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Review

Microbial Lignocellulolytic Enzymes for the Effective Valorization of Lignocellulosic Biomass: A Review

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Abstract: The urgent demand for alternative energy sources has been sparked by the tremendous burden on fossil fuels and the resulting acute energy crisis and climate change issues. Lignocellulosic biomass is a copious renewable and alternative bioresource for the generation of energy fuels and biochemicals in biorefineries. Different pretreatment strategies have been established to overcome biomass recalcitrance and face technological challenges, such as high energy consumption and operational costs and environmental hazards, among many. Biological pretreatment using microbial enzymes is an environmentally benign and low-cost method that holds promising features in the effective pretreatment of lignocellulosic biomass. Due to their versatility and eco-friendliness, cellulases, hemicellulases, and ligninolytic enzymes have been recognized as "green biocatalysts" with a myriad of industrial applications. The current review provides a detailed description of different types of lignocellulolytic enzymes, their mode of action, and their prospective applications in the valorization of lignocellulosic biomass. Solid state fermentation holds great promise in the microbial production of lignocellulolytic enzymes owing to its energy efficient, environment friendly, and higher product yielding features utilizing the lignocellulosic feedstocks. The recent trends in the application of enzyme immobilization strategies for improved enzymatic catalysis have been discussed. The major bottlenecks in the bioprocessing of lignocellulosic biomass using microbial enzymes and future prospects have also been summarized.

Keywords: circular bioeconomy; lignocellulosic biomass; pretreatment; lignocellulolytic enzymes; solid state fermentation; enzyme immobilization

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1. Introduction

The world's population is increasing at an exponential rate, with 8 billion recorded towards the end of 2022, and is expected to grow by more than one billion people within the coming 15 years, reaching 8.5, 10, and 11.2 billion in 2030, 2057, and 2100, respectively [1–3]. With regard to environmental issues and food security, the Sustainable Development Goals are facing urgent challenges due to uncontrolled global population growth [2]. Moreover, massive anthropogenic activities have risen at an alarming rate, resulting in grave environmental concerns including dwindling of fossil fuels, climate change, global warming, waste disposal, pollution, etc. [4,5]. As a consequence, the global research focus has shifted to discovering alternative renewable natural resources which have a

potential to address the energy crisis with limited effects on the environment. However, in order to utilize natural resources to supply the demand for food and energy, the "take, make, use and throw" paradigm has become a prevalent practice worldwide [6]. The largest producers of waste, which primarily consists of lignocellulosic waste, are the agriculture and agro-food processing industries. According to estimates, agro-food industries lose about 30% of the world's total food production [7]. Additionally, every year, almost 1.3 billion tons of food is wasted, which is about one third of global production [6]. Therefore, for sustainable development a change in policy is required towards the implementation of the 5R principles, including reduce, reuse, recycle, recovery, and restore, which contribute to the process of circular bioeconomy. Circular bioeconomy involves the flow of bio-waste of one industry to act as the raw material for another industry for the production of value-added products, and provides a rational waste disposal strategy for a systemic approach towards economic development [8].

Profusely present lignocellulosic biomass (LB) may serve as an intriguing substitute to non-renewable natural resources to produce energy in a viable way [9]. Tons of lignocellulosic biomass in the form of agro-industries, crop waste, weed biomass, and plant waste are generated annually worldwide. This biomass is either burnt causing air pollution or dumped in the landfills [6,10]. Nevertheless, a "waste to use" program can be applied wherein LB, which is rich in carbohydrates such as cellulose (32–54%), hemicellulose (11–37%), and non-carbohydrate polymer lignin (17–32%) can be exploited for generating multiple value- and energy-added products, viz., biofuel, organic acids, bioplastics, hydrogels, vanillin, resins, etc. [5,11]. Cellulose, lignin, and hemicellulose are linked together in an intense complex bonding that provide the plant cell wall with a rigid and tough nature, which therefore are not easily accessible for value addition. The production of valuable biochemicals from LB involves the extraction of a particular biopolymer, followed by its breakdown and subsequent conversion into the desired product [12]. However, the natural recalcitrance of LB and high processing cost impedes the extraction and conversion process [13,14]. Numerous physical, chemical, biological, or integrative methods have been tested to break down lignocellulosic biomass and reduce its inherently rebellious nature [5,12–16]. However, most of the physical, chemical, or physicochemical pretreatment strategies are very energy and cost intensive, and may result in the production of inhibitory products, restricting the upscaling of the biomass processing. On the contrary, the LB valorization by biological methods is an environmentally benign approach which involves the use of different lignocellulolytic enzymes from different microorganisms [17,18]. Enzymes are regarded as "green" industrial chemicals with a wide array of industrial applications and can be employed in environmentally friendly bioprocesses [19]. Diverse lignocellulolytic enzymes such as cellulases and hemicellulases attack and break down cellulose and hemicellulose into simpler sugars for subsequent conversion into different products, whereas ligninolytic enzymes break down lignin into different aromatic compounds [18]. Moreover, various auxiliary enzymes, such as glucose oxidase, aryl alcohol oxidase, glyoxal oxidase and gluco-oligosaccharide oxidase, aid in enhancing the activity of peroxidases and promote lignin disruption, while lytic polysaccharide monooxygenases play a role in the degradation of crystalline cellulose (Figure 1). The enzymatic conversion of lignocellulose offers the advantage of being highly specific and cost effective with minimal or no production of inhibitors [20]. Numerous variables, including the source of the enzyme, the substrate, and the amount and type of enzymes involved, influence the reaction rate of enzymatic hydrolysis and overall effectiveness in the degradation of lignocellulosic biomass [18].

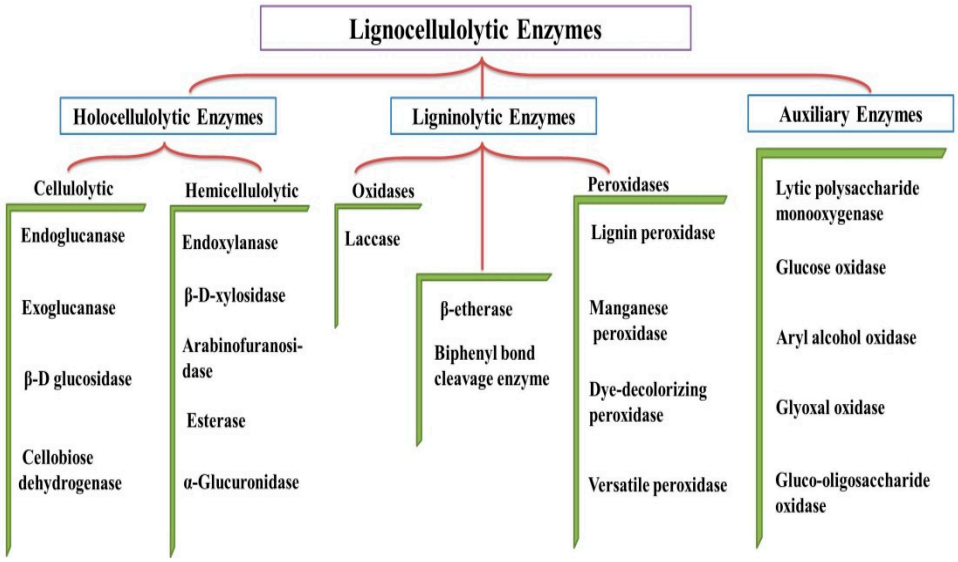

Figure 1. Different lignocellulolytic enzymes involved in the degradation of lignocellulosic biomass.

Lignocellulolytic enzymes' production source, mode of production/fermentation, and ability to recover and reuse enzymes are also major factors which govern the efficacy of the conversion process. Although LB-degrading enzymes are produced by various species of fungi, bacteria, and plants, fungal enzymes have gained commercial importance owing to their ability to produce extracellular and robust enzymes. Mycelial proliferation and an active enzymatic system are thought to be the causes of fungi's capacity to break down lignocellulosic biomass [17]. The cost-effective microbial fermentation for enzyme production also impacts the overall economy of the process. In this regard, solid state fermentation (SSF) has been widely recognised as a promising technique for the production of LB-degrading enzymes. SSF offers prospects for increased fermentation efficiency, increased end product concentrations, enhanced product stability, decreased catabolic suppression, cultivation of water-insoluble substrates, or integrated agriculture of several fungal species [18,21]. Another crucial factor which determines the cost effectiveness of the conversion process is the ability to recover and reuse lignocellulolytic enzymes owing to their high production cost. Enzyme immobilization is a promising technique to make the process cost effective and increase the usability of enzymes [22]. Immobilization aims to increase various properties of enzymes including their stability in extreme environments while improving the enzyme efficacy [23].

Considering all the aforementioned areas, this review discusses various lignocellulolytic enzymes which are involved in the degradation of LB and their mode of action. The present review also summarizes various microbes including fungi and bacteria which are known to be the producers of LB-degrading enzymes. Moreover, the importance of SSF and immobilization have also been highlighted in the current review article.

