

Biotechnological Transformation of Lignocellulosic Biomass in to Industrial Products: An Overview

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Received 15 January 2016; accepted 15 March 2016; published 18 March 2016

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Abstract

Lignocellulose—a major component of biomass available on earth is a renewable and abundantly available with great potential for bioconversion to value-added bio-products. The review aims at physio-chemical features of lignocellulosic biomass and composition of different lignocellulosic materials. This work is an overview about the conversion of lignocellulosic biomass into bio-energy products such as bio-ethanol, 1-butanol, bio-methane, bio-hydrogen, organic acids including citric acid, succinic acid and lactic acid, microbial polysaccharides, single cell protein and xylitol. The biotechnological aspect of bio-transformation of lignocelluloses research and its future prospects are also discussed.

Keywords

Lignocellulosic Biomass, Bio-Transformation, Bio-Energy, Organic Acids, Microbial Polysaccharides, Single Cell Proteins

1. Introduction

The amount of solar energy received on earth's surface is 2.5×10^{21} Btu/year (1 Btu = 55.05585 Joules), more than 12,000 times the present human requirement of 2.0×10^{17} Btu/year, and approximately the projected demand of energy in 2050 would be about 4000 times [1] [2]. The solar energy, stored as carbon via photosynthesis is 10 times the world usage. Throughout the world, terrestrial plants produce 1.3×10^{10} metric tons (dry weight basis) of wood per year, which has the energetic equivalent of 7×10^9 metric tons of coal or about

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two-third of world's energy requirement. Available cellulosic feedstocks from agriculture and other sources are about 180 million tons per year [1] [2]. Lignocellulose is the major component of biomass, consisting of around half of the plant matter produced by photosynthesis and it is the most abundant renewable organic resource in soil. It consists of cellulose, hemicelluloses and lignin that are strongly intermeshed and chemically bonded by covalent linkages and non-covalent forces [3] [4]. The chemical properties of components of lignocellulosic materials make them suitable substrate of enormous biotechnological values [5] [6]. Large amounts of lignocellulosic materials are generated through forestry and agricultural practices, timber, pulp and paper, and many agro-industries and they generate an environmental pollution problem. A large fraction of these lignocellulosic materials is often disposed of by burning, which is not restricted to developing countries alone, but is considered as a global phenomenon [5] [7]. However, the huge amount of residual plant biomass considered as "waste" can potentially be converted into different value-added products such as bio-ethanol, bio-methane, and other value added products. These lignocellulosic wastes can also be used as energy sources for microorganism during fermentation to produce various lignocellulolytic enzymes [5].

2. Lignocellulosic Biomass

Lignocellulosic biomass is a major component of plants that provides them structure and is usually present in stalks, leaves and roots. Lignocellulosic biomass consists mainly of three types of polymers: Cellulose (30% - 60%), hemicelluloses (20% - 40%) and lignin (10% - 25%) which are interlinked to each other in a hetero-matrix. Approximately 90% of dry matter in lignocellulosics consists of cellulose, hemicelluloses and lignin, whereas the rest comprises of ash and extractives [8]-[11]. The relative abundance of cellulose, hemicelluloses and lignin depends on type of biomass and vary in different lignocellulosic biomass (Table 1) [3] [5] [6] [10] [12]-[27]. Composition of lignocellulosic biomass is influenced by the plant's genetic and environmental factors that vary considerably [6] [8] [10].

Cellulose ($C_6H_{10}O_5)_n$ is a homopolysaccharide composed of linear chains of β -D-glucose units linked by β -1, 4 glycosidic linkage. These chains are linked by strong hydrogen bonding which forms the cellulose chains into microfibrils, making it crystalline in nature. These microfibrils are bundled together to form cellulose fibres. Cellulose consists of crystalline (organized) region which is resistant to degradation and amorphous (not well organized) region which is easy to degrade [28]-[30]. The cellulose fibres are embedded in an amorphous matrix of hemicelluloses, lignin and pectin. Lignin and hemicellulose are present in the space between cellulose microfibrils in primary and secondary cell walls and middle lamellae [31] [32].

Hemicelluloses are the branched heteropolymers consisting of pentose sugars (D-xylose and L-arabinose) and hexose sugars (D-mannose, D-glucose and D-galactose) with xylose being most abundant [1] [33]. Hemicelluloses are composed of xylan, mannan, arabinan and galactan as main heteropolymer [34]. Xylan is the major structural component of the plant hemicelluloses and it is the second most abundant renewable polysaccharide in nature after cellulose. Xylan represents approximately one-third of all the renewable organic carbon on earth [35] [36]. Xylan is a complex polysaccharide consisting of a backbone of xylose residues connected by β -1, 4-glycosidic linkage along with traces of L-arabinose [34] [37]. The xylan layer with its covalent interaction to lignin and its non-covalent linkage with cellulose may be essential in maintaining the integrity of cellulose in situ and in protecting the cellulosic fibers against degradation to cellulases [34] [38].

Lignin is an aromatic polymer, consisting of phenyl propane units which are organized in to a large three dimensional network structure. The phenyl propane unit's p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol are joined by C-O-C and C-C linkages. Lignin also contains methoxyl, phenolic, hydroxyl and terminal aldehyde groups in the side chains. Lignin acts as glue and fills up the gap between and around cellulose and hemicelluloses in lignocellulosic biomass which binds them tightly. Lignin is an amorphous heteropolymer which makes the cell wall impermeable, resistant against microbial and oxidative attack [3] [8] [39] [40]. Generally, softwoods have higher lignin content compared to hardwoods while higher amount of holocellulose is present in hardwoods. The presence of lignin in lignocellulosic biomass makes difficult the release of monomer sugars from holocellulose [8].

Extractives are low molecular weight and non-structural components of lignocellulosic biomass which are soluble in neutral organic solvents or water. Extractives consist of biopolymers such as terpenoids, steroids, resin acids, lipids, waxes, fats, and phenolic constituents in the form of stilbenes, flavanoids, tannins, and lignans. Generally, percentage of extractives is higher in leaves, roots and bark compared to stem wood [8] [41] [42]. The inorganic matter in lignocellulosic biomass is regarded as ash content which consists of major elements (Si,

Table 1. Composition of different lignocellulosic biomass.

Lignocellulosic material	Lignin (%)	Hemicellulose (%)	Cellulose (%)	References
Bamboo	21 - 31	15 - 26	26 - 43	[3] [16]
Banana waste	14	14.8	13.2	[3]
Barley straw	14 - 15	24 - 29	31 - 34	[15] [16]
Bast fibre jute	21 - 26	18 - 21	45 - 53	[3] [16]
Bast fibre kenaf	15 - 19	22 - 23	31 - 39	[3] [16]
Black gram residue	23.14	32.48	26.80	[17]
Coastal Bermuda grass	6.4	35.7	25	[5] [18]
Coconut coir	19.4	13.3	47.8	[14]
Coconut coir	18	26	48	[19]
Corn cob	15	35	45	[3] [5] [18]
Corn stalks	4.5 - 6.6	38 - 42	35	[13]
Corn stalks	17	24	43	[19]
Corn stover	18	22	40	[20]
Corn stover	18	20.5	41.7	[21]
Cotton gin waste	-	16	78	[19]
Elephant grass	24	24	22	[3]
Esparto grass	17 - 19	27 - 32	33 - 38	[3] [16]
Flax straw	22	27	29	[15]
Grasses (average)	10 - 30	25 - 50	25 - 40	[6]
Hardwood stem	18 - 25	24 - 40	40 - 55	[3] [5] [6] [18]
Leaves	0	80 - 85	15 - 20	[5] [18]
Millet husk	14	27	33	[19]
Newspaper	18 - 30	25 - 40	40 - 55	[5] [18]
Nut shells	30 - 40	25 - 30	25 - 30	[5] [18]
Oat straw	16 - 19	27 - 38	31 - 37	[3] [16]
Orchard grass (medium maturity)	4.7	40	32	[3] [5]
Pinewood	20	24	39	[10]
Poplar wood	26	17	35	[22]
Rice husk	14	24	31	[19]
Rice straw	18	24	32.1	[3] [5] [14] [18]
Rye straw	16 - 19	27 - 30	33 - 35	[3] [16]
Sabai grass	20.88	23.72	49.90	[23]
Softwood stem	25 - 35	25 - 35	45 - 50	[3] [5] [6]
Softwood stem	19 - 24	27 - 32	32 - 44	[16] [19]
Sugarcane bagasse	18.4	26.9	38.1	[24]
Sugarcane bagasse	24	25	43	[21]
Sugarcane tops	36.1	24.2	33.3	[25]
Sunhemp residue	17.4 - 18.4	11.9 - 13	43.4 - 48	[26]
Sweet sorghum bagasse	18	25	45	[22]
Switchgrass	12	31	45	[3]
Switchgrass	18	22	31	[21]
Timothy grass	18	30	34	[10]
Waste papers from chemical pulps	5 - 10	10 - 20	60 - 70	[5] [18]
Wheat bran	3 - 10	22 - 25	7 - 11	[27]
Wheat bran	16 - 21	26 - 32	29 - 35	[5]
Wheat bran	7.7	30.8	41.3	[12]
Wheat straw	15	50	30	[5]
Wheat straw	17	23	33	[21]
Wheat straw	14.5	24.8	36	[24]

Na, K, Mg and Ca) and minor elements (Al, Fe, Mn, P and S). Ash content in dry wood and shells is less than 1% (wt/wt) while it may be up to 25% in straws and husks [8] [41] [42].

3. Biotransformation of Lignocellulosic Biomass

Lignocellulosic biomass from wood, grasses, crop residues, forestry waste, and municipal solid waste are particularly abundant in nature and have a potential for bioconversion into various value added biological and chemical products. Accumulation of lignocellulosic biomass in large quantities presents a disposal problem which results not only in deterioration of environment but also loss of valuable materials. This lignocellulosic biomass can be used in paper manufacture, animal feed, biomass fuel production, and composting [3]. Biotechnological transformation of lignocellulosic biomass can make significant contribution for the production of organic chemicals. Over 75% of organic chemicals are synthesized from five primary base chemicals which are ethylene, propylene, toluene, xylene and benzene [5] [43]. These lignocellulosic biomass resources can also be used to produce various organic chemicals such as ethanol [44] [45], acetone [46] [47], butanol [46] [48], bio-hydrogen [49] [50], bio-methane [51]-[53], acetic acid [54] [55], citric acid [56] [57], fumaric acid [58], lactic acid [59], xylitol [60] etc. Aromatic compounds might be produced from lignin whereas the low molecular weight aliphatic compounds can be derived from ethanol produced by fermentation of sugars (glucose, mannose and xylose) generated from saccharification of lignocellulosic biomass [5]. Biotechnological conversion of lignocellulosic biomass in various industrial products is cost effective and environmentally sustainable route.

4. Pretreatment and Hydrolysis of Lignocellulosic Biomass

Solid-state and submerged fermentation conditions have been used for the production of compounds of industrial interest from lignocellulosic biomass. In solid-state fermentation (SSF), lignocellulosic biomass is utilized directly without any pretreatment or after some physical, chemical, or biological pretreatments. Lignocellulosic biomass are recalcitrant against enzymatic attack therefore, a pretreatment step is required which makes lignocellulosic biomass suitable for fermentation. Lignocellulosic biomass-derived sugars are economically attractive feedstock for large scale fermentation of different chemicals. Sugars released after hydrolysis of cellulose and hemicelluloses are converted into different industrial products like ethanol, butanol, glycerol, organic acids, bioactive polysaccharides, and others through submerged fermentation (Figure 1) [40] [61].

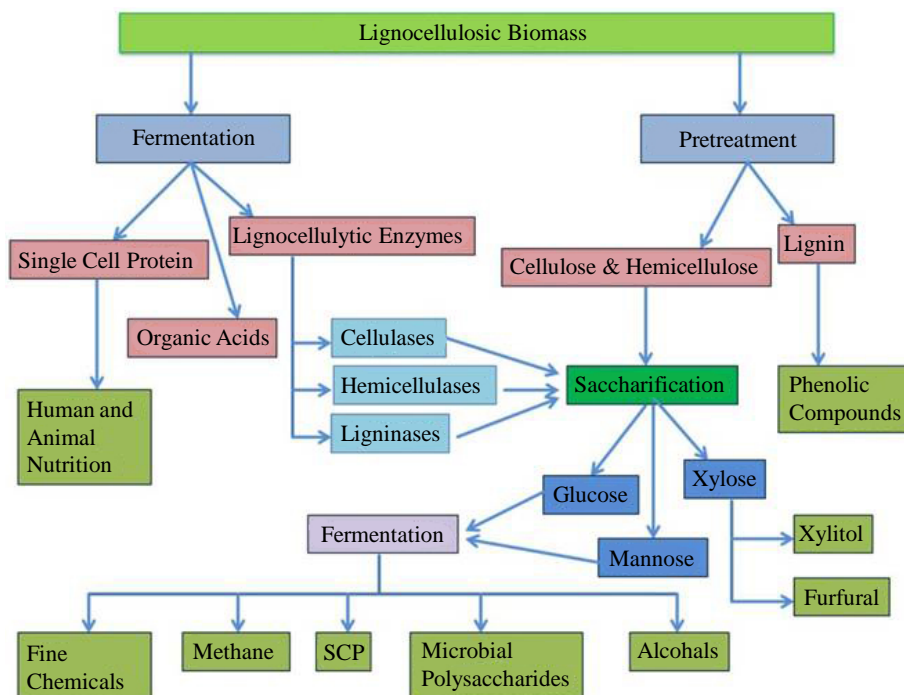


Figure 1. Bioconversion of lignocellulosic biomass into value added products.

5. Industrial Enzymes

From the last several years, the demand of industrially important enzymes such as cellulases, xylanases, lignases, pectinases, and proteases increased due to their wide applications in various industries. These enzymes are produced from by different microorganisms by solid-state fermentation or submerged fermentation of lignocellulosic biomass cost effectively. Different lignocellulosic biomasses such as wheat bran, wheat straw, rice bran, rice straw, sugarcane bagasse, corn cob, corn stover and other agro-industrial residues have been utilized for the production of industrial enzymes (Table 2) [44]-[60] [62]-[92]. Lignocellulolytic enzymes are most important among them because they are also used for hydrolysis of lignocellulosic biomass in to other enzyme-based products [39]. Carbohydrates (cellulose and hemicelluloses) are hydrolyzed by cellulases and xylanases to monomer sugars such as glucose, xylose, mannose, arabinose and galactose. These monomer sugars are utilized as carbon sources for the production of different industrial products such as ethanol, xylitol, biobutanol, bio-hydrogen, microbial polysaccharides, organic acids, and single cell proteins etc [93] [94].

Table 2. Bioconversion of different lignocellulosic biomass into industrial products.

Bioconversion of different lignocellulosic biomass into industrial products	References
Wheat bran	
Total cellulase (8.03 FPU/gds), endoglucanase (27.49 IU/gds), xylanase (2,165.44 IU/gds) by <i>Trichoderma harzianum</i> PPDDN10 using wheat bran under SSF	[62]
Xylanase (727.78 IU/ml), endoglucanase (0.92 IU/ml), laccase (0.64 IU/ml) produced by <i>Coprinellus disseminates</i> SH-1 using wheat bran under SSF	[63]
Xylanase (698.75 IU/ml), cellulase (1.01 IU/ml) and laccase (25.6 ± 3.2 IU/ml) by <i>Coprinus cinereus</i> AT-1 MTCC 9695 using wheat bran as substrate under SSF	[64]
Maximum laccase activity (416.4 U/ml) obtained by submerged fermentation of wheat bran by <i>Cerrena unicolor</i> C-139	[65]
Amylase (327 IU/ml) produced by <i>Aspergillus fumigatus</i> NTCC1222 using wheat bran as substrate	[66]
Lipase activity (9.14 IU/g of dry substrate) obtained by <i>Aspergillus niger</i> under SSF using wheat bran as substrate	[67]
Lactic acid yield of 0.73 g/g substrate achieved by fermentation by <i>Lactobacillus pentosus</i> using wheat bran as substrate	[59]
Fumaric acid 20.2 g/l was achieved by fermentation by <i>Rhizopus oryzae</i> using wheat bran hydrolysate as substrate	[58]
The maximum hydrogen yield of 128.2 ml/g total volatile solid from pre-treated wheat bran by mixed anaerobic cultures	[68]
Wheat straw	
Yields of endoglucanase, cellobiohydrolase, β -glucosidase, xylanase and β -xylosidase were found 1709, 4, 79, 5.5, 4490 and 45 U per g of dry wheat straw by <i>Thermoascus aurantiacus</i> under SSF	[69]
Pretreated wheat straw hydrolyzed and fermented into acetone-butanol-ethanol (0.31 g·L ⁻¹ ·h ⁻¹) by <i>Clostridium beijerinckii</i> P260.	[70]
Specific methane and biogas production yield of 165.9 L/kg VS and 353.2 L/kg VS respectively was obtained by the NaOH pretreated wheat straw	[71]
Rice straw	
Maximum endoglucanase, Fpase, β -glucosidase, cellobiohydrolase and xylanase produced 240.2, 9.73, 470, 15 and 2800 (units/g of substrate) of activities by <i>Aspergillus fumigatus fresenius</i> by using rice straw as substrate	[72]
Ethanol yield (0.48 g/g) and xylitol concentration of 0.89 g/l were obtained from rice straw hydrolyzate <i>Candida tropicalis</i> ATCC13803	[44]
Alkali-pretreated rice straw decomposed up to 68.21% by cellulase from <i>Trichoderma reesei</i> ZM4-F3	[73]
Enzymatic hydrolysis of organosolv pretreated rice straw resulted in glucose yield of 46.2%, which was fermented to 80.3 g butanol, 21.1 g acetone, and 22.5 g ethanol by <i>Clostridium acetobutylicum</i> .	[59]
Maximum methane yield of 225.3 mL/g VS achieved by anaerobic digestion of Ca(OH) ₂ treated rice straw	[51]
Methane yields of (0.33 - 0.35) m ³ /kg-VS loaded observed by anaerobic digestion of rice straw	[52]
Rice bran	
Highest Fpase, avicelase and CMCase activities found 11.68, 99.75 and 94.21 U/g dry weight of substrate respectively by <i>Trichoderma reesei</i> QM9414 under SSF using rice bran as substrate	[74]
Enzymatic hydrolysate of de-oiled rice bran treated with XAD-4 resin, having 30 g/l of sugars produced acetone, butanol, and ethanol 3.18, 7.72 and 1.23 g/l respectively by fermentation through <i>Clostridium saccharoperbutylacetonicum</i> N1-4.	[47]

Continued

- Lactobacillus brevis* produced maximum lactic acid concentration (39.1 g/l) by the fermentation of acid hydrolysate of corncob with 56.9 g/l total sugars in 48 h. [75]
- Rice husk**
- Through co-culture of *Saccharomyces cerevisiae* and *Scheffersomyces stipitis*, maximum 20.8 g/l of ethanol produced from rice husk hydrolyzate containing 70 g/l of reducing sugars [76]
- Acid hydrolysate of rice husk fermented to xylitol by *Candida guilliermondii* and *Candida tropicalis* and highest yield of xylitol was achieved upto 64.0% (w/w). [77]
- Maximum hydrogen yield (0.74 mmol H₂/g-VS added straw) was obtained from anaerobic co-digestion of rice straw and sewage sludge [50]
- Corn cob**
- Cellulase activity observed (213.4 IU/g cellulose) in submerged fermentation by *Trichoderma reesei* ZU-02 using corn cob as substrate [78]
- Fermentation of corn cob hemicellulose powder containing 4.5 g/l as xylan content produced 3.01 g/l of xylitol by *Candida tropicalis*. [79]
- Maximum 119 ml H₂/g corn cob produced from enzymatic hydrolysate of corn cob by the fermentation through *Clostridium hydrogeniproducens* HR-1 [80]
- Maize (corn) stover**
- Highest yields of endoglucanase, cellobiohydrolase, β -glucosidase, xylanase and β -xylosidase were observed 304, 4.1, 0.140, 1840 and 0.041 U/g of corn stover by *Fusarium oxysporum* under SSF conditions [81]
- Hydrolysis of corn stover released 97% of the sugars and fermented completely by *Clostridium beijerinckii* in 60 h resulting in a productivity of acetone-butanol (0.34 g·L⁻¹·h⁻¹). [48]
- Total soluble sugar (562.1 mg/g-TVS) obtained by enzymatic hydrolysis of acid pretreatment of cornstalk which produced maximum hydrogen yield (209.8 ml/g-TVS) achieved by anaerobic mixed microflora [82]
- Highest biogas yield of 372.4 L/kg VS was obtained by anaerobic digestion of 5% NaOH-pretreated corn stover [83]
- Highest methane yield of 216.7 and 206.6 mL CH₄/g VS obtained from 3% H₂O₂ and 8% Ca(OH)₂ treated corn straw by anaerobic digestion [84]
- Sugarcane bagasse**
- FPase (24.15 U/gds) achieved in optimized conditions by *Trichoderma reesei* RUT C30 using sugarcane bagasse as substrate under SSF [85]
- Pretreated sugarcane bagasse was hydrolyzed by crude enzyme from *Penicillium chrysogenum* BCC4504 and *Aspergillus flavus* BCC7179 and bagasse hydrolysate was converted into ethanol (0.29 g ethanol/g available fermentable sugars). [45]
- Sugarcane bagasse hydrolysate converted into xylitol (yield 61.5%) by *Candida guilliermondii* FTI 20037. [60]
- Hydrogen yield of 1.86 mol H₂/mol total sugar achieved by the fermentation of acid hydrolysate of sugarcane bagasse [49]
- Paper mill sludge**
- Yield of cellulase (307 FPU/g glucan of de-ashed paper mill sludge) was achieved by *Trichoderma reesei* Rut C-30 and simultaneous saccharification and fermentation was performed to produce 24.4 g/L of ethanol [86]
- Fermentation by *Pichia stipitis* produced 18.6 g/L of ethanol from 178.6 g/L of dried recycled paper sludge with conversion yield of 51% of the available carbohydrates. [87]
- In Semi-continuous simultaneous saccharification and co-fermentation of paper sludge containing 100 g/L cellulose equivalent, with 4 days residence time and 15FPU/g of cellulase loading, two strains of *Bacillus coagulans* produced 80.6 and 81.7 g/L of lactic acid respectively. [88]
- Highest methane yield (0.32 m³ CH₄/kg VS) was obtained from pretreated paper mill sludge [89]
- Sunflower**
- Pretreated sunflower hulls hydrolyzed by cellulase from *Trichoderma reesei* Rut C 30 up to 59.8% saccharification yield and ethanol produced (0.454 g/g) by *Saccharomyces cerevisiae* var. *ellipsoideus* using the concentrated hydrolyzate. [90]
- Highest methane production (259 mL CH₄/g VS) achieved after pretreatment of sunflower stalk at 55°C with 4% NaOH by anaerobic digestion [53]
- Water-hyacinth (*Eichhornia crassipes*)**
- Maximum ethanol yield (0.35 g/g sugars) obtained from water-hyacinth hemicellulose acid hydrolysate by *Pichia stipitis* NRRL Y-7124. [91]
- Maximum saccharification yield (71%) obtained by using cellulases and xylanases from *Trichoderma reesei* RUT C30 and *Aspergillus niger* MTCC 7956 and the hydrolyzate was converted into ethanol (4.4 g/L) by *Saccharomyces cerevisiae*. [92]

6. Bio-Energy

The world energy demand continues to increase, according to U.S. Energy Information Administration data; consumption of energy in the world will rise by 56% between 2010 and 2040 [95]. This dramatic increase of world energy consumption (154 to 240 quadrillion Watt-hour) is very difficult to achieve from diminishing fossil fuel reserves. Therefore, efforts have been directed towards promising alternatives for fossil fuels and the conversion of lignocellulosic biomass to biofuels is the sustainable choice for that [96]. Lignocellulosic biomass is a natural renewable resource for second generation bioenergy products. Bioethanol, biobutanol, biomethane and biohydrogen are the bioenergy products that are produced from lignocellulosic biomass.

6.1. Bioethanol

Ethanol produced from lignocellulosic biomass provides unique environmental, economic, and strategic benefits [97]. Bioethanol is an important replacement of fossil fuel, production of bioethanol is increasing rapidly. Lignocellulosic biomass such as agricultural, industrial and forest residuals are recognized widely as excellent low cost and abundantly available feedstock for bioethanol production [76] [97]. Ethanol presently has the largest market due to its use as a chemical feedstock or as a fuel additive or primary fuel [1] [98]. Conversion of lignocellulosic biomass into bioethanol consists of three steps. In the first step, pretreatment is carried out to make cellulose and hemicellulose available for hydrolysis by breaking the compact lignocellulosic structure [76]. Several physical, chemical and biological pretreatment methods have been studied for improving the hydrolysis of lignocellulosic biomass [99]. The second step aims at hydrolysing the holocellulose into fermentable sugars by the action of lignocellulolytic enzymes. In the third step, fermentable sugars during enzymatic hydrolysates are converted in to ethanol after proper detoxification process [100]. Fermentation of fermentable sugars is carried out with different microorganisms such as *Saccharomyces cerevisiae*, *Saccharomyces cerevisiae* var. *elliipoides*, *Scheffersomyces stipitis*, *Escheria coli*, *Zymomonas mobilis*, *Pachysolen tannophilus*, *Candida brassicae*, *Candida glabrata*, *Candida shehate*, *Candida tropicalis*, *Pichia stipitis*, *Kluyveromyces marxianus*, *Mucor indicus* etc. [44] [45] [76] [92] [97] [101]-[106]. Various lignocellulosic biomass such as sugarcane bagasse, water hyacinth, rice straw, rice husk, wheat straw, reed, bermuda grass, and rapeseed stover, corn cob, sunflower hulls, sunflower stalks, lemon peel waste, empty fruit bunches of oil palm, sweet sorghum have been tested for ethanol production [1] [14] [73] [76] [90]-[92] [106]-[110].

6.2. Biobutanol

Biobutanol is considered as future biofuel which have potential to replace gasoline. 1-Butanol as fuel is advantageous over ethanol in terms of energy density, engine compatibility and safety [111] [112]. 1-Butanol is also an important precursor for paints, polymers, and plastics. [113] Different members of genus *Clostridium* such as *C. acetobutylicum*, *C. beijerinckii*, *C. saccharoperbutylacetonicum*, *C. saccharoperbutylicum*, *C. sporogenes*, *C. perfringens*, *C. pasteurianum*, *C. carboxidivorus*, *C. tetanomorphum*, *C. aurantibutyricum*, *C. cadaveris*, *C. butylicum* etc. are used for the production of biobutanol through acetone-butanol-ethanol (ABE) fermentation [47] [48] [70] [111] [113]-[115]. For the production of butanol various substrates such as molasses, whey permeate, corn, cassava, and potato etc. have been used traditionally. These biomasses are costly and compete with food supply therefore, lignocellulosic biomass is the suitable source for cost effective and sustainable production of biobutanol [111] [114]. A number of lignocellulosic substrates like rice bran, corn stover, wheat bran, wheat straw, palm kernel cake, rice straw and wood chips have been utilized for the production of biobutanol in various studies [46]-[48] [70] [111] [113] [114] [116].

6.3. Biomethane

Biomethane has potential to yield more energy than any other current of biofuels like bioethanol and biodiesel. Anaerobic digestion or biomethanation is the microbial process which converts organic materials into biogas in the absence of oxygen. Biogas mainly consists of methane and carbon dioxide, used for the production of electricity and heat for local needs [117] [118]. Biogas can also be used as vehicle fuel where biogas is cleaned and upgraded to biomethane which is combusted in an internal combustion engine [119] [120]. El-Mashad [121] reported in a study that estimated gross energy (6774 MJ tonne⁻¹) in the form of biomethane through anaerobic digestion of untreated switchgrass was significantly higher than gross energy (3904 MJ tonne⁻¹) which was

estimated in terms of bioethanol, produced from alkali-treated and saccharified switchgrass. Cattle manures have low biogas yield which can be improved by co-digestion of manure, crop residues and organic wastes. Various studies showed the production of biomethane from wide range of lignocellulosic biomass such as rice straw, sorghum forage, pulp and paper sludge, softwood spruce, birch, corn stover, wheat straw, sunflower stalk and fallen leaves [1] [51]-[53] [71] [83] [91] [117] [122]-[126].

6.4. Bio-Hydrogen

Bio-hydrogen is also regarded as a viable energy option in future which is clean and renewable energy carrier as its combustion produces the water as the sole end product. Hydrogen has higher energy content as compared to hydrocarbon fuels and fossil fuels which are the main source for hydrogen production worldwide [61] [127]. Hydrogen can be produced from carbohydrate containing biomass by bacterial hydrogen fermentation to satisfy hydrogen demand in future [61]. Different mesophilic, thermophilic and extreme thermophilic microorganisms such as *Clostridium tyrobutyricum*, *C. butyricum*, *C. beijerinckii*, *Enterobacter aerogenes*, *E. cloacae*, *Thermoanaerobacterium thermosaccharolyticum*, *Caldicellulosiruptor saccharolyticus*, *Thermotoga neapolitana*, *Thermotoga elfii*, *Ethanoligenens* etc. are utilized for the production of hydrogen [61] [127]-[133]. Pure cultures and mixed cultures both are used for conversion of lignocellulosic biomass into hydrogen. Anaerobic digested sludge or compost which contains various microorganisms are the natural source for the hydrolysis of cellulose [128]. Song *et al.* [129] enumerated natural microbial consortium from compost for hydrogen fermentation and reported *Clostridium* sp, *Enterobacter* sp, *Bacteroides* sp, *Veillonella* sp, and *Streptococcus* sp. as essential members of natural microbial consortium. Different lignocellulosic biomasses including hemp, newspaper, barley straw, rice straw, corn stalk, corn cob, wheat bran, wheat straw, compost, sugarcane bagasse, and sweet sorghum bagasse, have been utilized for the production of hydrogen (Table 2) [49] [50] [68] [80] [82] [127]-[129] [134]-[136].

7. Organic Acids

Organic acids are the natural products or at least natural intermediate of major metabolic pathways of microorganisms. Organic acids are extremely useful products due to their functional group which make them suitable substrate for the synthesis of other important chemicals. [137] Organic acids can be produced either by using sugars such as glucose, xylose and sucrose or by using hydrolysate from lignocellulosic biomass. Different organic acids such as citric acid, acetic acid, succinic acid, gluconic acid, oxalic acid, lactic acid, malic acid, butyric acid, fumaric, etc. are produced by microbial fermentation of by using the lignocellulose as substrate [137]-[140].

