Role of Glycosyl Hydrolases in Breakdown of Lignocellulosic Waste and Its Industrial Applications

Pamela Jha, Moksha Pathan, Akshara Iyer, Renitta Jobby, and Neetin Desai

Abstract

Due to depletion of non-renewable resources at an alarming rate, the need for utilization of renewable resources to make valuable chemicals is of profound importance. Though lignocellulose is most widely available renewable resource on earth, yet it is utilized much below its potential. The conversion of lignocellulose, especially from agricultural wastes and forest residues to vast array of fuels and polymeric precursors is of crucial relevance in the sustainability and development of energy and chemical industries. But, there are technical and economical hindrances to the development of a commercial processes utilizing lignocellulose. There are few promising technologies developed and many are being developed which will allow the conversion of lignocellulose commercially viable. The conversion of lignocellulose to simple sugars requires daunting biological processes which includes delignification and depolymerization. In the second step, the liberation of free sugar can be done by enzymes which can efficiently carry out the process. Hence, understanding the mechanisms, limitations and improvement of these key enzymes, especially the glycosyl hydrolases dictate the efficiency and viability of the entire conversion.

Keywords

Glycosyl Hydrolases · Lignocellulose · Cellulase · Mechanism · Applications

Moksha Pathan and Akshara Iyer contributed equally to this work.

P. Jha (✉) · M. Pathan · A. Iyer · R. Jobby
Amity Institute of Biotechnology, Amity University, Mumbai, Maharashtra, India

N. Desai
Sunandan Divatia School of Sciences, NMIMS, Mumbai, Maharashtra, India

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Introduction

The accumulation of large quantities of lignocellulosic wastes over the years, cause big environmental concerns. However, due to their uniques chemical composition based on sugars and other compounds of commercial interest, they could be utilized for the production of a number of value added products, such as ethanol, food additives, organic acids, enzymes etc. The reuse of carbon obtained from breakdown of lignocellulose can be one of the approach towards decreasing the carbon footprint (Isikgor and Becer 2015). Therefore, along with the associated environmental hazards caused by their accumulation, the failure of the use of these materials encompasses a huge loss of potentially useful sources.

Lignocellulose Composition

Chemical Composition

The Lignocellulosic biomass is an organic material representing the most abundant source of biomass on earth (Lin and Tanaka 2006). The cells of woody and non-woody plant are majorly composed of lignocellulosic material, which includes cellulose, hemicellulose and lignin (Yang et al. 2001). The major component of lignocellulose biomass is cellulose, which is the potential substrate as it is renewable, biocompatible and biodegradable (Ahn et al. 2012). These major polymer constituents are closely associated with each other, constituting the cellular complex of the plant biomass (Fig. 1). Hemicellulose wraps around the cellulose backbone. This core is guarded by the lignin molecule forming the lignocellulosic structure and it act like cellular glue (Isikgor and Becer 2015).

Cellulose, hemicellulose and lignin consists 30–60%, 20–40% and 15–25% of the lignocellulosic material, respectively (Hamelinck et al. 2005). The properties of each component of lignocellulose is mentioned in Table 1.

The lignocellulosic biomass is a major component of disposed wastes obtained from industries such as agriculture, forestry and municipal waste treatment (Perez et al. 2002). These wastes are plentiful, renewable and of meagre expense as energy sources, and has been mostly under utilized. The percentage of each component in lignocellulose varies, depending on the source of biomass. The wastes include sponge gourd fibers, bagasse, banana waste, wheat straw, grasses, newspaper, nut shells, rice straw, corn stover, corn cobs, softwood, hardwood, sweet sorghum, sugarcane bagasse (Fig. 2).

Tertiary Architecture

The management of the tertiary architecture of lignocellulose structures is done by a diverse covalent and non-covalent linkages between its major components. As cellulose is enmeshed with hemicellulose, lignin, and other components, hence

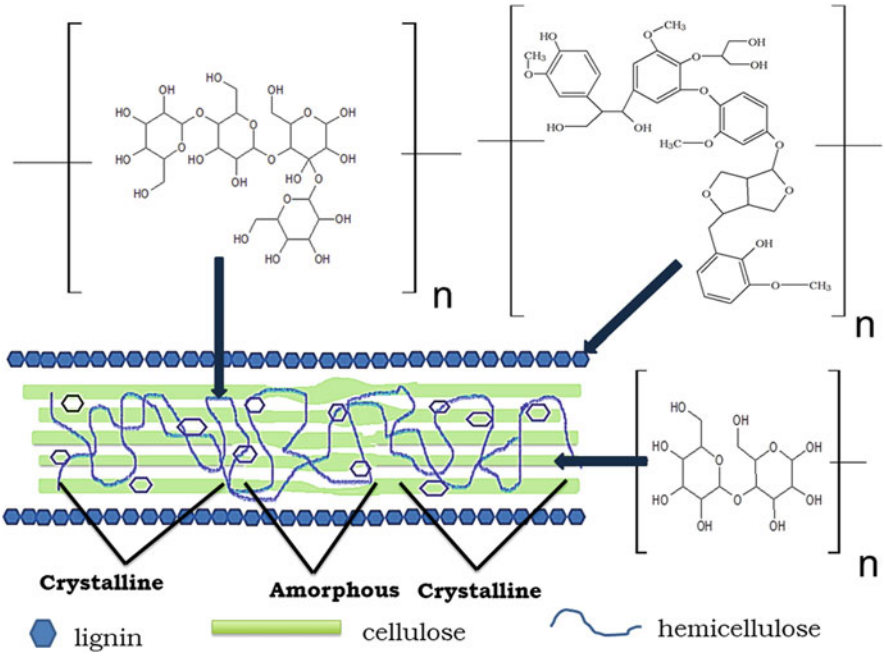

Fig. 1 Representation of lignocellulose structure showing cellulose, hemicellulose and lignin fractions

their hydrolysis is a daunting task (Leonowicz et al. 1999; Tomme et al. 1995). The microfibrils of cellulose are stabilized by intra- and intermolecular H-bonds and encircled by hemicellulose (mannans and xylans) which linked to cellulose by covalent and H-bonds (Heredia et al. 1995). The complicated H-bonding network found within and between glycan units merged with high degree of polymerization containing thousands of glucose monomers promote additional limitation of the linkages for the.