2. Lignocellulolytic Enzymes

Lignocellulosic biomass is abundantly present around the globe and is the cheapest and most promising bioresource for the production of value-added chemicals and metabolites [16,20,24]. LB is broadly categorized into agricultural waste, energy crops, softwood, hardwood, weed biomass, etc., and comprises three main components, viz., cellulose (35–50%), lignin (15–30%), and hemicellulose (20–35%) [5,25]. A protective layer of lignin covering the polysaccharides leads to biomass recalcitrance, which is described as the molecular and chemical resistance of biomass to enzymatic or microbial breakdown of cellulose and hemicellulose [26,27]. Additionally, lignin is known to hinder the efficient enzymatic saccharification of biomass by binding to saccharification enzymes ineffectively and non-specifically, hence reducing the amount of enzyme available for hydrolysis [28]. The main

obstacle to the effective use of LB for the production of valuable chemicals is its recalcitrance, which might be overcome by using an effective pretreatment method [6,24,29]. Pretreatment reduces the lignin content and aids in decreasing biomass recalcitrance [12,30]. Post pretreatment, the hydrolysis of LB constituents is a key step in the production of various biochemicals, which is carried out by lignocellulose-digesting enzymes. These enzymes are essential for the transformation of extremely complicated matrices into sugars that may be used for the production of a wide range of chemicals and products with high industrial importance [20]. Lignocellulose-degrading enzymes mainly include cellulases, hemicellulases, and ligninolytic enzymes. Cellulases and hemicellulases break down cellulose and hemicellulose into simpler sugars which can be used for the production of various products such as biofuels (bioethanol, biodiesel), hydrogels, biofilms, drug delivery coatings, organic acids, etc. [5]. Lignin, which was earlier considered as a hindrance in LB biorefineries, in recent times have been used to develop various products such as bioplastics, vanillin, carbon-based nanomaterial, etc. [31]. A variety of ligninolytic enzymes are used for the hydrolysis of lignin and its conversion into useful products [32].

The enzymes required for LB breakdown into simpler forms are categorized as carbohydrate-active enzymes (CAZymes) in the carbohydrate active enzyme database [33]. The CAZy database provides online access to the family categorization of CAZymes in a constantly updated form [34,35]. The discovery of new CAZymes can be performed using the omics technology such as metagenomics, proteomics, and transcriptomics that eliminate the need for isolation and culturing of the microorganisms for enzyme production. A metagenomic investigation of an enriched rumen consortium derived from sugarcane bagasse by Tomazetto et al. [36] revealed 41 metagenome-assembled genomes, several of which contained CAZymes and had little sequence similarity to known sequences. In a different study, the CAZyme from *Parascedosporium putredinis* NO1 growing on wheat straw was identified using a combined transcriptomics and proteomics approach [37]. As a result, a wide range of CAZymes were discovered, including esterases, hemicellulases, multicopper oxidases and lytic polysaccharide monooxygenases. However, the majority of new enzyme discoveries to date have been based on sequence similarity, which prevents the discovery of novel enzymatic activities that have only slight similarities to already known analogues. Therefore, the search for novel enzymes must be better directed, and computational/bioinformatics methods are required to aid in the identification of potential research targets.

2.1. Cellulase

Cellulose is a linear homopolymer formed by the repeated β-D-glucopyranose units which are linked together by β, 1 → 4 glycosidic bonds [38,39]. The strength and stability of plants is due to the cellulose chain aggregation that spontaneously forms cellulose microfibrils in plant cell walls [11]. Depending on the plant species, the degree of polymerization of cellulose might range from 500 to 15,000 glucose units [27]. Van der Waals forces and inter- and intramolecular hydrogen bonds strengthen the parallel arrangement of cellulose with microfibrils, which makes up crystalline cellulose. These linkages are weaker in amorphous cellulose and result in a less ordered arrangement of the cellulose molecules, making it hydrolyze 3–30 times easier than crystalline cellulose [27,31]. The paracrystalline structure of cellulose is made up of both amorphous and crystalline regions that are connected by β-1,4 glycosidic linkages [40].

Cellulases are a group of hydrolysing enzymes that belong to the O-glycoside hydrolases family and hydrolyse β-1,4 glycosidic bonds in cellulose to produce glucose, cellobiose, and cellooligosaccharides as major products [27]. These are classified as CAZymes, having functional domains that may bind to carbohydrates and change, degrade, or create glycosidic linkages. Cellulases are categorised on the basis of their catalytic mechanism of action and include endoglucanases, exoglucanases, or cellobiohydrolases (CBH) and β-glucosidases. They function simultaneously and synergistically as a multifaceted machinery based on internal bonding in cellulose as shown in Figure 2 [27,41]. Depending upon

the enzymes involved, there can be four different types of synergism: endo-exo synergy between endoglucanases, and CBH-I (reducing end cellobiohydrolase) and CBH-II (non-reducing end cellobiohydrolase); exo-exo synergy between CBH-I and CBH-II; synergy between CBH-I and CBH-II, and β-glucosidases; as well as intramolecular synergy between catalytic modules and carbohydrate-binding modules (CBMs) [42]. They work together to hydrolyze cellulose in a two-stage process. The first stage involves the breakdown of the cellulose substrate by endoglucanases and exoglucanases, which releases complex structured sugars into the liquid phase with up to six degrees of polymerization. This is followed by a second stage wherein β-glucosidase cleaves cellobiose to glucose [20]. The three-dimensional structure of over 50 cellulases are reported, and exhibit a range of topologies, including all β-sheet proteins, β/α-barrels, and all α-helical proteins [43]. One or more CBMs which are non-catalytic proteins associated with the catalytic domain (CD) are frequently present in cellulases that facilitate the binding of the enzyme to the substrate. CBM binds to oligo- and polysaccharides [44]. These three enzymes, viz., endoglucanases, cellobiohydrolases, and β-glucosidases are produced by many bacteria and fungi. However, lytic polysaccharide monooxygenases and cellobiose dehydrogenases are also produced by fungi that act on cellulose [20].

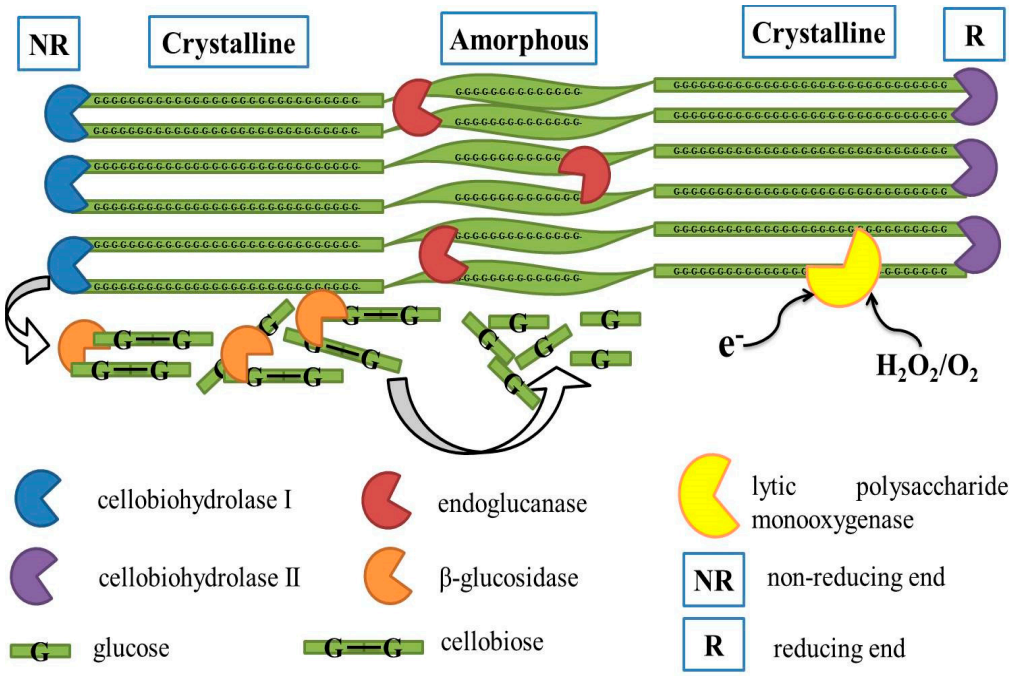

Figure 2. Mode of action of different cellulolytic enzymes for the hydrolysis of cellulose.

2.1.1. Endoglucanase

Endoglucanase (EC 3.2.1.4), a member of the parent glycosyl hydrolase (GH) family that has been categorized based on amino acid residues and three-dimensional structure, plays a crucial part in the biodegradation process [45]. Also known as endo-1,4-β-D-glucan glucanohydrolases, endoglucanase initiates the enzymatic breakdown of cellulose to reduce its degree of polymerization. They randomly act on β (1,4) glycosidic bonds in the internal amorphous areas of cellulose chains to produce oligosaccharides [27,46]. With both inverting and retaining the catalytic mode of action depending on the distance between two carboxylic groups, endoglucanases are distributed among 13 GH families and most thermostable endoglucanase belong to the GH12 family [45]. Endoglucanases are produced by numerous organisms ranging from bacteria, both anaerobic and aerobic, fungi, archaea and protozoa. However, for commercial applications, fungi are used for the production of these enzymes including *Trichoderma* and *Aspergillus* sp. [20].

2.1.2. Exoglucanase

Exoglucanases (EC. 3.2.1.91) or cellobiohydrolases (CBH) include CBHI and CBHII which act on the reducing and non-reducing ends of the cellulose chain, respectively, to produce cellobiose and a meagre quantity of cellotriose [27,47,48]. About 70% of the cellulases released by cellulolytic fungi are exoglucanases and among them CBHs are the most widely studied exoglucanases belonging to GH 6 and 7, as well as 48 families [48]. Cellobiose is produced at the reducing end of the cellulose chain by exoglucanases, primarily from glycoside hydrolase families 7 and 48, whereas exoglucanases from the GH6 family mainly produce cellobiose from the non-reducing end of the chain [47]. Cellobiohydrolases are produced by a wide range of bacteria and fungi, however, CBHs belonging to GH family 7 are produced by fungi and bacteria mostly produced by GH family 48 CBHs. Efficiently breaking down microcrystalline cellulose, cellobiohydrolases are thought to remove cellulose chains from the microcrystalline cellulose structure. CBHs are competitively inhibited by cellobiose [48].

