Role of Enzymes in Deconstruction of Waste Biomass for Sustainable Generation of Value-Added Products

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Nisha Bhardwaj, Komal Agrawal, Bikash Kumar, and Pradeep Verma

Abstract

The enzymes and its utility have increased tremendously over the past decade, as the focus presently is diverting toward the development of technologies that are cyclic in nature. This idea depends on the fact that both the substrate and the end product should be biodegradable and should fit well with the idea of it being recycled and reused. The enzymes are biological molecules when used commercially can solve many issues e.g., agro-residues waste disposal, replacement of synthetic processes to natural more environment reliable processes. The effective utilization of agro-residues in biorefinery has been gaining attention but its application has been restricted due to higher lignin content and expensive chemical treatment. The biological delignification involving xylanase, cellulose, and ligninolytic enzymes is an effective method, cheap and carbon neutral as well. These enzymes have wide utility and with the advancement of techniques i.e., protein engineering has enabled the synthesis of enzymes that are industrially feasible, higher production yield and can tolerate harsh conditions. This has widened the application to the areas which were previously not known and were either not possible due to the restrictions. This chapter focuses on different enzymes, the method involved in the production, and its application in the bio-based economy.

Keywords

Agro-residues · Biorefinery · Delignification · Waste biomass

N. Bhardwaj · K. Agrawal · B. Kumar · P. Verma (✉)
Bioprocess and Bioenergy Laboratory, Department of Microbiology, Central University of Rajasthan, Ajmer, Rajasthan, India

H. Thatoi et al. (eds.), *Bioprospecting of Enzymes in Industry, Healthcare and Sustainable Environment*, https://doi.org/10.1007/978-981-33-4195-1_11

11.1 Introduction

The bio-based economy revolves around the reuse of waste lignocellulosic biomasses (LCB) which are abundantly available on earth and are renewable (Kim et al. 2019). They have proven to be an effective source for the production of various value-added bioproducts. The LCB is available universally and the sources include trees, agro-residues, industrial by-products, grasses, etc. (Anwar et al. 2014; Isikgor and Becer 2015; Watkins et al. 2015). These LCB consist of the lignocelluloses, which comprises three main components i.e., cellulose (40–50%), hemicellulose (25–30%), and lignin (15–20%) (Gray et al. 2006; Singla et al. 2012). These components together form a three-dimensional network complex structure (Sánchez 2009). Cellulose and hemicellulose in the plant cell wall are less accessible to the microorganisms due to their chemical association, tightly bound interaction with lignin, and their ratio of monomers (Ni and Tokuda 2013; Li and Zheng 2017). The deconstruction of the renewable lignocelluloses for the generation of value-added bioproducts can be done by various physical, chemical, and biological methods, however, as the concerns over the environment conservation is gaining impetuous the use of biological methods are more preferred over other methods (Binod et al. 2018; Wagner et al. 2018; Kumar et al. 2020; Kumar and Verma 2020b). As the LCB has gathered attention worldwide among the researcher's several methodologies for LCB utilization have been developed of which enzymatic hydrolysis is an effective method and environmentally friendly (Chaturvedi and Verma 2013).Thus, keeping in prospect the above points the present chapter focuses on the components of LCB, different enzymes involved in efficient delignification of LCB, mechanism of action of various biocatalyst, methodologies to improve its yield, and its application in the bio-based economy.

11.2 The Lignocellulosic Biomass (LCB) Components

Lignocellulose is a reinforced structure comprising of lignin, cellulose, and hemicelluloses, which are bound together with help of different covalent and noncovalent interactions to form a rigid three-dimensional structure. The three components have been shown Fig. 11.1 and described as follows.

11.2.1 Cellulose

Cellulose is a homopolysaccharide consisting of β-D-glucopyranose moieties linked via β-(1, 4) glycosidic bonds. The amount of celluloses in lignocellulosic materials can range from 30 to 50% of the dry biomass weight (Mussatto and Dragone 2016). Celluloses are mainly located in the secondary wall and the degree of polymerization of cellulose chain can be as low as 10,000 glucose residues in wood and as high as 15,000 glucose residues in cotton (Frederick 2012; Guha et al. 2010). Intra and intermolecular hydrogen bonds result in aggregation of cellulose molecules which

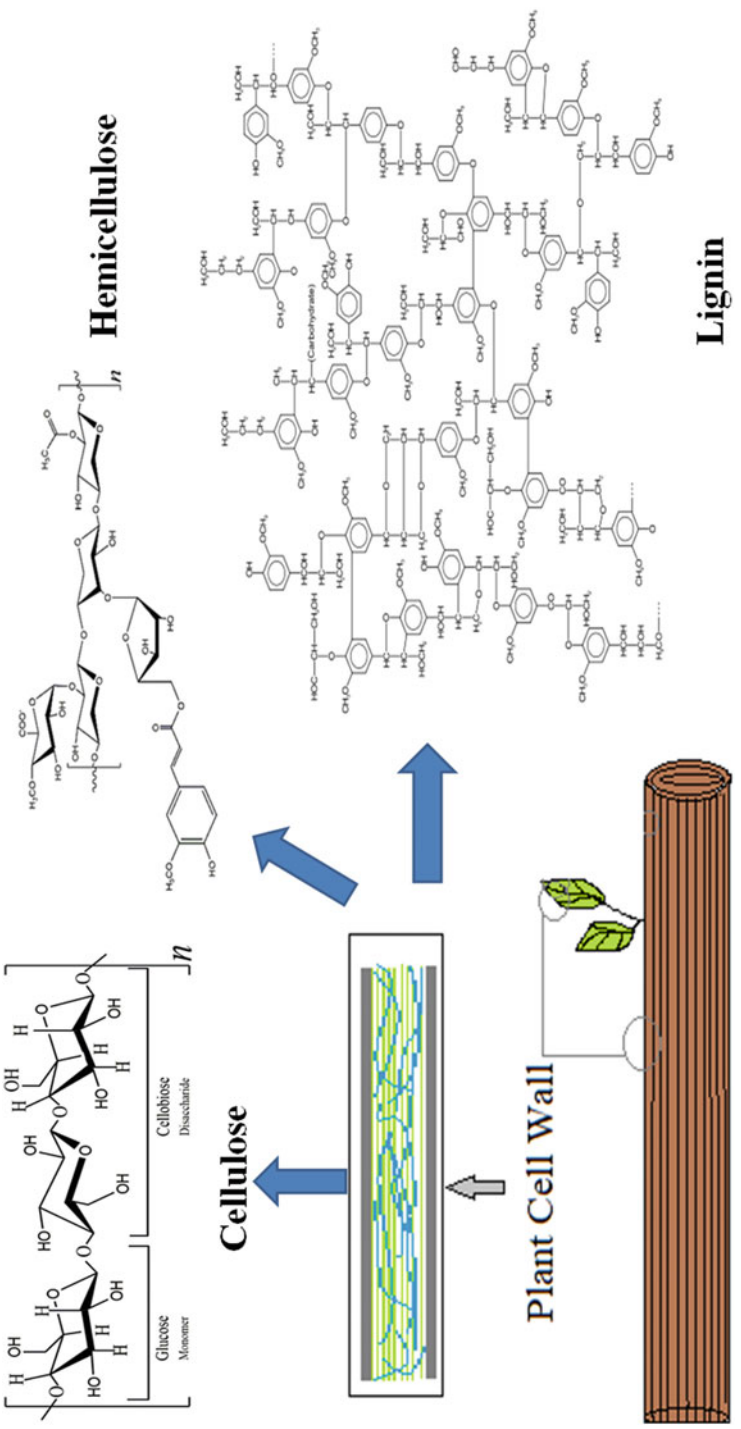

Fig. 11.1 Structural makeup of lignocellulosic biomass (LCB)

are called micro-fibrils that can gather together to form fibrils that subsequently bundle together to form cellulose fibers. The cellulose fibers consist of highly ordered crystalline regions and less ordered amorphous regions as a result of intra- and intermolecular hydrogen bonding. These strong hydrogen bonds and the crystalline structure render cellulose relatively stable toward chemical and enzyme attack and render it insoluble in most of the solvents (Rios-Fránquez et al. 2019).

11.2.2 Hemicellulose

Hemicelluloses are the cluster of various homo and heteropolymers (Perkins 2012). These polymers consist of the main chain of xylopyranose, mannopyranose, glucopyranose, and galactopyranose along with various substituents and together they form a complex polymeric structure (Collins et al. 2005; Shallom and Shoham 2003). Hemicelluloses are mostly found in different plants with varying composition and structure. The major component of hemicelluloses is β-1, 4-xylan, which is the second most abundant polysaccharide in nature after cellulose (Collins et al. 2005; Polizeli et al. 2005; Chávez et al. 2006). Hemicelluloses cover one-third of total renewable LCB found on earth and also comprises around 20–30% of total dry weight of annual plants and tropical hardwood (Collins et al. 2005; Singh et al. 2003).

11.2.3 Lignin

Lignin is made up of phenylpropane units (*p*-coumaryl, coniferyl, guaiacyl, syringyl, and sinapyl) linked with ether and C–C bonds. Phenolic compounds found in lignocellulose are considered as cross-linking agents by ester or ether bonds and by arabinoxylans esterification (Sánchez 2009; Ni and Tokuda 2013). According to Bermek and Eriksson (2009) the 3D structure of lignin is not known, but its composition varies in softwood and hardwood. Softwood comprises of guaiacyl units (14–25% in herbs) and hardwood mainly comprises of syringyl and guaiacyl units (27–32% in woody trees). Higher lignin's with *P*-hydroxyphenyl units along with syringyl and guaiacyl units are found on more woody plants, old trees, and annual plants, deposited in their cell wall which provide rigidity, water proof nature, and protection against microbes.

11.3 The Role of Lignocelluloytic Enzymes in the Bioconversion of LCB to Value-Added Products

The LCB components have the presence of complex structure which requires the activity of various enzymes for its hydrolysis and efficient conversion into monomeric units such as glucose, xylose, *p*-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol, and oligomers such as trioses and tetraoses (Annamalai et al. 2009; Irfan

et al. 2012). Several microorganisms utilizes LCB as their nutrient source and produce several hydrolytic enzymes collectively called as lignocelluloytic enzymes which include cellulase, xylanase, and laccase, lignin peroxidase (LiP), manganese peroxidase (MnP), and versatile peroxidase (VP). Overviews of these enzymes are described below.

11.3.1 Cellulolytic Enzymes

Cellulases are a multi-enzyme complex which hydrolyzes cellulose. The enzyme complex consists of mainly three enzymes i.e., endoglucanases, cellobiohydrolases, and β-glucosidases. These three enzymes act synergistically on the cellulose polymers to generate glucose monomers (Legodi et al. 2019).

11.3.1.1 Endoglucanases or Endo-1,4-β-D-Glucanase

Endoglucanases (EC 3.2.1.4) hydrolyze internal β-1,4-glucosidic bonds randomly in the amorphous regions of the long cellulose chain resulting in the formation of reducing and nonreducing ends of long-chain oligosaccharides (Singhania et al. 2017; Binod et al. 2018). The crystal structure of endoglucanases (Cel5A) protein of *Thermoascus aurantiacus* consist of a 335 amino acids and these amino acids mold into an eightfold $(\beta/\alpha)_8$ barrel architecture. The catalytic subunit of this enzyme consists of a compact structure containing short loops. Secondary structure of the protein is also represented with a short double-stranded anti-parallel β sheet in β/α-loop$_3$ and 3 one turn helices (Leggio and Larsen 2002). Several biocatalysis of cellulose processes require psychrophilic enzymes and thus study of these enzymes has gained impetus (Violot et al. 2005; Kasana and Gulati 2011). Recently, oxidative type of cellulase has been recognized, this oxidative cellulase utilizes free radical reaction mechanism for depolymerization of the cellulose (Violot et al. 2005; Juturu and Wu 2014).