hydrolysis. These covalent bonds are intensely resistant to chemical and biological hydrolysis (Ezeilo et al. 2017). On contrary, amorphous regions within the cellulose crystalline structure have a heterogeneous composition characterized by a various types of bonds. Finally, this asymmetrical arrangement, which characterizes amorphous regions, is critical to the biodegradation of cellulose. The accessibility of enzymes towards cell wall polysaccharides is directed by the extent to which they are interconnected with phenolic polymers (Chesson 1981; Kuhad et al. 1997).

Table 1 Various components of the lignocellulosic biomass

Components	Composition (%)	Monomeric units	Type of polymer	Nature	Degree of polymerisation	References
Cellulose	30–60	d-glucopyranose	Homopolymer	Mostly crystalline	500–25,000	Himmel et al. (1994)
Hemicellulose	20–40	Xylans, mannans glucans and acid sugars	Heteropolymer	Amorphous	100–200	Saha (2000)
Lignin	15–25	Phenylpropanoid precursors	Heteropolymer	Amorphous	6–41	Demirbas (2005), Balat (2011), Molina-Sabio and Rodríguez-Reinoso, (2004), Yang et al. (2009)

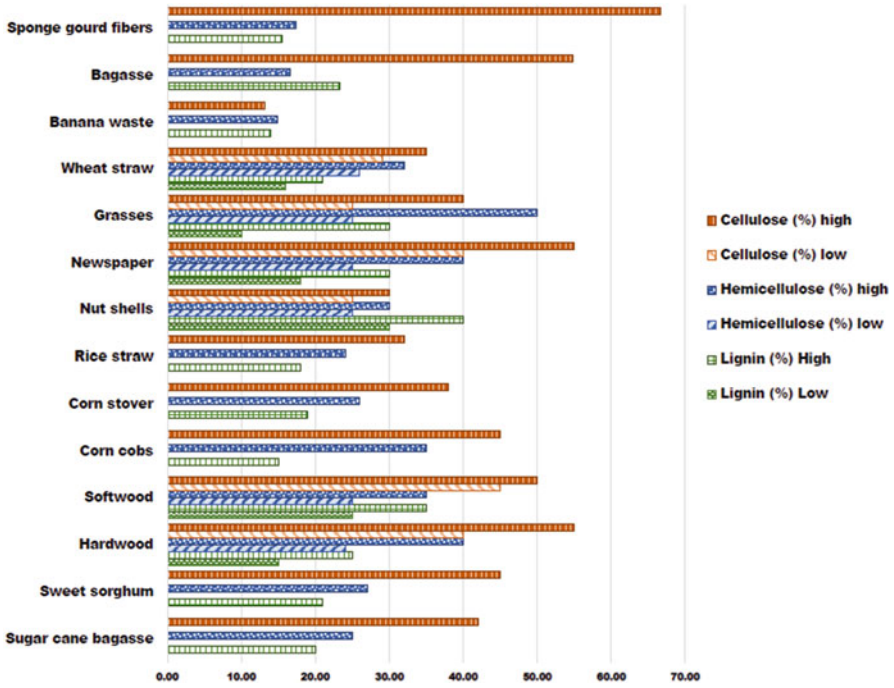

Fig. 2 Percentage of each component variation in lignocellulose from different sources (Reproduced from Iqbal et al. 2013)

Lignocellulose Breakdown

The conversion of lignocellulose to simple sugars requires daunting biological processes i.e.:

1. Delignification—release of free cellulose and hemicellulose from the lignocellulosic biomass;
2. Depolymerization—conversion of cellulose and hemicellulose to generate free sugars.

In the second step, the liberation of free sugar can be done by enzymes which can efficiently carry out the process. But, a complicated and detailed sequence arrangement between polysaccharides (hemicellulose and cellulose) and lignin makes the lignocellulosic material a challenge for carbohydrase and ligninase enzyme systems (de Siqueira et al. 2010).

Delignification

There are many conventional pretreatment techniques reported for the delignification of lignocelluloses which includes physical (grinding and milling), chemical (acid and alkali treatment), physicochemical (use of steam, hot air or ammonia fibres) and biological (fungi) treatments (Sun and Cheng 2002). But conventional methods have several disadvantages: they are time consuming, elaborate and cause damages to the environment by generating secondary pollutants. Of late, lignin modifying enzymes have been used such as laccases, peroxidases and enzymes hydrolyzing lignin-carbohydrate complexes.

Depolymerization

The hydrolysis of lignocellulose is a major obstruction in the technology of utilization of lignocellulose to valuable products. Presently, there are two major processes known for hydrolysis of lignocellulose into free sugars, includes

- catalytic hydrolysis and
- enzymatic hydrolysis.

