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Review

Microbial Enzyme Systems in the Production of Second Generation Bioethanol

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Abstract: The primary contributor to global warming has been the careless usage of fossil fuels. Urbanization's threat to the depletion of these resources has made it necessary to find alternatives due to the rising demand. Four different forms of biofuels are now available and constitute a possible replacement for fossil fuels. The first generation of biofuels is generated from the edible portion of biomass, the second generation is made from the non-edible portion of biomass, the third generation is made from algal biomass, and the fourth generation is made using molecular biology to improve the algal strain. Second-generation biofuels are extremely important because they are derived from non-edible biomass, such as agricultural and agro-industrial wastes rich in cellulose, hemicellulose, pectin, and starch impregnated with lignin, and are hydrolyzed after delignification by physio-chemical or biological pretreatments using ligninases. The enzymes involved in the hydrolysis of feedstocks for the production of second-generation bioethanol, a highly acceptable biofuel, are discussed in this article. Furthermore, the article discusses various fermentation technologies as well as significant developments in second-generation biofuel production by combining various microbial enzyme systems.

Keywords: biofuels; bioethanol; lignocellulose; cellulases; amylases; hemicellulases

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1. Introduction

Society's advancement has raised the standard of living and made jobs easier, but it has also resulted in environmental issues as a result of excessive use of automobiles, machines, and other items, which has contributed to the depletion of fossil fuel sources. Urban areas house 52.5% of the world's population, with that figure expected to rise to 70% by 2050 [1]. This urbanization is causing excessive use of fossil fuels in the transportation sector. Cities contribute significantly to CO_2 emissions and the indiscriminate use of fossil fuels has put their reserves at risk [2]. Annual global carbon dioxide emissions are increasing and are expected to reach 38,836.98 MT (Metric Ton) in 2025. China's expected CO_2 emissions in 2025 are 11,521.21 MT, the United States' is 11,521.21 MT, India's is 3158.37 MT, Canada's is 699.65 MT, Brazil's is 605.61 MT, Argentina's is 207.44 MT, Germany's is 738.77 MT, Turkey's is 374.40 MT, Iran's is 822.46 MT, Saudi Arabia's is 714.08 MT, South Africa's is 338.17 MT and Japan's is 1091.78 MT [3]. This has prompted researchers all over the world to focus on environmentally friendly alternatives to fossil fuels. Biofuels are one type of such fuel that emits fewer GHGs over their entire life cycle [4]. A biofuel is any fuel that is made from plant biomass and can generate energy for use in a variety of ways [5]. For the production of biofuels and energy, biomass that primarily consists of starchy crops, such as cereals, and root tubers, sugary crops, such as sugar cane and beet, agricultural residues, such as grasses, straws, bagasse, and brans, forestry crops, wood processing residues, dedicated energy crops, and biodegradable municipal solid waste, can be used [6]. Solid, liquid, or gaseous biofuels are all possible. Wood, and refuse-derived fuel (RDF), are some examples of solid biofuels. Biodiesel, biomethanol, bioethanol, biobutanol, etc are examples of liquid

biofuels, while biohydrogen and biomethane are examples of gaseous biofuels. Given the increasing global biofuel consumption trend, major research attention has been directed toward feasible and low-cost biofuel resources, as reported by research publications in the last 20 years around the world, particularly in Asia, Europe, and the United States [7].

According to the proposed sustainable development scenario, biofuels must meet 9% of total transportation fuel demand by 2030, up from 3% in 2018. Between 2010 and 2021, the use of modern bioenergy increased by about 7% per year on average, and it is on the rise. More efforts are required to accelerate modern bioenergy deployment to meet the Net Zero Scenario. Biofuel production is not increasing at a rate sufficient to meet this demand, and it grew 6% year on year in 2019, with an average of 3% growth expected over the next five years, leaving total production short of 10% by 2030 to meet the pace required for sustainable development [8]. Food crops account for the majority of biofuels produced. For better sustainability, advanced biofuel production using non-food feedstocks must improve and gain a significant share of total biofuel production. Scaling up the production of these biofuels to a commercial level will require a great deal of effort and innovative research. Bioethanol and biomass-to-liquid synthetic fuels are among the most important advanced biofuels because they can be produced using low-cost, abundantly available feedstocks such as agricultural and agro-industrial residues [9,10].

Traditional biofuels are made from edible feedstocks such as sugar cane juice, molasses, sugar beet juice, molasses, cereals such as corn, rice, barley, wheat, sorghum, and oils such as soybean oil and palm oil. These are known as first-generation biofuels. Advanced biofuels are made from non-edible parts of biomass and are classified into three types based on the type of substrate used in the production process: second, third, and fourth-generation biofuels. Waste biomass resources such as agricultural, agro-industrial, municipal solid waste, and forest residue are used in second-generation biofuels. Third-generation biofuels are primarily made from algal biomass, which can be used to produce a wide range of biofuels and other value-added products [11]. The fourth generation of biofuels is a newer type that uses synthetic biology tools to create electro fuels and photobiological solar fuels by converting solar energy directly into fuels [12,13]. Recent concerns about the production of first-generation biofuels caused by the conflict between food and fuel have prompted experts to investigate alternative biofuel production routes [14]. According to numerous reports, the cost of food ingredients has risen due to the production of first-generation bioethanol [15]. The primary reason for preferring second-generation biofuels over first-generation biofuels is the use of waste and inedible agricultural biomass as a substrate for fuel generation. Because of its abundance and underutilization in comparison to other natural resources, lignocellulosic, agro-industrial, and biodegradable municipal solid waste biomass is a promising feedstock for the production of biofuels.

Due to the extensive food versus fuel debate associated with first-generation biofuels, the emphasis has shifted to the production of second-generation biofuels because the feedstock is easily accessible and has a less significant impact on the food web, water resources, and ecosystem [16–18]. The current methods for producing second-generation bioethanol are neither cost-effective nor eco-friendly [19]. As a result, the entire manufacturing process must be improved to be environmentally friendly and to make the cost of the fuel produced competitive with other fuels already on the market [20,21]. Biologically mediated lignocellulosic biomass conversion into biofuels appears to be more promising. The primary goal of this article is to review the environmentally friendly approaches used in biofuel production, with a focus on the enzymes used in the production of second-generation bioethanol, a highly acceptable liquid biofuel.

2. Composition of Agricultural and Agro-Industrial Waste Biomass, the Feedstocks for Second Generation Bioethanol

The majority of plant waste biomass, also known as lignocellulosics, consists primarily of carbohydrates in the form of cellulose, hemicellulose, and phenolic polymers such as lignin. Starch, pectin, proteins, acids, salts, and minerals are also present in varying amounts

in some agro-industrial and biodegradable municipal solid waste biomass residues [18]. The structural composition of some common lignocellulosic biomass residues with the potential to be used as feedstocks in the production of second-generation ethanol, also known as cellulosic ethanol, is shown in Table 1 and discussed along with the structural architecture of pectin and starch, commonly found in agro-industrial wastes such as brans, spent grains and kitchen waste residues, etc.

Table 1. Lignocellulosic composition (%) of various agricultural wastes on a dry basis of the substrate.

Substrate	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Rice straw	32–47	19–27	5–24	[21]
Rice husk	34.40	29.30	19.20	[22]
Wheat straw	35–45	20–30	8–15	[21]
Corn straw	42.60	21.30	8.20	[21]
Corn cobs	45.00	35.00	15.00	[21]
Corn stover	38.00	26.00	19.00	[23]
Wheat bran	25.30	14.60	3.20	[24]
Sugarcane bagasse	42.00	25–36	19–20	[16]
Sweet sorghum	48–49	20–26	19–20	[25]
Coconut fiber	36–43	0.15–0.25	41–45	[21]
Cocoa pods husk	35	10	14	[26]
Soft wood	40–44	25–29	25–31	[21]
Banana fiber	60–65	6–8	5–10	[21]
Switch grass	36–38	27	17–19	[27]
De-oiled rice bran	9.80	20.60	3.90	[28]
Barley straw	31–45	27–38	14–19	[21]

2.1. Cellulose ($(C_6H_{10}O_5)_n$)

One of the major constituents of plant cell walls which is abundantly available on earth is cellulose which exists as a fibrous structure. It is an unbranched long-chain polymer consisting of several repeated units of cellobiose which are linked to each other by β-1,4-glycosidic bonds [29]. These long chains of cellulose are linked together by Van der Waals and hydrogen bonds packing the cellulose into microfibrils which further bundle together to build cellulose fibers. The straightness of the chain is determined by the hydrogen bonds within these microfibrils. The crystalline and amorphous structures within the cellulose are introduced by interchain hydrogen bonding which imparts order or disorder to the cellulose structure [18].