2.1.3. β-D Glucosidase

β-D glucosidase (BGL) or cellobiases (EC 3.2.1.21) carry out the final reaction of cellulose hydrolysis and therefore is the rate-limiting enzyme. They hydrolyze soluble cellodextrin and cellobiose to yield D-glucose units [49]. Owing to the fact that they activate the cellulase enzyme complex by synthesizing gentiobiose and sophorose, β-D glucosidases are essential for the cellulase degradation system [50]. Based on the sequences of their amino acids, BGLs have been grouped into the GH families, GH1, GH3, GH5, GH9 and GH30. Fungal β-D glucosidase belongs to GH family 3 and 1 [49,51]. Additionally, stored glucose reversibly limits BGL action, making the regulation of BGL rather laborious. However, BGL production is also stimulated by glucose and are categorised in GH1 and GH3 families [51,52]. BGLs being the rate-limiting enzymes are highly important for the production of biofuel and to prevent catabolite repression on endoglucanase and cellobiohydrolase. However, these are produced in very scanty amount by the microorganisms or even in commercial cellulase. Therefore, in order to form an effective cellulolytic cocktail, the augmentation of BGL to the enzyme cocktail is ineluctable and may result in increased sugar yield [51].

2.1.4. Cellobiose Dehydrogenase

Cellobiose dehydrogenases (EC 1.1.99.18) are extracellular enzymes produced by white-rot fungus containing two cofactors, heme and flavin, in separate domains [53]. A flexible proteolysis-sensitive linker connects a flavodehydrogenase domain bearing a non-covalently bonded FAD cofactor to a heme having a cytochrome domain [54]. Cellobiose dehydrogenases function in synergy with lytic polysaccharide monooxygenases. This intramolecular interaction, which has been studied from a structural and mechanistic perspective, entails electron transfer from the flavin domain, where cellobiose is oxidized to cellobionolactone with the assistance of catalytic histidine and other residues in the heme domain [53].

2.1.5. Lytic Polysaccharide Monooxygenase

Lytic polysaccharide monooxygenases (LPMO) (EC 1.14.99.54), a new class of enzymes, are copper-containing reductases that play a vital role in cellulose degradation and perform synergistically with cellulases. They use an oxidative method to break down cellulose, which involves electron donors and molecular oxygen [27,53]. In order to activate the molecular oxygen in its copper-containing active site, LPMO needs a reducing substrate [20]. The reduction of a catalytic cupric ion, which has a methylated terminal histidine and a tyrosine as ligands, is necessary for the action of a few fungal LPMO. This activation can be achieved by the use of an artificial reductant such as ascorbic acid that reduces Cu^{2+} to Cu^{+}, subsequently reacting with O_2 to form a responsive copper-

superoxide complex. This reaction facilitates oxidative degradation of crystalline carbohydrate chains via monooxygenase activity [53]. The generation of aldonic acid and the breakdown of cellulose are the results of oxidation at the level of the C1 carbon or, in some fungi, the C4 carbon of glucose molecules on cellulose [55]. Some reports have also suggested that hydrogen peroxide (H_2O_2) is a favored co-substrate of LPMOs, rather than O_2 for cellulose oxidation [56]. LPMOs can operate without oxygen while controlling the supply of H_2O_2, where monocopper enzymes can catalyze the biochemical reactions. Kont et al. [57] compared the reference enzymes and LPMOs for the H_2O_2 co-substrate for the characterization of LPMO-catalyzed cellulose oxidation. Their study suggested that the bacterial and fungal LPMOs exhibited high peroxygenase efficiencies compared to the reference enzymes.

LPMO are now classified as the family of auxiliary activity (AA) enzymes including fungal enzymes (AA9, AA11, AA13, AA14, AA16, AA17), bacterial enzymes (AA10), and enzymes from arthropods and oomycetes (AA15) [58,59]. AA9 mainly breaks down cellulose and hemicelluloses, including glucans, xylan, xyloglucans and pectins. AA11 and AA13 specifically act on chitin and starch, respectively. The cellulose oxidation is specifically carried out by AA16 and the xylan breakdown is performed by AA14 [60]. All of these enzymes are produced by aerobic organisms and are absent in anaerobic organisms [27,55].

Cellulases have huge potential in different biotechnological applications and are extensively used in many industries including biofuels, alcohol, wine, textiles, animal feeds, food, juices and pulp [39]. The exploration of cellulases from different sources has been boosted by their potential use in the biofuel production chain, especially given that the market for biofuels is anticipated to expand over the coming years and supplant 30% of petroleum fuels by 2025 [61]. Cellulase is the second most significant enzyme among the carbohydrases used to make second generation biofuels, only after amylases which are used for first generation biofuel production [40]. One of the earliest cellulolytic microbes discovered was *Trichoderma reesei* in the 1950s [62]. At the commercial scale, *Trichoderma reesei* is the leader in the enzyme sector for the production of cellulase cocktail [49]. *Penicillium* spp. and *Aspergillus* spp. are also used for industrial cellulase production [63].

2.2. Hemicellulases

Hemicellulose is a heteropolymer and the second most prevalent polysaccharide in the plant cell wall [27]. It is heterogeneous, branched, and amorphous in character, and by encircling the cellulose microfibrils, it gives the plant structural endurance. The primary purpose of hemicellulose is to inhibit microbial degradation by attaching packages of cellulose to microfibril and covalently crosslinking lignin via diferulic acid bridges and lignin-glucuronic acid ester links to establish structural endurance [11,31]. The simple sugars D-xylose, D-arabinose, and D-mannose (pentoses), as well as D-glucose, D-galactose, and D-galactose (hexoses), are all present in hemicellulose, with xylose serving as the predominant sugar [27]. Uronic acids such as d-galacturonic, d-glucuronic, and methylgalacturonic are also present in hemicellulose [5,27]. Covalent and hydrogen bonding are involved in the linking of polymers that make up hemicellulose together. It forms a close link between cellulose and lignin by binding to lignin via aromatic esters and to cellulose by hydrogen bonds. Moreover, hemicellulose has a hydrophilic and hygroscopic characteristic [64]. The chemical makeup of hemicellulose in LB differs depending on the kind of plant, with hardwood or angiosperms containing largely xylans and softwood, or gymnosperms, primarily glucomannans [65].

The breakdown of hemicellulose is mediated by a number of enzymes, the majority of which are hydrolytic and function similarly to cellulolytic enzymes [20]. The primary chain of xylan is attacked by the xylanase endoenzymes, which reduces the substrate's ability to polymerize by hydrolyzing the β-d-xylopyranosyl links and releases xylobiose, xylooligosaccharides, and xylose [66,67]. The exoenzymes, β-xylosidases, begin a progressive disintegration process after the xylanase action is completed, commencing from the

non-reduced extremes of the xylooligosaccharides and producing xylose as the end product [68,69]. Xylan and glucomannan-specific enzymes have received the greatest attention among hemicellulose-active enzymes. Broadly, hemicellulolytic enzymes include those which hydrolyze the main chain, viz., endo-β-1,4-xylanases (xylanases), endo-β-1,4-mannanases (mannanases), and debranching enzymes which aid in the removal of substitutions from the polysaccharide backbone such as deacetylases, arabinosidases, and galactosidases [70].

2.2.1. Endoxylanase

Endoxylanases break β-1,4 glycosidic linkages in the xylan backbone of hemicellulose [20]. Endo-1,4-beta-xylanase (EC 3.2.1.8) breaks down xylan to produce xylooligosachharides, whereas endo-1,3-beta-xylanase (EC 3.2.1.32) produces xylobiose, xylotriose, and xylotetrose by hydrolysing glycosidic bonds between xylans at carbon 1 and 3. The terminal residues of non-reducing alpha-D-xylose are hydrolyzed by α-D-xyloside xylohydrolase (EC 3.2.1.177), which releases α-D-xylose [20,71,72]. During hydrolysis, the degree of branching, chain length, and the presence of substituents in hemicellulose all influence which bonds are chosen for attack during the hydrolysis of xylan, rather than being chosen at random [73]. Endoxylanases are classified into glucohydrolase families 10 and 11. GH10 endoxylanases typically have the ability to utilize smaller substrates and produce xylose whereas GH11 enzymes preferentially target longer xylan chains and do not yield xylose [66,74]. Different organisms, viz., bacteria, fungi, archaea, marine algae, protozoans, etc., are capable of producing xylanases, however, for commercial applications, xylanases from filamentous fungi are mostly reported [74].

2.2.2. β-D-Xylosidase

β-D-xylosidases (EC 3.2.1.37) act on the non-reducing end from xylooligosaccharides such as xylose residues. Following the progressive hydrolysis of xylan by xylanases, β-xylosidases play a crucial role by converting short oligomers into monomers. The suitable substrate for these enzymes is xylobiose and the affinity of oligosaccharides is inversely correlated with degree of polymerization [73,75]. β-xylosidases mainly belong to the GH3 family. All β-xylosidases, despite their three-dimensional structural variations, contain a characteristic pocket-shaped active site which is negatively charged due to the presence of acidic residues, and also holds hydrophobic patches of aromatic residues [76]. The catalytic activity of most of the β-xylosidase is competitively inhibited by its product xylose when p-nitrophenyl-β-d-xyloside (pNPX) is used as a substrate [76].