7.1. Citric Acid

Citric acid is the second largest fermentation product after ethanol worldwide with 1.7 million tons of annual production. Citric acid is a commodity chemical which has broad range of versatile applications in biomedicine, nanotechnology, bioremediation of heavy metals [138] [141]. Citric acid is produced dominantly by *Aspergillus niger* under submerged and solid-state fermentations and other producers of citric acid are *Absidia* sp, *Acremonium* sp, *Botrytis* sp, *A. flavus*, *A. awamori*, *A. nidulans*, *A. phoenicus*, *A. wenti*, *Penicillium citrinum*, *P. janthinellu*, *P. Luteum*, *P. restrictum*, *Trichoderma viride*, and *Talaromyces* sp. [56] [138] [141]-[144]. Citric acid is produced using different lignocellulosic biomass such as sugarcane bagasse [56] [57], oil palm empty fruit bunches [145], apple pomace [46] [138], cassava bagasse [139] [142], cotton waste [147], corn cobs [148], corn husk [149], pineapple waste [150], grape and pomace [146] etc.

7.2. Succinic Acid

Succinic acid is a C4 dicarboxylic acid which is a very useful chemical in food, agricultural and pharmaceutical industries. Succinic acid is a platform chemical which is used as feedstock for the production various high value derivatives such as adipic acid, 1, 4 butanediol, methyl ethyl ketone, 1, 3-butadiene, ethylene diamine disuccinate [151]-[153]. Currently, succinic acid is synthesized from petroleum based chemical processes commercially. Due to depleting of oil reserves, rising prices and environmental pollution, succinic acid production through fermentation using low cost substrates such as lignocellulosic biomass has attracted more and more attention in

recent years [151] [153] [154]. To date, different renewable lignocellulosic biomass used for succinic acid production are wood hydrolysate [155], corn stover [153] [156], corn stalk hydrolysate [151] [154], sugarcane bagasse hydrolysate [152], pinewood [156], and *Cannabis sativa* L [157]. Microorganisms that naturally produce the succinic acid are *Actinobacillus succinogenes* [153] [156] [157], *Anaerobiospirillum succiniciproducens* [156], *Klebsiella pneumonia* [158], and *Mannheimia succiniciproducens* [155] etc. Along with these microbial strains, genetically engineered *E. Coli*. [151] [152] [154] and *Saccharomyces cerevisiae* [159] have also been used successfully for the production of succinic acid [156].

7.3. Lactic Acid

Lactic acid is one of the most versatile organic acids which have broad range of applications in food, textile, and pharmaceutical cosmetic and chemical industries [160]. World demand for lactic acid have been estimated 600,000 tons by 2020 and is expected to keep increasing in due to its use in production of poly-lactic acid and lactate solvents [161]. Poly-lactic acid is biodegradable and biocompatible polymer which can replace plastics derived from petrochemicals [162] [163]. Lactic acid is synthesized chemically or produced by microbial fermentation. Currently, almost all lactic acids produced globally by microbial fermentation due to several advantages including production of optically pure L-or D-lactic acid, low production temperature, and decreased energy consumption. However, traditional substrates including starch and refined sugars constitutes for the major proportion of production cost. Therefore, lignocellulosic biomass is cost effective and non-food material for the production of lactic [162]-[164]. Lignocellulosic biomass substrates such as rice bran [165], corn stover [166], corn cob [166], paper sludge [88], sugarcane bagasse [167] [168], wheat bran [169] [170], and office waste paper [171] etc. are utilized for the production of lactic acid. Lactic acid is produced by fermentation using different microorganisms such as *Bacillus coagulans* [88] [162], *Lactobacillus brevis* [166], *Lactobacillus coryniformis* [172], *Lactobacillus casei* [167], *Lactobacillus delbrueckii* [170], *Lactobacillus rhamnosus* [165] [169], *Lactococcus lactis* [173], *Lactobacillus pentosus* [173], *Streptococcus thermophilus* [167] [173], and *Rhizopus oryzae* [171].

7.4. Acetic Acid

Acetic acid, formic acid and levulinic acid are formed by acid-catalyzed conversion of lignocellulosic biomass. Acetic acid is formed by hydrolysis of acetyl group of hemicelluloses. Formic acid is produced by degradation of furfural and 5-hydroxymethylfurfural (HMF) while levulinic acid is degradation product of HMF. Furfural and HMF are formed by pentose (e.g. xylose and arabinose) and hexose (e.g. glucose, mannose and galactose) sugars respectively [54] [55]. Levulinic acid is a versatile platform chemical that can be used for the synthesis of different chemicals such as γ -valerolactone, succinic acid, resin, polymers, herbicides, pharmaceuticals and flavouring agents [174] [175]. Acetic acid and formic acid are effective in the fractionation of lignocellulosic biomass to produce the cellulosic pulp and other products. Acetic acid and formic acid have been used for the fractionation of lignocellulosic biomass from different sources such as dhaincha (*Sesbania aculeata*), kash (*Saccharum spontaneum*), banana stem (*Musa cavendish*) and jute fibre [176]-[178].

8. Microbial Polysaccharides

Exopolysaccharide are produced by wide variety of microorganisms which are very useful in different industries due to their novel and unique physical properties [179]. Microbial polysaccharides have diverse applications in different industrial sectors such as food, petroleum, and pharmaceutical industries. Because of their higher cost of production, microbial polysaccharides comprise of a small fraction of current polymer market. Low cost fermentation substrates are required to get down the cost of microbial polysaccharides and lignocellulosic biomass are the potential sources for their production [180]. Different microbial bioactive polysaccharides such as schizophyllan, pullulan, xanthan, dextran, curdlan etc. are produced by microorganisms using fermentable sugars as the substrate. Hydrolysates from different lignocellulosic biomass are the potential source of fermentable sugars which can be utilized for the production of microbial polysaccharides cost effectively. Schizophyllan is a polysaccharide produced by the strains of a white rot fungus, *Schizophyllum commune*. Schizophyllan consists of β -1, 3 linked glucose backbone with single β -1, 6 linked glucose side chains at every other residues. Shu and Hsu [181] used rice hull hydrolysate for the production of schizophyllan and found 81.3 mg/l of schizophyllan by *Schizophyllum commune*. Pullulan is polysaccharide consisting of maltotriose units joined by

α -(1→6) linkage, produced by a fungus *Aureobasidium pullulans* [182]-[184]. Wang *et al.* [182] studied the production of pullulan and obtained 22.2 g/l of pullulan by using rice hull hydrolysate as the substrate from the mutant of *Aureobasidium pullulans*. Sugumaran *et al.* [184] studied the production of pullulan by using rice bran, wheat bran, coconut kernel and palm kernel as the substrate and observed maximum pullulan production by palm kernel. Another very important microbial polysaccharide is xanthan which is hetero-polysaccharide of pentasaccharide repeating units, containing D-glucose, D-mannose, D-glucuronic acid (at the ratio-2:2:1). Xanthan is produced by aerobic fermentation of bacteria *Xanthomonas campestris* on glucose or sucrose based media [185] [186]. Moreno *et al.* [186] tested hydrolysate of different lignocellulose biomass including *Lycopersicon esculentum*, *Cucumis melo*, *Citrullus lanatus*, *Cucumis sativus* for xanthan production and reported maximum xanthan production using *Cucumis melo* hydrolysate.

9. Single-Cell Proteins

Continuous growth of population in developing countries needs an increase protein enriched animal feed and human food supply. Single-cell proteins are such alternatives which can solve the global food problems [187]. Term single-cell protein refers the dried microbial cell or total protein extracted from pure microbial cultures including algae, bacteria, fungi and yeasts. Single-cell proteins are used as human food supplement or animal feed [187]-[189]. Lignocellulosic wastes are low cost substrates for the production of single-cell proteins. Different lignocellulosic wastes such as apple waste, banana peel, and cucumber peel, Eichornia waste, mango waste, papaya waste, pineapple waste, orange peel, rice bran, watermelon skin, and wheat bran etc have been used for the production for single-cell protein successfully [187]-[191].

10. Xylitol

Xylitol is a five carbon high value sugar alcohol, derived from xylose which is naturally found in some fruits and vegetables. Xylitol is used as an anticarcinogenic agent in toothpastes, as coating on vitamin tablets, in chewing gum, in soft drinks, and in bakery products. Xylitol is equivalent to sucrose in sweetness and metabolized by an insulin independent pathway therefore, it is used as sweetener agent for diabetic persons [79] [192] [193]. Currently, xylitol is produced by conventional method in which chemical hydrogenation of pure xylose takes place in the presence of nickel catalyst at high temperature and pressure. The yield of xylitol is 50% - 60% of xylan fraction and the chemical process is cost and energy intensive. Microbial production of xylitol is the highly attractive and alternative method which is able to produce high quality product cost effectively because it can be achieved without high pressure, temperature or xylose purification [79] [193]-[195]. Microorganisms like bacteria, yeasts, and filamentous fungi are able to metabolize xylose for the production of xylitol but yeasts are considered the most efficient producers of xylitol. Among wild type of xylitol producing yeasts, various species of *Candida* are capable for the production of xylitol [79] [195].

11. Conclusion

In this review, chemical and physical properties of lignocellulosic biomass and their components viz. cellulose, hemicelluloses, and lignin as well as bioconversion of lignocellulosic biomass in to industrial products have been discussed. The bio-conversion of lignocellulosic biomass by industrial enzymes is a potential sustainable approach to develop value-added bio-products. A large fraction of these lignocellulosic materials is often disposed of by burning, which is not restricted to developing countries alone. However, the huge amount of residual plant biomass considered as “waste” can potentially be converted into different value-added products such as bio-ethanol, bio-methane, organic acids, microbial polysaccharides, single cell protein, lignocellulolytic enzymes, and other value added products. Biotechnological conversion of lignocellulosic biomass in various industrial products is cost effective and environmentally sustainable route.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Abbreviations

ABE	—Acetone-butanol-ethanol
Btu	—British thermal unit
CMCase	—Carboxymethyl cellulase activity
FPase	—Filter paper activity
FPU	—Filter paper unit
G	—Gram
Gds	—Gram dry substrate
IU	—International unit
Kg	—Kilogram
L	—Litre
MJ	—Mega joule
M	—Meter
N ml	—normalized ml
SSF	—Solis-state fermentation
TS	—Total solids
TVS	—Total volatile solids
VL	—Volatile solids