2.2. Hemicellulose ($(C_5H_8O_4)_n$)

Hemicellulose is the second notable and prevalent polymer in plant waste. Being chemically heterogeneous sets it apart from cellulose. These pentoses (xylose, rhamnose, and arabinose), hexoses (glucose, mannose, and galactose), and uronic acids (4-o-methyl-glucuronic, D-glucuronic acids) are branching, heterogeneous polymers [29]. In various materials, hemicelluloses have varying proportions. For instance, conifers and hardwoods have widely different proportions and types of xylans and mannan. In conifers, galactoglucomananas (5–8%), arabinoglucouronoxilanes (7–15%), and glucomannan (10–15%) are the primary components, whereas glucomannans (2–5%) and glycoronoxilanes (15–35%) predominate in hardwoods. The primary hemicellulosic components of grass and cereal cell walls are arabinoxylans [18]. The general structure of hemicellulose is depicted in Figure 1.

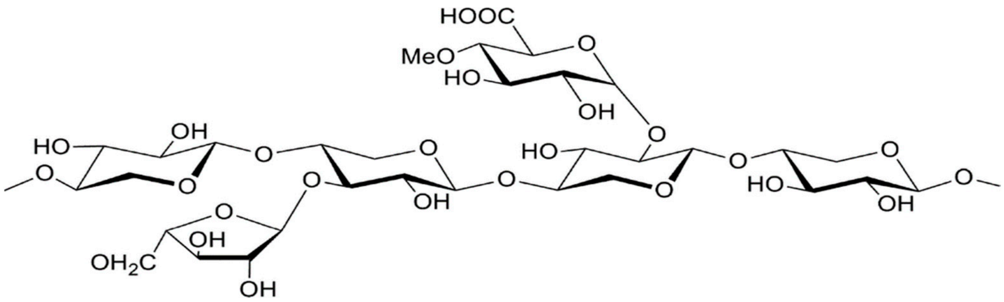

Figure 1. Generalized structure of hemicellulose (Xylan type) (Modified from [18]).

2.3. Lignin

Lignin is the third polymer that is widely distributed in nature (Figure 2). This polymer, which is found in plant cell walls, gives the cell wall of the plant a strong defense against any microbial invasion. The major three forms of phenyl propane units found in lignin are guaiacyl propanol also known as coniferyl alcohol, syringyl alcohols also known as sinapyl alcohol, and p-hydroxyphenyl propanol also known as coumaryl alcohol. Lignin is primarily viewed as the glue that binds the various parts of lignocellulosic biomass together, making it water-insoluble. It is extremely challenging to hydrolyze biomass using enzymatic or microbiological processes because of how tightly lignin is bound to the cellulose structure [18,30].

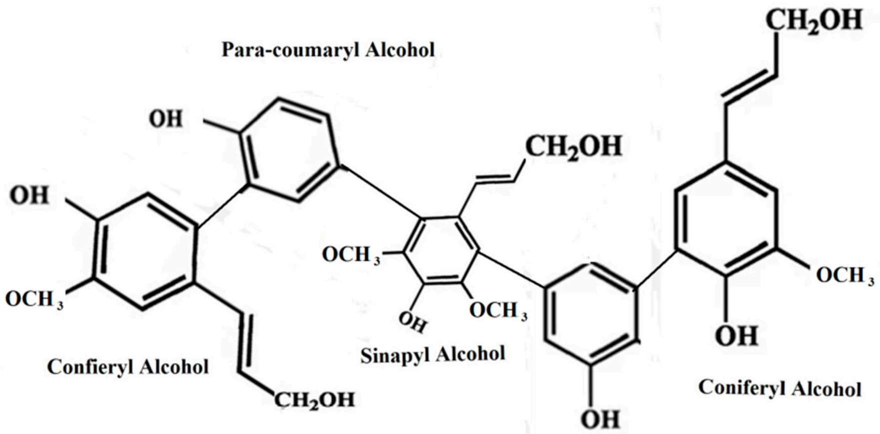

Figure 2. Generalized structure of lignin (Modified from [18]).

2.4. Pectin

Only a limited amount of pectin can be found in plant cell walls. Pectins are heteropolysaccharides comprised of 1,4-linked units of α-D-galactosyluronic acid residues. Rhamnogalacturonan-I, homogalacturonan, and substituted galacturonans are the three main pectins that have been identified from plant cell walls [31]. The general structure of pectin is shown in Figure 3.

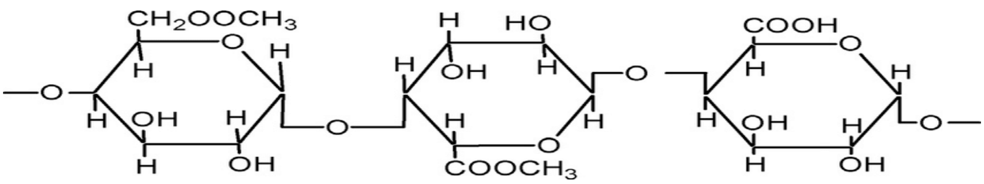

Figure 3. Generalized structure of pectin (Modified from [31]).

2.5. Starch

Glucose units in starch are connected by glycosidic linkages. Figure 4 shows the architecture of the two types of polymeric units that make it up: amylose and amylopectin. By

α-1,4 glycosidic linkages, amylose is made up of linearly linked glucose units. Amylopectin is made up of linear glucose chains with an α-1,4 linkage that is joined to the side chains by α-1,6 linkage [32,33].

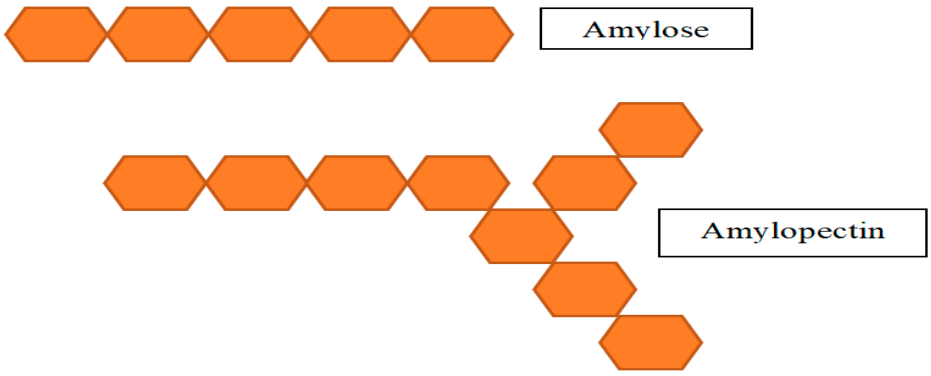

Figure 4. Generalized structure of starch.

The preceding section summarised the various carbohydrates in the form of cellulose, hemicellulose, phenolic polymer, and other ingredients in lesser amounts such as pectin and starch that comprise the overall skeleton of agricultural and agro-industrial waste biomass used in the production of second-generation biofuels. Following the hydrolysis of polysaccharides into simpler sugar molecules to be converted into bioethanol, the phenolic polymers are disintegrated first for conversion into various value-added products. Many developed countries are investing heavily in microbial fermentation and product regeneration from lignocellulosic feedstock, which necessitates complete exploitation of the lignocellulosic biomass. Knowing the lignocellulosic biomass composition allows industries, researchers, and biorefineries to invest in and exploit microorganisms and their enzyme systems for the development of second-generation bioethanol.

3. Conversion of Agricultural and Agro-Industrial Residues into Bioethanol

The development of a biorefinery for the production of numerous value-added products, including second-generation biofuels from plant biomass waste, has been the subject of extensive research. Effective cellulose utilization is crucial for making use of lignocellulosic biomass because it produces sugars that can be fermented further. But because lignin acts as a significant barrier to the existing carbohydrates, pretreatment is an extremely important step in the processing of biomass to disrupt lignin and hemicellulose for efficient hydrolysis of cellulose in the following stage. Pretreatment, enzymatic hydrolysis, and fermentation are the three primary processes in the bioconversion of lignocellulosic biomass into bioethanol [33–35].

3.1. Pretreatment

The fundamental obstacle to the generation of biofuels seems to be the resistant and crystalline structure of plant biomass [36]. Enzyme interaction with cellulose is necessary for enzymatic hydrolysis, however, cellulose's crystalline structure makes enzymatic attacks difficult. The lignin and hemicellulose matrices are another obstacle because they operate as physical barriers that reduce the accessibility of activated cellulose to enzymes. Additionally, lignin reduces the effectiveness of enzymes by binding cellulase [37]. Therefore, a pretreatment technique is needed to soften the crystalline structure of plant biomass before enzymatic hydrolysis [38]. The pretreatment process alters the structure and composition of the biomass and increases the surface area of the cellulose, making it more porous and more accessible for enzymatic hydrolysis [39–41].

3.1.1. Goal of Pretreatment

Different pretreatment techniques have been proposed and put into practice for the maximum release of fermentable sugars from lignocellulosic biomass to improve the enzymatic hydrolysis of biomass and fermentation yields [42,43].

Pretreatment must have the following qualities to be effective: (i) it must be economical and environmentally friendly, (ii) the most lignin can be eliminated, (iii) minimum production of phenols, furans, and furfurals, which prevents fermentation, (iv) recovering lignin to create other products with extra value, (v) minimal energy required, (vi) pretreatment chemicals must be recovered for future use, (vii) minimum costs of operation and minimum labor needs.

3.1.2. Factors Affecting the Choice of Pretreatment

Several considerations need to be taken into account when choosing a pretreatment method for a certain feedstock. These variables primarily comprise the biomass's total hemicellulose and lignin contents, cellulose's degree of crystallization, polymerization, and permeability [44–46].

3.1.3. Types of Pretreatments

Different types of pretreatment technologies have been studied so far and basically, four types of strategies have been categorized including (i) mechanical or physical involving mechanical milling and exposure to high temperature using steam (ii) chemical involving the use of acids, bases, oxidizing agents or ionic liquids alone or in combination with steam and are energy intensive (iii) physicochemical involving acid or ammonia explosion which are also energy intensive, (iv) biological involving the microorganisms or microbial enzyme systems for disrupting lignin and hemicellulose. Table 2 summarises different pretreatment methodologies and their effects on biomass. Because this manuscript is about enzyme systems for the production of second-generation biofuels, biological pretreatment is more relevant here and will be discussed in detail hereafter.

Table 2. Various methods, processes, and their impact on lignocellulosic biomass during the pretreatment.

Nature of Pretreatment	Method	Process	Impact	Reference
Mechanical or physical	Milling	Roll, ball, hammer, disk, and colloid milling	Decreases polymerization and crystalline structure of cellulose, increases specific surface area	[47]
	Extrusion	Mixing, heating, and shearing of biomass	Alterations in the physical and chemical structure. Defibrillation and fiber shortening	[48]
	Pulse electric field	A sudden burst of high voltage between 5.0–20.0 kV/cm for nano to milliseconds	Disruption of the cell wall and electroporation	[49]
	Microwave	Irradiation with 2450 MHz microwaves (170–200 °C)	Alterations in the ultra-structure of cellulose, partially removes hemicelluloses and lignin	[50,51]
Chemical	Acidic	Treatment with dilute HCl, H_3PO_4, HNO_3, H_2SO_4, acetic acid, citric acid, oxalic acid, maleic acid, fumaric acid, etc	Hydrolysis of hemicellulose	[9]
	Alkaline	Treatment with dilute NaOH, KOH, $Ca(OH)_2$, NH_4OH	Efficient removal of lignin	[9]

Table 2. *Cont.*

Nature of Pretreatment	Method	Process	Impact	Reference
Physicochemical	Wet Oxidation	Treatment with oxidative agents such as peracetic acid, sodium chlorite, $KMnO_4$, and H_2O_2 at high temperatures	Higher lignin and hemicelluloses solubilization	[52]
	Organosolv	Treatment with organic or aqueous–organic solvent systems with or without added catalysts in the temperature range of 100–250 °C	Hydrolysis of lignin and hemicellulose	[53]
	Ammonia Fibre Expansion treatment (AFEX)	Treatment with anhydrous or liquid ammonia at a temperature ranging from 90 to 100 °C followed by a successive lowering of pressure	Lignin removal	[54]
	Steam Explosion	Exposure to saturated steam under high pressure followed by a sudden lowering of pressure	Lignin removal and hemicellulose solubilization	[55]
	Liquid hot water	Use of high temperature of 170°–230 °C and pressure more than 5 MPa	Removal of hemicelluloses	[56]
Biological	Enzymes or microorganisms	Acton of lignin-degrading enzymes such as peroxidases and laccases	Lignin degradation	[46,57]

Biological Pretreatment

Biological pretreatment uses less energy and is less harmful to the environment than chemical and physical procedures. Natural diversity includes a variety of ligninolytic and hemicellulolytic microorganisms that can be used for the pretreatment of biomass [38]. Because they destroy lignin and hemicellulose with only a small amount of cellulose, a variety of white, brown, and soft rot fungi have been employed for biological pretreatment [57]. White-rot fungi degrade lignin due to the presence of lignin-degrading enzymes including peroxidases and laccases. With the aid of mediators, laccase can directly target the nonphenolic and phenolic subunits of lignocellulosic biomass, causing structural changes [58].

Some of the white-rot fungal species that have been investigated for the biological pretreatment of biomass include Pycnoporus cinnarbarinus. Phanerochaete chrysosporium, Cyathus stercolerus, Ceriporia lacerata, Ceriporiopsis subvermispora, Pleurotus ostreaus. Other basidiomycetes used for biological pretreatment include Fomes fomentarius, Ganoderma resinaceum, Lepista nuda, Irpex lacteus, Trametes versicolor, and Pycnoporus sanguineus [59–64]. The biological pretreatment of the biomass can be accomplished in three different ways, which include the use of enzymes, a consortium of microorganisms, or fungi that can degrade lignin [22]. Ma and Ruan [65] explored simultaneous delignification and hydrolysis of corn stover by co-culturing Coprinus comatus and Trichoderma reesei. A range of white-rot fungi was investigated in a study to discover the optimum biological pretreatment for corn stover, and Cyathus stercoreus NRRL-6573 produced the highest carbohydrate conversion [62]. Although biological pretreatment has advantages, it is not favored on an industrial scale because it is too sluggish [66]. Therefore, for biological pretreatment to be applied at the industrial level, it is necessary to discover more fungi that can delignify biomass but at faster rates. Rastogi et al. [67] observed that Pyrenophora phaeocomes S-1 cultivation on rice straw led to 63 and 51% lignin and hemicellulose breakdown, respectively. Further extraction of these components using a mild alkali revealed that the overall losses for lignin and hemicellulose were 78 and 60%, respectively. An increase in hydrolytic efficiency was seen in a study by Yan et al. [68] by using the Cupriavidus basilensis B-8 strain of bacteria in conjunction with diluted acid pretreatment. By forming pores in the biomass and removing the lignin droplets created by the acid treatment, the bacteria increased the surface area available for enzymatic action.

3.2. Hydrolysis to Release Free Sugars for Fermentation into Ethanol

Pretreatment is followed by hydrolysis of the pretreated substrate to saccharify it leading to the release of monomeric sugars. Hydrolysis can be performed by acid or enzymatic treatments.

3.2.1. Acid Hydrolysis

For a remarkably long time, diverse substrates have been hydrolyzed using acid. The two most frequently used acids are H_2SO_4 and HCl, which can be utilized in both diluted and concentrated forms and at varied concentrations. Dilute acid hydrolysis involves two processes. The first step in the process is the saccharification of carbohydrates, and if the reaction persists, sugars will then be converted to furfurals. Because cellulose breaks down more slowly than hemicellulose, a two-stage process is necessary to prevent the formation of furfurals from the sugars released from hemicellulose. The first stage of the process recovers the sugars from the hemicellulose under mild conditions, and stage two recovers the sugars from the cellulose under harsher conditions. The effective enzyme from *Penicillium* consortium and acid hydrolysis of poplar were also compared by Liang et al. [69], who concluded that the sugar yield from enzymatic hydrolysis is superior.

3.2.2. Enzymatic Hydrolysis

Since it does not result in the production of inhibitors, enzymatic hydrolysis of the pretreated substrate is preferred to acid hydrolysis. Furthermore, the enzymes contain no secondary reactions and work in a highly precise manner. By pretreating the substrate, cellulose and hemicellulose's crystalline structure is broken down, allowing the enzymes to attack them and liberate sugars (Figure 5). Cellulases and hemicellulases are needed to break down cellulose and hemicellulose, which are the two main carbohydrates found in the cell wall structure [70]. The pretreated substrate must also include starch and pectin for amylases and pectinases, the corresponding enzymes, to fully saccharify the substrate.

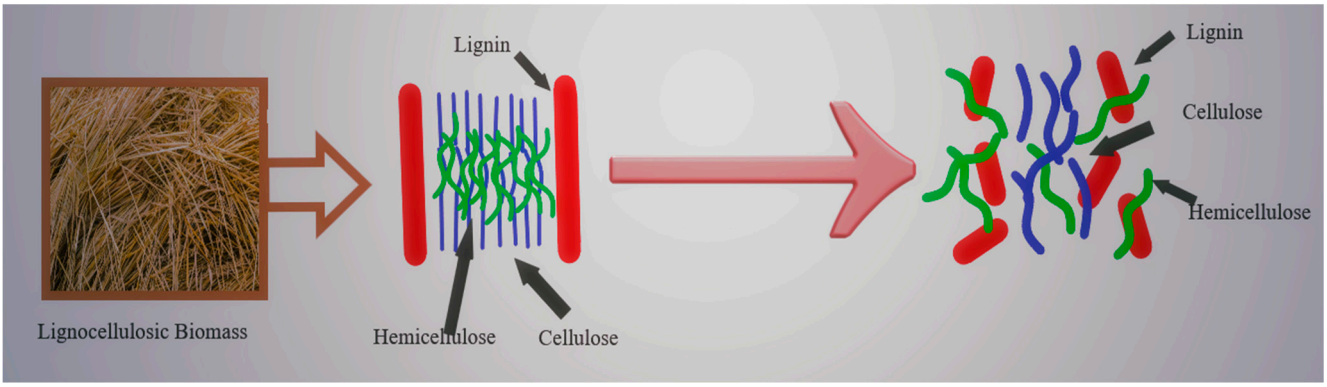

Figure 5. Schematic representation of pretreatment of lignocellulosic residue (Modified from [21]).

Enzymatic hydrolysis has several benefits, such as high specificity, a higher sugar yield, milder reaction conditions, and a reduced formation of undesirable products [71]. Additionally, enzymatic saccharification offers a more cost-effective, environmentally friendly method for releasing sugars from lignocellulosic biomass.

Microbial Enzymes Involved in the Hydrolysis of Feedstocks for the Production of Second-Generation Bioethanol

Rice straw, wheat straw, corn stover, corn cobs, barley straw, sugarcane bagasse, rice husk, switchgrass, cotton stalks, and poplar biomass, among others, contain 30–48% cellulose and 15–30% hemicellulosic carbohydrates [72]. Cellulases and hemicellulases are thus essential for the efficient saccharification of these residues and the production of free sugars from them. Other agro-industrial residues, such as wheat bran, fruit peels, vegetable waste, rice bran, maize bran, and apple pomace, contain starch and pectin in

addition to cellulose and hemicellulose [28,73,74]. As a result, amylases and pectinases are required for the hydrolysis of these biomass residues. Enzyme systems containing cocktails of various hydrolytic enzymes are required for complete and simultaneous hydrolysis of all carbohydrates in various feedstocks for the production of second-generation bioethanol. The following sections discuss the individual enzymes of various systems, along with their modes of action, required for the efficient hydrolysis of various polysaccharides in feedstocks for the generation of second-generation bioethanol.

Cellulases

The majority of the time, lignocellulosic biomass requires a combination of numerous enzymes, the most crucial of which are cellulases. Cellulases are classified structurally as glycosyl hydrolases, which hydrolyze cellulose's β-1,4-D-glucan connections to create cellobiose and glucose [75]. To completely dissolve the cellulose framework, three enzymes must act together as depicted in Figure 6 and the role of various enzymes is as follows:

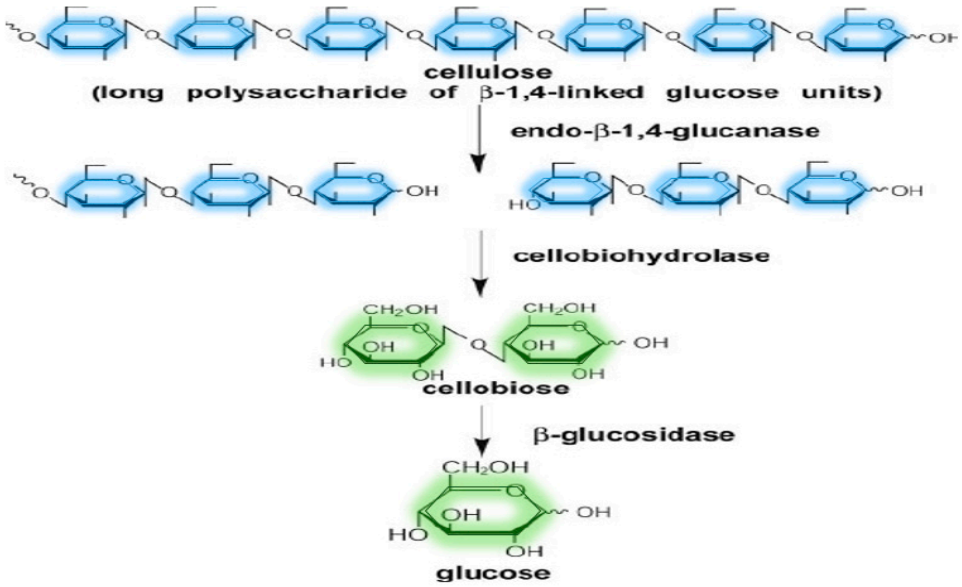

Figure 6. Mode of action of enzymes involved in the breakdown of cellulose (Modified from [21]).

Endoglucanase or Endo-β-1,4-glucanase (EC 3.2.1.4): It makes short-chain oligomers containing non-reducing and reducing tails by randomly cutting the amorphous area of cellulose.

Cellobiohydrolase or Exo-β-1,4-glucanase (EC 3.2.1.91): Endoglucanase's catalytic activity produces non-reducing endings that are hydrolyzed to produce cellobiose, a repetitive unit containing two glucose molecules.

Cellobiase or β-glucosidase (BG) (EC 3.2.1.21): To generate monomeric glucose units, it hydrolyzes cellobiose units.

Cellulose is the primary growth medium needed by the microbes that make cellulases, while they can also use other carbohydrates. Cellulase-producing microorganisms include fungi such as *Aspergillus flavus*, *Aspergillus fumigatus*, *Aspergillus niger*, *Aspergillus oryzae*, *Fusarium oxysporum*, *Trichoderma viride* [60–65].

Hemicellulases

The second most abundant polymer in nature is hemicellulose which comprises xylan, mannan, arabinan, and galactan. It is soluble in aqueous alkali but not in water or any chelating agent [76]. The enzyme market for hemicellulases is expanding quickly because these enzymes are used in a variety of industrial processes. The second-most prevalent carbohydrate in lignocellulosic is called xylan, which is a hetero-polysaccharide made up of 1,4-β-D-xylose monomers with different substituents [77]. Figure 7 shows the mode

of action of xylanase for the breakdown of xylan [18]. When xylan is hydrolyzed by xylanase, oligosaccharides are produced, which are then hydrolyzed by 1,4-β-xylosidase to produce xylose [78]. For complete hydrolysis of xylans, other enzymes such as ferulic and p-coumaric esterases, xylan esterases, α-4-O-methyl glucoronosidases, and α-1-arabinofuranosidases work in concert [57].

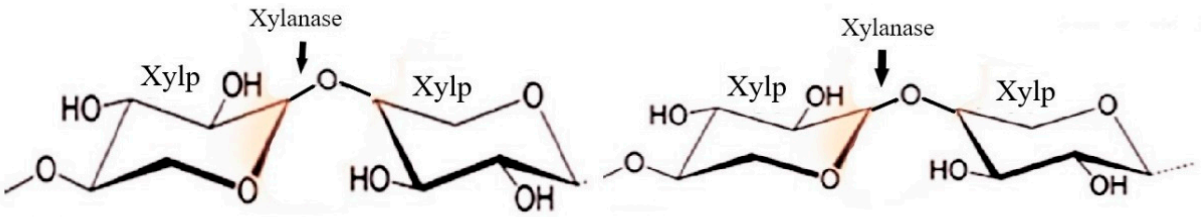

Figure 7. Mode of action of enzymes involved in the breakdown of xylan (Modified from [18]).

In addition to xylanase, mannans, and heteromannanas are additional polysaccharides that are found in the hemicellulose of plant cell walls. D-mannose, a six-carbon sugar, makes up the majority of mannan, but because plant mannans have a complex and heterogeneous structure, it takes a combination of endo-1,4-β-mannanases, exo-mannosidases, and other enzymes to completely break them down [79]. These enzymes can also remove the side chain sugars that are present at various locations on mannans. The following enzymes are involved in the hydrolysis of different hemicellulosic structures. Xylan degradation is carried out by three different types of xylanases [80].

Endo-β-1,4-xylanase (EC 3.2.1.8): By hydrolyzing glycosidic linkages to release linear and branching oligosaccharides, it randomly splits the xylan chain.

Exo-β-1,4-xylanase or β -1,4-xylan xylohydrolase: It eliminates monomeric xylose units from the xylan polymer's non-reducing terminus.

β-1,4-xylosidase or Xylobiase. (EC 3.2.1.37): This enzyme hydrolyzes disaccharides such as xylobiose and the higher xylooligosaccharides that have a lower specific affinity.

The following enzymes, whose modes of action are also shown in Figure 8, are considered to be involved in the hydrolysis of mannan and galactomannans by Moreira and Filho [81].

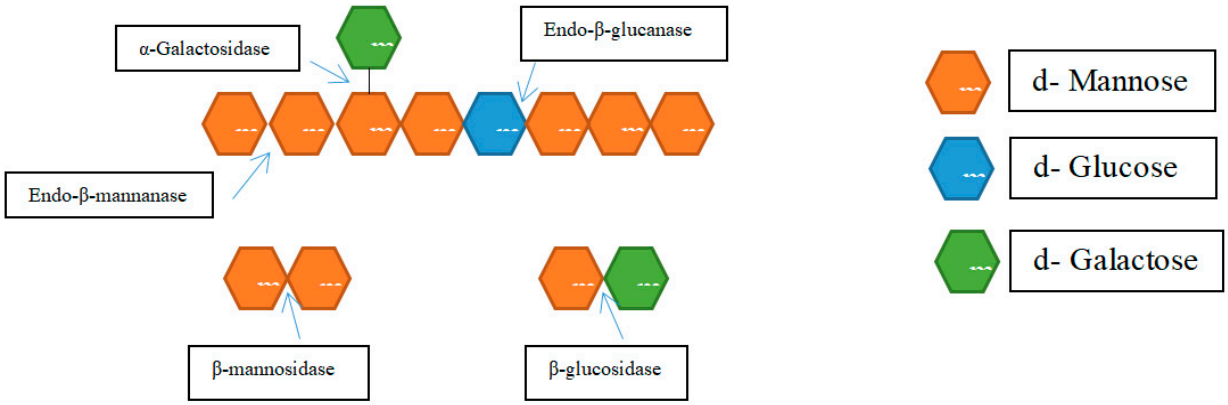

Figure 8. Schematic representation of O-acetylated galacto-glucomannan and enzymes involved in its degradation and the oligosaccharides released.

Endo-β-1,4-mannanase (EC 3.2.1.78): It generates new chain endpoints by randomly cleaving the mannan's β-1,4-linkage internal links.

Exo-β-mannosidase (EC 3.2.1.25): It releases mannose sugar moieties by cleaving β-1,4-linked mannosides from the non-reducing ends of mannan and mannooligosaccharides.

β-glucosidase (EC 3.2.1.21): This enzyme hydrolyzes the 1,4-β-D-glucopyranose found at the non-reducing ends of the oligosaccharides produced from glucomannan and galactoglucomannan.

α-galactosidase (EC 3.2.1.22): It is a debranching enzyme that breaks down the α-1,6-linked D-galactopyranosyl side chains of galactomannan and galactoglucomannan.

Acetyl mannan esterase: It is a debranching enzyme that causes galactoglucomannan to release its acetyl groups.

Agaricus [82], *Aspergillus* [83,84], *Fusarium* [84,85], and *Trichoderma* [86–89] are fungi that have been discovered to break down hemicellulose. Hemicellulases are produced mostly by gram-positive bacteria, such as *Bacillus* species [90,91] and *Clostridia* species [92,93]. Among the actinomycetes, some species of *Streptomycetes* group [94].

Pectinases

Pectinases are the enzymes that hydrolyze pectic polysaccharides into monomers such as galacturonic acids. Pectin is a major component of plant cell walls, so to completely break down the lignocellulosic biomass, pectinases are required to completely hydrolyze the pectic materials. This lowers the viscosity of the medium and creates an ideal environment for the other enzymes to act on different polysaccharides. The following are the primary enzymes [95] involved in the hydrolysis of pectic substances:

Protopectinases: To liberate soluble form polymerized pectin, they dissolve protopectin. These are divided into two types: type A, which acts with protopectin at the polygalacturonic acid chain area, and type B, which acts with the polysaccharide chains tying the polygalacturonic acid chain to the components of the cell wall.

Pectin Methyl Esterases (PME) (EC 3.1.1.11): Pectin methyl esterases de-esterify the methyl group of pectin, releasing pectic acid and methanol in the process. Before pectate lyases and polygalacturonases, which require non-esterified substrates, it catalyzes de-esterification.

Pectin Acetyl Esterases (PAE): To liberate pectic acid and acetate, it catalyzes the hydrolysis of the acetyl esters found in pectin.

Polymethylgalacturonases (PMG): The pectin backbone's α-1,4-glycosidic linkages are broken down, resulting in the formation of 6-methyl-D-galacturonate. It has both endo and exo modes of action. Exo-PMG catalyzes a reaction at the non-reducing end of the substrate while endo-PMG randomly cleaves the substrate.

Polygalacturonases (PG): To create D-galacturonate, it cleaves the polygalacturonic acid's α-1,4-glycosidic linkages. It can act in both endo and exo modes, just as PMG. Exo-PG (EC 3.2.1.67) catalyzes the reaction at the non-reducing end of the substrate while endo-PG (EC 3.2.1.15) randomly cleaves the substrate.

Pectate Lyases (PGL): To release α-4,5-D-galacturonate from the glycosidic bonds in polygalacturonic acid, it performs a trans-elimination reaction. Exo-PGL (EC 4.2.2.9) cleaves the substrate at the nonreducing end, whereas endo-PGL (EC 4.2.2.2) operates on the substrate at random.

Pectin Lyases (PL): It performs trans elimination of glycosidic connections to randomly break the esterified pectin and create unsaturated methyloligogalacturonates.

Numerous bacteria and fungi that cause plant disease produce pectinolytic enzymes to aid in host invasion. Additionally, they aid in the recycling of carbon ponds in nature by decomposing dead plant materials. Numerous organisms have been shown to generate pectinolytic enzymes, including *Aspergillus* [96], *Fusarium* [97], *Penicillium* [98], *Trichoderma* [99], *Bacillus*, *Erwinia*, and actinomycetes such as *Streptomycetes* [100].

Amylases

The three main categories of amylases, also known as glycosyl hydrolases (GH), according to the International Union of Biochemistry and Molecular Biology (UIBMB), are endo-amylases, exo-amylases, and debranching enzymes. Figure 9 shows how all of these enzymes work to break down starch. The various types of starch-degrading enzymes are as follows [101].

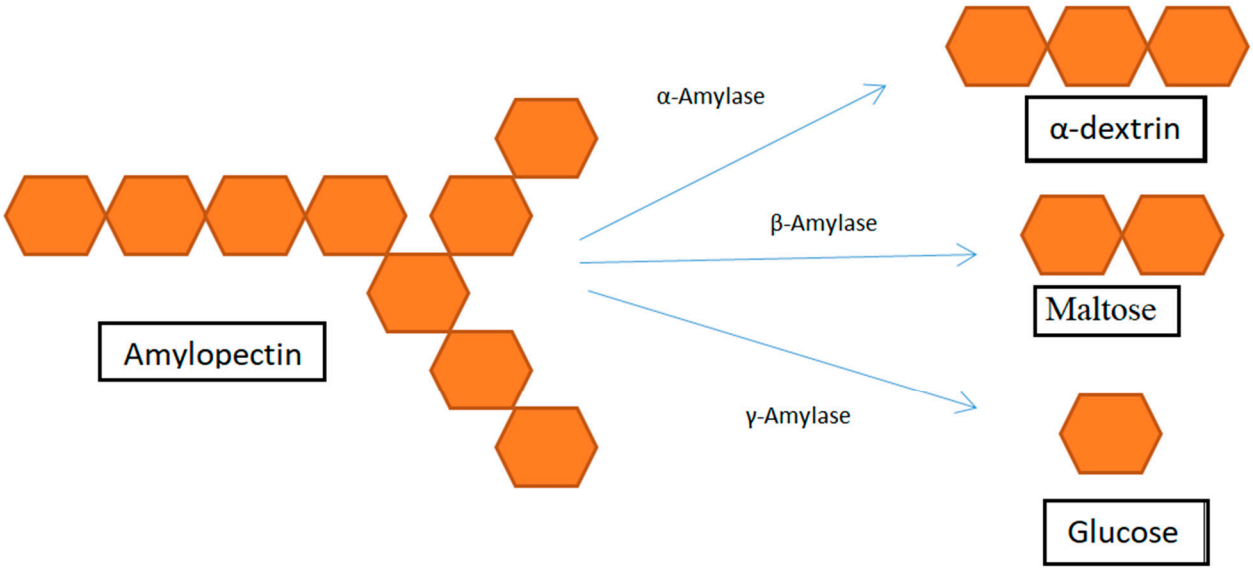

Figure 9. Generalized mode of action of amylases.

Endoamylases or α-amylase (EC 3.2.1.1): It cleaves the α-1,4-bonds present in the inner regions of amylose and amylopectin to break into oligosaccharides and dextrins, decreasing the solution's viscosity.

Exoamylase or β-amylase (EC 3.2.1.2): Only the α-1,4-bonds at the non-reducing ends are broken, releasing limit dextrins and β-maltose.

γ-amylase or Amyloglucosidase or Glucoamylase (EC 3.2.1.3): It functions as a debranching enzyme by cleaving the final α-1,4 links at the non-reducing end of amylase and amylopectin, which releases glucose.

Many fungi, bacteria, and actinomycetes have been found to produce amylases. Several species of the genera *Aspergillus* and *Penicillium* are effective fungal amylase producers. *Aspergillus flavus*, *Aspergillus fumigatus*, and *Aspergillus niger* are among the fungi that produce amylases [102–104]. *Bacillus* species are the most common types of the many bacteria that produce amylases. *Rhodothermus*, *Corynebacterium*, *Geobacillus*, *Lactobacillus*, and *Pseudomonas* are some more species. *Streptomyces* and *Thermonospora* have been discovered to make amylase among the actinomycetes [105].

Enzyme technology is typically regarded as the most environmentally friendly method of saccharification in any biorefinery. Using additional enzymes to allow for more extensive exploitation of plant biomass could result in processing that uses less energy and chemicals while recovering more fermentable sugar. Table 3 depicts the use of multiple hydrolytic enzymes produced by fungi and bacteria to aid in the process of polysaccharide bioconversions in various biomass residues for the production of second-generation bioethanol.

To completely hydrolyze biomass residues and produce second-generation bioethanol, a large number of enzymes are required. These enzymes are required for hydrolyzing a specific linkage at a specific phase in any biorefinery. Furthermore, the method of action provides any biorefinery with critical information for overcoming any flaws in the hydrolysis of any type of sugar or linkage between them. A microorganism with the ability to release a variety of enzymes involved in the hydrolysis of lignocellulosic biomass could be a candidate for use in a biorefinery producing second-generation biofuel.

Table 3. Application of various hydrolytic enzymes in the degradation of polysaccharides in various biomass residues.

Hydrolytic Enzyme	Classification	Mode of Action	Common Lignocellulosic Biomass	References
Cellulases	Endoglucanase or Endo-β-1,4-glucanase	Random hydrolysis of the interior glycosidic bonds in cellulolytic biomass	Wheat straw, rice straw, corn cobs, wheat bran, oat bran, Arundo donax, Populus tremuloides, deoiled rice bran, kitchen waste	[9,73,75,106]
	Cellobiohydrolase or Exo-β-1,4-glucanase	Hydrolysis of beta-D-glucosidic linkages by releasing mainly cellobiose		
	Cellobiase or β-glucosidase (BG)	Cleavage of cellobiose		
Hemicellulases	Endo-β-1,4-xylanase	Release of xylose from xylan by Endohydrolysis of (1 → 4)-beta-D-xylosidic linkages	Wheat bran, kitchen waste, Banana peels, Peanut oil cake, Brewer's spent grain	[9,80,81,84,106–108]
	Exo-β-1,4-xylanase or β-1,4-xylan xylohydrolase	Release monomeric xylose from the non-reducing end of xylan		
	β-1,4-xylosidase or Xylobiase	hydrolyzes disaccharides such as xylobiose and the higher xylooligosaccharides		
	Endo-β-1,4-mannanase	Randomly cleaving the mannan's β-1,4-linkage internal links		
	Exo-β-mannosidase	Releases mannose sugar moieties by cleaving β-1,4-linked mannosides from the non-reducing ends of mannan		
	β-glucosidase	Hydrolyzes the 1,4-β-D-glucopyranose found at the non-reducing ends of the oligosaccharides		
	α-galactosidase	breaks down the α-1,6-linked D-galactopyranosyl side chains of the oligosaccharides		
	Acetyl mannan esterase	The debranching enzyme releases acetyl groups.		
Pectinases	Protopectinases	Liberate soluble form polymerized pectin	Wheat bran, mango peel, banana peel, kitchen waste, Orange peels, exhausted sugar beet cassettes	[84,85,109,110]
	Pectin Methyl Esterases	Deesterify the methyl group of pectin, releasing pectic acid and methanol		
	Pectin Acetyl Esterases	Hydrolysis of the acetyl esters found in pectin		
	Polymethylgalacturonases	Breaks α-1,4-glycosidic linkages in pectin		
	Polygalacturonases	Cleaves the polygalacturonic acid's α-1,4-glycosidic linkages		
	Pectate Lyases	Release α-4,5-D-galacturonate from the glycosidic bonds in polygalacturonic acid		
	Pectin Lyases	randomly break the esterified pectin and create unsaturated methyloligogalacturonates.		
Amylase	Endoamylases or α-amylase	Cleaves the α-1,4-bonds present in the inner regions of amylose and amylopectin	Rice bran, wheat bran, black gram bran, Soybean husk, flour mill waste	[101,105,111]
	Exoamylase or β-amylase	Release limit dextrins and β-maltose		
	ɣ-amylase or Amyloglucosidase or Glucoamylase	Debranching enzyme releases glucose		

4. Production of Microbial Enzymes for Use in the Generation of Second-Generation Bioethanol

Two different fermentation procedures can be used to produce enzymes at the industrial level while taking production costs and using natural substrates into account. There are two types of fermentation: liquid-state fermentation and solid-state fermentation.

4.1. Solid-State Fermentation (SSF)

For the growth of microorganisms, this type of fermentation often uses a moist solid substrate. SSF is a fermentation procedure that uses either a natural or inert solid substrate in the absence of freely flowing water [112,113]. A key component of SSF is the choice of solid material, which must be insoluble and serve as both a physical support and a source of nutrition for the bacteria. This imitates their natural environment and promotes the synthesis of enzymes and other useful metabolites for industry [114,115]. Due to the utilization of lignocellulosic as a medium or substrate for the development of microorganisms to create cellulases, hemicellulases, pectinases, and amylases, this fermentation is cost-effective. SSF cultures were discovered to produce more enzymes as compared to liquid cultures. SSF might be viewed as a superior method for the industrial synthesis of enzymes while taking into account production costs and employing natural substrates. Higher fermentation productivities, higher product stability, higher product concentration, decreased chances of contamination due to lower water activity need, and development of microorganisms specialized for water-insoluble substrates are all benefits of SSF [116]. Other benefits include the use of straightforward instrumentation, compactness of the fermenter due to a smaller volume of water, lack of foam formation, higher fermentation capacity, decreased catabolic repression, cost-effectiveness, and a reduced need for solvents in the product recovery process [117,118].

Various researchers have used different lignocellulosic, agro-industrial, and biodegradable municipal solid waste feedstocks to produce various hydrolytic enzyme systems important in the industries working in the field of second-generation biofuels using bacterial and fungal cultures. In an attempt to investigate the potential of *Aspergillus niger* CECT2088 on brewer's spent grain for the production of cellulases and xylanases, Leite et al. [108] used brewer's spent grain. Kaur et al. [119] used a natural variant of *Aspergillus niger* P-19 to produce a cellulase-hemicellulase consortium on rice straw for efficient and low-cost saccharification, whereas Chugh et al. [9] produced multiple carbohydrases including cellulases, hemicellulases, pectinases, and amylases through solid-state fermentation of de-oiled rice bran. Recently, our group developed an enzyme cocktail comprised of 19 hydrolytic enzymes for the generation of bioethanol from various lignocellulosic and agro-industrial waste biomass residues in solid, surface, and submerged state fermentation using a standardized kitchen waste-based medium [120]. More studies on optimizing various physical and cultural factors, as well as enzyme characterization, have been published in the literature to achieve the highest enzyme productivity and activity. Table 4 compiles some examples of solid-state fermentations for the production of various hydrolytic enzymes important in second-generation biofuels with significant breakthroughs.

Table 4. Examples of the production of hydrolytic enzyme systems by solid-state fermentations using various substrates and breakthroughs.

Substrate	Microorganism	Enzymes	Major Breakthrough	References
Wheat straw, rice straw, corn cobs, wheat bran, oat bran, Arundo donax, Populus tremuloides	*Thermoascus aurantiacus*	Cellulases	Thermostable cellulolytic components production	[121]
Wheat bran	*Aspergillus awamori Nakazawa* (MTCC 6652)	Glucoamylase	Optimization of extraction and purification of glucoamylase	[122]

Table 4. *Cont.*

Substrate	Microorganism	Enzymes	Major Breakthrough	References
Wheat bran	*Aspergillus niger NS-2*	Cellulases xylanase, mannanase, pectinase, amylases	Co-production of multiple enzymes for Bioethanol Production	[123]
Deoiled rice bran	*Aspergillus niger, Aspergillus oryzae, Trichoderma reesei*	Cellulase, amylase	Co-production of the thermostable multi-enzyme system for ethanol production	[9,124]
Kitchen waste	*Aspergillus niger* CJ-5	Cellulases, xylanase, mannanase, pectinase, amylases	Co-production of multiple enzymes for Bioethanol Production from kitchen waste residues	[73]
Brewer's spent grain	*Fusarium oxysporum* SS-25	Cellulases	Production of cellulases for the production of ethanol from brewer's spent grain	[125]
wheat straw, paddy straw, sugarcane waste, maize straw	*Bacillus licheniformis*	α-amylase	Production of amylase from the mixture of agricultural residue waste	[126]
Rice bran, wheat bran, black gram bran	*Achromobacter xylosoxidans*	Amylase, cellulase, xylanase	Co-production of multiple enzymes from various agro waste	[127]
Peanut oil cake	*Aspergillus oryzae*	Cellulase, xylanase, amylase	Enhancement in various functional properties during fermentation in addition to enzyme activities	[107]
Brewer's spent grain	*Aspergillus niger* CECT2088	Cellulase, xylanase	Simultaneous production of lignocellulolytic enzymes	[108]
Orange peel, apple pomace, and rice fiber	Compost from Municipal Solid Waste as inoculum	Cellulases	Development of a framework for a zero-waste enzyme production process	[128]
Coffee husk and wood chips	Compost from MSW as inoculum	Cellulases	Enhanced cellulase production	[129]
Orange peels and exhausted sugar beet cassettes	*Aspergillus awamori* 2B.361 U2/1	Cellulase, xylanase, pectinase	Enhanced sugar production	[109]
Sugarcane bagasse	*Penicillium* sp., *Rhizomucor* sp., *Trichoderma* sp.	Cellulases	Use of sugarcane bagasse as an inducer for cellulase	[130]
Grape pomace with wheat bran	*Aspergillus niger* 3T5B8	Cellulase, xylanase	Production of a cocktail of hydrolytic enzymes using Grape pomace with wheat bran	[131]
Wheat bran, banana peel, orange peel, rice bran, pine apple peel	*Bacillus subtilis* D19	Amylase	Enhanced amylase production on various agro-waste residues	[132]
Mango peels	*Aspergillus tamarii*	Pectinase	Enhanced polygalacturonase and pectin lyase	[110]
Wheat chaff	*Trichoderma reesei* QM 9414	Cellulases and xylanase	Simultaneous production of cellulase and xylanase	[133]
Rice straw	*Aspergillus niger* P-19	Cellulases, hemicellulases	Enhanced sugars and ethanol from rice straw	[119]
Rice straw	*Penicillium* spp.	Cellulase	Potent cellulase cocktail production for lignocellulosic degradation	[69]
Soybean husk and flour mill waste	*Aspergillus oryzae*	Amylase	Production and purification of alpha-amylase	[111]
Wheat bran	*Bacillus* sp. TC-DT13	Xylanase	Optimized production of extracellular xylanase	[134]
Wheat bran	*Trichoderma reesei, Neurospora crassa*	Cellulases	Optimization and standardization of various factors for cellulase production	[24]
Banana peels	*Aspergillus fumigatus*	Pectinase and xylanase	Coproduction of pectinase and xylanase	[84]
Kitchen waste	*Aspergillus niger S-30*	Cellulases, Hemicellulases, Pectinases, Amylases	19 hydrolytic enzymes from a single substrate and organism	[120]

4.2. Liquid State Fermentation (Submerged and Surface)

Under stationary or shaking circumstances, liquid-state fermentation involves the development of microorganisms in a liquid medium that contains the necessary nutrients. This type of fermentation is appealing for the development of microbes and the creation of products with added value due to several factors, including (a) homogenous distribution of nutrients for the proliferation of microorganisms; (b) simplicity of monitoring of variables such as moisture, temperature, pH, agitation, oxygen, and nutrient levels; (c) powerful technology that has already been best adapted with automatic grade and equipment availability. Cellulolytic enzymes, ligninolytic enzymes, and other beneficial metabolites can all be produced through liquid-state fermentation [135].

Liquid-state fermentation is divided into submerged and surface culture fermentation depending primarily on whether the incubation is being carried out in stationary or rocking circumstances. In surface culture, fermentation microorganisms develop on the shallow nutritional media's surface, consume the nutrients necessary for their growth, and simultaneously release products into the medium. Since fungi are filamentous in nature and agitation might break their mycelia, segregating biomass from the liquid medium, this mode of fermentation does not call for agitation in the case of fungi [136].

However, surface culture fermentation has a lower bio-reaction rate and longer fermentation periods as compared to submerged fermentation, which involves robust aeration and agitation [137]. Submerged fermentation is preferred over surface culture fermentation as a result of this drawback. Through submerged cultivation, many strains of bacteria, yeast, fungus, and algae have been employed for fermentation. These methods of fermentation can use either synthetically manufactured or lignocellulosic biomass-produced fermentation media.

The fungal hyphae are not desiccated as a result of the continual immersion in a liquid medium during liquid-state fermentation, which is also the most effective, easiest to sterilize, and most cost-effective approach for producing bioagents in large quantities [138]. Except for high-density cultures, microorganisms are exposed to a fixed temperature throughout their life cycle. Additionally, oxygen availability to biomass can be regulated at a specific level of medium saturation. When compared to solid substrates, submerged culture has various benefits, including easier control of fermentation parameters such as pH and temperature, improved contamination control, and a lower labor and space demand. The nature and amplitude of forces in a bioreactor are studied using fermenters that offer the organism a low-shear environment. Surface culture fermentation is preferred to submerged fermentation for several reasons, including equipment expense, energy usage, aeration breakdown, improved productivity, and yield [139].

Elegbede et al. [140] synthesized in-house xylanases in submerged fermentation conditions using corn cob as the substrate. Irfan et al. [141] used a peanut shell to produce cellulases in a submerged fermentation process. Recent studies investigated the much-needed potential of the submerged fermentation process in the production of various hydrolytic enzymes involved in the production of second-generation biofuels. Table 5 depicts a few examples of liquid-state fermentation producing hydrolytic enzymes on various substrates, as well as a significant breakthrough in their production.

Table 5. Examples of the production of hydrolytic enzyme systems by liquid-state fermentations using various substrates and breakthroughs.

Substrate	Microorganism	Enzymes	Major Breakthrough	References
Rice bran	*Aspergillus niger*	Pectinase	Enhanced Polygalacturonase and Pectinmethylesterase activity	[142]
Solka-Floc cellulose	*Penicillium brasilianum* IBT 20888	Cellulases, xylanase	Coinduction of cellulolytic and xylanolytic	[143]
Mandarin peels and tree leaves	*Pleurotus dryinus*	Cellulases, xylanase, laccase, manganese peroxidase	Enhanced activity of cellulases, xylanase, laccase, manganese peroxidase	[144]
Starch	*Bacillus* sp.	Amylase	Optimization of enhanced amylase production	[145]
Partially delignified cellulignin	*Trichoderma harzianum* IOC-4038	Cellulases	Simultaneous saccharification and fermentation process development using partially delignified cellulignin	[146]
Sugarcane bagasse, corn stover	*Acremonium* sp.	Cellulases, xylanase	Enhanced reducing sugar conversion	[147]
Wheat bran	*Aspergillus tamarii* MTCC5152	Amylase	Production of a cellulase-free and alkali-stable xylanase	[148]
Corn cob	*Aspergillus fumigatus* SD5A	xylanase	Use of eight fungal strains in xylanase production	[140]
Pineapple stem	*Bacillus subtilis* BKDS1	Pectinase	Economical production of the enzyme, pectinase using pineapple stem extract (PSE) medium	[149]
Coffee waste	*Penicillium humicola*	Mannanase	Statistical experimental designs to enhance the β-mannanase production	[150]
Wheat bran and citrus peel waste	*Bacillus pumilus*	Xylanase and pectinase	Maximum production of xylanase and pectinase in a short submerged fermentation cycle	[151]
Banana peels	*Bacillus subtilis* TYg4-3 and *Bacillus amyloliquefaciens* SW106	Pectinase	Optimization of bacterial pectinsae	[152]
Coffee residue powder, date seeds powder, prickly pear seeds	*Bacillus subtilis* US191	Mannanase	Statistical experimental designs to enhance the bacterial β-mannanase production	[90]
Peanut shells	*Bacillus paralichniformis*	Cellulases	Utilization of peanut shells for cellulase production through Box-Behnken Design	[141]
Wheat chaff	*Trichoderma reesei* QM 9414	Cellulases and xylanase	Simultaneous production of cellulase and xylanase	[133]
Wheat bran, rice husk	Aspergillus niger	Amylase	Production and purification of amylase using an aqueous two-phase system	[153]
Corn stover	*Phanerochaete chrysosporium* PC2	Cellulases and hemicellulases	Revealed the importance of carbohydrate-binding module in the hydrolysis process of lignocellulose	[154]
Corn bran	*Aspergillus niger*	Xylanase	Use of UV- rays for enhanced xylanase	[155]
Wheat bran and citrus peel waste	*Bacillus safensis* M35, *Bacillus altitudinis* J208	Xylanase and pectinase	Concentration values for wheat bran and citrus peel substrates are to be amended in one single production medium for enhanced xylanase and pectinase	[156]
Banana peels	*Aspergillus fumigatus*	Pectinase and xylanase	Coproduction of pectinase and xylanase	[84]
Kitchen waste	*Aspergillus niger S-30*	Cellulases, Hemicellulases, Pectinases, Amylases	19 hydrolytic enzymes from a single substrate and organism	[120]

Enzymatic saccharification of lignocellulosic feedstock is followed by fermentation of the hydrolysate by suitable fermentative microorganisms for ethanol production. The hydrolysate produced by enzymes after saccharification of pretreated lignocellulosic feedstock contains a mixture of hexoses and pentoses, including glucose, mannose, xylose, arabinose, galactose, and some oligosaccharides. *Saccharomyces cerevisiae, Pachysolen tannophilus, Escherichia coli, Zymomonas mobilis, Candida brassicae, Candida shehatae, Bacillus macerans, Clostridium* sp., etc. are used to ferment these monomeric sugars to produce ethanol [157,158]. However, for an effective ethanol production method, the fermentative microorganism should be able to use a wide range of substrates, including pentoses and hexoses, and have high ethanol productivities, tolerance for high ethanol concentrations and inhibitors present in the hydrolysate [159,160]. So far, four types of fermentation have been studied: (i) separate hydrolysis and fermentation (SHF), (ii) simultaneous saccharification and fermentation (SSF), (iii) simultaneous saccharification and co-fermentation (SSCF), and (iv) Consolidated bioprocessing (CBP), and the key features of each are summarised in Table 6.

Table 6. Salient features of various types of fermentation technology involved in second-generation bioethanol production.

Fermentation Technology	Steps Involved	Advantages	Disadvantages	Reference
Separate hydrolysis and fermentation (SHF)	1. Pretreatment 2. Saccharification 3. Fermentation	The conditions can be optimized separately for each step	End product inhibitionRequire separate reactors for each step High energy and time consumption	[161]
Simultaneous saccharification and fermentation (SSF)	1. Pretreatment 2. Saccharification and Fermentation	• Elimination of end-product inhibition • Removes the need for separate reactors • Cost-effective • Reduction in time	Differences in the optimum condition for hydrolytic enzymes and fermenting microorganisms	[162]
Simultaneous Saccharification and Co-Fermentation (SSCF)	1. Pretreatment 2. Saccharification and Co-Fermentation	• Saccharification of both hexose and pentose sugars • High sugar and ethanol yield	Differences in the optimum condition for hydrolytic enzymes and fermenting microorganisms	[163]
Consolidated Bio-Processing (CBP)	Pretreatment, enzyme production, Saccharification, and Fermentation	• All the steps are carried out in a single reactor • Elimination of cost involved in the purchase or production of enzymes	Differences in the optimal conditions for enzymes or microorganisms involved in the process	[164]

Many reports from around the world suggested that the use of enzymes in the conversion of lignocellulosic and other waste biomass residues to second-generation bioethanol provides a much-needed boost to this sector. Roberto et al. [162] reported SSF using a vertical ball mill reactor with a high loading of rice straw. The study concluded that feeding the substrate gradually at an initial load of 16% with 4% additions after 10 and 24 h using an inoculum level of 3 g/L resulted in a high ethanol concentration of 52.3 g/L. As a result, the findings demonstrated that a suitable fed-batch feeding strategy of biomass aids in overcoming the limitations of SSF in batch mode. Zhu et al. [163] used SSCF to ferment ethylenediamine-treated corn stover with *Saccharomyces cerevisiae* and xylose utilizing yeast, yielding 59.8 g/L ethanol at 42 °C. In a study by da Silva et al. [165], pretreatment used alkaline hydrogen peroxide, which efficiently removed lignin and hemicellulose from carnauba waste, yielding 57.49% and 56.13%, respectively. Chen et al. [166] obtained 72.3% ethanol yield on total sugar by co-fermenting with *S. cerevisiae* IPE005 in corn stover hydrolysate. In another study, using a statistical approach significantly increased sugar yields and the tool

was successful in designing simple conditions of pre-treatment and hydrolysis of deoiled rice bran for maximum saccharification of all carbohydrates present in the substrate [9].

Recently, our group investigated the potential of biodegradable solid waste, primarily kitchen waste, as a feedstock for the production of second-generation biofuel. A multiple hydrolytic enzyme cocktail was created using 19 concentrated enzyme components with an enzymatic yield of 150–250 IU/mL of CMCase. 30–40 IU/mL of FPase, 25–35 IU/mL of Avicelase, 30–40 IU/mL of β-glucosidase, 135–145 IU/mL of cellobiase, 160–175 IU/mL of salicinase, 800–900 IU/mL of xylanase, 50–70 IU/mL of xylosidase, 260–275 IU/mL of mannanase, 25–35 IU/mL of mannosidase, 25–35 IU/mL of pectin-lyase, 25–35 IU/mL of polygalacturonase, 12,500–15,000 U/mL of α-amylase, 50–75 IU/mL of pullulanase, 400–500 IU/mL of glucoamylase, 140–165 IU/mL of α-glucosidase, 2100–2300 U/mL of protease, 190–210 U/mL of lipase and 190–210 U/mL of alginate lyase [120]. This breakthrough has paved the way for biodegradable solid waste to be used as a substrate for enzymes in second-generation biofuels.

Different countries use different feedstocks for bioethanol production based on regional availability, local climate, and economic drivers. Sugars and starches are the primary feedstocks for commercial bioethanol production. The ethanol produced in the United States and Brazil accounts for 85% of all bioethanol produced globally [167]. The United States, the world's largest bioethanol producer, primarily uses corn as a feedstock, which is also used in China and Slovakia whereas Brazil, the world's second-largest bioethanol producer, primarily uses sugarcane juice and molasses as a feedstock which are also employed in India, Indonesia, Brazil, China, Thailand, and Colombia. Wheat is generally used in Denmark, Austria, Germany, Canada, Belgium, France, and Russia [75]. Because most of these feedstocks compete with human feed, lignocellulosic biomass, as well as agro-industrial and biodegradable municipal solid waste residues, which are abundant and the most untapped natural reservoir on the planet, are promising feedstocks for second-generation bioethanol generation.

5. Conclusions and Future Outlook

The world's increasing energy requirements as a result of urbanization, excessive use of fossil fuels, and the issue of disposing of agricultural waste residues are all scenarios that make the use of biofuels made from waste biomass an essential solution that can solve all of these problems. Second-generation ethanol production is significantly more expensive than first-generation ethanol, which uses existing technology for converting biomass to bioethanol, and it is difficult to predict when its cost will approach that of corn/sugarcane ethanol. Cellulosic ethanol's superior environmental benefits require drastic cost reductions at all levels. The cost of pretreatment, enzymes for hydrolysis, fermentation of all sugars, and distillation, all significantly increase the final cost of producing cellulosic ethanol. Many countries around the world have launched Ethanol Blending Programmes to reduce their reliance on crude oil imports, reduce carbon emissions, and increase farmer income. Because of the coordinated efforts of the Public Sector Oil Marketing Companies, the program's target of 10% blending has been met much ahead of the November 2022 deadline in India. The Government of India announced its 'National Policy on Biofuels' in 2018, with an indicative target of 20% ethanol blending in gasoline by 2030. However, given the encouraging performance and various interventions implemented by the government since 2014, the target of 20% ethanol blending has been pushed back from 2030 to 2025–26. In this context cellulosic ethanol and enzyme systems especially cellulases and hemicellulases are emerging as the stronger contenders to increase the indigenous production of second-generation bioethanol. Globally, research at all levels is currently being conducted to reduce the overall cost of the process. Furthermore, government-level incentives for second-generation ethanol and mandated ethanol blending into gasoline in several countries may pave the way for future bioethanol production from waste biomass.

The scientific community has switched to biofuels that are made from a variety of biomass residues, including municipal and agricultural waste, as a result of the rising cost of

fossil fuels, the global warming caused by the careless use of these fuels, and the unscientific disposal of agricultural and agro-industrial waste residues. The commercial manufacture of bioethanol, which is now the highest-volume industrial fermentation product, generally uses sweet and starchy substrates. However, specialists are careful about their utilization due to the utility of such starchy residues as human nourishment. Even yet, many nations have established limitations on their permissible usage. Scientists are working to use agricultural, agroindustrial, and municipal solid waste as second-generation bioethanol feedstocks as the biofuel industry develops as a result of the rise in ethanol demand. These feedstocks are used by a small number of companies that pretreat and hydrolyze materials using chemical processes, which results in increased costs and significant chemical loading that eventually enters our life and environment. Enzymatic hydrolysis is advised, even though it adds between 30 and 50% to the overall cost of producing ethanol from lignocellulosic wastes. Enzymes with higher substrate specificity, lower dose requirements, and improved cost-effectiveness are required. The process economy as a whole can gain from the creation of innovative enzymes that can hydrolyze a variety of substrates, high-titer production of such enzymes, further development using genetic and molecular methods, and lower costs associated with the enzyme production process. Technologies that reuse the enzyme that washed away during hydrolysis can help address the issue of enzyme cost. The development of effective and environmentally friendly process technology for converting lignocellulosic residues to bioethanol may be made possible by advancements in enzyme technology and commercialization. This technology may prove to be a panacea for pressing global issues such as the depletion of fossil fuels and the improper disposal of these priceless resources.

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