Catalytic

The catalytic hydrolysis is usually carried out with homogeneous acid or solid acid. The catalysts used are relatively inexpensive. These catalysts are mineral acids such as acetic acid, oxalic acid etc. and organic acids such as H_2SO_4, HCl for hydrolysis of cellulose (Amiri and Kamiri 2013). However, there are multiple disadvantages of their use such as energy-inefficiency, requires separation, recycling, and treatment of the waste acids. Of late, recyclable solid acid catalysts are being used to replace mineral acids for cellulose hydrolysis (Zhou et al. 2013).

Enzymatic

The enzymatic hydrolysis is a promising method to obtain fermentable sugars from lignocellulosic biomass, which can proceed under mild conditions with high selectivity. But, the high cost and low efficiency of recycling enzymes are a problem for the application of enzymatic hydrolysis (Mascal and Nikitin 2008).

Main Enzymes in Cellulose and Hemicellulose Hydrolysis

The enzymes employed in depolymerization of cellulose and hemicellulose are as follows:

Cellulases

- Endo-β-1,4-glucanases, cellobiohydrolases, β-glucosidases
- Fungal cellulases e.g. *Trichoderma, Humicola, Acremonium*
- Bacterial cellulases e.g. *Clostridium thermocellum*

Hemicellulases

- Backbone degrading enzymes
- Enzymes removing the side groups
- β-xylosidases

Other helper enzymes/proteins

- Swollenin

Inhibitors of Enzymatic Degradation

The inhibitors of enzymatic degradation are as follows:

- Phenolics

Aromatic compounds show varied effects depending on the functional groups attached and it is related to their interference with the cell membrane composition and function (Larsson et al. 2000).

- Aliphatic acids

Acids diffuse through the cell membranes and dissociate in the neutral environment of the cytoplasm which causes the pH of the cell to go down and ultimately lead to cell death. It may also compromise on the formation of biomass by producing ethanol (to reverse the lowered pH) (Verduyn et al. 1992).

Glycosyl Hydrolases (GH)

The enzymes are usually classified on the type of the bond that they break. The class of enzymes which hydrolytically break the bonds are grouped under class 3 enzymes and are called hydrolases (Fig. 3) (IUBMB 1992). In this class, the enzymes that hydrolyze glycosidic bonds between two or more sugars and non-sugars within carbohydrate and oligonucleotides are called GH. There are 115 families of these enzymes known, on the basis of mode of action and amino acid sequence (Sathya and Khan 2014). These enzymes hydrolytically breaks the bonds such as ester, glycosidic, ether, and peptide bonds, and also transfers the specific group to water, which acts as an acceptor (IUBMB 1992). GHs are key enzymes involved in the depolymerization of cellulose, which is the most crucial step in formation of fermentable sugars for production of fuels and chemicals. GH catalysed reactions are accelerated by 17 folds compared to spontaneous hydrolysis, which makes them lucrative biocatalysts (Wolfenden et al. 1998).

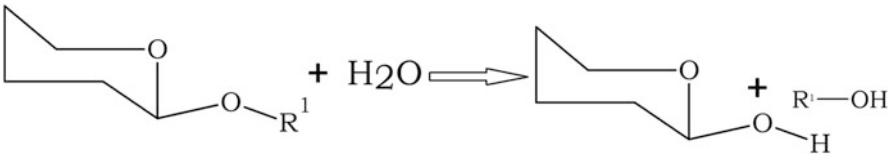

Fig. 3 Hydrolysis reaction of glycosidic bond

Classification of GH

GH also known as glycosidases or carbohydrases (EC 3.2) comprises of a wide spectrum group of enzymes that has the catalytic properties to cleave N-, S- and O-glycosidic bonds. They either cleave two sugar moieties or a sugar and a non-sugar region of carbohydrate. There are 115 families (based on the amino acid sequence and action) of GH, which have been identified (Lehninger 2004). There are few glycosidic bond, which are most stable covalent bonds found between monomers in biopolymers, especially between two glucose residues in some polysaccharides (Wolfenden et al. 1998). The domain, E.C., CATH, CAZY FAM, and CAZY clan cells, show different entries could be assigned to the given classes (Table 2).

Structure of GH

The 3D structure of Lysozyme was the first to be resolved and it was found that aspartate and glutamate are the major amino acids involved in catalysis. Further studies proved that most glycosyl hydrolases has conserved regions of aspartate or glutamate that were involved in catalysis. Recent examples of neuraminidase show that tyrosine is used in stabilising the intermediates of the reaction (Burmeister et al. 1993; Crennel et al. 1993).

GH catalyse all the hydrolytic reactions of glycosidic bonds and are studied thoroughly. They cleave the C–O exo-cyclic acetal bond.

Study of the spontaneity of the reaction reveal their extremely slow action with the half life a hydrolytic cleavage estimated to be 4.7 million years. Thus GH act as an efficient and powerful catalyst speeding up the reaction by more than 1000× (Stick and Williams 2009).

The most important structural aspect of an enzyme is its active site conformation and GH is found to have three distinct conformation in its active site (Davies and Henrissat 1995).

Active Site Topology

22 families of the protein have been studied and it has been found that the active sites can be classified into three classes:

Table 2 Summary of the structurally homologous classes of GH and their sources

Domains	Class	Domains	EC	CATH	Cazy FAM	CAZY CLAN	Representative enzymes	Sources
N-glycosyl catalytic (A)	1	25	1	1	–	–	Shiga Toxin A subunit	*Shigella dysenteriae*
	2	30	1	4	–	–	Ricin A chain	Castor beans
	3	14	1	1	–	–	ADP-ribosyl cyclase	Sea urchins
	4	10	2	1	–	–	Pyrimidine nucleoside hydrolase	*E. coli*
	5	5	2	2	–	–	3-Methyladenine DNA glycosylase	Recombinant human
	6	2	1	1	–	–	Uracil-DNA glycosylase	Recombinant human
	7	2	1	1	–	–	MTA/SAH nucleosidase	*Escherichia coli*
N-glycosyl binding (B)	8	5	2	2	1	–	Endo-1,4-beta-xylanase A	*Trichoderma longibrachiatum*
O-(S)-glycosyl catalytic (C)	1	171	2	2	3	–	Lysozyme	Albumin
	2	12	2	4	2	1	Chitosanase	*Penicillium chrysogenum, E. coli*
	3	13	1	1	1	1	Polygalactouronidase	Agro wastes (pectin)
	4	303	33	35	28	4	Beta-galactosidase	*Aspergillus niger*
	5	48	2	2	3	2	Endo-1,4-beta-Xylanase	*Trichoderma longibrachiatum*
	6	54	5	7	6	2	Cellobiohydrolase	*Saccharomyces cerevisiae*
	7	34	2	6	4	2	Neuraminidase	*Influenza virus*
	8	2	2	–	1	–	6-Phospho-beta-glucosidase	*Escherichia coli*
	9	3	1	1	1	–	Endoglucanase	*Aspergillus terreus*
	10	17	4	2	2	1	Beta-Agarase B	*Alteromonas sp. C-1*

(continued)

Table 2 (continued)

Domains	Class	Domains	EC	CATH	Cazy FAM	CAZY CLAN	Representative enzymes	Sources
O-(S)-glycosyl binding (D)	11	3	1	1	1	–	Endo-1,4-beta-Xylanase Y	*Clostridium thermocellum*
	12	2	2	1	1	–	Glucoamylase	*Aspergillus niger*
	13	2	1	–	1	–	Cellobiohydrolase	*Trichoderma reesei*
	14	8	3	2	1	–	Endo-1,4-beta-Xylanase D	*Talaromyces funiculosus* (*Penicillium funiculosum*) (*Bacteroides ruminicola*)
	15	2	1	1	1	–	Endo-1,4-beta-Xylanase A	*Trichoderma longibrachiatum*
	16	10	2	3	4	–	Endoglucanase C	*Cellulomonas fimi*

Reproduced from Fülöp and Ponyi (2015)

- Pocket or crater
  This is mainly when non-reducing saccharides are substrates (example: monosaccharidases like neuraminidase and galactosidase and exopolysaccharidases like amylase). These enzymes act on substrates which have exposed non-reducing ends. They have limited activity on fibrous substrates with no free ends (Davies and Henrissat 1995).
- Cleft or groove
  These are the binding points for endo-acting polymeric substrates like lysozymes and chitinase (Davies and Henrissat 1995).
- Tunnel
  These are modified clefts with the protein loops covering the clefts to form a tunnel shaped structure. Cellobiohydrolases are the only class of enzyme with this structure and they pass through the site for the reaction to occur (Rouvinen et al. 1990). Products are released while the polysaccharide chain is still bound to the enzyme enabling better processivity. Although the exact mechanism of action is unknown, it is observed that the direction of enzyme motion changes during the reaction based on the enzyme class (Divne et al. 1994).

Mechanism of Glycosyl Breakdown

During enzyme hydrolysis of the glycosidic bond, two essential components required are proton donor and a nucleophile (Fig. 4).

GH in Lignocellulose Breakdown

The breakdown of lignocellulosic biomass for the production of valuable products can add to the economics as well as alleviate the detrimental effect on environment caused due to their disposal into soil or landfills (Taherzadeh and Karimi 2008). The cellulose-degrading systems are pertinent for industrial cellulose breakdown as well as to sustain the carbon cycle. The class of enzymes which are crucial in liberation of free sugars after delignification of lignocellulosic biomass is cellulase. Cellulases are the class of enzymes that are associated with the breaking down of cellulose and other related polysaccharides. Although produced by various organisms like bacteria, fungi and yeast, termites and their intestinal symbionts form the major source of cellulase (Watanabe and Tokuda 2001).

Classes of GH in Cellulosic Breakdown

They exist as complexes of various enzymes from the class exocellulase, endocellulase, cellobiolases, cellulose phosphorylases and oxidative cellulases (Tsai et al. 2012). The families of GH with different types of cellulases is mentioned in Table 3.

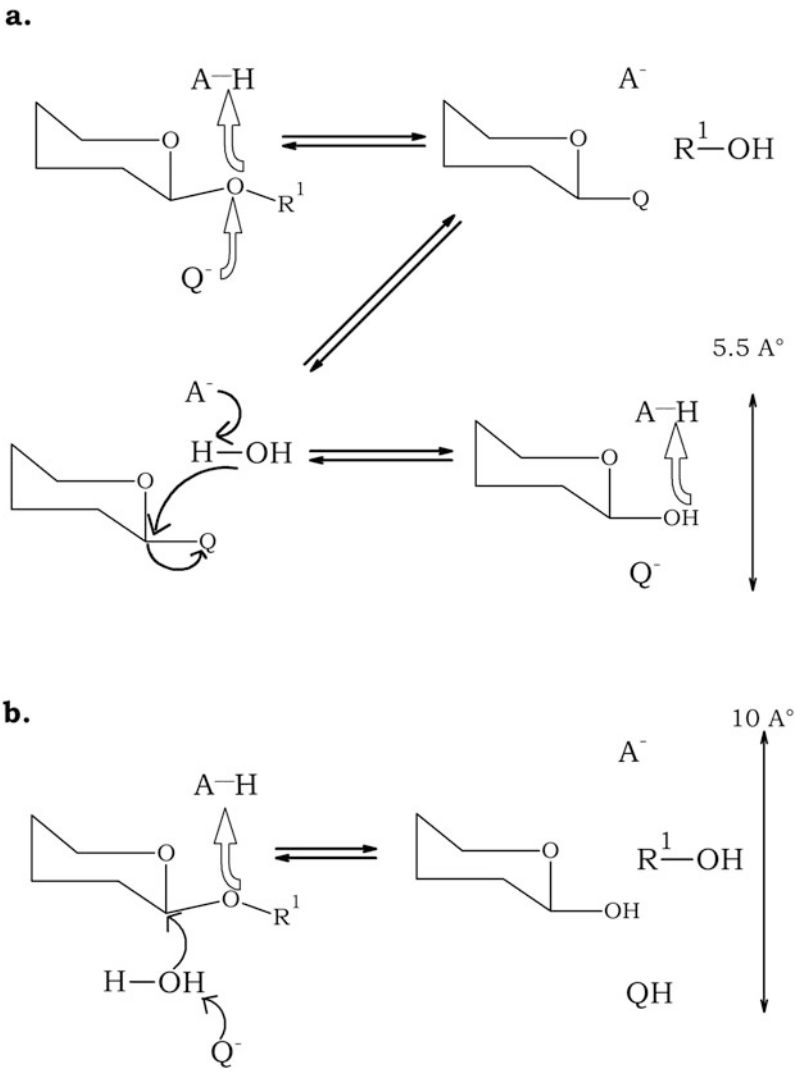

Fig. 4 Mechanism of breakdown of lignocellulose. (**a**) The retaining method, the acid catalyst AH protonate the oxygen in the glucose and base Q- avails the nucleophilic function to knockout the aglycon group. The glycosyl enzyme is then undergoes hydrolysis. (**b**) The inverting method, the oxygen of the glucose is protonated and aglycon group knockout occurs simultaneously by the attack of the water molecule which is activated by the base Q- (Reproduced from Davies G. and Henrissat B. 1995)

The major families of Cellulases belong to GH class of 5,9,17 and 48 (Ezeilo et al. 2017). These cellulase of particular class, have the following properties:

- Enzymes of GH 5—These are characterized by the presence of conserved glutamic acid residues which are the major catalytic groups. They exhibit the retaining mechanism

Table 3 Cellulases, functions and their corresponding GH families

Enzyme	EC number	Functions	GH family
1. Name: β-1,4-glucanase Systematic name: 4-(1,3;1,4)-β-D-glucan 4-glucanohydrolase	EC 3.2.1.4	Endohydrolysis of (1 → 4)-β-D-glucosidic linkages in cellulose, lichenin and cereal β-D-glucans. Randomly hydrolyses b-(1,4)-glycosidic bonds exposing reducing and non-reducing ends of the linear polymer of glucose units	GH5, GH9, GH12, GH44, GH45, GH48, GH51, GH74, GH124
2a. Name: glucan 1,4-β-glucosidase Systematic name: 4-β-D-glucan glucohydrolase	EC 3.2.1.74	Hydrolysis of (1 → 4)-linkages in (1 → 4)-β-D-glucans, to remove successive glucose units Cleaves glucose successively from the non-reducing ends of the glucan to liberate glucose units, with preference for substrates of longer chain length and giving rise to inverted products	GH3, GH5, GH6, GH7, GH9, GH48
2b. Name: β-1,4-glucan cellobiohydrolase Systematic name: 4-β-D-glucan cellobiohydrolase (non-reducing end)	EC 3.2.1.91	Hydrolysis of (1 → 4)-β-D-glucosidic linkages in cellulose and cellotetraose, releasing cellobiose from the non-reducing ends of the chains Acts at the reducing ends of -b-(1,4)-glucans, produced by endoglucanases, cleaving cellobiose and cellooligosaccharides	GH5, GH6, GH7, GH9, GH48
3. Name: β-1,6-glucosidase Systematic name: β-D-glucoside glucohydrolase	EC 3.2.1.21	Hydrolysis of terminal, non-reducing β-D-glucosyl residues with release of β-D-glucose Hydrolyses cellobiose and other very short chain b-D-oligosaccharides up to cellohexaose to form glucose; unlike exoglucosidases the rate of hydrolysis decreases markedly as the degree of polymerization of the substrate increases	GH1, GH3, GH5, GH9, GH30, GH116

Reproduced from Saini et al. (2015), Gilbert and Hazlewood (1993), and Xiros et al. (2016)

- Enzymes of GH 9—These are subdivided as E1 (source: aerobic and anaerobic bacteria) and E11 (Source: mainly non-bacterial). They exhibit the inverting mechanism.
- Enzymes of GH 17—These exhibits retaining mechanism. It includes 2 major enzyme families: 1,3-β-D-glucan endohydrolases and 1,3;1,4-β-D-glucan endohydrolases
- Enzymes of GH 48—These have high efficiency for amorphous or crystalline cellulose than carboxymethylcellulose or cellobiose as the latter inhibits its activity. They too exhibit inverting mechanism.

The mechanisms stated above for each class were obtained from CAZYPedia.

Model of Cellulose Degradation

The model known for enzymatic degradation of cellulose is depicted (Fig. 5).

The diffusion of enzymes into the substrate has been simulated and the biological conditions understood. The model is based on (Luterbacher et al. 2013a, b):

1. The dependency of the hydrolysis on the particle size (it can be modified by a suitable pretreatment)
2. Sudden decrease in the reaction rate after the initial rush of the enzyme into the substrate.

Cellulosome Complex

Cellulosomes have the capability to breakdown cellulose. The understanding of structure, mechanism and functions of this multi-enzyme complex began from *Clostridium thermocellum* (Lamed et al. 1983). The key features of cellulosome are stability and flexibility, composed of many subunits, its organization promotes synergistic action, and contains catalytic and non catalytic units. The components of cellulosome are the scaffoldin subunit (1800 amino acids), cohesin modules,

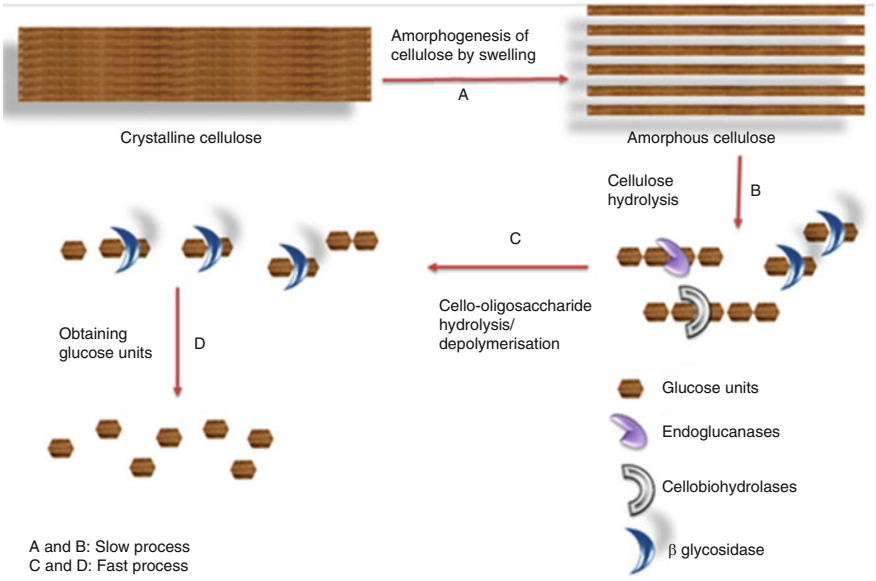

Fig. 5 Enzymatic cellulose degradation model (Reproduced from Lynd et al. 2002)

dockerin modules, and catalytic subunits (Bayer et al. 2004). The catalytic subunits of cellulosomes consist of enzymes such as endoglucanases, xylanases and cellobiohydrolases. These enzymes portray array of substrate specificities and catalytic mechanisms Apart from the catalytic module, the dockerin module modulates enzyme interaction alongside the scaffoldin protein, responsible for assembly of the cellulosome complex (Bayer et al. 2004). The synergism of different subunits ensures a well-harmonized enzymatic coordinations, thus making cellulosomes the most efficient system for the breakdown of cellulose (Xiros et al. 2016). Recently, artificial cellulosomes are being built for the dedicated aim of enhancing the catalytic efficiency for the depolymerization of cellulose (Gefen et al. 2012).

Factors Influencing the Enzymatic Hydrolysis of Lignocellulose

Complexity of the Substrate

Cellulose is a complex and heterogeneous molecule which makes its breakdown difficult to achieve. Thus achieving a fool-proof model for its breakdown is an issue. Cellulose structure has both intra and inter-chain bondings forming a tightly packed crystalline structure interspaced with some amorphous regions each of which are at different complexity and availability (Yang et al. 2011; Bubner et al. 2013).

The enzymatic breakdown of the biomass is affected by various factors like (Fox et al. 2013; Luterbacher et al. 2013a, b):

- Biomass content
- Available surface area
- Bond accessibility
- Pretreatment used (minimal inhibitors produced)
- Degree of polymerization
- Organization of cellulose

Heterogeneity of the Enzymes

Microbial cellulases have been in use since the 1990s. The demand for the enzymes has only increased with time making it imperative to find other sources for the bulk production of the enzymes. The search led to a finding that both bacteria and fungi are efficient cellulase producers with organisms like *Clostridium, Bacillus, Erwinia* and *Streptomyces* being some of them (Yang et al. 2011; Bubner et al. 2013).

Based on the enzyme source they can be generally classified as (Coughlan and Ljungdahl 1988; Sun and Cheng 2002; Elkins et al. 2010; Bayer et al. 1998):

1. Non-complexed system: Produced by fungi and aerobic bacteria.
2. Complexed system: Produced by anaerobic organisms.

Recently, the study on cellulases produced by *Trichoderma reesei* has gained momentum due to the large amount of enzyme released which is beneficial economically. It is the only non-complexed system studied as the degradation of the biomass

by the organism occurs simultaneously (Coughlan and Ljungdahl 1988); Sun and Cheng 2002; Elkins et al. 2010; Bayer et al. 1998). On the other hand complexed system has various advantages like:

- A coordinated process
- Only specific interaction

Applications of Cellulase

The addition of novel cellulases to the existing list of GH in lignocellulosic breakdown is increasing the applications of these enzymes in various industries (Fig. 6).

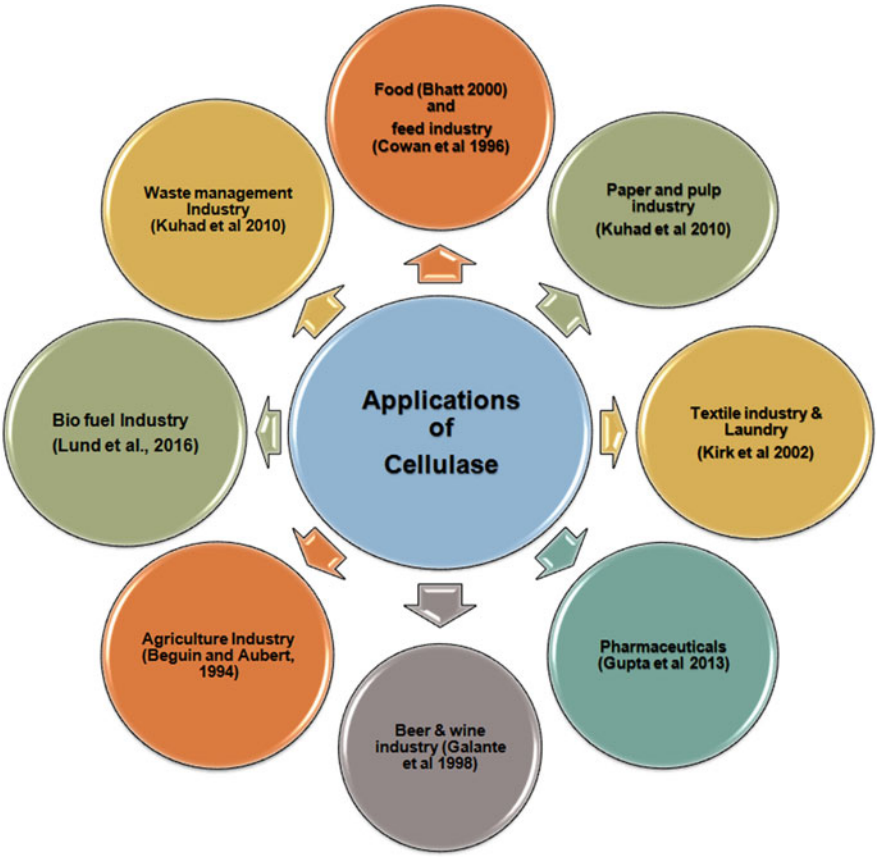

Fig. 6 Diverse applications of cellulases

Conclusion

The requirement of huge energy and chemicals demand is compelling the human race to find alternative to renewable clean technologies. In this context, one of the most lucrative substrate which promises to partially fulfil our demand is lignocellulosic biomass. The usage of lignocellulose at industrial scale is limited due to the huge expenses incurred in enzymes used for their hydrolysis. Thus, in present scenario the focus is being targeted to improve enzymes with respect to increased stability, wider substrate affinity, and magnus increase in catalytic activity at wide range of pH and temperature.

References

Ahn Y, Lee SH, Kim HJ, Yang YH, Hong JH, Kim YH, Kim H (2012) Electrospinning of lignocellulosic biomass using ionic liquid. Carbohydr Polym 88(1):395–398

Amiri H, Karimi K (2013) Efficient dilute-acid hydrolysis of cellulose using solvent pretreatment. Industr Eng Chem Res 52(33):11494–11501

Balat M (2011) Production of bioethanol from lignocellulosic materials via the biochemical pathway: a review. Energy Convers Manag 52:858–875

Bayer EA, Chanzy H, Lamed R et al (1998) Cellulose, cellulases and cellulosomes. Curr Opin Struct Biol 8(5):548–557

Bayer EA, Belaich JP, Shoham Y, Lamed R (2004) The cellulosomes: multienzyme machines for degradation of plant cell wall polysaccharides. Annu Rev Microbiol 58:521–554

Bubner P, Plank H, Nidetzky B (2013) Visualizing cellulase activity. Biotechnol Bioeng 110:1529–1549

Burmeister WP, Henrissat B, Bosso C, Cusack S, Ruigrok RWH (1993) Influenza B virus neuraminidase can synthesize its own inhibitor. Structure 1(1):19–26

Chesson A (1981) Effects of sodium hydroxide on cereal straws in relation to the enhanced degradation of structural polysaccharides by rumen microorganisms. J Sci Food Agric 32:745–758

Coughlan MP, Ljungdahl LG (1988) Comparative biochemistry of fungal and bacterial cellulolytic enzyme system. In: Aubert JP, Beguin P, Millet J (eds) FEMS symposium: biochemistry and genetics of cellulose degradation. Academic Press, London, pp 11–30

Crennel SJ, Garman EF, Laver WG, Vimr ER, Taylor GL (1993) Crystal structure of a bacterial sialidase (from *Salmonella typhimurium* LT2) shows the same fold as an influenza virus neuraminidase. Proc Natl Acad Sci USA 90:9852–9856

Davies G, Henrissat B (1995) Structures and mechanisms of glycosyl hydrolases. Structure 3 (9):853–859

de Siqueira FG, Ferreira F, Ximenes E (2010) Plant cell wall as a substrate for the production of enzymes with industrial applications. Minirev Organic Chem 7(1):54–60

Demirbas A (2005) Bioethanol from cellulosic materials: a renewable motor fuel from biomass. Energy Sources 27:327–337

Divne C et al (1994) The three-dimensional crystal structure of the catalytic core of cellobiohydrolase I from *Trichoderma reesei*. Science 265:524–528

Elkins JG, Ramen B, Keller M (2010) Engineered microbial systems for enhanced conversion of lignocellulosic biomass. Curr Opin Biotechnol 21(5):657–662

Ezeilo UR, Zakaria II, Huyop F, Wahab RA (2017) Enzymatic breakdown of lignocellulosic biomass: the role of glycosyl hydrolases and lytic polysaccharide monooxygenases. Biotechnol Biotechnol Equip 31(4):647–662

Fox JM, Jess P, Jambusaria RB (2013) A single-molecule analysis reveals morphological targets for cellulase synergy. Nat Chem Biol 9:356–361
Fülöp L, Ponyi T (2015) Classification of glycosyl hydrolases based on structural homology. J Univ Sci 2(1):1–9
Gefen G, Anbar M, Morag E (2012) Enhanced cellulose degradation by targeted integration of a cohesin-fused β-glucosidase into the *Clostridium thermocellum* cellulosome. Proc Natl Acad Sci USA 109:10298–10303
Gilbert HJ, Hazlewood GP (1993) Bacterial cellulases and xylanases. J Gen Microbiol 139:187–194
Hamelinck CN, Van Hooijdonk G, Faaij AP (2005) Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle-and long-term. Biomass Bioenergy 28(4):384–410
Heredia A, Jimenez A, Guillen R, Lebensm Z (1995) Composition of plant cell walls. Lebensm Unters Forsch 200:24–31
Himmel ME, Baker JO, Overend RP (1994) Enzymatic conversion of biomass for fuels production. Am Chem Soc, Washington, DC, pp 292–324
Iqbal HMN, Kyazze G, Keshavarz T (2013) Advances in valorization of lignocellulosic materials by biotechnology: an overview. Bioresources 8:3157–3176
Isikgor FH, Becer CR (2015) Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. Polym Chem 6(25):4497–4559
IUBMB (1992) Enzyme nomenclature. Recommendations. Academic Press, San Diego
Kuhad RC, Singh A, Eriksson KEL (1997) Microorganisms and enzymes involved in the degradation of plant fiber cell walls. Adv Biochem Engin/Biotechnol 57:45–125
Lamed R, Setter E, Bayer EA (1983) Characterization of a cellulose-binding, cellulase-containing complex in *Clostridium thermocellum*. J Bacteriol 156:828–336
Larsson S, Quintana-Sáinz A, Reimann A, Nilvebrant NO, Jönsson LJ (2000) Influence of lignocellulose-derived aromatic compounds on oxygen-limited growth and ethanolic fermentation by *Saccharomyces cerevisiae*. In: Twenty-first symposium on biotechnology for fuels and chemicals. Humana Press, Totowa, NJ, pp 617–632
Lehninger AL, Nelson DL, Cox MM (2004) Lehninger principles of biochemistry. W. H. Freeman, New York
Leonowicz A, Matuszewska A, Luterek J, Ziegenhagen D, Wojtas Wasilewska M, Cho NS, Hofrichter M, Rogalski J (1999) Biodegradation of lignin by white rot fungi. Fungal Genet Biol 27:175–185
Lin Y, Tanaka S (2006) Ethanol fermentation from biomass resources: current state and prospects. Appl Microbiol Biotechnol 69:627–642
Luterbacher JS, Parlange JY, Walker LP (2013a) A pore-hindered diffusion and reaction model can help explain the importance of pore size distribution in enzymatic hydrolysis of biomass. Biotechnol Bioeng 110(1):127–136
Luterbacher JS, Walker LP, Moran-Mirabal JM (2013b) Observing and modeling BMCC degradation by commercial cellulase cocktails with fluorescently labeled *Trichoderma reseii* Cel7A through confocal microscopy. Biotechnol Bioeng 110(1):108–117
Lynd LR, Weimer PJ, Van Zyl WH, Pretorius IS (2002) Microbial cellulose utilization: fundamentals and biotechnology. Microbiol Mol Biol Rev 66(3):506–577
Mascal M, Nikitin EB (2008) Direct, high-yield conversion of cellulose into biofuel. Angewandte Chemie 47(41):7924–7926
Molina-Sabio M, Rodríguez-Reinoso F (2004) Role of chemical activation in the development of carbon porosity. Colloid Surf A Physicochem Eng Aspect 241:15–25
Perez J, Munoz-Dorado J, De la Rubia TD, Martinez J (2002) Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. Int Microbiol 5(2):53–63
Rouvinen J, Bergfors T, Teeri T, Knowles JKC, Jones TA (1990) Three-dimensional structure of cellobiohydrolase II from *Trichoderma reesei*. Science 249:380–386
Saha BC (2000) Alpha-l-arabinofuranosidases—biochemistry, molecular biology and application in biotechnology. Biotechnol Adv 18:403–423

Saini JK, Saini R, Tewari L (2015) Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments. Biotechnology 5 (4):337–353

Sathya TA, Khan M (2014) Diversity of glycosyl hydrolase enzymes from metagenome and their application in food industry. J Food Sci 79(11):R2149–R2156

Stick RV, Williams SJ (2009) Enzymatic cleavage of glycosides: mechanism, inhibition and synthetic applications. In: Stick RV, Williams SJ (eds) Carbohydrates: the essential molecules of life, 2nd edn. Elsevier, Amsterdam, pp 253–284

Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 83(1):1–11

Taherzadeh M, Karimi K (2008) Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. Internat J Mol Sci 9(9):1621–1651

Tomme P, Warren RA, Gilkes NR (1995) Cellulose hydrolysis by bacteria and fungi. Adv Microb Physiol 37:1–81

Tsai SL, DaSilva NA, Chen W (2012) Functional display of complex cellulosomes on the yeast surface via adaptive assembly. ACS Synth Biol 2(1):14–21

Verduyn C, Postma E, Scheffers WA, Van Dijken JP (1992) Effect of benzoic acid on metabolic fluxes in yeasts: a continuous-culture study on the regulation of respiration and alcoholic fermentation. Yeast 8(7):501–517

Watanabe H, Tokuda G (2001) Animal cellulases. Cellu Mol Life Sci 58(9):1167–1178

Wolfenden R, Lu X, Young G (1998) Spontaneous hydrolysis of glycosides. J Am Chem Soc 120 (27):6814–6815

Xiros C, Topakas E, