Glycosyl Hydrolases and Biofuel

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Abstract

Paucity of non-renewable energy sources has created a vital requirement for renewable and sustainable biofuels from lignocellulosic biomass. Exploitation of lignocelluloses for the production of second generation fuels such as bioethanol, biodiesel and biogas etc forms an attractive energy alternative since they are naturally abundant and easily accessible throughout the year. Efficient pretreatment methodologies such as alkali, acid treatment, enzymatic hydrolysis and steam explosion are useful for enhancing the digestibility of major lignocellulosic components, cellulose and hemicellulose, followed by the fermentation of obtained sugars exists as a prerequisite for effective transformation of lignocelluloses to diverse value added products. Present chapter compiles different approaches made by eminent scientists and researchers for competent use of celluloses and hemicelluloses for enhancing bioethanol production and also describes recent innovative techniques exploited for the same. The chapter gives an overview of simple sugars utilization by bacteria and fungi and also highlights the influence of consolidated bioprocess systems on ethanol production from various agro-industrial wastes.

Keywords

Bioethanol · Lignocelluloses · Glycoside hydrolases · Xylanases · Cellulases

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Introduction

Glycoside hydrolases (GHs) are catalysts responsible for hydrolysis of the glycosidic bonds in glycoconjugates, oligo- and polysaccharides, thereby forming a reducing sugar and the corresponding free aglycon (Zhang et al. 2010, Van Niël et al. 2017). Sometimes they are also referred to as glycosyl hydrolases and can catalyze the hydrolysis of O-, N- and S-linked glycosides. There are two types of glycoside hydrolases: exo- and endo-, which refers to their ability to cleave a substrate at the end or within the middle of a chain, respectively.

Glycosidases are ubiquitously found in nature. About 1% of the genome of any organism encodes for GHs where they are involved in processes that are essential for life including cell wall metabolism, signaling, biosynthesis of glycans, defence in plants as well as mobilization of storage reserves (Roth 2002; Ardèvol and Rovira 2015). Varying kinds of GHs are involved in different applications such as cellulase, hemicellulase, and amylase are involved in the degradation of biomass, lysozyme in anti-bacterial defense strategies and mannosidases in normal cellular function.

Biofuels eliminate the concerns arising from continuous usage of fossil fuels. Since they are produced through biological processes they offer an ecological and economical alternative for improving energy security. For more than a decade, primary biofuels such as fuel-wood have been used for cooking, heating and generation of electricity. Conversely, biomass can be processed into secondary biofuels like bioethanol and biodiesel to be used in vehicles and industries (Dragone et al. 2010). Biofuels (solid, liquid or gas) can be produced from a variety of biomass including aquatic, agricultural and forestry wastes (Rastogi and Shrivastava 2017). Biofuels can be characterized into first, second, third and fourth generation subject to their source and production technique. First generation biofuels are quite easy to obtain since they are directly processed from food crops such as vegetable oil, starch, sugar and also animal fats. However, utilization of food crops as feed for energy production not only competes with food consumption but also deteriorates the quality of agricultural areas. Inedible crops including lignocellulosic biomass and bio-wastes can be processed into fuels which constitute the second generation biofuels. Algal feedstocks and photobiological solar fuels (presently on paper) are categorized into third and fourth generation biofuels, respectively (Rastogi and Shrivastava 2018).

The abundant supply and low cost of plant biomass favors its usage as energy crops for biofuel production making it one of the highlighted areas for research and industry currently. Mostly, the biotransformation emphasizes on establishing a sugar platform of simple sugar moieties which can be subsequently converted into fuels (such as ethanol, hydrocarbons and butanol) through biological or chemical processes (Cherubini 2010, Singh et al. 2015). Glycoside hydrolases or glycosidases are biocatalysts that play a significant role in industrial and biotechnological processes via hydrolytic degradation of carbohydrates. These versatile enzymes have been applied for a wide variety of processes from biomass degradation to cell surface engineering due to their high specificity and remarkable catalytic efficiency. Moreover, glycosidases aid in the synthesis of glycan through transglycosylation wherein

Fig. 1 Hydrolysis reaction by GHs (cazypedia.org)

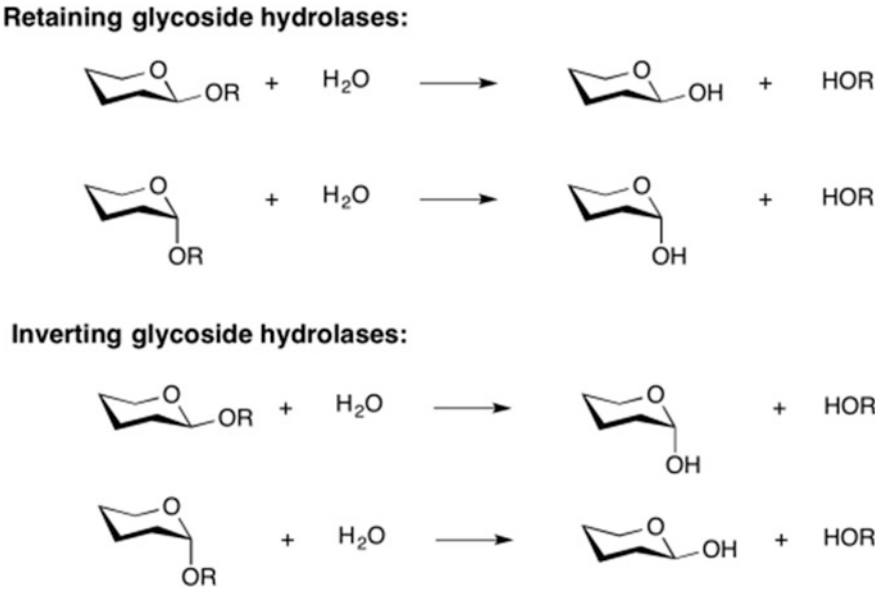

Fig. 2 Reaction mechanism of glycosyl hydrolases (cazypedia.org)

a sugar moiety is transferred from one glycoside to another, rather than to water as in the case of hydrolysis (Wang and Huang 2009) (Fig. 1).

Industrially Important Glycosyl Hydrolases

Glycosyl hydrolases hydrolyze the glycoside bonds by the universal acid catalysis method that entails two main residues: a proton donor and a nucleophile/base as initially suggested by Koshland (1953). The hydrolysis reaction occurs via two different mechanisms resulting in either retaining (via a double-displacement) or inverting of the anomeric configuration of the substrate as shown in Fig. 2 (Van Niël et al. 2017). Hydrolysis of a glycosidic bond via GHs is always stereospecific (Naumoff 2011).

Glycosyl hydrolases have found numerous applications in industrial as well as biotechnological areas. Some applications of these enzymes, ranging from biofuel production to drug designing, have been discussed in brief in Table 1.

Cellulases which are predominantly produced by bacterial, fungal and protozoal organisms are crucial for the hydrolysis of cellulose polymers into monomers of

Table 1 Various applications of commonly used glycosyl hydrolases

Enzyme	GH family	Industry	Applications	References
Cellulase	GH-5, -9, -17, -48	• Biofuel • Detergent • Textile • Food processing • Wine and Brewery • Paper and pulp	• For degradation of cellulose to glucose, to be used for bio-ethanol production • In detergents for washing of cotton fabrics for maintenance of colours • For bio-stoning of denim jeans and bio-polishing of cotton clothes • For maceration and clarification of fruits and vegetable juices, nectars, oils and purees; Olive paste malaxation and olive oil extraction • To improve skin maceration, must clarification, color extraction, filtration, and wine quality and stability • For pulping and deinking of waste papers	Sajith et al. (2016), Kuhad et al. (2011), Sathya and Khan (2014)
Invertase	GH-32, -100	• Food and beverage • Drug and pharmaceutical	• For manufacture of invert sugar; production of non-crystallizable sugar syrup from sucrose for candies and fondants • In the manufacture of artificial honey and plasticizing agents used in cosmetics	Samarth et al. (2013), Willem et al. (2009)
Amylase	GH-13, -14, -15, -31, -57	• Starch • Detergent • Biofuel • Food • Textile • Paper	• For starch hydrolysis in the starch liquefaction process • For laundry and dishwashing to degrade the residues of starchy foods • For bioconversion of starch into ethanol via liquefaction and saccharification	De Souza and De Oliveira Magalhães (2010), Sathya and Khan (2014)

(continued)

Table 1 (continued)

Enzyme	GH family	Industry	Applications	References
			• For production of maltodextrins; in baking, brewing, preparation of digestive aids, production of cakes, fruit juices and starch syrups; to improve viscosity of dough for better volume and texture of the product • As a desizing agent to strengthen and prevent breaking of the warp thread during the weaving process • For modification of starch of coated paper	
Xylanase	GH-5, -7, -8, -9, -10, -11, -12,-16, -26, -30, -43, -44, -51, -62	• Biofuel • Paper and pulp • Animal feed • Baking • Fruit juice and Brewery • Detergent • Others	• To convert hemicellulose to simple sugars for bioethanol production • To remove hemicelluloses from paper pulp • To stimulate animal growth rates by improving digestibility and quality of animal litter • To increase the elasticity of the gluten network • To increase yield in the maceration process, reduces viscosity of fruit juice, extraction of more fermentable sugar from barley • In detergents to remove stains • To produce xylo-oligosaccharides to be used in pharmaceuticals, food and feed formulations, agricultural applications	Walia et al. (2017), Goswami Girish and Seema (2015), Garg (2016)

(continued)

Table 1 (continued)

Enzyme	GH family	Industry	Applications	References
Mannanase	GH-5, -26	• Paper • Detergent • Food • Pharmaceutical • Others	• For biobleaching of pulp and paper • For removal of stains of mannan containing gums, ice-creams, hair gels, sauces, shampoos, and tooth-pastes • In coffee processing to reduce viscosity; to produce prebiotic manno-oligosaccharides, maceration of fruits and vegetables • To provide fast dissolving and structure forming properties to the tablets • Gas and oil exploitation, production of animal feed, bioethanol production, textile printing	Chauhan (2012)
Pectinase	GH-28	• Food • Wine • Bioenergy • Textile • Animal feed • Paper and pulp	• To reduce viscosity, increase the yield and juice clarification by liquefaction of pulps; in maceration of vegetables; extraction of vegetable oils in an aqueous process; tea and coffee processing; • To maximise juice extraction, facilitate filtration and strengthen the flavour and colour • To hydrolyze pectin present in agro-wastes into simple sugars to be converted into bioethanol • In bio-scouring, to remove impurities and prevent fiber damage • To decrease feed viscosity for better absorption of nutrients	Garg et al. (2016)

(continued)

Table 1 (continued)