11.3.1.2 Cellobiohydrolases (CBH) or Exoglucanases

Cellobiohydrolases (EC 3.2.1.91) cleaves the long-chain oligosaccharides releasing cellobiose (Singhania et al. 2017; Binod et al. 2018). The crystal structure of *Clostridium thermocellum* cellobiohydrolase CelS protein folds into an $(\alpha/\alpha)_6$ barrel with tunnel-shaped binding region. At the N-terminal side of the inner α-helices, tunnel cover one-third of the $(\alpha/\alpha)_6$ barrel side and play a crucial role in the substrate binding. Even in the absence of substrate the loops defining the tunnel are stable and thus suggest a dynamic mode of action of cellobiohydrolases (Guimarães et al. 2002).

11.3.1.3 β-Glucosidases or β-Glucoside Glucohydrolases

β-glucosidases (EC 3.2.1.21) hydrolyses the glycosidic bonds of β-D-glucosides or cellobioses and oligosaccharides and generate glucose monomers (Singhania et al. 2017; Binod et al. 2018). Based on the crystal structure of β-glucosidase A (BglA) of *Bacillus polymyxa*, these proteins belong to clan GH-A and GH family. The BglA

protein exists in octameric form, on further screening it was observed that these octamers exist as a tetramer of the dimer in a fourfold axis. These dimmers are strongly stabilized by 14 H-bonds and water molecules. The monomeric units adopt a adopts a single $(\alpha/\beta)_8$ barrel topology and between the α/β subunits secondary structure is inserted (Sanz-Aparicio et al. 1998; Juturu and Wu 2014).

11.3.2 Xylanolytic Enzymes

Xylanases that are also known as "endo-1, 4-β-xylanase" helps in the hydrolysis of 1, 4-β-D-xylosidic bond of xylan (Kuhad et al. 1997; Bhardwaj et al. 2019b). They are the highly preferred catalyst for the endohydrolysis of xylan because of their high specificity, mild reaction condition, and negligible substrate loss. The xylanolytic enzyme can be of six different types, which are as follows.

11.3.2.1 Endo-1,4-β-D-xylanases

Endo-1,4-β-D-xylanases (EC 3.2.1.8) also known as 1, 4-β-D-xylanxylanohydrolase cleaves the glycosidic bonds of backbone of the xylan by reducing the degree of polymerization of the substrates (Kumar and Shukla 2016, 2018). Different xylanases have difference in the substrate specificity which has an important role in the destruction of xylan (Prajapati et al. 2018). The selection of cleaving sites by these enzymes depends on the presence and arrangement of molecules with a specific degree in the side chain and the chain length (Liab et al. 2000; Polizeli et al. 2005).

11.3.2.2 1,4-*β*-Xylosidases

The1,4-*β*-xylosidases (EC 3.2.1.37) plays a very important role after endo-1,4-β-xylanases in xylan degradation by hydrolyzing soluble xylooligomers formed by the endoxylanase hydrolysis of insoluble xylan into xylose from the non-reducing ends (Lasrado and Gudipati 2013). Transglycosylation reactions were also catalyzed by 1,4-*β*-xylosidases in which xylose units release the monosaccharide units or alcohols attached to it (Jordan et al. 2013). Biely et al. (1986) explained the classification of 1,4-*β*-xylosidases, which can be in two forms i.e., xylobiases for xylobiose and exo-1, 4-β-xylanases for larger xylooligosaccharides. Xylobiose is the most suitable substrate for the 1,4-*β*-xylosidases and its xylooligosaccharides affinity depends on the degree of polymerization which is inversely proportional to each other (Terrasan et al. 2016). These enzymes can also cleave some artificial substrates e.g., *o*-nitrophenyl- and *p*-nitrophenyl- c-D-xylopyranoside (Jordan et al. 2013).

11.3.2.3 Acetyl Xylan Esterase

Acetyl xylanesterase (EC 3.1.1.72) primarily hydrolyze the acetyl xylan esters by removing the O-acetyl groups from 2 and/or 3 positions on the β-D-xylopyranosyl residues. Xylan from different plant origin varies in their arrangement of the side chain. The xylopyranoside units with acetic acid were found in the C2 and C3 position in the hardwood and annual plants, 4-*O*-methyglucuronic acid at C2

position in hardwood, softwood, and annual plants and arabinose at the C3 position of softwood and annual plants (Adesioye et al. 2016). The enzymatic approach that cleaves the backbone of xylan can be interfered with due to the presence of acetyl side-groups, acetyl xylan esters play an important role by the steric hindrance and elimination of these groups and facilitating the endoxylanase activity (Polizeli et al. 2005).

11.3.2.4 Arabinase

The L-arabinase is a branched polymer made up of (1-5)-, (1-2)-and (1-3)-α-linked L-arabinofuranosyl residues and its component are occupied with covalent cross-linking of polysaccharides of the cell wall. Mode of action of arabinase differentiate it into two types i.e., *p*-nitrophenyl-α-L-arabinofuranosides and branched arabinans degrading exo-α-L-arabinofuranosyl (EC 3.2.1.55) and linear arabinans hydrolyzing endo-1,5-α-L-arabinase (EC 3.2.1.99) (Semenova et al. 2018).

11.3.2.5 α-Glucuronidase

The α-glucuronidase (EC 3.2.1.139) hydrolyzes the α-1, 2-linkage of glucuronic acid residues, and nonreducing terminal β-D-xylopyranosyl backbone units of glucuronoxylan (aldouronic acids) and releases MeGlcA of GlcA (Yan et al. 2017). Uronic acid and xylose ratio depends on the source of xylan e.g., in softwood the ratio is 1:5 which contains a large amount of 4-*O*-methyglucuronic acids, whereas in hardwood very less uronic acid is found with the ratio of 1:10. Similarly, in annual plants uronic acids quantity depends upon the plants species and it varies even on their parts (Asmadi et al. 2017; Sporck et al. 2017).

11.3.2.6 Ferulic Acid Esterase and *p*-Coumaric Acid Esterase

These enzymes cleave the ester bonds present on the xylan. Ferulic acid esterase (EC 3.1.1.73) between arabinose and side group of ferulic acid and *p*-coumaric acid works with arabinose and *p*-coumaric acid (EC 3.1.1.) (Hunt et al. 2017; Morris et al. 2017).

11.3.3 Ligninolytic Enzymes

The ligninolytic enzymes consist of laccases, hemeperoxidase which are of two types namely lignin peroxidises (LiP) and manganese peroxidase (MnP), and lastly the versatile peroxidises (VP), which are described as follows.

11.3.3.1 Laccase

Laccases (E.C. 1.10.3.2) also known as benzenediol: oxygen oxidoreductase or *p*-diphenoloxidase belongs to the oxidoreductase class. The laccase is universally present however the laccase from white-rot fungi are the most commonly studied. The laccase can break the lignocellulosic wall, complex polyphenol structure which consists of lignin. These enzymes have a broad substrate range, though they do not require an inducible component for its production or enhancement, but considering

the industrial prospect and utility it can be considerably induced in the presence of copper, dyes, or other recalcitrant compounds (Minussi et al. 2007). The enzyme is capable of degrading the phenolic compounds in the absence of mediator, however, the degradation of the non-phenolic compounds require the mediator to initiate the reaction, which is contributed due to the redox potential of both the enzyme and the substrate which plays an important part in the acting capability of the enzyme on various substrates (Kudanga and Le Roes-Hill 2014; Agrawal et al. 2019).

11.3.3.2 Heme-Peroxidases Consisting of MnP and LiP

The heme-peroxidases are an important part of ligninolytic enzymes consisting of lignin peroxidase (LiP) and manganese peroxidase (MnP). LiP and MnP have three reactions of the catalytic cycle which are as follows a) Hydrogen peroxide oxidizes the enzyme to produce compound I (modified enzyme) and water, (b) The compound I (modified enzyme) catalyzes the production of compound II (second modified form of an enzyme), formed by the electron transfer from the reduced substrate along with a generation of free radical, (c) The compound II reacts with the molecule of a reduced substrate to produce another free radical and water. As the reaction continues the enzymes reduces to its native form, (Piontek et al. 1993; Sundaramoorthy et al. 1994; Choinowski et al. 1999; Martínez 2002; Dias et al. 2007; Piontek et al. 1993) and are represented in Fig. 11.2.

11.3.3.2.1 Lignin Peroxidise

LiP's (E.C. 1.11.1.14) were originally discovered in *Phanerochaete chrysosporium* (Dias et al. 2007). LiP possesses high redox potential and can catalyze the degradation of a broad range of aromatic structures. It oxidizes aromatic rings which are moderately activated by electron-donating substitutes whereas the common peroxidases participate in the catalysis of aromatic substrates. An explanation for

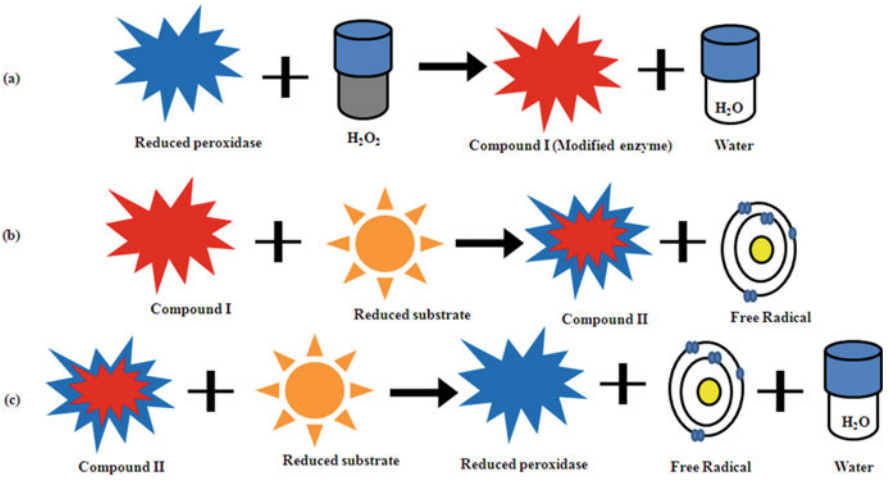

Fig. 11.2 The schematic representation of the three reactions in the catalytic cycle of LiP and MnP

this type of catalysis is the production of veratryl alcohol radicals which have higher redox potential than LiP's compounds I and II and can eventually participate in the degradation of compounds with high redox potential (Khindaria et al. 1996).

11.3.3.2.2 Manganese Peroxidise

MnP (EC 1.11.1.13) are glycoproteins with a molecular weight in the range from 38 and 62.5 kDa (Hofrichter 2002), MnP structure has two domains which are as follows: first heminic group in the middle, second consist ten major helixes, third is a minor helix, and fourth consist of five disulfide bridges. Among those bridges, one bridge participates in the manganese (Mn) binding site, and is this site distinguishes MnP from other peroxidases (Sundaramoorthy et al. 1994). The catalytic reaction has been previously described in Fig. 11.2. However, in case the compound II mandatorily requires the presence of Mn^{2+} for its reaction to proceed. The compound II then oxidizes Mn^{2+} to Mn^{3+} which is responsible to oxidize aromatic compounds. The converted Mn^{3+} are than stabilized by organic acids which react nonspecifically with organic molecules thereby removing an electron and a proton from the substrates (Hofrichter 2002), The attack of the Mn^{3+} which is a small size compound having high redox potential diffuses easily in the lignified cell wall thereby attacking inside the plant cell wall facilitating the penetration as well as the action of other enzymes (Martínez 2002; Hammel and Cullen 2008).

11.3.3.2.3 Versatile Peroxidises

The VP (EC 1.11.1.16) can directly oxidize Mn^{2+}, methoxybenzenes, phenolic aromatic substrates similarly to MnP, LiP, and horseradish peroxidase. VP has a very broad substrate specificity range and can oxidize the substrates even in the absence of manganese. It can efficiently oxidize both phenolic and nonphenolic lignin model dimers (Polak and Jarosz-Wilkolazka 2012). Thus considering the broad range of substrate overproduction system is desired for biotechnological and industrial sectors (Plácido et al. 2013; Hoopes and Dean 2004).

11.4 Mode of Action of Various Lignocellulolytic Enzymes

The mode of action of the lignocellulolytic enzymes has been represented in Fig. 11.3 and described as follows:

11.4.1 Mode of Action of Cellulolytic Enzymes

Cellulolytic enzyme works in synergism and thus cellulose hydrolysis is a stepwise process where the first step is called primary hydrolysis followed by secondary hydrolysis. The primary hydrolysis occurs in the presence of endoglucanases and exoglucanases, these enzymes act on the cellulosic substrate and results in the release of cellobioses. Thus the primary hydrolysis (depolymeriztion) is often regarded as rate-limiting step. The cellobioses are subjected to secondary hydrolysis

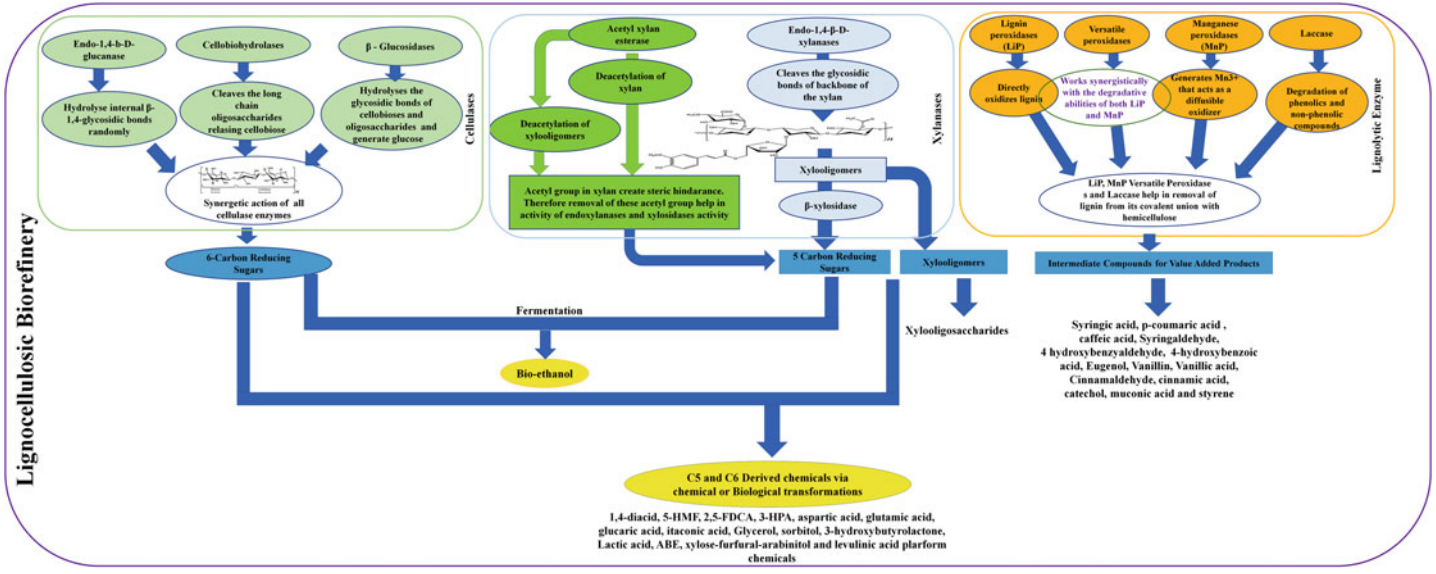

Fig. 11.3 Schematic representation of mode of action and application of lignocelluloytic enzymes in deconstruction of LCB and production of value-added products

in presence of β-glucosidase for the generation of glucose monomers (Kubicek 1992; Binod et al. 2018).

Cellulase enzyme has been broadly divided into two types: non-complex system and complex system. The non-complex system i.e., endoglucanases and cellobiohydrolases have a characteristic two-domain structure a catalytic domain and a cellulose-binding domain (CBD) or carbohydrate-binding module (CBM) (Kuhad et al. 2016). The catalytic domain consists of catalytic site and carbohydrate/cellulose-binding domain as the name suggests help in the binding of enzyme to cellulose and these domains are linked by glycosylated flexible linker peptide. The CBD plays a vital role in ensuring the orientation of the substrate with the catalytic domain for perfect binding and subsequent degradation of cellulose. The complex system consists of high-molecular-weight complexes known as "cellulosomes" (Behera et al. 2017). These complex cellulases are characteristics of the anaerobic bacteria but observed in certain anaerobic fungi as well. The cellulosomes are protuberance from the bacterial cell wall, which harbor stable enzyme complex that causes degradation of cellulose by binding to it (Doi and Kosugi 2004).

11.4.2 Mode of Action of Xylanolytic Enzymes

Xylan hydrolysis done by xylanolytic enzymes either by inversion or retention of the anomeric centers of monomeric units suggesting the participation of one or two chemical transition state (Moreira et al. 2016). During retention two glutamate residues being employed in the catalytic mechanism, which is double displacement mechanism having an acid catalyst protonating the substrate, a carboxyl group situated with a covalent glycosyl enzyme intermediate with the carboxylate in which substrate is opposite to the sugar anomeric configuration. This can reach both sides through transition state including oxo-carbonium ions (Collins et al. 2005; Uday et al. 2016), whereas in inversion mechanism aspartate along with glutamate is involved (Bhardwaj et al. 2019b). This is a single displacement mechanism, in which only one carboxylate in offers for overall acid-catalyzed group departure. This enzyme also acts as a base for activating a nucleophilic water molecule to attack the anomeric carbon (depending upon the distance between two molecules) for breaking the glycosidic bonds and causing an inversion of anomeric carbon configuration (Subramaniyan and Prema 2002).

11.4.3 Mode of Action of Ligninolytic Enzymes

The action of the enzyme on lignin is an oxidative process where the dissimilar fungal oxidases e.g., glyoxal oxidase, pyranose-2 oxidase, and aryl-alcohol oxidase release extracellular H_2O_2, which oxidizes the polymer in a reaction which has been catalyzed by LiP, MnP, and laccase (Martínez et al. 2005; Kersten and Cullen 2007; Hammel and Cullen 2008). The high redox potential of LiP and VP has enabled it to

Table 11.1 Various strain reported for the production of cellulase

Bacteria	Fungi
Acetivibrio cellulolyticus	*Aspergillus niger*
Bacteroides cellulosolvens	*Fusarium oxysporum*
Clostridium	*Penicillium funiculosum*
Ruminococcus	*Penicillium pinophilum*
Pseudomonas fluorescens	*Sclerotium rolfsii*
Bacillus sp.	*Schizophyllum commune*
Cellulomonas	*Trichoderma ressei*
Cellvibrio	*Caecomyces*

act on a wide range of substrates including lignin which oxidizes the benzenic ring irrespective of the degree of methylation and interunit linkages (Ruiz-Dueñas and Martinez 2009), resulting in the formation of unstable aromatic cation radicals, which leads to depolymerization as well as other reactions (Martínez et al. 2005). The released H_2O_2 activates the heme group and enables it to gain a cofactor via an access channel, thus blocking the ability to oxidize lignin as it is unable to reach the site (heme pocket) where oxidation takes place. Thus these enzymes then oxidize the lignin with the help of the bare tryptophanyl radical (Ruiz-Dueñas and Martinez 2009). As the redox potential of laccase is ($\leq$0.8 V), it can directly attack the phenolic moiety which constitutes 10% of the polymer, but the action of a non-phenolic moiety (redox potential is >1.3 V in comparison to laccase) the direct action would be difficult. However, this problem can be overcome by the use of redox mediators effectively known as laccase mediator system (LMS) (Ralph et al. 2008).

11.5 Microbial Sources for the Production of Lignocellulolytic Enzymes

Naturally, all living beings are capable of degrading carbohydrates; however, capacity to produce cellulase is limited to microorganisms along with some molluscs. Both anaerobic and aerobic bacteria and fungi are capable of producing cellulase. The anaerobic bacteria are mostly found in soil, in cattle rumens, in the termite gut, decomposing plant materials, and isolated from different paper and wood processing industries wastes (Table 11.1) (Rees et al. 2003). As the application of cellulases in various industrial processes requires stability over ambient temperature it has also led to the production of cellulases from thermophilic fungi e.g., *Chaetomium thermophilum, Humicola grisea, Myceliopthora thermophila, Sporotrichum thermophile,* and *Thermoascus aurantiacus* (Singhania et al. 2017; Binod et al. 2018).

Over the decades many microorganisms such as fungi and bacteria have been reported by many researchers that utilizes hemicelluloses (Table 11.2) (Pokhrel and Yoo 2009; Dong et al. 2012; Liao et al. 2014). Fungi are known as a potential source of xylanases as they produce high titer of extracellular xylanase from various cheap

Table 11.2 Various strain reported for the production of xylanase

Bacteria	Fungi
Bacillus altitudinis	*Aspergillus tamari*
Bacillus mojavensis	*Aspergillus niger*
Bacillus pumilus	*Penicillium purpurogenum*
Bacillus tequilenis	*Aspergillus flavus*
Bacillus licheniformis	*Trichoderma reesei*
Bacillus aerophilus	*Aspergillus welwitschiae*
Bacillus polymyxa	*Aspergillus nidulans*
Pichia stipitis	*Trichoderma longibrachiatum*

Table 11.3 Various strain reported for the production of laccase, manganese peroxidase, lignin peroxidase and versatile peroxidase

Laccase	
Insects	Fungi
Nephotettix cincticeps	*P ostreatus*
Manduca sexta	*Trametes versicolor*
Reticulitermes flavipes	*Cerrena unicolor*
Tribolium castaneum	*Aspergillus flavus*
Bacteria	Plants
Lysinibacillus sp.	*Rhus vernicifera,*
Streptomyces psammoticus	*Pinus taeda*
Bacillus subtilis	*Populus trichocarpa*
Azospirillum lipoferum	*Liriodendron tulipifera*
Manganese peroxidase	
Bacteria	Fungi
Serratia marcescens	*Pleurotus eryngii*
Bacillus pumilus	*Bjerkandera adusta*
Paenibacillus sp.	*Cerrena maxima*
Lignin peroxidase	
Bacteria	Fungi
Pseudomonas aeruginosa	*Phanerochaete chrysosporium*
Bacillus megaterium	*Lentinula edodes*
Serratia marcescens	*Phellinus pini*
Versatile peroxidase	
Fungi	
Bjerkandera sp	
Phanerochaete chrysosporium	
Pleurotus eryngii	
Pleurotus ostreatus	

sources such as agricultural residues by degrading their cell wall (Su et al. 2011). Various mesophilic fungi, some white-rot fungi (Schimpf and Schulz 2018), and filamentous fungi (Bhardwaj et al. 2017) are most commonly reported for xylanase production as they produce stable enzymes.

The ligninolytic enzymes are universally present and present in different types of organisms as plants, bacteria, insects, and fungi (Table 11.3). The presence of

laccase in plants was studied in Japanese lacquer tree, mango, mung bean, peach, tobacco, Zea mays, etc. (Polak and Jarosz-Wilkolazka 2012), bacteria includes actinomycetes, α-proteobacteria, and γ-proteobacteria (Bugg et al. 2011). The presence of laccase has been detected in insects. In the case of fungi, ligninolytic enzymes occur in *Ascomycetes*, *Basidiomycetes*, and *Deuteromycetes* (Dos Santos et al. 2007).

11.6 Various Approaches Implemented for the Enhanced Production of Lignocellulolytic Enzymes

With advent of biotechnology, several pre-existing harmful chemical mediated processes have been replaced by the enzymatic processes. The applications of enzymes in these industries are limited due to low enzyme yield, temperature, and pH stability and cost of production and suitable downstream processing and reusability. Therefore several researchers are trying to overcome these limitations by adopting various approaches which are as follows:

11.6.1 Fermentation Process Used for the Production of Lignocellulolytic Enzymes

The choice of fermentation technology significantly affects the level of production. Submerged fermentation (SmF) is most accepted for lignocelluloytic enzyme production strategy due to extracellular nature of the enzyme. In SmF method, microbes are cultivated in an aqueous medium rich in essential nutrients for microbial growth. However the cost of the concentration and extraction of enzyme is high. Therefore an alternative i.e., solid state fermentation (SSF) was adapted, it involved the growth of microbes on solid materials (moist), and this method mimicked the natural habitat of the microbes (Hölker et al. 2004). However, the easy handling and monitoring associated with the liquid medium have given an upper hand to the SmF over SSF. Different fermentation method employed for lignocellulolytic enzyme production and their yield have been mentioned in Table 11.4.

11.6.2 Lignocellulose as Substrate Used for Enzyme Production

As the cost associated with the production is very high, thus cheap substrates are essential for the enhanced enzyme production. The lignocellulosic substrates such as different agro and forest residues have been used for cellulase, xylanase, and laccase production and help in lignocelluloytic enzyme synthesis without the supplementation other culture medium component and inducers (Elisashvili and Kachlishvili 2009; Ravindran and Jaiswal 2016; Luo et al. 2019; Novy et al. 2019).

Table 11.4 Reported microbial strains, methodology adapted, substrate used for lignocelluloytic enzymes production and its application in various fields

Enzyme	Strain	Method	Substrate	Yield	Properties and application	References
Cellulase	*Sporothrix carnis*	SmF	CC	285.7 U/mL	Enzyme is thermostable at 80–90 °C and suitable for biofuel industries	Olajuyigbe and Ogunyewo (2016)
Cellulase	*Phialophora* sp. G5	SmF	CMC-Na	Specific activity 10.3 U/mg	Stability of 47% at 90 °C	Zhao et al. (2012)
Cellulase (Endoglucanase)	*Aspergillus terreus*	SSF	RS, WS, CS, ZS,J, W BS	141.29 U/g	Enzymatic degradation of delignified RS	Narra et al. (2014)
Cellulase (Endoglucanase)	*Thermoanaerobacter tengcongensis* MB4	SmF	NA	294 U/mg	Stability at a high temperature and is halo tolerant. Suitable for industrial applications	Liang et al. (2011)
Cellulase (Endoglucanase)	*Aspergillus fumigates*	SmF and SSF	WS	SmF: 6294 IU/mg SSF: 9158 IU/mg	Higher specific activity in SSF as compared to SmF	Saqib et al. (2010)
Cellulase	*Schizophyllum commune* NAIMCC - F –03379	SmF	WB	CMCase 195 ± 3.5 IU/mL, FPase 245 ± 1.12 IU/mL	Acid/ alkali and thermo tolerant cellulase efficiently hydrolyzed RS with sugar yield of 1.162 mg/ mL	Kumar et al. (2018)
Cellulase and xylanase	*Aspergillus fumigatus* SK1	SSF	OPT	Endoglucanase (CMCase) 54.27 U/g, exoglucanase (FPase) 3.36, β-glucosidase 4.54 and xylanase 418.70 U/g	Thermotolerant enzyme and saccharification of untreated oil OPT and NaOH-treated OPT gave sugar yield of 8.55 g/land 5.09 g/L	Ang et al. (2013)
Cellulase and Xylanase	*Myceliophthora thermophila* JCP	SSF	SB, SBM, WB and oat	Endoglucanase 357.51 U/g β-glucosidase, 45.42 U/g, xylanase931.11 U/g, avicelase 3.58 U/g	Saccharification of microwave pre-treated SB gave glucose and xylose yields of 15.6 and 35.13%	de Cassia Pereira et al. (2015)

(continued)

Table 11.4 (continued)

Enzyme	Strain	Method	Substrate	Yield	Properties and application	References
Xylanase	*Fusarium proliferatum*	SmF	OSX	Specific activity of 591 U/mg protein	Conversion of xylan to oligosaccharides such as xylobiose and short-chain XOS	Saha (2002)
Xylanase	*Penicillium canescens*	SSF	SOC	18,895 IU/gds	Stable at freezing temperature for 6 months and at room temperature for 3 months	Antoine et al. (2010)
Xylanase	*Clostridium strain* DBT-IOC-DC21	SmF	RS	Ethanol yields 26.61 mM with Xylan, 43.63 mM with xylose, 40.22 mM with mixture of cellulose and xylan and 19.48 mM with untreated RS	Direct microbial conversion of untreated rice straw to ethanol.	Singh et al. (2018b)
Xylanase	*Streptomyces* sp.	SmF	BWX	10,220 U/mL	Purified enzyme could successfully clarify orange, mousambi, and pineapple juice to 20.87%, 23.64%, and 27.89% clarify juices of orange (20.87%), mousambi (23.64%), and pineapple juice (27.89%)	Rosmine et al. (2017)
Xylanase	Aspergillus niger JL-15	SSF	Orange peel	917.7 U/g	Generation of XOS such as xylotriose from birchwood xylan and wheat bran	Dai et al. (2011)
Xylanase	*C. pseudorhagii* SSA-1542T	SmF	Xylan and D-xylose	Activity of 1.73 U/mL with xylan and 0.98 U/mL D-xylose	60.7% fermentation efficiency in 48 h	Ali et al. (2017)
Cellulase and Xylanase	*Aspergillus niger*	SSF	SMB	FPase activity 0.55 IU/g, endoglucanase 35.1 IU/g, xylanase-47.7 IU/g	Hydrolysis of SB yielded 4.4 g/L of glucose after 36 h	Vitcosque et al. (2012)

Xylanase	*Aspergillus niger*LC1	SmF	RS	1245 ± 2.4 IU/mL	Generation of XOS: xylobiose, xylotriose from different untreated agro-residues by partially purified xylanase	Bhardwaj et al. (2018)
Laccase	*Pleurotus ostreatus*	SSF	Na	13,000 U/L	The strain performs better in SmF than in SSF	Téllez-Téllez et al. (2008)
Laccase	*Trametes versicolor*	SSF	SCS	2600.33 ± 81.89 U/g	The SCS improved laccase production and enabled the production of low cost enzyme	Adekunle et al. (2017)
Laccase	*Cerrena unicolor*	SmF	OP	56.3–78.5 U/mL	Removal of phenolic compounds	Elisashvili et al. (2018)
Laccase	*Lysinibacillus* sp.	SSF	SBM as inducer	2.39-fold increase	The phenolic-rich waste can be potential enhancers for the laccase production	Sharma et al. (2017)
Laccase	*Aspergillus flavus*	SmF	NA	15.96 U/mL	An alternate for the valorization of agro-waste	Ghosh and Ghosh (2017)
Laccase	*Myrothecium verrucaria* ITCC-8447	SmF	Glucose	1675 U/L	Delignification of agro-residues	Agrawal et al. (2019)
Lip and MnP	*Phanerochaete chrysosporium*	SSF	SWS	Lip and MnP activity 2600 and 1375 U/L	Effective use of agro-residues for large scale enzyme production	Fujian et al. (2001)
LiP	*Pleurotus* ostreatus (PLO 9) *Ganoderma lucidium* (GRM 117)	SSF	J. curcas L. seed cake	PLO 9-10602.68 U/mL and GRM 117-9419 U/mL	Dye decolorization	Oliveira et al. (2018)

(continued)

Table 11.4 (continued)

Enzyme	Strain	Method	Substrate	Yield	Properties and application	References
VP, laccase	*P. eryngii, P. ostreatus and P. sajor-caju*	SmF	To the media 2,4-DCP was added	The activity was similar for all the three strains 400–700 mU/mL VP, 10–20 mU/mL	The enzyme activity was detected during the degradation of 2,4-DCP	Rodriguez et al. (2004)

RS rice straw, *WS* wheat straw, *CS* cotton, *ZG* zinjivo grass, *BS* bajra straw; *CC* corn cob, *WB* wheat bran, *OPT* oil palm trunk, *SB* sugarcane bagasse, *SBM* soybean meal, *OSX* oat spelt xylan, *SOC* soy oil cake, *BWX* beech wood xylan, *SCS* steam exploded corn stalk, *OP* olive pomace, *SWS* steam exploded wheat straw, *JW* jowar, *SmF* submerged fermentation, *SSF* solid state fermentation, *XOS* xylooligosaccharides, *LiP* lignin peroxidase, *MnP* manganese peroxidase, *VP* versatile peroxidase

11.6.3 Process Optimization for Enhanced Enzyme Production

The enzyme production by microbes are influenced by various nutrient and physical parameters such as substrates, salts in medium, pH, temperature, and light regulation, agitation/shaking the medium (Zhanga et al. 2019). Considering the high cost of commercially available enzymes and increase in their industrial demands, all the above mentioned factors can be optimized using a well-known conventional method One-Factor-at-a-Time (OFAT). However OFAT is time consuming and it can only give the effect of individual component in the fermentation and does not explain about the interaction among them (Deswal et al. 2011; Kumar et al. 2018). Later Response Surface Methodology (RSM) a statistical tool was designed which helped in analyzing multiple factors at the same time (Abdullah et al. 2018; Neelkant et al. 2019). Thus being economically feasible and time saving in contrast to OFAT, in the present time RSM is much more preferred over OFAT.

11.6.4 Strain Improvement for Enhanced Enzyme Production

Several attempts have been made for the improvement of strains by applying techniques such as (a) mutagenesis and selection, (b) gene cloning, and (c) genome shuffling (Peterson and Nevalainen 2012; Singhania et al. 2017). The strain improvement processes is one of the most exploited techniques for the enhanced production for different enzymes and have evolved greatly with time. The cloning of enzyme encoding genes in homologous and heterologous hosts has been attempted. *E.coli* is the most favored organism for expression as it has several advantages over other expression system such as yeast or plants. Mandels et al. (1971) had selected a mutant strain *Trichoderma viride* QM6a, from over 100 *Trichoderma* wild strains for enhanced cellulase production. In order to utilize xylose directly, D-xylose-utilizing pathway controlling genes was added to the recombinant *Saccharomyces cerevisiae* HZ3001 (Sun et al. 2012). Similarly Davidi et al. (2016) designed a dockerin-fused variant laccase from the aerobic bacterium *Thermobifida fusca*. The strain improvement processes is one of the most exploited techniques for the enhanced production for different enzymes and have evolved greatly with time.

11.7 Applications of Lignocelluloytic Enzyme in the Bio-Based Economy

LCB has a wide spectrum of applications in various industries. Traditionally, they are applied in food and brewery production, animal feed processing, detergent production, laundry, textile processing and paper pulp manufacturing. Due to the crisis in sustainable supply of fossil fuel, production of biofuels and chemicals from renewable resources are expected to increase rapidly in the foreseeable future. In biorefinery, generation of biofuels and value-added chemicals from renewable LCB

have gained much attention worldwide (Kumar et al. 2020). For utilization of biomass, their depolymerization in order to generate fermentable sugars is one of the basics requirements. Several chemical and physical pre-treatment methods have been suggested; however they are energy intensive and generate several pollutants. Therefore, biological pre-treatment or enzymatic hydrolysis have gained impetuous due to its environmental friendly nature and also has several advantages such as specificity over physic-chemical methods (Agbor et al. 2011). The Table 11.4 represents various strains responsible for cellulase, xylanase and laccase production along with various substrate used, enzyme yield and its application.

11.7.1 Recent Development of the Biocatalyst in the Bio-Based Economy

The recent scenario the conversion of biomass to value-added products, and the focus diverting toward greener methods have gained interest among the researchers. The lignocellulolytic enzymes have been greatly investigated for its ability to produce value-added products as shown in Fig. 11.4 and have been discussed as follows.

11.7.2 Bioethanol and Bio-Based Chemicals

Bioethanol generation from amorphous cellulose and cellulose soaked in ionic liquid were analyzed separately using the recombinant strain *S. cerevisiae* and highest ethanol yield was observed (Yanase et al. 2010; Nakashima et al. 2011). Kumar et al. (2018) demonstrated the application of in-house produced cellulase from *Schizophyllum commune* and xylanase from *A oryzae* LC1 in saccharification of wheat straw and rice straw alone and in combination. The in-house produced

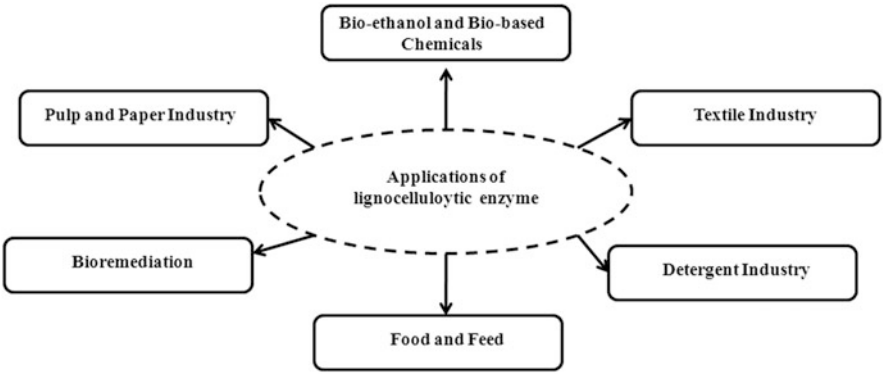

Fig. 11.4 Application of lignocelluloytic enzymes in various fields fitting into the concept of "reduce-reuse-recycle" and contributing toward "circular economy"

cellulase showed results in comparable with the commercial cellulase enzyme Onozuka R-10 from the *Trichoderma viridae.* Bhardwaj et al. (2018) used partially purified xylanase for generating xylooligosaccharides which included xylobiose, xylotriose and xylotetraose by the direct enzymatic hydrolysis of untreated sugarcane bagasse, wheat straw, and wheat bran. Xylan fermenting thermophilic *Clostridium* strain was used for direct conversion of LCB to bioethanol production. The strain showed preferential bioethanol production efficiency when wide ranges of substrates were tested with mixture of cellulose and xylan and untreated rice straw. This strain also presented broad range of primary metabolic end products such as acetate, lactate, and hydrogen substrate spectrum utilizing wide range of substrate spectrum (Singh et al. 2018b). Similarly laccase from *Lentinus squarrosulus* MR13 resulted in lignin removal from *Saccharum spontaneum (*karn grass) and subsequently resulting enhanced sugar yield (Rajak and Banerjee 2016).

Bhardwaj et al. (2020) demonstrated the synergistic action of laccase, cellulase and xylanase in generation of ethanol using single pot culture system performing simultaneous delignification, saccharification and fermentation. LCB is a sustainable platform for the production of the bio-based chemicals and polymer (Isikgor and Becer 2015; Kumar and Verma 2020b; Agrawal and Verma 2020b). The C5 and C6 carbon generating as a result of hydrolysis of xylanase and cellulase can be used for production of1,4-diacid, 5-HMF, 2,5-FDCA, 3-HPA, aspartic acid, glutamic acid, glucaric acid, itaconic acid, Glycerol, sorbitol, 3-hydroxybutyrolactone, Lactic acid, ABE, xylose-furfural-arabinitol, and levulinic acid platform chemicals.

11.7.3 Textile Industry

The specificity of enzyme has led to development of enzyme as important biochemical in textile industry. The enzymes are highly specific, nontoxic and therefore enzymes have replaced the intensive conventional chemical processes in textile processing. The cellulases and xylanases can effectively remove the hairiness of the cellulose thread with less weight loss, impart brightness and help in giving textile a smooth texture and glossy appearance. Acidic cellulases obtained from the *T. reesei* (Kuhad et al. 2011), neutral cellulases *H. insolens* (Anish et al. 2007) xylanases from *Bacillus pumilu*s (Singh et al. 2018a; Battan et al. 2012), and laccase from *Pleurotus ostreatus and Trametes versicolor* (Anish et al. 2007; Mojsov 2014) are widely used in the textile processing industries.

11.7.4 Detergent Industry

The detergents have several applications such as laundering, dishwashing and cleaning (Schäfer et al. 2005). Traditional chemical detergents have strong bleaching chemicals and phosphates and it adversely affect to the environment and the user (Olsen and Falholt 1998). Due to this drawback, development of detergents for industrial application using enzymes is one of the major research areas today. The

enzymes help in removal of proteins starch, fats oil stains and due to its hydrolytic properties increases effectiveness of detergents (Kirk et al. 2002; Hasan et al. 2010). Different hydrolyzing enzymes such as lipases, proteases, cellulases, pectinase, xylanases and laccases are used in different detergent composition for efficient cleaning and fabric care (Kuhad et al. 2011; Li et al. 2012). Apart from removing stains these enzymes cleaves off damaged cotton fabric and maintain color, whiteness and fabric smoothness. Different alkaline cellulases enzymes are used in detergents which are capable of passing through the inter fibril spaces of the cotton and help in efficient stain removal (Juturu and Wu 2014).

11.7.5 Food and Feed

At present, these so called wastes are judiciously utilized to produce valuable products such as enzymes, sugars, biofuels, chemicals, cheap energy sources for fermentation, improved animal feeds, human nutrients and intermediates compounds for generating value-added chemicals (Kuhad et al. 2011). The enzymes have huge applicability and food in food industry as well α-amylases and xylanases have been used for maintaining the softness and elasticity of bread. Cellulase and laccase has been effectively used for the clarification of juice where it catalyzes the cross-linking of polyphenols, thereby resulting in an easy removal of polyphenols by the help of filtration. It has also been used for flavor enhancement in beer. It is possible that better functional understanding of these enzyme classes will broaden its applications within the food industry. The use of enzyme mixtures containing pectinases, cellulases, and hemicellulases can also be used for improved extraction of olive oil as well.

The enzymes have been effectively used as feed additives as well; xylanases and β-glucanases have been used in cereal-based feed for monogastric animal's (Kirk et al. 2002). The use of pre-treatment of agricultural silage and grain feed by the combination of cellulases or xylanases has helped improve its nutritional value (Godfrey and West 1996) eliminate anti-nutritional factors; degrade certain feed constituents which would help improve its overall nutritional value for its effective use (Choct 2006; Juturu and Wu 2014; Vasconcellos et al. 2015).

11.7.6 Bioremediation

In the wastewater processing sector cellulase enzyme is employed in the bioremediation of the ink released during recycling of paper in pulp and paper industry (Karigar and Rao 2011). Thermo-alkaline tolerant cellulases are new favorites of the scientist working in the area biofuel production and waste management's (Annamalai et al. 2016; Khan et al. 2016) *Humicola* species cellulase is highly adaptive to the harsh environment so it is used in bioremediation of wastewater generated from detergents and washing powder industries (Imran et al. 2016). Laccase also play crucial role in decolorization of azo dyes by oxidizing the aromatic

ring and transform these azo dyes into less harmful by-products (Verma and Madamwar 2005). Agrawal et al. (2020a) and Agrawal and Verma (2020a) demonstrated the white laccase obtained from *Myrothecium verrucaria* ITCC-8447 has resulted in complete removal of hazardous chemical i.e., phenol and resorcinol. Similarly the same group has also reported that yellow laccase obtained from *Stropharia* sp. ITCC 8422 was efficient in degrading anthraquinone violet R and alizarin cyanine green dye (Agrawal and Verma 2019a,b; Agrawal et al. 2020b).

The Commercial laccase obtained from genetically modified *Aspergillus oryzae* effectively treated meat industry wastewater resulting in reduction of COD and color under optimum conditions (Thirugnanasambandham and Sivakumar 2015). Peroxidases has shown capability to treat wide spectra of aromatic compounds such as aromatic compounds (Chen et al. 2014), anilines (Nakamoto and Machida 1992), aromatic dyes (Bhunia et al. 2001), poly-carbonated biphenyls (Köller et al. 2000), poly-aromatic hydrocarbons (Baborová et al. 2006), and phenols (Bayramouglu and Arica 2008), along with different pollutant of industrial contamination (Cheng et al. 2006). These enzymatic biotransformation serve dual purpose in waste management i.e., treatment of waste and generating the several essential chemicals and intermediates.

11.7.7 Pulp and Paper Industry

The utilization of chemicals in the paper and pulp industry is very high, thus the environmental concern has now replaced the chemical based method to the bio-based methods. The use of enzymes has been an effective and promising tool in the paper and pulp industry. Cellulases individually, or in combination with xylanases, can be used for the deinking of various types of paper wastes (Kumar et al. 2018). Maximum applications involving the use of cellulases and hemicellulases leads to the release of ink from the fiber surface by the partial hydrolysis of carbohydrate molecules (Kuhad et al. 2011; Juturu and Wu 2014; Kumar et al. 2018). Similarly, laccase in the paper and pulp industry plays a role in the delignification and brightening of the pulp but can also remove the lipophilic extractives responsible for pitch deposition from both wood and non-wood paper pulps. It can also improve the physical, chemical, as well as mechanical properties of pulp either by forming reactive radicals with lignin or by functionalizing lignocellulosic fibers. Further it also targets the colored and toxic compounds which are released as effluents from various paper and pulp industries rendering them nontoxic by the polymerization and depolymerization reactions (Virk et al. 2012).

11.8 Overcoming the Limitations and Future Prospects Toward Making "Circular Bio-Economy" a Reality

The major challenges toward making circular based bio-economy a reality through feasible solutions are mentioned below:

1. Selection of suitable strains for the lignocellulolytic enzyme production which can be used in synchronization for biomass deconstruction and development of low cost enzyme production process and effective downstream production technologies.
2. Development of biological and environmental friendly pre-treatment technology for minimizing the natural recalcitrance of LCB.
3. Selection of promising strains or development of suitable technology which can be employed for conversion of lignin, xylan, and cellulose to several reactions intermediated for economically important compounds.
4. Supply chain mechanisms of the wastes collection from field to industries and the development of decentralized system for continuous supply of the biomass to the bio-based industries.

These are the major points may be taken into consideration in order to make concept of circular bio-economy a reality in the future (Kumar and Verma 2020a). In this participation of governments, different stack holders, scientist, economist and engineers will play a pivotal role. The cooperation and synergy among these institutions will lead to a sustainable system of the bio-based economy where recycling and waste reduction is reality.

11.9 Conclusion

The application of lignocellulolytic in biomass deconstruction for generation of sugars and value-added products have to a parallel economy where waste materials such as agricultural residues which were earlier considered as waste are now part of the bio-based economy also known as circular bio-economy. The conversion of hemicelluloytic content of LCB by cellulase and xylanase to reducing sugar which can further be converted to bioethanol can act as green substitute to fossil fuels. Xylanase can help in direct conversion of xylan to different xylooligosaccharides which can be used as dietary supplements and essential pharmaceutical The removal of lignin using laccase can enable the better utilization of the agro-residues and contribute toward green environment and circular economy as well. This parallel bio-based economy where the concept of reduce-reuse-recycle is applied on reutilization of waste material, the concept of circular bio-economy evolves mostly around the LCB and these hydrolyzing lignocellulolytic enzymes. The combination of both the concepts by efficient utilization of wastes and technologies can help achieve the goal of "reduce-reuse-recycle" and contribute toward "circular economy" as well.

Acknowledgments PV is thankful to DBT (Grant No.BT/304/NE/TBP/2012; Grant No.BT/PR7333/PBD/26/373/.

2012) and Central University of Rajasthan for laboratory and library facilities. NB acknowledges University Grants Commission for providing Non-NET and Rajiv Gandhi National Fellowship respectively for the doctoral studies. BK acknowledges Jawaharlal Nehru Memorial Fund, New Delhi, CSIR-SRF for providing funding for Doctoral Studies.

Competing Interests All the authors declare that they have no competing interests.

References

Abdullah A, Hamid H, Christwardana M, Hadiyanto H (2018) Optimization of cellulase production by *Aspergillus niger* ITBCC L74 with bagasse as substrate using response surface methodology. HAYATI J Biosci 25:115–125

Adekunle AE, Zhang C, Guo C, Liu C-Z (2017) Laccase production from *Trametes versicolor* in solid-state fermentation of steam-exploded pretreated cornstalk. Waste Biomass Valor 8:153–159

Adesioye FA, Makhalanyane TP, Biely P, Cowan DA (2016) Phylogeny, classification and metagenomic bioprospecting of microbial acetyl xylan esterases. Enzym Microb Technol 93:79–91

Agbor VB, Cicek N, Sparling R et al (2011) Biomass pretreatment: fundamentals toward application. Biotechnol Adv 29:675–685

Agrawal K, Verma P (2019a) Biodegradation of synthetic dye Alizarin Cyanine Green by yellow laccase producing strain Stropharia sp. ITCC-8422. Biocatal Agric Biotechnol 21:101291

Agrawal K, Verma P (2019b) Column bioreactor of immobilized *Stropharia* sp. ITCC 8422 on natural biomass support of L. cylindrica for biodegradation of anthraquinone violet R. Bioresour Technol Rep 8:100345

Agrawal K, Verma P (2020a) Potential removal of hazardous wastes using white laccase purified by ATPS--PEG--salt system: an operational study. Environ Technol Innov 17:100556

Agrawal K, Verma P (2020b) Production optimization of yellow laccase from Stropharia sp. ITCC 8422 and enzyme-mediated depolymerization and hydrolysis of lignocellulosic biomass for biorefinery application. Biomass Conversion Biorefinery. https://doi.org/10.1007/s13399-020-00869-w

Agrawal K, Shankar J, Kumar R, Verma P (2020a) Insight into multicopper oxidase laccase from Myrothecium verrucaria ITCC-8447: a case study using in silico and experimental analysis. J Environ Sci Health B:1–13

Agrawal K, Shankar J, Verma P (2020b) Multicopper oxidase (MCO) laccase from Stropharia sp. ITCC-8422: an apparent authentication using integrated experimental and in silico analysis. 3 Biotech 10(9):1–18

Agrawal K, Bhardwaj N, Kumar B et al (2019) Process optimization, purification and characterization of alkaline stable white laccase from *Myrothecium verrucaria* ITCC-8447 and its application in delignification of agroresidues. Int J Biol Macromol 125:1042–1055. https://doi.org/10.1016/j.ijbiomac.2018.12.108

Ali SS, Wu J, Xie R et al (2017) Screening and characterizing of xylanolytic and xylose-fermenting yeasts isolated from the wood-feeding termite, *Reticulitermes chinensis*. PLoS One 12: e0181141

Ang SK, Shaza EM, Adibah Y et al (2013) Production of cellulases and xylanase by *Aspergillus fumigatus* SK1 using untreated oil palm trunk through solid state fermentation. Process Biochem 48:1293–1302. https://doi.org/10.1016/j.procbio.2013.06.019

Anish R, Rahman MS, Rao M (2007) Application of cellulases from an alkalothermophilic *Thermomonospora* sp. in biopolishing of denims. Biotechnol Bioeng 96:48–56

Annamalai N, Thavasi R, Jayalakshmi S, Balasubramanian T (2009) Thermostable and alkaline tolerant xylanase production by *Bacillus subtilis* isolated form marine environment. Indian J Biotechnol 8:291–297

Annamalai N, Rajeswari MV, Balasubramanian T (2016) Thermostable and alkaline cellulases from marine sources. In: New and future developments in microbial biotechnology and bioengineering. Elsevier, Amsterdam, pp 91–98

Antoine AA, Jacqueline D, Thonart P (2010) Xylanase production by *Penicillium canescens* on soya oil cake in solid-state fermentation. Appl Biochem Biotechnol 160:50–62

Anwar Z, Gulfraz M, Irshad M (2014) Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: a brief review. J Radiat Res Appl Sci 7:163–173

Asmadi M, Kawamoto H, Saka S (2017) Characteristics of softwood and hardwood pyrolysis in an ampoule reactor. J Anal Appl Pyrolysis 124:523–535

Baborová P, Möder M, Baldrian P et al (2006) Purification of a new manganese peroxidase of the white-rot fungus *Irpex lacteus*, and degradation of polycyclic aromatic hydrocarbons by the enzyme. Res Microbiol 157:248–253

Battan B, Dhiman SS, Ahlawat S et al (2012) Application of thermostable xylanase of Bacillus pumilus in textile processing. Indian J Microbiol 52:222–229

Bayramouglu G, Arica MY (2008) Enzymatic removal of phenol and p-chlorophenol in enzyme reactor: horseradish peroxidase immobilized on magnetic beads. J Hazard Mater 156:148–155

Behera BC, Sethi BK, Mishra RR et al (2017) Microbial cellulases--diversity & biotechnology with reference to mangrove environment: a review. J Genet Eng Biotechnol 15:197–210

Bermek H, Eriksson K (2009) Lignin, lignocellulose, ligninase. In: Encyclopedia of microbiology. Elsevier, Amsterdam, pp 373–384

Bhardwaj N, Chanda K, Kumar B et al (2017) Statistical optimization of nutritional and physical parameters for xylanase production from newly isolated *Aspergillus oryzae* LC1 and its application on hydrolysis of lignocellulosic agro-residues. Bioresources 12:8519–8538

Bhardwaj N, Verma VK, Chaturvedi V, Verma P (2018) GH10 XynF1 and Xyn11A: the predominant xylanase identified in the profiling of extracellular proteome of Aspergillus oryzae LC1. Ann Microbiol 68(11):731–742

Bhardwaj N, Kumar B, Agarwal K et al (2019a) Purification and characterization of a thermo-acid/alkali stable xylanases from *Aspergillus oryzae* LC1 and its application in Xylo-oligosaccharides production from lignocellulosic agricultural wastes. Int J Biol Macromol 122:1191–1202

Bhardwaj N, Kumar B, Verma P (2019b) A detailed overview of xylanases: an emerging biomolecule for current and future prospective. Bioresour Bioprocess. https://doi.org/10.1186/s40643-019-0263-7. In Press

Bhardwaj N, Kumar B, Agrawal K, Verma P (2020) Bioconversion of rice straw by synergistic effect of in-house produced ligno-hemicellulolytic enzymes for enhanced bioethanol production. Bioresource Technol Rep 10:100352

Bhunia A, Durani S, Wangikar PP (2001) Horseradish peroxidase catalyzed degradation of industrially important dyes. Biotechnol Bioeng 72:562–567

Biely P, MacKenzie CR, Puls J, Schneider H (1986) Cooperativity of esterases and xylanases in the enzymatic degradation of acetyl xylan. Nat Biotechnol 4:731

Binod P, Gnansounou E, Sindhu R, Pandey A (2018) Enzymes for second generation biofuels: recent developments and future perspectives. Bioresour Technol Rep 5:317–325

Bugg TDH, Ahmad M, Hardiman EM, Singh R (2011) The emerging role for bacteria in lignin degradation and bio-product formation. Curr Opin Biotechnol 22:394–400

de Cassia Pereira J, Paganini Marques N, Rodrigues A et al (2015) Thermophilic fungi as new sources for production of cellulases and xylanases with potential use in sugarcane bagasse saccharification. J Appl Microbiol 118:928–939

Chaturvedi V, Verma P (2013) An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value-added products. 3 Biotech 3:415–431

Chávez R, Bull P, Eyzaguirre J (2006) The xylanolytic enzyme system from the genus *Penicillium*. J Biotechnol 123:413–433
Chen Z, Li H, Peng A, Gao Y (2014) Oxidation of polycyclic aromatic hydrocarbons by horseradish peroxidase in water containing an organic cosolvent. Environ Sci Pollut Res 21:10696–10705
Cheng J, Yu SM, Zuo P (2006) Horseradish peroxidase immobilized on aluminum-pillared interlayered clay for the catalytic oxidation of phenolic wastewater. Water Res 40:283–290
Choct M (2006) Enzymes for the feed industry: past, present and future. Worlds Poult Sci J 62:5–16
Choinowski T, Blodig W, Winterhalter KH, Piontek K (1999) The crystal structure of lignin peroxidase at 1.70 Å resolution reveals a hydroxy group on the Cβ of tryptophan 171: a novel radical site formed during the redox cycle1. J Mol Biol 286:809–827
Collins T, Gerday C, Feller G (2005) Xylanases, xylanase families and extremophilic xylanases. FEMS Microbiol Rev 29:3–23
Dai X-J, LiU M-Q, Jin H-X, Jing M-Y (2011) Optimization of solid-state fermentation of *Aspergillus niger* JL-15 for xylanase production and xylooligosaccharides preparation. Czech J Food Sci 29:557–567
Davidi L, Moraïis S, Artzi L et al (2016) Toward combined delignification and saccharification of wheat straw by a laccase-containing designer cellulosome. Proc Natl Acad Sci 113:10854–10859
Deswal D, Khasa YP, Kuhad RC (2011) Optimization of cellulase production by a brown rot fungus *Fomitopsis* sp. RCK2010 under solid state fermentation. Bioresour Technol 102:6065–6072
Dias AA, Sampaio A, Bezerra RM (2007) Environmental applications of fungal and plant systems: decolourisation of textile wastewater and related dyestuffs. In: Environmental bioremediation technologies. Springer, Berlin, pp 445–463
Doi RH, Kosugi A (2004) Cellulosomes: plant-cell-wall-degrading enzyme complexes. Nat Rev Microbiol 2:541
Dong X, Meinhardt SW, Schwarz PB (2012) Isolation and characterization of two endoxylanases from Fusarium graminearum. J Agric Food Chem 60:2538–2545
Dos Santos AB, Cervantes FJ, Van Lier JB (2007) Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. Bioresour Technol 98:2369–2385
Elisashvili V, Kachlishvili E (2009) Physiological regulation of laccase and manganese peroxidase production by white-rot Basidiomycetes. J Biotechnol 144:37–42
Elisashvili V, Kachlishvili E, Asatiani MD (2018) Efficient production of lignin-modifying enzymes and phenolics removal in submerged fermentation of olive mill by-products by white-rot basidiomycetes. Int Biodeterior Biodegradation 134:39–47
Frederick WJ Jr (2012) Thermochemical conversion of biomass to liquid fuels and chemicals. In: Integrated biorefineries. CRC Press, Boca Raton, pp 540–589
Fujian X, Hongzhang C, Zuohu L (2001) Solid-state production of lignin peroxidase (LiP) and manganese peroxidase (MnP) by *Phanerochaete chrysosporium* using steam-exploded straw as substrate. Bioresour Technol 80:149–151
Ghosh P, Ghosh U (2017) Statistical optimization of laccase production by *Aspergillus flavus* PUF5 through submerged fermentation using agro-waste as cheap substrate. Acta Biol Szeged 61:25–33
Godfrey T, West S (1996) Textiles. In: Industrial enzymology. Macmillan, London, pp 360–371
Gray KA, Zhao L, Emptage M (2006) Bioethanol. Curr Opin Chem Biol 10:141–146
Guha SK, Kobayashi H, Fukuoka A (2010) Conversion of cellulose to sugars. In: Crocker M (ed) Thermochemical conversion of biomass to liquid fuels and chemicals, vol 1, pp 344–364
Guimarães BG, Souchon H, Lytle BL et al (2002) The crystal structure and catalytic mechanism of cellobiohydrolase celS, the major enzymatic component of the *Clostridium thermocellum* cellulosome. J Mol Biol 320:587–596. https://doi.org/10.1016/S0022-2836(02)00497-7
Hammel KE, Cullen D (2008) Role of fungal peroxidases in biological ligninolysis. Curr Opin Plant Biol 11:349–355

Hasan F, Shah AA, Javed S, Hameed A (2010) Enzymes used in detergents: lipases. Afr J Biotechnol 9:4836–4844
Hofrichter M (2002) Lignin conversion by manganese peroxidase (MnP). Enzym Microb Technol 30:454–466
Hölker U, Höfer M, Lenz J (2004) Biotechnological advantages of laboratory-scale solid-state fermentation with fungi. Appl Microbiol Biotechnol 64:175–186
Hoopes JT, Dean JFD (2004) Ferroxidase activity in a laccase-like multicopper oxidase from Liriodendron tulipifera. Plant Physiol Biochem 42:27–33
Hunt CJ, Antonopoulou I, Tanksale A et al (2017) Insights into substrate binding of ferulic acid esterases by arabinose and methyl hydroxycinnamate esters and molecular docking. Sci Rep 7:17315
Imran M, Anwar Z, Irshad M et al (2016) Cellulase production from species of fungi and bacteria from agricultural wastes and its utilization in industry : a review. Adv Enzyme Res 4:44–55
Irfan M, Nadeem M, Syed Q, Baig S (2012) Effect of medium composition on xylanase production by *Bacillus subtilis* using various agricultural wastes. J Agric Environ Sci 4:2
Isikgor FH, Becer CR (2015) Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. Polym Chem 6:4497–4559
Jordan DB, Wagschal K, Grigorescu AA, Braker JD (2013) Highly active β-xylosidases of glycoside hydrolase family 43 operating on natural and artificial substrates. Appl Microbiol Biotechnol 97:4415–4428
Juturu V, Wu JC (2014) Microbial cellulases: engineering, production and applications. Renew Sust Energ Rev 33:188–203. https://doi.org/10.1016/j.rser.2014.01.077
Karigar CS, Rao SS (2011) Role of microbial enzymes in the bioremediation of pollutants: a review. Enzyme Res 2011:805187
Kasana RC, Gulati A (2011) Cellulases from psychrophilic microorganisms: a review. J Basic Microbiol 51:572–579
Kersten P, Cullen D (2007) Extracellular oxidative systems of the lignin-degrading Basidiomycete *Phanerochaete chrysosporium*. Fungal Genet Biol 44:77–87
Khan MN, Luna IZ, Islam MM et al (2016) Cellulase in waste management applications. In: New and future developments in microbial biotechnology and bioengineering. Elsevier, Amsterdam, pp 237–256
Khindaria A, Yamazaki I, Aust SD (1996) Stabilization of the veratryl alcohol cation radical by lignin peroxidase. Biochemistry 35:6418–6424
Kim JK, Yang J, Park SY et al (2019) Cellulase recycling in high-solids enzymatic hydrolysis of pretreated empty fruit bunches. Biotechnol Biofuels 12:138
Kirk O, Borchert TV, Fuglsang CC (2002) Industrial enzyme applications. Curr Opin Biotechnol 13:345–351
Köller G, Möder M, Czihal K (2000) Peroxidative degradation of selected PCB: a mechanistic study. Chemosphere 41:1827–1834
Kubicek CP (1992) The cellulase proteins of *Trichoderma reesei*: structure, multiplicity, mode of action and regulation of formation. In: Enzymes and products from bacteria fungi and plant cells. Springer, Berlin, pp 1–27
Kudanga T, Le Roes-Hill M (2014) Laccase applications in biofuels production: current status and future prospects. ApplMicrobiol Biotechnol 98:6525–6542
Kuhad RC, Singh A, Eriksson K-EL (1997) Microorganisms and enzymes involved in the degradation of plant fiber cell walls. In: Biotechnology in the pulp and paper industry. Springer, Berlin, pp 45–125
Kuhad RC, Gupta R, Singh A (2011) Microbial cellulases and their industrial applications. Enzyme Res 2011:1–10
Kuhad RC, Deswal D, Sharma S et al (2016) Revisiting cellulase production and redefining current strategies based on major challenges. Renew Sust Energ Rev 55:249–272

Kumar V, Shukla P (2016) Functional aspects of xylanases toward industrial applications. In: Frontier discoveries and innovations in interdisciplinary microbiology. Springer, Berlin, pp 157–165

Kumar V, Shukla P (2018) Extracellular xylanase production from *T. lanuginosus* VAPS24 at pilot scale and thermostability enhancement by immobilization. Process Biochem 71:53–60

Kumar B, Verma P (2020a) Application of hydrolytic enzymes in biorefinery and its future prospects. In: Microbial strategies for techno-economic biofuel production. Springer, Singapore, pp 59–83

Kumar B, Verma P (2020b) Enzyme mediated multi-product process: a concept of bio-based refinery. Ind Crop Prod 154:112607

Kumar B, Bhardwaj N, Alam A et al (2018) Production, purification and characterization of an acid/alkali and thermo tolerant cellulase from *Schizophyllum commune* NAIMCC - F - 03379 and its application in hydrolysis of lignocellulosic wastes. AMB Express 8:1–16

Kumar B, Bhardwaj N, Agrawal K, Chaturvedi V, Verma P (2020) Current perspective on pretreatment technologies using lignocellulosic biomass: an emerging biorefinery concept. Fuel Process Technol 199:106244

Lasrado LD, Gudipati M (2013) Purification and characterization of β-D-xylosidase from *Lactobacillus brevis* grown on xylo-oligosaccharides. Carbohydr Polym 92:1978–1983

Leggio LL, Larsen S (2002) The 1.62 Å structure of *Thermoascus aurantiacus* endoglucanase: completing the structural picture of subfamilies in glycoside hydrolase family 5. FEBS Lett 523:103–108

Legodi LM, La Grange D, van Rensburg EL, Ncube I (2019) Isolation of cellulose degrading fungi from decaying banana pseudostem and Strelitzia alba. Enzyme Res 2019:1390890

Li X, Zheng Y (2017) Lignin-enzyme interaction: mechanism, mitigation approach, modeling, and research prospects. Biotechnol Adv 35:466–489

Li S, Yang X, Yang S et al (2012) Technology prospecting on enzymes: application, marketing and engineering. Comput Struct Biotechnol J 2:e201209017

Liab K, Azadi P, Collins R et al (2000) Relationships between activities of xylanases and xylan structures. Enzym Microb Technol 27:89–94

Liang C, Xue Y, Fioroni M et al (2011) Cloning and characterization of a thermostable and halotolerant endoglucanase from *Thermoanaerobacter tengcongensis* MB4. Appl Microbiol Biotechnol 89:315–326

Liao H, Sun S, Wang P et al (2014) A new acidophilic endo-β-1, 4-xylanase from *Penicillium oxalicum*: cloning, purification, and insights into the influence of metal ions on xylanase activity. J Ind Microbiol Biotechnol 41:1071–1083

Luo X, Liu J, Zheng P et al (2019) Promoting enzymatic hydrolysis of lignocellulosic biomass by inexpensive soy protein. Biotechnol Biofuels 12:51

Mandels M, Weber J, Parizek R (1971) Enhanced cellulase production by a mutant of *Trichoderma viride*. Appl Microbiol 21:152

Martínez AT (2002) Molecular biology and structure-function of lignin-degrading heme peroxidases. Enzym Microb Technol 30:425–444

Martínez AT, Speranza M, Ruiz-Dueñas FJ et al (2005) Biodegradation of lignocellulosics: microbial, chemical, and enzymatic aspects of the fungal attack of lignin. Int Microbiol 8:195–204

Minussi RC, Pastore GM, Durán N (2007) Laccase induction in fungi and laccase/N--OH mediator systems applied in paper mill effluent. Bioresour Technol 98:158–164

Mojsov KD (2014) Biotechnological applications of laccases in the textile industry. Savrem Tehnol 3:76–79

Moreira LRS et al (2016) Insights into the mechanism of enzymatic hydrolysis of xylan. Appl Microbiol Biotechnol 100:5205–5214

Morris P, Dalton S, Langdon T et al (2017) Expression of a fungal ferulic acid esterase in suspension cultures of tall fescue (Festuca arundinacea) decreases cell wall feruloylation and increases rates of cell wall digestion. Plant Cell Tissue Organ Cult 129:181–193

Mussatto SI, Dragone GM (2016) Biomass pretreatment, biorefineries, and potential products for a bioeconomy development. In: Biomass fractionation technologies for a lignocellulosic feedstock based biorefinery. Elsevier, Amsterdam, pp 1–22

Nakamoto S, Machida N (1992) Phenol removal from aqueous solutions by peroxidase-catalyzed reaction using additives. Water Res 26:49–54

Nakashima K, Yamaguchi K, Taniguchi N et al (2011) Direct bioethanol production from cellulose by the combination of cellulase-displaying yeast and ionic liquid pretreatment. Green Chem 13:2948–2953

Narra M, Dixit G, Divecha J et al (2014) Production, purification and characterization of a novel GH 12 family endoglucanase from *Aspergillus terreus* and its application in enzymatic degradation of delignified rice straw. Int Biodeterior Biodegradation 88:150–161

Neelkant KS, Shankar K, Jayalakshmi SK, Sreeramulu K (2019) Optimization of conditions for the production of lignocellulolytic enzymes by *Sphingobacterium* sp. ksn-11 utilizing agro-wastes under submerged condition. Prep Biochem Biotechnol 49:927–934

Ni J, Tokuda G (2013) Lignocellulose-degrading enzymes from termites and their symbiotic microbiota. Biotechnol Adv 31:838–850

Novy V, Nielsen F, Seiboth B, Nidetzky B (2019) The influence of feedstock characteristics on enzyme production in *Trichoderma reesei*: a review on productivity, gene regulation and secretion profiles. Biotechnol Biofuels 12:238

Olajuyigbe FM, Ogunyewo OA (2016) Enhanced production and physicochemical properties of thermostable crude cellulase from *Sporothrix carnis* grown on corn cob. Biocatal Agric Biotechnol 7:110–117. https://doi.org/10.1016/j.bcab.2016.05.012

Oliveira SF, da Luz JMR, Kasuya MCM et al (2018) Enzymatic extract containing lignin peroxidase immobilized on carbon nanotubes: potential biocatalyst in dye decolourization. Saudi J Biol Sci 25:651–659

Olsen HS, Falholt P (1998) The role of enzymes in modern detergency. J Surfactant Deterg 1:555–567

Perkins HR (2012) Microbial cell walls and membranes. Springer, Berlin

Peterson R, Nevalainen H (2012) *Trichoderma reesei* RUT-C30--thirty years of strain improvement. Microbiology 158:58–68

Piontek K, Glumoff T, Winterhalter K (1993) Low pH crystal structure of glycosylated lignin peroxidase from *Phanerochaete chrysosporium* at 2.5 Å resolution. FEBS Lett 315:119–124

Plácido J, Imam T, Capareda S (2013) Evaluation of ligninolytic enzymes, ultrasonication and liquid hot water as pretreatments for bioethanol production from cotton gin trash. Bioresour Technol 139:203–208

Pokhrel S, Yoo YJ (2009) Designing active site pKa values to shift optimum pH of *Bacillus circulans* xylanase. New Biotechnol 25:S126

Polak J, Jarosz-Wilkolazka A (2012) Fungal laccases as green catalysts for dye synthesis. Process Biochem 47:1295–1307

Polizeli M, Rizzatti ACS, Monti R et al (2005) Xylanases from fungi: properties and industrial applications. Appl Microbiol Biotechnol 67:577–591

Prajapati AS, Pawar VA, Panchal KJ et al (2018) Effects of substrate binding site residue substitutions of xynA from Bacillus amyloliquefaciens on substrate specificity. BMC Biotechnol 18:9

Rajak RC, Banerjee R (2016) Enzyme mediated biomass pretreatment and hydrolysis: a biotechnological venture towards bioethanol production. RSC Adv 6:61301–61311

Ralph J, Brunow G, Harris PJ et al (2008) Lignification: are lignins biosynthesized via simple combinatorial chemistry or via proteinaceous control and template replication. Recent Adv Polyphen Res 1:36–66

Ravindran R, Jaiswal AK (2016) Microbial enzyme production using lignocellulosic food industry wastes as feedstock: a review. Bioengineering 3:30

Rees HC, Grant S, Jones B et al (2003) Detecting cellulase and esterase enzyme activities encoded by novel genes present in environmental DNA libraries. Extremophiles 7:415–421

Rios-Fránquez FJ, Rojas-Rejón ÓA, Escamilla-Alvarado C (2019) Microbial enzyme applications in bioethanol producing biorefineries: overview. In: Ray R, Ramachandran S (eds) In bioethanol production from food crops sustainable sources, interventions, and challenges. Elsevier, Amsterdam, pp 249–266

Rodriguez E, Nuero O, Guillén F et al (2004) Degradation of phenolic and non-phenolic aromatic pollutants by four Pleurotus species: the role of laccase and versatile peroxidase. Soil Biol Biochem 36:909–916

Rosmine E, Sainjan NC, Silvester R et al (2017) Statistical optimisation of xylanase production by estuarine *Streptomyces* sp. and its application in clarification of fruit juice. J Genet Eng Biotechnol 15:393–401

Ruiz-Dueñas FJ, Martinez ÁT (2009) Microbial degradation of lignin: how a bulky recalcitrant polymer is efficiently recycled in nature and how we can take advantage of this. Microb Biotechnol 2:164–177

Saha BC (2002) Production, purification and properties of xylanase from a newly isolated Fusarium proliferatum. Process Biochem 37:1279–1284

Sánchez C (2009) Lignocellulosic residues: biodegradation and bioconversion by fungi. Biotechnol Adv 27:185–194

Sanz-Aparicio J, Hermoso JA, Martinez-Ripoll M et al (1998) Crystal structure of β-glucosidase a from Bacillus polymyxa: insights into the catalytic activity in family 1 glycosyl hydrolases1. J Mol Biol 275:491–502

Saqib AAN, Hassan M, Khan NF, Baig S (2010) Thermostability of crude endoglucanase from *Aspergillus fumigatus* grown under solid state fermentation (SSF) and submerged fermentation (SmF). Process Biochem 45:641–646

Schäfer T, Kirk O, Borchert TV et al. (2005) Enzymes for technical applications. Biopolym Online Biol Chem Biotechnol Appl 557-617

Schimpf U, Schulz R (2018) Industrial by-products from white-rot fungi production. Part II: application in anaerobic digestion for enzymatic treatment of hay and straw. Process Biochem 76:142–154

Semenova MV, Volkov PV, Rozhkova AM et al (2018) Cloning, isolation, and properties of a new homologous Exoarabinase from the *Penicillium canescens* fungus. Appl Biochem Microbiol 54:387–395

Shallom D, Shoham Y (2003) Microbial hemicellulases. Curr Opin Microbiol 6:219–228

Sharma A, Gupta V, Khan M et al (2017) Flavonoid-rich agro-industrial residues for enhanced bacterial laccase production by submerged and solid-state fermentation. 3 Biotech 7:200

Singh S, Madlala AM, Prior BA (2003) *Thermomyces lanuginosus*: properties of strains and their hemicellulases. FEMS Microbiol Rev 27:3–16

Singh A, Kaur A, Patra AK, Mahajan R (2018a) A sustainable and green process for scouring of cotton fabrics using xylano-pectinolytic synergism: switching from noxious chemicals to eco-friendly catalysts. 3 Biotech 8:184

Singh N, Puri M, Tuli DK et al (2018b) Bioethanol production by a xylan fermenting thermophilic isolate *Clostridium* strain DBT-IOC-DC21. Anaerobe 51:89–98

Singhania RR, Adsul M, Pandey A, Patel AK (2017) Cellulases. In: Ashok Pandey A, Negi S, Soccol RR (eds) Current developments in biotechnology and bioengineering. Elsevier, Amsterdam

Singla A, Paroda S, Dhamija SS et al (2012) Bioethanol production from xylose: problems and possibilities. J Biofuels 3(1):17

Sporck D, Reinoso FAM, Rencoret J et al (2017) Xylan extraction from pretreated sugarcane bagasse using alkaline and enzymatic approaches. Biotechnol Biofuels 10:296

Su Y, Zhang X, Hou Z et al (2011) Improvement of xylanase production by thermophilic fungus *Thermomyces lanuginosus* SDYKY-1 using response surface methodology. New Biotechnol 28:40–46

Subramaniyan S, Prema P (2002) Biotechnology of microbial xylanases: enzymology, molecular biology, and application. Crit Rev Biotechnol 22:33–64

Sun J, Wen F, Si T et al (2012) Direct conversion of xylan to ethanol by recombinant Saccharomyces cerevisiae strains displaying an engineered mini-hemicellulosome. Appl Environ Microbiol 78:3837–3845

Sundaramoorthy M, Kishi K, Gold MH, Poulos TL (1994) The crystal structure of manganese peroxidase from *Phanerochaete chrysosporium* at 2.06-a resolution. J Biol Chem 269:32759–32767

Téllez-Téllez M, Fernández FJ, Montiel-González AM et al (2008) Growth and laccase production by Pleurotus ostreatus in submerged and solid-state fermentation. Appl Microbiol Biotechnol 81:675

Terrasan CRF, Guisan JM, Carmona EC (2016) Xylanase and β-xylosidase from *Penicillium janczewskii*: purification, characterization and hydrolysis of substrates. Electron J Biotechnol 23:54–62

Thirugnanasambandham K, Sivakumar V (2015) Enzymatic catalysis treatment method of meat industry wastewater using lacasse. J Environ Heal Sci Eng 13:86

Uday USP, Choudhury P, Bandyopadhyay TK, Bhunia B (2016) Classification, mode of action and production strategy of xylanase and its application for biofuel production from water hyacinth. Int J Biol Macromol 82:1041–1054

Vasconcellos VM, Tardioli PW, Giordano RLC, Farinas CS (2015) Production efficiency versus thermostability of (hemi)cellulolytic enzymatic cocktails from different cultivation systems. Process Biochem 50:1701–1709

Verma P, Madamwar D (2005) Decolorization of azo dyes using Basidiomycete strain PV 002. World J Microbiol Biotechnol 21:481–485

Violot S, Aghajari N, Czjzek M et al (2005) Structure of a full length psychrophilic cellulase from *Pseudoalteromonas haloplanktis* revealed by X-ray diffraction and small angle X-ray scattering. J Mol Biol 348:1211–1224

Virk AP, Sharma P, Capalash N (2012) Use of laccase in pulp and paper industry. Biotechnol Prog 28:21–32

Vitcosque GL, Fonseca RF, Rodriguez-Zúñiga UF et al (2012) Production of biomass-degrading multienzyme complexes under solid-state fermentation of soybean meal using a bioreactor. Enzyme Res 2012:248983

Wagner AO, Lackner N, Mutschlechner M et al (2018) Biological pretreatment strategies for second-generation lignocellulosic resources to enhance biogas production. Energies 11:1797. https://doi.org/10.3390/en11071797

Watkins D, Nuruddin M, Hosur M et al (2015) Extraction and characterization of lignin from different biomass resources. J Mater Res Technol 4:26–32

Yan R, Vuong TV, Wang W, Master ER (2017) Action of a GH115 α-glucuronidase from *Amphibacillus* xylanus at alkaline condition promotes release of 4-O-methylglucopyranosyluronic acid from glucuronoxylan and arabinoglucuronoxylan. Enzym Microb Technol 104:22–28

Yanase S, Yamada R, Kaneko S et al (2010) Ethanol production from cellulosic materials using cellulase-expressing yeast. Biotechnol J 5:449–455

Zhanga F, Bunterngsookc B, Lia J-X et al (2019) Regulation and production of lignocellulolytic enzymes from Trichoderma reesei for biofuels production. Adv Bioenergy 4:79

Zhao J, Shi P, Li Z et al (2012) Two neutral thermostable cellulases from Phialophora sp. G5 act synergistically in the hydrolysis of filter paper. Bioresour Technol 121:404–410