2.2.3. Arabinofuranosidase

Arabinofuranosidases or arabinases produce arabinose with exo- and endomodes of action from polysaccharides/arabino-oligosaccharides or from synthetic substrates [73]. In oligo- and polysaccharides containing arabinose, α-l-arabinofuranosidases (E.C. 3.2.1.55) cleave α-1,2-, α-1,3-, and α-1,5- l-arabinofuranosyl residues from non-reducing ends [77]. α-Arabinofuranosidases are also known to remove 4-O-methyl glucuronic acid substituent from xylan [75]. Glycoside hydrolase families GH30, GH43, GH51, GH54, and GH62 contain arabinofuranosidase with GH62 being the only family which is composed solely of arabinofuranosidases [73,77]. Arabinofuranosidases are categorized into three different types. The enzymes in type A category predominantly act on ϱ-nitrophenyl-α-l-arabinofuranoside and arabino-oligosaccharides; type B hydrolyzes arabinoxylan to produce xylose and l-arabinose; and the third type, known as 1 → 4-β-d-arabinoxylan arabinofurano-hydrolase, is extremely specific for arabinosidic linkages in various arabinoxylans, with the release of l-arabinose. Moreover, the third type is inactive on many synthetic substrates [77].

2.2.4. Esterase

Acetyl xylanesterase (E.C. 3.1.1.72) cleaves acetyl-ester linkages between acetic acid and xylose units of xylan to produce o-acetyl groups [20]. The acetyl groups from polymeric acetylated xylose, xylan, acetylated glucose, p-nitrophenyl acetate and α-napthyl acetate are hydrolyzed by the enzyme, while acetylated mannan and pectin remain unaffected [20]. Ferulic acid esterase (E.C.3.1.1.73) is another esterase which is known for removing ferulic acid from O–5 of arabinose of glucuronoarabinoxylan in monocots via breaking feruloyl ester bonds with xylan [75,78]. Acetoxylan esterases are classified into different carbohydrate esterase (CE) families (CE1–7, 16) and have a strong specificity for O-acetyl-4-O-methyl-D-glucurono-D-xylan [78]. Except for acetoxylan esterase assigned to CE4, the majority of acetoxylan esterase universally exhibit acetyl esterase activity [79]. Few feruloyl esterases are classified into the CE1 family along with other esterase. Glucuronoyl esterases are newly discovered esterases which catalyze the hydrolysis of ester bond between 4-O-methyl-D-glucuronic acid residues and lignin in lignin-carbohydrate complexes (LCCs) and belong to the CE15 family [78].

2.2.5. α–Glucuronidase

α-Glucuronidases (E.C.3.2.1.131) hydrolyze α-1,2-glycosidic bond between D-glucuronic acid or its 4-O-methyl ether and non-reducing end xylopyranosyl unit of small xylooligosaccharides [73]. Glucuronidases belonging to the GH67 family are usually produced intracellularly or are membrane associated and preferably act on short glucuronic acid substituted xylooligosaccharides, whereas glucuronidases from the GH115 family are extracellular and more effective on polymeric glucuronic acid-containing xylans [80].

Among all different hemicellulases, xylanases are of most importance due to a high content of xylan in the hemicellulose. It is anticipated that by 2023, the xylanase industry will have a 500 million USD market demand, up from the current estimate of 200–300 million USD [81,82]. Apart from their application in lignocellulosic biorefineries, they are widely used in feed and food industries such as poultry, baking, coffee extractions, functional foods and agriculture silage. Xylanases are also used at a large extent in the paper and pulp industry commercially. Geographically, the world's xylanase market is shared by five major geographical areas: Latin America, North America, Asia-Pacific, Europe, and Africa [82]. A number of different bacterial, yeast, fungal and actinomycetes species have been explored for xylanase production [73].

2.3. Ligninolytic Enzymes

Lignin, the second amplest heterogenous polymer after cellulose, comprises three aromatic alcohols, coniferyl, p-coumaryl, and sinapyl alcohol, connected via C-C and aryl ether bonding [5,83]. The amount of these three units varies depending on the plant species and isolation method. The lignin percentage is higher in softwood and lower in hardwood. Moreover, coniferyl alcohol makes up around 90–95% of the lignin in softwood, whereas coniferyl and sinapyl alcohols make up about 25–50% and 50–75%, respectively, of lignin in hardwood. All three monomer alcohols are usually present in lignin from grass [27]. These aromatic alcohols use free radical polymerization to form three equivalent phenylpropanoid monomeric units, namely guaiacyl unit, p-hydoxyphenyl unit, and syringyl unit. These units contain phenolic groups which serve as the primary substrate for enzymatic action [20,27]. The various lignin monomeric units are linked together via a series of condensed C–C (β-5′, 5–5′, β-β, β-1) and non-condensed C–O–C (β-O-4) ether bonds. The β-O-4 linkages are more prone to enzymatic hydrolysis as compared to C–C linkages [84].

Ether linkages, which account for at least 56% of all linkages in the lignin polymer, are the most prevalent type of linkage. Moreover, the percentage of linkages also varies among different plant species owing to the variation in the amount or ratios of the monomeric units. β-O-4 linkages are predominant, accounting to about 50% and 60% of all

linkages in softwood and hardwood, respectively. Owing to the abundance of β-O-4 linkages, hydrolysis of the β-O-4 ether bond is regarded as a crucial step in the depolymerization of lignin [83]. The association of lignin with cellulose and hemicellulose is favored by covalent, hydrogen, and ester bonding [27]. Lignin is the primary cause of the recalcitrance of LB due to its complex, amorphous, hetero-polymeric structure, which is resistant to breakdown [27]. The biological depolymerization of lignin requires the action of various enzymes, owing to the complex and different linkages in the lignin structure, and some of them are explained below.

2.3.1. Laccase

Laccases (EC 1.10.3.2) are multicopper oxidases produced by bacteria, fungi, and plants. They oxidize the substrate by transfer of electrons from a mononuclear copper center to a trinuclear copper center [20,85]. The laccase holoenzyme is made up of dimers or tetramers glycoprotein with four copper atoms per monomer coupled to the type 1, type 2, and type 3 redox sites [75]. The redox potential of laccases falls in the range of 0.4–0.8 V vs. normal hydrogen electrode. They use copper's redox capacities to oxidize aromatic compounds [20,83,86]. The unstable intermediate phenoxyl free radical is produced when laccase oxidizes phenolic substrates, and it then encourages Cα oxidation and polymer cleavage such as Cα-Cβ and alkyl-aryl cleavage [83,85]. Laccases are capable of hydrolyzing a variety of substrates such as diphenols, polyphenols, aliphatic and aromatic amines [75]. Although laccases are mostly known to act on phenolic compounds, they can also hydrolyze non-phenolic compounds using mediators. In combination with mediators, the oxidized non-phenolic substrates can facilitate β ether cleavage, aromatic ring cleavage, Cα-Cβ cleavage, and Cα oxidation [85]. Mediators such as 3-hydroxyanthranilic acid (HAA), 1-hydroxybenzotriazole (HBT), and 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate) are small low molecular-weight molecules with electron transfer ability. They aid in overcoming the steric hindrance between enzyme and substrate by assisting laccase to form a steady intermediate with the substrate, thereby enhancing the oxidation potential of laccase [20,83,85]. It has been reported that with the help of mediators, laccase can break down roughly 80–90% of the lignin. White-rot fungus is one of the main known laccase producers [83].

2.3.2. Manganese Peroxidase

Manganese peroxidases (EC 1.11.1.13), a glycosylated heme protein, oxidizes Mn^{2+} as a reducing substrate to generate Mn^{3+} ions that form bonds with dicarboxylic acids and alpha hydroxy acids [20,83]. Depolymerization of lignin by manganese peroxidases involves both oxidation and reduction steps. The catalytic cycle is initiated by manganese peroxidase which aids in the binding of hydrogen peroxide (H_2O_2) to the native ferric enzyme. This is followed by oxidation of Mn^{2+} to Mn^{3+} in the presence of chelators. Since the Mn^{3+} is a potent oxidant, it diffuses from the enzyme and oxidizes phenolic components in lignin to phenoxy radicals which cause lignin depolymerization. The organic acid chelators such as oxalate and malonate assist in enhancing enzyme activity and stabilizing Mn^{3+} [83,85]. Manganese peroxidases play a crucial part in lignin degradation during the early phase and, owing to higher redox potential than laccase, they degrade phenolic compounds in lignin to a better extent [87].

2.3.3. Lignin Peroxidase

Lignin peroxidases (EC.1.11.1.14) are glycosylated enzymes which contain a heme cofactor in the active center with an iron protoporphyrin prosthetic group [87]. These enzymes can act on both phenolic and non-phenolic compounds without the assistance of any mediator due to high redox potential and production of cation radicals [75,87]. Lignin peroxidases are dependent on hydrogen peroxide for initiating the catalysis of phenolic and non-phenolic substrates. Veratryl alcohol also aids in the action of these enzymes due

to its role as an electron donor and cofactor [83]. Commonly, the catalytic cycle of these enzymes is divided into three steps: first oxidation, followed by two steps of reduction. Initially, lignin peroxidases catalyze the reduction of H_2O_2 to water and oxidation of ferric [Fe (III)] to form oxoferryl iron porphyrin radical cation [Fe (IV)=O$^+$]. Then, in the next two consecutive one-electron reduction steps, [Fe (IV)=O$^+$] is converted to two [Fe (IV)=O] [85].

2.3.4. Dye-Decolorizing Peroxidase

Dye-decolorizing peroxidase, DyP (EC 1.11. 1.19), is another heme-based peroxidase that can degrade lignin via an oxidation process mediated by radicals. These recently discovered peroxidases, although different from other class II heme peroxidases in structure and sequence, possess similar H_2O_2 and mediator-dependent catalytic mode of action for degradation of lignin [87,88]. In contrast to other peroxidases that are primarily found in fungi, these are broadly distributed in a variety of bacteria. These enzymes have the ability to decarboxylase non-phenolic lignin-related substrates and produce p-anisaldehyde as a main product [83,89]. There are four classes, viz., type A, B, C and D, known for these enzymes which are categorized on the basis of sequence differences. Bacteria commonly produce type A, B, and C, while fungi primarily make type D. Type A and B are small and possess lower catalytic activity whereas type C and D are similar and exhibit higher activity for substrate oxidation [83].

2.3.5. β-Etherase

β-etherase, glutathione-dependent enzymes, are involved in lignin degradation by catalyzing the reductive hydrolysis of β-aryl ether linkages which is achieved via glutathione attack at the β position of an α ketone group containing an oxidized aryl unit [90]. The depolymerization of lignin can be accomplished with high efficiency by the β-etherases implicated in the β-O-4 ether and biphenyl catabolic pathways [85]. Since β-O-4 ether linkages are the most prominent linkages in lignin, the hydrolysis of these linkages is crucial and achieved by a group of enzymes involving Cα-dehydrogenase, β-etherase, and glutathione-S-transferase. Initially, the oxidation of hydroxyl group at Cα position in lignin takes place by the action of Cα-dehydrogenase LigD, followed by the action of either LigE or LigF β-etherase, which cleaves β-O-4 ether bond to produce intermediate products vanillin and α-glutathionyl-β-hydroxypropiovanillone (GS-HPV). In the final step, oxidation of GS-HPV occurs, catalyzed by glutathione-S-transferase LigG. After the glutathione is broken down, the residual hydroxypropiovanillone could be further oxidized to vanillin [83,91].

2.3.6. Biphenyl Bond Cleavage Enzyme

Apart from β-O-4 aryl-ether bonding, the biphenyl bonding is another major linkage in lignin that accounts for around 10% linkages in softwood lignin [85]. These linkages most commonly occur between two guaiacyl units. During the hydrolysis of 5, 5′-dehydrodivanillate, action of non-heme, iron-dependent demethylase enzyme LigX results in the demethylation of one methoxy group and the production of hydroxyl group. This product then acts as a substrate for oxidative breakdown by the LigZ (extradiol dioxygenase). Subsequently, LigY (C–C hydrolase) breaks the ring fission product to form to 5-carboxyvanillic acid and 4-carboxy-2-hydroxypentadienoic acid. In the final step, two decarboxylases, i.e., LigW and LigW2 converts 5CVA to vanillic acid or vanillate [92]. The hydrolysis of bi-phenyl linkage has been proven to encourage degradation of lignin.

3. Microbial Production of Lignocellulolytic Enzymes

Lignocellulolytic enzymes are the extracellular biocatalysts which are involved in the complete fractionation of lignocellulose. In nature, lignocellulolytic enzymes can be found in a wide variety of creatures, including microbes, insects, and plants. However, due to the economic advantages, microbial enzyme production has received the most attention

[18]. The study of the microorganisms involved in the synthesis of these enzymes has focused particularly on the quantity and variety of enzymes produced under their ideal growing conditions. Microorganisms present freely in nature or in the animals' digestive tract can possess the ability to breakdown lignocellulosic biomass [18]. Table 1 represents different bacterial and fungal species that are reported to produce lignocellulolytic enzymes for degradation of LB. However, fungal enzymes have more exciting features than bacterial enzymes for degradation of lignocellulosic biomass [17]. Fungi and their enzymes possess few advantages over bacterial enzymes, viz., extracellular enzyme production, easy recovery, robust to extreme environmental conditions, ability to utilize agro-industrial waste for growth, biodiversity, high enzyme yield, and production of auxiliary enzymes [66].

3.1. Fungal Lignocellulolytic Enzymes

Wood-degrading fungi are primarily in charge of lignocellulose degradation. Owing to their extremely adapted lives, which are evidenced by a significant phylogenetic and phenotypic diversity, they are able to degrade and assimilate even the most resistant organic polymers. The fungi engage a diverse array of extracellular enzymes to reduce the physical and chemical stability of lignocellulosic biomass [93]. The fungal systems have two different types of degradation systems: extracellular, crucial for polysaccharide degradation, and intracellular, associated with the outer cell envelope layer. Additionally, there are two different kinds of enzymes in the extracellular enzymatic system: hydrolytic enzymes, which break down polysaccharides, and oxidative enzymes, which break down lignin and open phenyl rings [94]. Three different kinds of fungi, i.e., brown-rot, white-rot, and soft-rot fungi have been described, each having distinct effects and processes for degrading lignocellulose [20].

3.1.1. Soft-Rot Fungi

Soft-rot fungi are ascomycetes and deuteromycetes which emerge when the process of brown and white rot has not begun. These are the slow decomposers which hydrolyze polysaccharides in the surface layers of plant biomass and possess an ability to degrade wood in harsh milieu [20,94]. They preferentially degrade cellulose and require fixed nitrogen to produce enzymes such as cellulases, which primarily digest cellulose from the cell wall to create microscopic voids in the secondary cell wall. Moreover, the enzyme laccases and peroxidases produced by fungi degrade lignin in the lignocellulosic biomass, which results in a darkening and softening of the wood [17,20,94]. Although soft-rot fungi have the ability to easily oxidize the syringyl units in lignin, they lack the capability to oxidize fractious guaiacyl lignin despite being the potent producer of extracellular peroxidases and oxidases [17]. Compared to the enzymes from white-rot and brown-rot fungus, these enzymes are less specific and have a smaller range of applications. These belong to genera *Trichoderma, Aspergillus* and *Neurospora* [17,94].

3.1.2. Brown-Rot Fungi

Brown-rot fungi are a member of basidiomycetes and a few ascomycetes species that rapidly disintegrate polysaccharides of lignocellulosic biomass, i.e., cellulose and hemicellulose as compared to lignin [17,95]. These fungi lack exoglucanase and have a different mode of action compared to other fungi since the reduction mechanism for the hydrolysis of complex carbohydrates in the biomass is enzyme independent and certain low molecular weight compounds such as oxalic acid play a vital role [95,96]. Brown-rot fungi follow an iron-dependent Fenton chemistry called the chelator-mediated Fenton system (CMF) for non-enzymatic fractionation of lignocellulosic biomass. The demethylation of lignin is also carried out by these fungi [94,95]. In biofuel production, these fungi are mainly engaged for the pretreatment of lignocellulosic biomass and the subsequent saccharification process to overcome the chemical conversion of complex sugars into monomeric forms

[17]. Several brown-rot fungi have been used for hydrolysis of LB for biofuels and other value-added materials' production. *Serpula lacrymans* was able to produce monosaccharaides and phenol from five different agricultural wastes, i.e., cacao pod, sugarcane bagasse, rice straw, corn leaves and corn cobs. The results depicted that rice straw yielded the highest quantity of total soluble phenols (0.140 mg g^{-1}), while corn leaves produced the highest amount of total reducing sugars (207.37 mg g^{-1}) [97]. The enzymatic hydrolysis of *Eucalyptus globulus* and *Pinus radiate* was shown to be increased by 7% and 11%, respectively, by the basidiomycetous fungus *Laetoporeus sulphurous* [98]. A sequential pretreatment of wheat straw using brown-rot fungi (*Gloeophyllum trabeum*) and white-rot fungi (*Ganoderma lobatum*) resulted in the disruption of hemicellulose and lignin, respectively. The sequential pretreatment effectively yielded a 2.8-fold higher glucose yield than untreated wheat straw [99].

3.1.3. White-Rot Fungi

White-rot fungi fractionate all the three polymers of lignocellulosic biomass, i.e., cellulose, hemicellulose, and lignin. They belong to the phylum basidiomycota, the largest phylum of the kingdom Fungi [94]. Due to their special ability to completely mineralize lignin to CO_2, they can efficiently degrade lignin faster than other organisms including soft-rot and brown-rot fungi and use it as the only source of carbon and energy [17,94]. White-rot fungi produce different enzymes such as lignin peroxidase, laccase, manganese peroxidase and versatile peroxidases for effective lignin disruption [53]. They are categorized into two groups, viz., selective delignifiers and non-selective delignifiers depending on their mode of action and substrates. Selective delignifiers predominantly hydrolyze lignin and hardly impact cellulose and hemicellulose, whereas non-selective delignifiers simultaneously disintegrate all the polymers of LB [100,101]. The property of selective delignifying enzymes that release lignin from intact cellulose has diverted more research attention towards them as compared to non-selective delignifying enzymes [17]. Numerous white-rot fungi have been studied for the conversion of lignocellulosic biomass into various useful products. Pretreatment of radiata pine wood chips with two white-rot fungi, *Stereum hirsutum* and *Trametes versicolor*, yield a cellulose rich biomass and decreased crystallinity to 37% and 44%, respectively, as compared to that of untreated biomass (46%) [102]. An enhanced glucose yield of over 90% was achieved from the wheat straw treated with *Pleurotus ostreatus* in the presence of manganese [103]. A corn stover was pretreated with six different white-rot fungi, viz., *P. sajor-caju*, *T. versicolor*, *C. gallica*, *P. ostreatus*, *P. chrysosporium*, *L. edodes.* The highest lignin degradation, sugar yield, and ethanol yield obtained, respectively, was 38.29%, 71.24%, and 0.124 g/g corn stover biomass after *P. sajor-caju* assisted pretreatment [104].

3.2. Bacterial Lignocellulolytic Enzymes

Biological pretreatment of lignocellulosic biomass for lignin disruption using bacterial enzymes is also reported. Bacteria offer advantages of higher growth rate and metabolic activity over fungi and thus reduce the pretreatment time. Nonetheless, the ability of bacteria to degrade lignin is not as strong as that of the fungal species [101]. It is generally believed that bacteria produce a cluster of ligninolytic enzymes which cleave lignin into smaller aromatic compounds that can be brought into the cell for further aromatic hydrolysis [105]. Various bacterial strains have been stated for the degradation of lignin and mainly include α-proteobacteria, actinomycetes, and γ-proteobacteria [20]. Actinomycetes are the bacteria which grow in the form of filaments and produce many enzymes required for biodegradation. The disruption of the organic substrate by these bacteria is attributed to their morphology which aids them to penetrate and proliferate throughout the organic matter. They are also known to produce extracellular enzymes for the hydrolysis of lignin, cellulose, and hemicellulose [106].

Anaerobic cellulolytic bacteria produce multienzyme complexes called cellulosomes that are used to break down the cell wall polysaccharides of lignocellulosic biomass [107].

Because of their frequency and the significance of the microbial enzymatic approach, cellulosome-producing bacteria have been isolated from a wide range of growth environments. In a study, the disposition of the cell-anchored cellulosome complex of *Clostridium clariflavum* was explored [108]. The results showed that the amount of cellulosome which was visible on the surface of bacterial cells during cell development on wheat straw and microcrystalline cellulose dramatically increased. Shinoda et al. [109] performed the comparative analysis of cellulosomes from *Clostridium clariflavum* DSM 19732 and *Clostridium thermocellum* growing on pretreated rice straw, showing the effectiveness of *C. clariflavum* cellulosome than that from *C. thermocellum*. To better understand the synergistic effect produced by cellulosomal diversity, additional research on the combined effects of cellulosome complexes from various species for substrate breakdown is required.

The laccases produced by bacteria are usually intracellular that occur in monomeric, multimeric, or homotrimeric structure, lacking a carbohydrate group. Laccases are used by bacteria in nature to protect their spores and produce pigmentation [110]. Actinobacteria *Microbacterium phyllosphaerae* and *Rhodococcus jostii* RHA1, α-Proteobacteria *Ochrobactrum* sp., and γ-Proteobacterium *Pseudomonas putida* KT2440 are reported as lignin-degrading bacteria [111]. A study reported lignin degradation of 28.55% from tobacco straw by *Bacillus amyloliquefaciens* SL after degradation of 15 days. The bacteria also exhibited a high titer of manganese peroxidase, lignin peroxidase, and laccase enzymes [112]. Methane production was carried out from microaerobical *Bacillus subtilis* pretreated corn straw. The methane yield was increased after anaerobic digestion of corn straw after microaerobic pretreatment using *Bacillus subtilis* [113]. A total of 20 bacterial lignin degraders were used for delignification and gas production from soil containing 1% pine lignocellulose. *Pseudomonas putida* exhibited enhanced gas release from the pretreated sample [114].

3.3. Lignocellulolytic Enzyme Production from Recombinant Microorganisms

A number of microbial species have been studied for a diverse range of cellulolytic enzymes with stability under extreme conditions. The hurdles related to the secretion of recombinant cellulolytic enzymes from microbial species are the sole obstacles that need to be identified and optimized. The economical valorization of LB, especially via consolidated bioprocessing, has advanced in the recent past due to the cellulase engineering in fermenting microorganisms such as *Saccharomyces cerevisiae* [115]. In a study, a cell-surfaced yeast consortium was developed using a consolidated bioprocessing approach for heterologous expression of active lignocellulolytic enzymes. The results exhibited that synergistic cellulase-xylanase activities and proximity effect considerably enhanced the reducing sugar yield from corn stover biomass [116]. Similarly, the engineered *Bacillus subtilis* secreted xylanase that caused in situ depolymerization of xylan, yielding a maximum xylose of 7.1 g/L which was 66.7% of the total xylose initially contained in 13.3 g/L xylan [117]. Consequently, the use of recombinant cellulolytic enzymes from microbial species is also a crucial factor for the effective implementation and success of lignocellulosic biorefineries.

Table 1. Degradation of different lignocellulosic feedstocks by various fungal and bacterial lignocellulolytic enzymes.

Microorganism	Enzyme	Lignocellulosic Feedstock	Significant Results	Reference
		Fungi		
Aspergillus niger ITV02	Cellulase (β-glucosidase and endoglucanase)	Wheat straw	Glucose yield 24.58 g/L ± 0.08 with a conversion rate of 40.2% ± 0.14; xylose 8.32 g/L ± 0.02 with a conversion rate of 77.54% ± 0.2	[118]

Penicillium aurantiogriseum	Endoglucanase, cellobiohydrolase and β-glucosidase	Corn stover	Methane yield (281 $mL_{N/g}$ oTS);	[119]
Geobacillus sp.	Laccase	Corn stover and bagasse	Corn stover hydrolysis increased by 1.31–2.28 folds (used along with commercial enzymes); bagasse hydrolysis increased by 1.32–2.02 folds (used along with commercial enzymes)	[120]
Trametes hirsuta F13	Laccase and manganese-dependent peroxidase	Beechwood sawdust	63.58 ± 1.47 mg/mL fermentable sugar from 18-days treated substrate	[121]
Aspergillus niger CBS 513.88	Lytic polysaccharide monooxygenases	Rice straw	2.31 times more reducing sugar yield together with commercial cellulase	[122]
Trichoderma asperellum BPLMBT1	Laccase	Sweet sorghum stover	Lignin removal of 76.93%; biohydrogen production 402.01 mL	[123]
P. citrinum LMI01, *Aspergillus* sp. LMI03, *T. reesei* QM9414	(CMCase), Endoglucanase, β-glucosidase and xylanase	Cellulose pulp and cassava peel	Cellulose pulp-hydrolytic efficiency of 93%; cassava peel-hydrolytic efficiency of 78%	[124]
Lentinus squarrosulus MR13, *Trichoderma reesei* Rut C30	Laccase and cellulase	*Saacharum spontaneum* or Kans grass	81.67% delignification and reducing sugar yield of 500.30 mg/g	[125]
Pycnoporus sanguineus MCA 16	Exoglucanase, endoglucanase, β-glucosidase, xylanase, β-xylosidase, manganese peroxidase laccase and lignin peroxidase	Sugarcane bagasse	Glucose yield-7.32 g/L; total phenolic reduction-82.3%	[126]
Marasmiellus palmivorus VE111, *Penicillium echinulatum* S1M29	Laccases, peroxidase, cellulase and xylanase	*Eucalyptus globulus* wood	31% decrease in the lignin content; 10% increase in the glucose yield; 15% increase in xylose yield	[127]
Aspergillus aculeatus PN14	Cellulase and xylanase	*Parthenium hysterophorus*	Reducing sugar yield-213.89 mg/g biomass	[26]
Aspergillus assiutensis VS34	Cellulase and xylanase	Sugarcane bagasse	Total reducing sugar yield-224 mg/g biomass	[30]
		Bacteria		
Ruminiclostridium thermocellum M3	Endoglucanase, exoglucanase, β-glucosidase, and xylanase	Corn straw, corn cobs, rice straw, poplar sawdust	High oligosaccharide yields: corn cobs (77.8 mg/g), corn straw (89.4 mg/g), rice straw (107.8 mg/g), poplar sawdust (52.7 mg/g)	[128]
Chromohalobacter salexigens	Laccase	Almond shell	Delignification efficiency strengthened up to 58%	[129]
Streptomyces ipomoeae (SilA)		Wheat straw	Decreased phenol content by up to 35%	[130]
Acinetobacter sp. B213,	Manganese peroxidase, lignin peroxidase	Corn straw	98.51% cellulose retention rate and 12.02%, lignin degradation rate.	[131]

Micromonospora sp. G7, *Streptomyces* sp. H1, *Saccharomonospora* sp., *Mycobacterium* sp.	Xylanase, CMCase, lignin peroxidase, manganese peroxidase, laccase	Rice straw, corn straw, wheat straw, soybean straw	Degradation ratio increase: cellulose-46.2%, hemicellulose-22.5%, Lignin-28.9%	[132]
Bacillus sp. CX6	Cellulase and xylanase	Wheat straw	Glucose-6.03 ± 0.12 mg/mL and xylose-6.16 ± 0.07 mg/mL	[133]
Cellulomonas sp. CX4	Cellulase and xylanase	Wheat straw	Glucose-2.36 ± 0.06 mg/mL and xylose-2.43 ± 0.06 mg/mL	[133]
Paenibacillus illinoisensis CX11	Cellulase and xylanase	Wheat straw	Glucose-2.56 ± 0.09 mg/mL and xylose-2.64 ± 0.03 mg/mL [133]	[133]
Bacillus cereus CX15	Cellulase and xylanase	Wheat straw	Glucose-3.39 ± 0.19 mg/mL and xylose-3.61 ± 0.03 mg/mL	[133]
Paenibacillus barcinonensis CX17	Cellulase and xylanase	Wheat straw	Glucose-3.97 ± 0.07 mg/mL and xylose-4.2 ± 0.11 mg/mL	[133]
Bacillus ligniniphilus L1	Laccase	Rice straw	Lignin content decrease-8.93%; phenolic content decrease-44.8%	[134]
Thermus sp. 2.9	Laccase	*Eucalyptus*	Reducing sugar- 0.96 ± 0.05 mg/mL	[135]

4. Solid State Fermentation for Enzyme Production

The global enzyme market in different industrial sectors is expected to reach 7 billion USD in 2023. In terms of sales of industrial enzymes, lignocellulolytic enzymes account for more than 20% of global sales owing to their wide application in different industries, viz., biofuel, pharmaceutical, textile, paper and pulp, fruit juice, etc. The production of these commercially important enzymes from microbes can be achieved by exploiting various lignocellulosic wastes as substrate. These substrates favor high microbial growth and thus aid in enzyme production [6,136]. In this regard, solid state fermentation (SSF) is a potential technology utilizing LB for microbial enzyme production. SSF has been used in Asian and Western countries since antiquity, however, Western nations almost completely neglected the significance of SSF, probably as a result of the 1940s discovery of penicillin using submerged fermentation (SmF) technology. Nonetheless, lately SSF has regained a lot of attention due to the growing application of various organic wastes for the production of goods and chemicals with added value [61,137]. SSF is a technique that uses solid particles with an inter-particle continuous gaseous phase as either a substrate or an inert solid support for the growth of microorganisms in the lack or almost absence of free water [138]. Traditionally, the industrial enzymes production used to be carried out by SmF due to easier process control and more bioreactors; however, owing to the multiple advantages of SSF over SmF, the focus has been shifted to enzyme production via SSF. The advantages of SSF over SmF include cost and energy effectiveness, environment friendly, higher enzyme yield, low risk of contamination, less water wastage, minimal degradation of enzymes, shorter fermentation duration, and less susceptible to substrate inhibition issues [136,139]. Both fungi and bacteria are reported for the production of enzymes under SSF but, generally, fungi have been more exploited for the production of enzymes, especially lignocellulolytic enzymes, since fungi prefer low-moisture conditions for growth in a natural habitat. SSF appears to be the most apt strategy to mimic and provide the natural conditions for fungal growth and enzyme production [18,61].

Various LBs such as rice bran, brewer's spent grain, coffee husk, grape pomace, wood chips, oilseed cakes, wheat bran, corn stover and olive pomace have been used as crude substrates for the production of fungal and bacterial enzymes via SSF [136,140]. A study reported the use of brewer's spent grain for the production of cellulase (51–62 U/g) and xylanase (300–313 U/g) enzyme from *A. ibericus* under SSF. Moreover, *A. niger* CECT2088 efficiently produced β-glucosidase (94 ± 4 U/g) using brewer´s spent grain as a substrate

[141]. Laccase production from *Streptomyces ipomoeae* CECT 3341 using wheat straw as a substrate under SSF has been reported [142]. Production of carboxymethyl cellulase has been studied from *Bacillus subtilis* MS 54 using maize bran as a substrate under SSF. A cellulase activity of 14.23 IU/g of maize bran was stated [143]. *Phanerochaete chrysosporium* PC2 was grown under SSF using corn stover as a substrate for the production of different enzymes, including endoglucanase, cellobiohydrolase, β-glucosidase, xylanase, β-xylosidase, mannanase and esterase with 68.6 ± 1.9 U/mg, 13.4 ± 0.1 U/mg, 31.6 ± 0.2 U/mg, 159.7 ± 1.9 U/mg, 8.5 ± 0.3 U/mg, 2.9 ± 0.0 U/mg and 39.1 ± 0.4 U/mg enzyme activities, respectively [140]. Lignocellulolytic enzyme production from various bacterial and fungi sources under SSF has been summarized in Table 2.

Table 2. Microbial enzyme production under SSF using lignocellulosic biomass as a substrate.

Microorganism	Enzyme	Lignocellulosic Substrate	Enzyme Activity	Reference
Coriolus versicolor	Lignin peroxidase, laccase, polyphenol peroxidase, manganese peroxidase, aryl alcohol oxidase and xylanase	Sweet sorghum bagasse	Laccase-115.1 ± 7.1 U/g, Lignin peroxidase-2.86 ± 0.1 U/g, Manganese peroxidase-11.1 ± 1.0 U/g, Xylanase-13.1 ± 0.9 U/g, Polyphenol peroxidase-6.2 ± 0.4 U/g, Aryl alcohol oxidase-3.1 ± 0.2 U/g,	[144]
Aspergillus ibericus	Xylanase, cellulase and β-glucosidase	Olive mill and winery wastes	Xylanase-96.4 U/g, Cellulase-84.2 U/g, β-glucosidase-25.5 U/g	[145]
Aspergillus niger	Xylanase, cellulase and β-glucosidase	Olive mill and winery wastes	Xylanase-129.4 U/g, Cellulase-38.8 U/g, β-glucosidase- 17.9 U/g	[145]
Bacillus halodurans FNP 135 and *Bacillus* sp.	Xylanase, laccase	Wheat bran	Xylanase-1685 IU/g, Laccase-2270 nkat/g	[146]
Bacillus nealsonii PN-11	Mannanase	Wheat bran	Mannanase-834 U/g	[147]
Pleurotus ostreatus	Laccase, manganese peroxidase, lignin peroxidase and aryl alcohol oxidase	Potato peel waste	Manganese peroxidase-2503.6 ± 5 U/L, Laccase-6708.3 ± 75 U/L, Lignin peroxidase-231.2 ± 9 U/L, Aryl alcohol oxidase-677.4 ± 17 U/L	[148]
Aspergillus niger CCUG33991	Xylanase	Wheat bran, sorghum stover, corn cob and soybean meal	Wheat bran-1137 ± 104 U/g, sorghum stover-257 ± 35 U/g, corn cob-380 ± 25 U/g, soybean meal-365 ± 20 U/g	[149]
Trichoderma asperellum TF1	Cellulase	Mixture of jatropha cake, vine shoots, olive oil, olive pomace	Cellulase-10.68 ± 0.21 U/g biomass	[150]
Cellulomonas uda	Cellulase	Banana stem waste	Cellulase-6.97 IU/mL	[151]

Although several advantages are associated with SSF, its utilization at an industrial level is still limited. The fluctuations in parameter which impact the growth of microorganism and metabolite production such as temperature, pH, moisture, oxygen and various other factors inside the bioreactor that result from the challenging agitation of the solid substrate are few of the fundamental issues with scaling up the production of enzymes by SSF. Moreover, there are very few fully developed bioreactors available in the market with an easy design and autonomous process control [136]. Therefore, in order to make production of lignocellulolytic enzymes by SSF more successful, the focus has to be

shifted in aspects of bioreactor technology in designing efficient bioreactors with automatic process control, which may result in higher product yield.

5. Enzyme Immobilization

Lignocellulolytic enzymes contribute a noteworthy share in various industries such as pulp and paper, animal feed, textile and, more recently, the biofuel industry. About 20% of all industrial enzyme sales in the late 1990s were made up of just three lignocellulose-degrading enzymes, i.e., xylanases, cellulases, and pectinases [152]. Over the past two decades, the use of lignocellulose-degrading enzymes has increased significantly, and it is anticipated that this trend will continue in the years to come. This is due to strong government and industrial initiatives to produce renewable fuels and chemicals through the enzymatic hydrolysis of lignocellulosic biomass [152]. However, the expense of lignocellulose-degrading enzymes continues to be a significant barrier in developing efficient production methods for fuels and chemicals from LB. For enzyme prices to be competitive, they would need to be on an average 0.10 USD per gallon [153]. The techno-economic analysis methods may assist in lowering enzyme cost to achieve practical industrial scale applications. The contribution of enzyme cost in the final market cost of the lignocellulosic bioethanol production may exceed up to 50%, which is higher than the starch ethanol. Other obstacles that lessen the overall viability of the method include the high sensitivity of free enzymes, the difficulty of removing them from the reaction media, the inability to be reused, and poor stability under situations of extreme environmental adversity. As a result, their poor operating stability, limited availability, and short lifetime significantly impede the entire catalytic process [23]. Enzyme immobilization is a single solution to these multiple issues related to enzymes and their catalytic function. Enzyme immobilization has drawn a lot of interest recently as a crucial bio-engineering strategy to modify and improve a variety of enzyme catalytic properties, including its activity, physicochemical stability, specificity, selectivity, and inhibitor tolerance [6].

It is crucial to evaluate the viability of immobilized enzyme-mediated bioprocesses at an early stage in order to assess their economic and environmental impact. As more immobilized enzymes are assessed for use in commercial-scale biocatalytic processes, life-cycle evaluations (LCAs) and techno-economic studies are viewed as powerful tools. In order to develop a sustainable process for enzyme production, Lima et al. [154] recently found that the techno-economic analysis of the process indicated an enzyme cost of about 3.2 USD.kg^{-1} which was lower than the projected 4.24 USD.kg^{-1} in the National Renewable Energy Laboratory's (NREL) report (NREL/TP-5100–47764). Additionally, the life-cycle analysis revealed a roughly 50% reduction in carbon footprint compared to a standard commercial enzyme. This displays that immobilized enzymatic processes generally consume less energy and are economical, showing their potential to be both commercially successful and environmentally friendly.

In general, enzymes are used in aqueous media on a single-use basis, which is neither cost-effective nor consistent with the idea of a circular economy. The enzyme can be immobilized as a heterogeneous catalyst in solid form with insolubility in water and, therefore, readily binds with the solid substrate to perform the biocatalytic reaction [155]. Enzyme immobilization entails the binding or localization of enzymes onto a solid support surface or within a particular matrix. When coupled to a support surface, immobilized enzymes emulate their usual mode of action and are more resilient to hostile environments [23,156]. Enzyme immobilization for any enzyme broadly involves three basic steps: the first step involves the choice of a support material with which the enzyme adsorption takes place; the second step is the assessment of experimental parameters throughout the procedure to maximize process output such as high immobilization yield, enzyme activity, and stability; and finally, the third step includes characterizing the immobilized biocatalyst's performance [156]. Immobilizing the commercially important enzyme may lower the overall cost of any enzymatic process [23]. The selection of the supporting matrix and immobilization method is crucial for producing reusable, durable, and

stable immobilized biocatalysts. Enzymes are immobilized using a variety of organic and inorganic support materials with varying porosities, sizes, and configurations. Various organic support matrices including agro-food wastes, biopolymers, starch, dextran, alginate, agar and chitosan, as well as inorganic matrices including silica, zeolite, clays, pumice, alumina, glass, ceramics and magnetic nanoparticles have been used and reported [6,38].

For enzyme immobilization schemes, a variety of techniques can be applied, each one specifically designed to complement the intrinsic features of the target enzyme and the intended use of the resultant biocatalysts. Moreover, an immobilized enzyme system's performance is influenced by the properties of the support. Some of the reported properties of ideal support matrix include: inert towards enzymes, resistant to microbial attack, readily and abundantly available at low cost, easy to obtain/derive/regenerate, resistant to physical compression, large surface area with high permeability, good chemical and thermal stability, and the presence of sufficient functional groups for enzyme attachment under non-denaturing conditions [157]. Broadly, the immobilization technique can be divided into two categories, i.e., reversible immobilization, which includes adsorption, and irreversible immobilization, which includes crosslinking, covalent bonding, entrapment and encapsulation [118]. The different methods of immobilization are shown in Figure 3. The covalent bonding method of enzyme immobilization is the most widely accepted technique at an industrial level owing to the interactions between a functional group of enzymes and the support matrix [38].

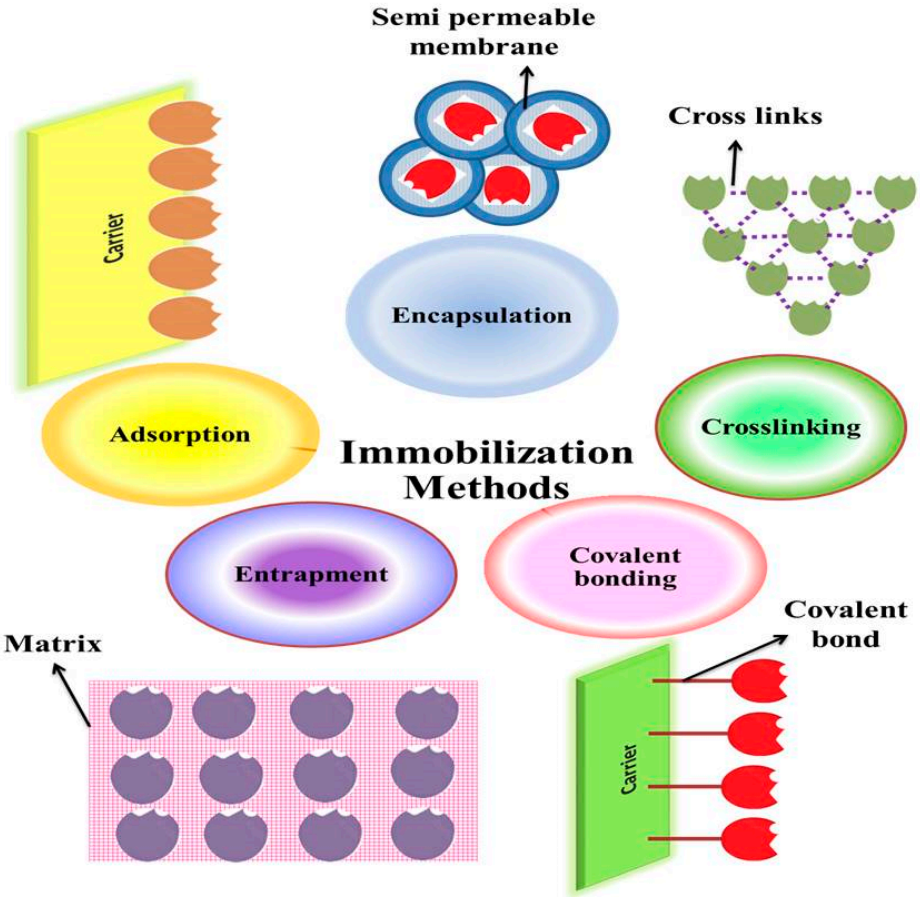

Figure 3. Schematic representation of different enzyme immobilization methods.

Various lignocellulolytic enzymes have been immobilized on different support materials with appreciable reusability to enhance the process productivity and cost effectiveness. Enzyme preparation containing xylanase and cellulase from *Aspergillus flavus* PN3

was immobilized on magnetic nanoparticles. Immobilization efficiencies for cellulase and xylanase enzymes obtained were 73.88% and 50.12%, respectively, with an immobilization yield of 79.74%. The immobilization also resulted in the same amount of sugar yield as a free enzyme; however, the immobilized enzyme mixture was successfully reused until the 5th cycle with almost 100% reusability [22]. Immobilization of laccase from *A. flavus PUF5* was reported on pretreated coconut fiber through crosslinking by glutaraldehyde. Immobilization resulted in increased melting temperature from 73 °C (free enzyme) to 82.5 °C. Moreover, immobilized laccase was able to retain >80% of its initial activity up to 6 cycles of reusability [158]. Recombinant cellulase from *Clostridium thermocellum* expressed in *E. coli* was immobilized using regenerated cellulose membrane modified by two approaches: one to form immobilized metal ion affinity membranes (IMAMs) and a second to form aldehyde functional group membranes (AMs). Both immobilization techniques increased the thermal stability of bound cellulase and the IMAMs and AM immobilized enzyme was able to retain 63% and 53% relative activity, respectively, after the 5th cycle of reuse [23]. A study reported the immobilization of bacterial cellulase from *Glutamicibacter arilaitensis* strain ALA4 on different matrices (calcium alginate, agar-agar, gelatin and k-carrageenan). The immobilized cellulase was used for the saccharification of NaOH pretreated aquatic weeds (*Alternanthera philoxeroides* and *Brachiaria mutica*) biomass. The saccharification using calcium alginate immobilized cellulase resulted in an enhanced total reducing sugar yield with maximum yield of 17.85 ± 0.18 mg/g and 19.51 ± 0.2 mg/g, from pre-treated *A. philoxeroides* and *B. mutica* biomass, respectively [159]. Lignin peroxidase from *Pichia methanolica* was also immobilized on Fe_3O_4@SiO_2@polydopamine (PDA) nanoparticles. The immobilized enzymes showed high thermal stability and retained over 30% of initial activity until the 8th cycle of reuse [160]. β-xylosidases are the type of xylanases that possess potential application in bioethanol production from lignocellulosic biomass. These enzymes cause the release of xylose units from xylooligosaccharides by acting on their non-reducing ends. Murguiondo et al. [161] immobilized a recombinant β-xylosidase from *Talaromyces amestolkiae* in the form of magnetic cross-linked enzyme aggregates. These immobilized enzyme aggregates maintained excellent O-transxylosylating and hydrolytic activity with high recyclability, and improved pH and thermal stability. These findings support the beneficial impact of immobilization in enzyme mediated processes which may pave the way for the economic bioconversion of LB into value-added products.

6. Future Prospects and Concluding Remarks

The microbial enzymes have several potential applications in a wide array of industrial bioprocesses [162]. However, despite the advantages of lower energy consumption and environment friendliness, the large-scale production of biofuels and other bioproducts from microbial enzymes in lignocellulosic biorefineries is constrained by a number of significant obstacles. When converting lignocellulosic biomass to fermentable sugars, pretreatment is thought to be the most expensive processing step [163,164]. The primary barrier in the complete deconstruction of LB by enzymes is the lack of enough exposure of polysaccharides to cellulolytic enzymes owing to the presence of lignin on their surface. Moreover, the current research regarding biological pretreatment using microbial enzymes is still below the target for industrial needs. The slow reaction rate of lignocellulolytic enzymes is also a major hurdle that causes the progressive degradation of carbohydrates, resulting in low sugar yields.

Consequently, there is a need for the development of a technological bioprocess which overcomes these hurdles in an economical and sustainable manner. The exploration of a suitable microbial consortia by optimization of different physiochemical parameters are nowadays being practiced. The scientific societies are showing their interests in novel genetic and enzyme engineering techniques involving the manipulation of gene sequences or amino acid residues cantered on the high yield of target specific enzymes. The complete breakdown of the complex structure of LB to its monomeric forms will be made

possible by these genetic and enzyme engineering techniques for better enzyme cocktails. Enhancing the substrate selectivity and transcending their basal features have been made possible by site-directed mutagenesis or transcriptomic technologies. This is advantageous for enzymatic expression, which may be easily influenced by variables such as temperature and pH. The characterization of the genetic makeup of microbial strains facilitates rapid microbial prospecting, which speeds up the proteomic evaluation of microbes and identifies the genes of interest. A deeper understanding of microbial physiology and the manipulation of microbial strains is essential for the augmented production of lignocellulolytic enzymes for their potential role in consolidated the bioprocessing of LB into biofuels and value-added products. In fact, engineered cellulase enzyme cocktails are now being developed by several industries worldwide with an emphasis on enzyme production for valorization of lignocellulosic feedstocks. The joint initiatives of industry and academia can enable interdisciplinary discussion to exchange developments and issues that can open up space for technological advancement in building better enzyme-based biorefineries.

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