Enzyme	GH family	Industry	Applications	References
			by ruminants and thus reduce amount of faeces • In bio-bleaching of kraft pulp to reduce cationic demand in the filtrate thereby reducing yellowness of paper	
Pullulanase	GH-13	Starch Processing	To hydrolyse the α-1,6 glucosidic linkages in starch, amylopectin and pullulan during starch saccharification; production of high-maltose/fructose corn syrup and cyclodextrins; in dishwashing and laundary detergents	Hii et al. (2012)
Chitinase	GH-18, -19, -20	• Waste management • Medical	• To convert chitinous waste of marine organisms into simple components and reduce water pollution • As an antifungal agent in combination with antifungal drugs to treat fungal infections	Rathore and Gupta (2015)
Inulinase	GH-32, -91	• Food • Others	• Production of high fructose syrup and fructo-oligosaccharides • Assist citric acid, lactic acid, ethanol and butanediol production	Singh et al. (2017)
Agarase	GH-16, -50, -86, -96	• Biotechnological • Others	• To recover DNA bands from the agarose gel; to produce oligosaccharides having antioxidant properties; preparation of seaweed protoplasts • Used as low-calorie additives to improve qualities of food; in cosmetics and medical fields	Fu and Kim (2010), Sathya and Khan (2014)

fermentable sugars (glucose) to produce biofuels. They break the β-1,4-d-glucan bonds present in the cellulose and liberate glucose, cellobiose and cello-oligosaccharides. This enzymatic complex includes endo-glucanases (EG; EC 3.2.1.4), exoglucanases (cellobiohydrolases, CBH; EC 3.2.1.91) and β-glucosidases (BGL; EC 3.2.1.21) (Rawat et al. 2014; Srivastava et al. 2017). These enzymes are required to work synergistically for efficient conversion of celluloses to sugar monomers for effective biofuel production. The enzyme hydrolysis commences with the release of nicks in the cellulosic structure by the endoglucanases thereby revealing the reducing and non-reducing ends, in order for the cellobiohydrolases to liberate cellobioses and cello-oligosaccharides by acting upon both the ends. Subsequently, β-glucosidases breakdown the cellobioses into glucosemonomers during the hydrolysis reaction (Bhat and Bhat 1997; Srivastava et al. 2014, 2017).

Owing to the structural heterogeneity of hemicellulosic constituent of plant biomass, complete degradation requires an array of hemicellulolytic enzymes. These enzymes include endo-1,4-β D-xylanase (E.C.3.2.1.8) which randomly cleave the xylan backbone to produce xylooligomers; xylan-1,4-β-xylosidase (E.C.3.2.1.37) cleaves these xylooligomers into xylose monomers; α-l-arabinofuranosidase (E.C. 3.2.1.55) remove the side groups from the main chain; acetylxylan esterases (E.C. 3.1.1.72) and α-D glucuronidases (E.C. 3.2.1.139) act synergistically to remove phenolic and acetyl side branches from the complex polymer (Ahmed et al. 2009; Uma Shankar et al. 2016). Xylanases are ubiquitous in both eukaryotes and prokaryotes as they have been accounted from bacterial (terrestrial, marine or rumen), fungal, protozoans and algal sources in addition to snails, insects and crustaceans (Walia et al. 2017).

Lignocelluloses comprise nearly 5% mannan apart from softwoods or coniferous sources that usually contain more mannan (10%) than xylan. Mannans are polysaccharides that consist of β-1,4-linked backbone of mannose as the major constituent unit. Mannans are non-starch carbohydrate reserves and are one of the constituents of hemicellulose. There are two major mannan-degrading enzymes: β-mannanase (1,4-β-D-mannan mannohydrolase, EC 3.2.1.78), an endo-acting enzyme catalyzing the random cleaving of β-1,4-linked internal linkages of the mannan, galactomannans and glucomannans via double displacement mechanism and an exo-acting β-mannosidase enzyme (1,4-β-D-mannopyranoside hydrolase, EC 3.2.1.25) which works on the non-reducing ends of the chain to release β-1,4-linked mannosides (Moreira and Filho 2008). The two enzymes work in collaboration with each other on mannans and its oligosaccharides to form mannose, which is utilized as a sugar substrate by some microbes for subsequent fermentation (Ishii et al. 2016). In addition to the key enzymes (cellulases and xylanases), β-mannanases are essential for the efficient bioconversion of lignocellulose biomass to fermentable sugars (Yamabhai et al. 2016).

Pectinases remain as one of the significant enzymes in the current biotechnological perspective due to their wide-ranging application. Based upon the mode of action, they are broadly categorized into three types: pectin esterase, hydrolases and lyases. Pectin esterases are responsible for the de-esterification of methoxyl

moieties present in pectin to form pectic acid. The polygalacturonases and polymethylgalacturonases hydrolases cleave the α-1,4-glycoside bonds in pectic acid and pectin, respectively, while lyases (polygalacturonate lyase and polymethylgalacturonate lyase) disintegrate the α-1,4-glycosidic linkages in pectic acid and pectin, respectively by trans-elimination reaction forming unsaturated galacturonates and methyl galacturonates, respectively (Garg et al. 2016; Ismail et al. 2016). Pectins, being the main components of the middle lamella in the cell wall, not only hamper second generation bioethanol production via inhibition of release of sugars but also obstruct the dilapidation of cells from tissues in first generation bioethanol process (Latarullo et al. 2016).

Biodiesel is manufactured via transesterification of vegetable oils. The presence of precipitates in biodiesel is of utmost importance as it declines the quality. These precipitates have been accounted to contain steryl glucosides (SGs) which give a hazy appearance to biodiesel while forming white sediments during storage. Thus, SGs need to be selectively removed to circumvent the blockage of filters as well as engine failures, hence producing biodiesel of superior quality to be accepted by the consumers. At present, distillation is the solitary means for complete removal of SGs from biodiesel that happens to be an expensive process requiring a lot of energy. This compromises with the cost efficiency and net energy gain of biodiesel production. In such scenario, glycoside hydrolases provide an alternative for cost-effective industrial methods to eradicate these compounds. Steryl-beta-glucosidase (EC 3.2.1.104) enzymes have been proposed to catalyze the hydrolysis of SGs while forming glucose and a sterol. This enzyme belongs to the family of O- and S-glycosyl hydrolases. The sterols thus generated completely solubilize in biodiesel, whereas the glucose is subsequently eliminated during the water-washing steps after transesterification (Peiru et al. 2015).

Agricultural Residues/Wastes/Industrial Effluents (Sources of Carbon)

A variety of wastes including agricultural residues, municipal solid waste and industrial effluents can be utilized for efficient production of biofuels. Lignocellulosic biomass can either be derivatives of agricultural practices or related industries. Lignocelluloses entail agro-wastes such as sugarcane bagasse, corn cobs, wheat and rice straw, cotton stalks, jute sticks, rice husks, coconut shells; forest wastes like wood chips, bark and sawdust; and organic fractions of sewage treated sludge and municipal solid wastes (MSW). Cellulose forms a major fraction of lignocellulosic feedstocks with 40–60% of the total dry weight followed by hemicellulose and lignin constituting about 20–40% and 10–25%, respectively (Kang et al. 2014). These are present in the cell walls of practically all plant materials. Cellulose is a homopolysaccharide of glucose residues attached to each other by β-1,4-glycosidic linkages. The linear cellulose chains are packed into crystalline microfibril bundles by means of hydrogen bonds (internal and external). Hemicelluloses are considered to be heterogeneous as these complex polysaccharides constitute different hexose

Table 2 Composition of various lignocellulosic biomass (Rastogi and Shrivastava 2017)

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
Sugarcane bagasse	32–48	19–24	23–32	1.5–5
Corn stalk	39–47	26–31	3–5	12–16
Rice husk	31.3	24.3	14.3	23.5
Rice straw	28–36	23–28	12–14	14–20
Wheat straw	33–38	26–32	17–19	6–8
Groundnut shell	35.7	18.7	30.2	5.9
Coconut shell	29.7	NA	44.0	0.5
Corn stover	38–40	28	7–21	3.6–7.0
Cotton waste	80–95	5–20	–	–
Softwoods	45–50	25–35	25–35	NA
Hardwoods	40–55	24–40	18–25	NA
Newspaper	40–55	25–40	18–30	8.8–1.8
Algae (green)	20–40	20–50	NA	NA

NA Not available. Composition is represented in percent weight on dry weight of the samples

and pentose sugars including glucose, galactose, mannose, xylose, arabinose and glucuronic acid. Hemicelluloses differ in plants depending upon their species and type of tissues. Some of the side residues in hemicellulosic structures have been found to be acetylated or methylated. Hemicelluloses are covalently linked to lignin, which comprises of three aromatic monomers- guaiacyl (G-lignin), syringyl (S-lignin), and *p*-hydroxyphenyl (H-lignin). The enzyme accessibility to cellulose is blocked due to the orientation of the cellulose microfibrils between the lignin and hemicellulose matrix which is a major problem regarding biofuel production (Xiao et al. 2016). Plant species differ in lignocellulosic composition (Table 2) with the abundance (on average) of major macromolecules in the following order: glucan > lignin > xylan > mannan > arabinan > galactan (Ishii et al. 2016).

Industries such as paper, pulp, food processing, dairy, sugar, poultry, tanneries, distilleries and biodiesel generate large volumes of inadequately treated solid and liquid wastes that pose a serious threat to ecosystems causing environmental distress. Industrial effluents rich in organic matter having high BOD/COD levels form potential fermentable substrates for bio-ethanol, methane, bio-hydrogen and surfactants production (Diwan et al. 2018). In food industry, waste generation occurs at every stage of food supply chain from production, transportation and storage to processing, packing, distribution and consumption. Fruit and vegetable wastes contain cellulose, hemicellulose and pectin in high quantities and can be used either directly or after pretreatment for production of bioethanol, biodiesel and biogas (Eleren et al. 2018). Industrial effluents act as sustainable feedstock for algal growth which accumulates nutrients and metals and degrading toxic compounds present in the effluents. Algal ponds containing wastewater has been used for production of biodiesel which also aid in sequestering the carbon dioxide emitted by the industries utilizing it for their photosynthesis. Table 3 describes various industrial effluents and its applications.

Table 3 Industrial effluents and its applications

Industries	Wastes generated	Applications	References
Sugar mills	Bagasse	Production of bio-ethanol and bio-methane, heat and electricity in sugar mills, cattle feed and paper making	Bhatnagar (2016)
	Press mud	Fertilizer and wax production; cement and paint manufacturing, foaming agent, animal feed	
	Molasses	Ethanol production	
	Fermentative yeast biomass	Biogas production and digestate	
	Bagasse fly ash	As an adsorbent for the removal of different metal ions, dyes from effluents, phenol and its derivatives, pesticide removal from wastewater	
Slaughter houses	Organs, tissues, hides, blood, animal excreta, carcass	Biogas production; fat for making grease, animal feed, candles, soap and biodiesel; tallow as a lubricant in steel rolling industry	Franke-Whittle and Insam (2013)
Paper mills	Pulp	Biogas production and digestate	Chakraborty (2019)
	Paper shavings	Heat and power	
	Wood wastes and paper boards	Heat and power	
Dairy plants	Whey and milk cream	Biogas production and digestate	Chakraborty (2019)
Sago factories	Starch materials and peels	Biogas production and digestate	
Tanneries	Hides and skins	Biogas production and digestate	
Animal husbandries	Animal excreta and body fluids	Biogas production and digestate	
Fruits and vegetable processing units	Pulp wastes	Biogas production and digestate	

Processing of These Wastes

Biofuels obtained as metabolites of microbial processes (as in the case of bioethanol production) primarily target cellulose component of biomass. A major challenge is to accomplish high titers of fermentable sugars from lignocelluloses that usually requires the aid of different microbial GHs, which catalyze the saccharification of varying polysaccharides present in the biomass. The microbial glycoside hydrolases disintegrate the complex carbohydrate compounds into mono or oligosaccharides, allowing their uptake and subsequent metabolism by a suitable microorganism for their conversion into desirable biofuels. Due to the structural, physicochemical and

compositional complexity, cellulose is resistant to enzymatic degradation. Moreover, many microorganisms are deficient of a competent enzyme machinery essential for the effective degradation of lignocellulosic biomass. Thus, lignocellulosic biomass requires a pretreatment step for their efficient conversion to biofuels, thereby reducing the crystallinity of the cellulose, removing the lignin and hemicellulosic components and improving the permeability of the biomass. The enzyme accessibility to cellulose is further enhanced which leads to improved production of fermentable sugars from cellulose (Mamo et al. 2013). This has led to the development of numerous pre-treatment methods to breakdown the intertwined interaction between the lignocellulosic constituents (cellulose, hemicellulose and lignin), and have been summarized in Table 4.

Bioethanol Production (Native/Biotechnological or Cloning)

The biochemical conversion of lignocelluloses to bioethanol comprises of four major processes: physicochemical pretreatment, enzymatic hydrolysis of the complex sugar polymers, ethanol production via sugar fermentation and distillation (Sánchez and Cardona 2008). This conversion route can be accomplished by utilizing highly proficient microbial strains (native as well as recombinant) that are able to produce both glycosyl hydrolases and ethanol. The celluloses and hemicelluloses in the biomass are acted upon by varying cellulases and hemicellulases for their respective conversion into glucose and xylose. Upon saccharification, the hexose and pentose monomeric sugars so formed can be sequentially fermented to ethanol by diverse microorganisms. Microorganisms like *C. thermocellum* and *T. reesei* have been extensively interrogated for their natural ability to produce ethanol. On the other hand, prospective microorganisms such as *F. oxysporum, C. thermocellum*, *K. oxytoca* and *T. mathranii* that are naturally cellulolytic have been genetically altered to be ethanologenic and potential fermenting microbes such as *P. stipitis*, *S. cerevisiae*, *H. polymorpha*, *E. coli*, *K. marxianus* and *Z. mobilis* have been transformed to be cellulolytic (Jouzani and Taherzadeh 2015).

Different strategies integrating the hydrolysis and fermentation processes have been proposed with the aim of escalating the efficacy of bioethanol production. The process of separate hydrolysis and fermentation (SHF) allows the hydrolysis and fermentation processes to operate distinctly. The pretreated biomass is degraded first into sugar monomers that are subsequently converted to ethanol via fermentation. Although, both enzyme hydrolysis and fermentation operate at their respective optimum conditions during the process, yet accumulation of sugars inhibits the enzymatic activity ultimately affecting the ethanol yield (Jambo et al. 2016). Simultaneous saccharification and fermentation (SSF) permits the saccharification and fermentation to occur simultaneously in a single reactor, that is, as soon as the sugars are released from the biomass, they are quickly converted into ethanol. The major constraint in this process is to optimize the process parameters suitable for both the microorganisms as well as enzymes since they are operating at the same time (Vohra et al. 2014). Simultaneous Saccharification and Co-Fermentation (SSCF) is focused

Table 4 Comparative analysis of various pre-treatment techniques (Rastogi and Shrivastava 2017)

Pretreatment	Mode of action	Advantages	Disadvantages
Mechanical	Milling, grinding, shredding or chipping reduces particle size	• Increase in specific surface area and digestibility of biomass • Reduced crystallinity and degree of polymerization of cellulose	• High energy consumption renders this method economically inefficient
Extrusion/ pyrolysis	Treatment at high temperature (>300 °C) following by mixing and shearing causes defibrillation, fibrillation and shortening of the fiber		Parameters in bioreactor need to be highly efficient
Liquid hot water	Liquid hot water (160–240 °C) under high pressure (>5 MPa) for time ranging from few minutes up to an hour removes hemicellulose from lignocellulosic biomass making the cellulose more accessible	• Better pH control minimizes non-specific degradation of polysaccharides • High pentose recovery and lower formation of inhibitors • No chemicals and corrosion resistant materials are required	• High energy requirement and water demand • Not feasible for commercial scale
Steam explosion (Autohydrolysis)	Exposure of chopped biomass to hot steam (160–260 °C) under high pressure for specific period of time followed by sudden release in pressure causes autohydrolysis of acetyl groups of hemicellulose. Individual fibers are separated disrupting the cell wall structure	• Improved enzymatic hydrolysis • Lower environmental impact • Less hazardous chemicals required • High sugar yield • Feasible for industries	• Less effective for softwoods • Formation of inhibitory products (eg furfural and HMF[a]) • Partial degradation of hemicelluloses and lignin • Additional equipment requirement for acid addition • High cost
Ammonia fiber expansion (AFEX)	Treatment with liquid ammonia at moderate temperature (60–100 °C) for 30–60 min at high pressure (250–300 psi) followed by sudden pressure release causes	• Increases the surface area accessible for enzymes and thus enhanced digestibility • Less inhibitory or	• Not very effective for the biomass with high lignin content • High cost of large amount of ammonia • Hemicelluloses are not significantly

(continued)

Table 4 (continued)

Pretreatment	Mode of action	Advantages	Disadvantages
	disruption of biomass fibers and partial decrystallization of cellulose	toxic compound formation	reduced affecting the sugar yield
Acid	Dilute rather than concentrated acid is used either at high temperature (e.g., 180 °C) for short period of time or lower temperature (e.g., 120 °C) for longer retention time (30–90 min) to solubilize hemicelluloses and lignin	• Enhanced hydrolysis of hemicelluloses and amount of amorphous cellulose • High sugar yield	• High energy input so cost is high • Acids are corrosive so the process requires specific reaction vessels • Formation of inhibitory compounds (furfural, 5-HMF[a], phenolic acids and aldehydes)
Alkali	Treatment with alkali such as sodium, potassium, calcium and ammonium hydroxides disrupts the ester and glycosidic side chains causing alteration in lignin structure, cellulose swelling and its partial decrystallization and partial solubilization of hemicelluloses	• Efficient removal of all lignin • Increased accessibility of hemicelluloses-degrading enzyme • Decrease in the degree of polymerization and crystallinity of cellulose	• Downstream processing costs are high • Not efficient for industrial scale
Organosolv	Organic or aqueous organic solvent mixtures (such as ethanol, ethylene glycol, acetone, methanol, etc.) with inorganic acid catalysts are used to extract lignin	• Improvement in enzymatic digestibility of lignin and hemicelluloses	• Cost of solvent and the catalysts are high • Risk of fires and explosions as organic solvents are inflammable
Ozonolysis	Ozone treatment degrades lignin by attacking aromatic rings structure, hardly affecting cellulose and hemicelluloses	• No toxic residues produced • Reaction is carried out at room temperature and pressure	• Highly expensive due to requirement of large amount of ozone
Biological	Microorganisms specifically white rot fungi such as *P. chrysosporium,C. lacerata, C. stercolerus,* etcproduce lignin peroxidases and	• Low capital cost • No chemicals required • Low energy requirement • Mild environmental	• Slow rate of hydrolysis so inefficient for industrial purposes • Operational costs increase in large scale operation

(continued)

Table 4 (continued)

Pretreatment	Mode of action	Advantages	Disadvantages
	manganese-dependent peroxidases and laccase that causes lignin degradation	conditions required • Improved productivity • Control of pH during sugar utilization	• More microbes need to be identified and isolated to delignify the plant material quickly and efficiently

[a]*HMF* hydroxymethylfurfural

on the microbial assimilation of the entire sugars that are released from the pretreatment in addition to the hydrolytic processes of biomass. For instance, a mixture of yeast cultures can assimilate both type of sugars but a higher rate of hexose conversion to ethanol will be seen as hexose utilizing microbes grow faster than pentose-utilizing microbes (Koppram et al. 2013).

Consolidated bioprocessing (CBP), on the other hand, integrates all the reactions essential for the conversion of lignocellulosic biomass into ethanol. This approach emphasizes on the usage of a single microbe which can carry out all the processes of enzyme production and hydrolysis as well as fermentation in a single step (Vohra et al. 2014). Naturally occurring cellulase-producing microbial strains can be improved for their biofuel yield or cellulolytic microorganisms can be altered to be ethanologenic while ethanologenic strains can be engineered to be cellulolytic to generate CBP organisms. Different bacterial species such as *Clostridium thermocellum* (Maki et al. 2013; Kumagai et al. 2014; Tian et al. 2016), *Clostridium phytofermentans* (Jin et al. 2011), *Clostridium cellulolyticum* (Li et al. 2012), *Thermoanaerobacterium saccharolyticum* (Shaw et al. 2012), *Caldicellulosiruptor bescii* (Chung et al. 2015), *Escherichia coli* (Shin et al. 2014; Luo et al. 2014), *Zymomonas mobilis* (Wu et al. 2014); fungi such as *Fusarium oxysporum* (Ali et al. 2013), *Trichoderma reesei* (Huang et al. 2014), *Paecilomyces variotii* (Zerva et al. 2014), *Aspergillus oryzae* (Hossain 2013); and yeasts including *Kluyveromyces marxianus* (Hu et al. 2012; Chang et al. 2013), *Clavispora* (Liu et al. 2012), *Pichia stipitis* (Watanabe et al. 2011; Puseenam et al. 2015) and *Saccharomyces cerevisiae* (Yamada et al. 2011, Sakamoto et al. 2012, Fan et al. 2016) have been extensively studied, modified by various strategies such as adaptive evolution, directed mutagenesis and engineered genetically and metabolically to enhance ethanol yield and tolerance for their widespread use in bioethanol production (Table 5).

Discussion

Varied families of glycoside hydrolases are responsible for conversion of lignocellulosic polysaccharide chains into oligomeric and monomeric sugars that can be processed into several value added products, specifically biofuels. Different cellulases, xylanases and mannanases act synergistically on complex sugars present

Table 5 Genetically modified microbes for consolidated bioprocess system (Rastogi and Shrivastava 2017)

Substrate	Microorganism	Description	Ethanol concentration/ yield
Inulin Jerusalem artichoke tuber powder	*S. cerevisiae*	Co-expression of exo-inulinase (InuMK1) and endo-inulinase (InuB) genes from *A. niger* and *K. marxianus* respectively, with repression of proteinase gene PEP4 and switch between haploid and diploid strains	2.44 g/l/h 3.13 g/l/h
20 g/l galactose + 10 g/l CMC 20 g/l galactose + PASC (10 g/l)	*S. cerevisiae*	Cell-displayed minicellulosome consisting of endo- and exo-glucanase with intracellular cellodextrin utilization pathway mimicking the one in *C. thermocellum*	62.61 mg/g cell/h 56.37 mg/g cell/h
60 g/l cellulose (Avicel PH105)	*C. thermocellum* strain AG553	Mutation: adaptive evolution strategy. Apparent changes in Clo1313_1831-2, AdhE and GapDH genes in adapted strain (LL1210)	22.4 ± 1.4 g/l (75% of the theoretical maximum)
Natural sorghum Triticale	*S. cerevisiae* strains M2n and MEL2	Integration of codon optimized variants of *T. lanuginosus*glucoamylase (TLG1) and *S. fibuligera*α-amylase (SFA1) genes	62% and 73% (theoretical maximum)
2% (w/v) Avicel 2% (w/v) Switchgrass	*C. bescii*	Expression of bi-functional acetaldehyde/alcohol dehydrogenase (AdhE) from *T. pseudethanolicus* 39E in the *C. bescii* strain lacking lactate dehydrogenase gene	2.3 mM 1.6 mM
Xylan and β-glucan	*S. stipitis* strain BCC15191	Co-expression of endoxylanase and endoglucanase from *Aspergillus niger* and *Aspergillus aculeatus* respectively	2.7 g/l
50 g/l Glucose 50 g/l Sugarcane bagasse	*T. reesei*CICC 40360	Genome shuffling and mutagenesis to improve production of ethanol under aerobic condition and increased ethanol tolerance (4% v/v)	9.7 g/l 3.1 g/l

(continued)

Table 5 (continued)

Substrate	Microorganism	Description	Ethanol concentration/ yield
20 g/L CMC	*S. cerevisiae*	Co-expression of endoglucanase (eg3) and β-glucosidase (bgl1) were obtained from *Trichoderma viride*	4.63 g/l
Wheat straw	*F. oxysporum*	Post-translational gene silencing of the sugar transporter (Hxt) in the fungus	33.8% (theoretical maximum)
10 g/l crystalline cellulose	*C. cellulolyticum*	Inactivation of L-lactate dehydrogenase (*ldh*) and L-malate dehydrogenase (*mdh*) genes	2.7 g/l

in biomass leading to the formation of monosaccharides such as glucose, xylose and mannose, respectively. Other accessory enzymes such as glucuronidases and arabinofuranosidases cleave branching components from the backbone chains forming glucuronic acid and arabinose, respectively as end products (Walker et al. 2017). Hexose sugars (such as glucose, mannose and galactose) and pentose sugars (such as xylose and arabinose) are typically assimilated in all microorganisms through specific metabolic processes, Embden-Meyerhof-Parnas (EMP) and Pentose Phosphate pathway (PPP), respectively. A detailed description and interaction of the pathways has been described in Fig. 3. Xylulose kinase converts D-xylose into D-xylulose-5-phosphate via an intermediary reaction, which is directed to the native pentose phosphate pathway. Xylose conversion to xylulose, an intermediary product, occurs directly in bacteria whereas fungi and yeasts employ xylose reductase and xylitol dehydrogenase through a two-step oxidation-reduction pathway (Koppram et al. 2013; Poszytek et al. 2016). The synergistic action of phosphopentose epimerase, transketolase and transaldolase further converts D-xylose-5-phosphate through non-oxidative rearrangement into fructose-6-phoshate and glyceraldehyde-3-phosphate, the latter being metabolized into pyruvate by EMP.

In most fungi, L-arabinose is metabolized into D-xylulose-5-phosphate through a series of oxidation-reduction reactions involving reductases and dehydrogenases while in bacteria, arabinose assimilation occurs via the formation of ribulose by arabinose isomerase. A series of reactions involving ribulokinase and ribulose-5-phosphate-4-epimerase further convert ribulose into D-xylulose-5-phosphate which enters the PPP. Pyruvate, the end product of EMP has several fates subject to the environmental circumstances befitting the microorganism. In anaerobic environments, pyruvate is converted to acetaldehyde and carbon dioxide via a decarboxylation reaction by pyruvate decarboxylase. The acetaldehyde is subsequently reduced to form ethanol by alcohol dehydrogenase (De Souza et al. 2013). In

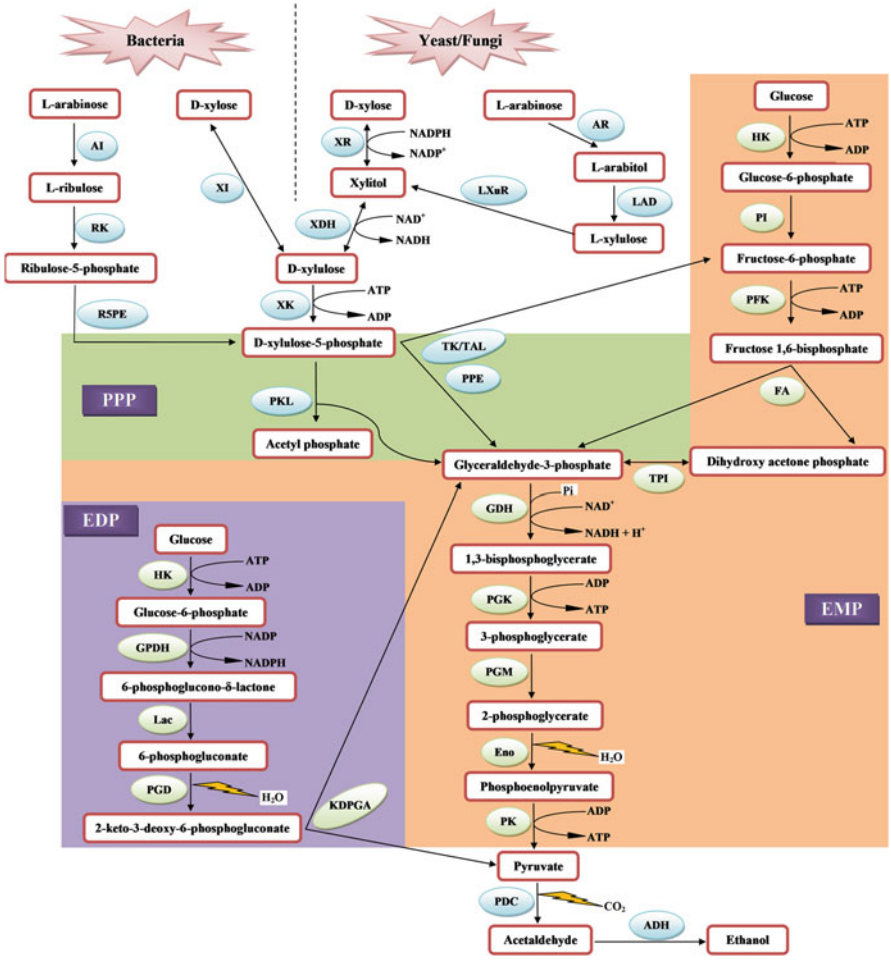

Fig. 3 Hexoses (glucose) and pentoses (xylose and arabinose) assimilation via different pathways in microorganisms. *AI* arabinose isomerase, *RK* ribulokinase, *R5PE* ribulose-5-phosphate-4-epimerase, *XI* xylose isomerase, *XK* xylulose kinase, *XR* D-xylose reductase, *XDH* xylitol dehydrogenase, *AR* arabinose reductase, *LAD* L-arabitol dehydrogenase, *L-XuR* L-xylulose reductase, *PKL* phosphoketolase, *HK* hexokinases, *PI* phosphoglucose isomerase, *PFK* Phosphofructokinase, *FA* fructose bisphosphate aldolase, *TPI* triosephosphate isomerase, *PPE* phosphopentose epimerase, *TA* transaldolase, *TK* transketolase, *GDH* 3-phosphate dehydrogenase, *PGK* phosphoglycerate kinase, *PGM* phosphoglycerate mutase, *Eno* enolase, *PK* pyruvate kinase, *GPDH* glucose-6-phosphate dehydrogenase, *Lac* lactonase, *PGD* 6-phosphogluconate dehydratase, *KDPGA* 2-keto-3-deoxy-6-phosphogluconate aldolase, *PDC* pyruvate decarboxylase, *ADH* alcohol dehydrogenase

E. coli instead of decarboxylase, pyruvate formate lyase catalyzes the conversion of pyruvate to ethanol (Maki et al. 2013). In some bacteria such as *Pseudomonas*, *Rhizobium*, *Agrobacterium* and *Zymomonas mobilis* glycolysis is substituted by the Entner-Doudoroff pathway (EDP). Glucose-6-phosphate is formed via same

reactions through the PPP. The serial conversion of glucose-6-phosphate to 2-keto-3-deoxy-6-phosphogluconate (KDPG), a key intermediate, is assisted by glucose-6-phosphate dehydrogenase, lactonase and 6-phosphogluconate dehydratase enzymes. The formation of pyruvate and glyceraldehyde 3-phosphate occurs via the cleavage of KDPG by the action of 2-keto-3-deoxy-6-phosphogluconate aldolase. Glyceraldehyde 3-phosphate is further converted to pyruvate similarly as in the glycolytic pathway followed by its subsequent conversion to ethanol.

One of the most valuable renewable energy source is biogas. Biogas is a mixture of different gases, naturally produced via decomposition of organic matter in the absence of oxygen. This multilateral biofuel can be utilized for the production of heat and power and also as a gaseous fuel in automobiles. Apart from reducing the greenhouse gases emissions, the digestate of anaerobic digestion (AD) technology acts as a high-value fertilizer for crop cultivation thereby replacing the mineral fertilizers (Achinas et al. 2017). The microbial decomposition of organic substances to biogas comprises of four stages: (1) hydrolysis of complex organic polymers to simple soluble compounds, (2) fermentation of hydrolytic products into intermediates such as alcohols and fatty acids (acidogenesis); (3) anaerobic oxidation of these intermediary compounds to produce acetate, hydrogen and carbon dioxide gases (acetogenesis) and lastly (4) methane production by methanogenic Archaea (methanogenesis) (Sun et al. 2013). Lignocellulosic biomass is popularly utilized for biogas production since they do not compete with food but the recalcitrance of plant material results in its slow or incomplete digestion. Lignocelluloses are degraded into sugars which are subsequently utilized by microbial consortium to produce biogas. The complexity of lignocellulosic biomass acts as an obstacle for enzyme accessibility and thus the hydrolysis process is a rate-limiting step. Therefore, the efficacy of anaerobic digestion, and thus yield of biogas is not always adequate. In such scenario, using glycosyl hydrolases either in pure form or as enzyme complexes or utilizing microorganisms producing such enzymes in situ seems to be the potent solution.

Mixed cultures of cellulolytic and non-cellulolytic bacteria have been used. Many species of fungi, especially white rot fungi (e.g., *Phanerochaete chrysosporium, Coriolus versicolor*, *Fusarium* sp., *Cyathus stercoreus*, *Pleurotus ostreatus* and *Ceriporiopsis subvermispora*) have been used in consortia for pretreatment of lignocelluloses. These organisms secrete unique ligninolytic enzymes useful for boosting the enzymatic disintegration of lignocellulosic biomass (Pinto et al. 2012). They require strict anaerobic conditions which is often provided by using pre-reduced media (Poszytek et al. 2016; Prasertsan et al. 2017). Nonetheless, many factors such as type of substrate, environmental conditions (such as pH, temperature), pre-treatment time, restrict the efficiency of enzymatic pretreatment. Also, usage of free enzymes is less effective as compared to the propagation of microbial consortia, which can stably and constantly produce glycosyl hydrolases for the degradation of lignocelluloses (Parawira 2011).

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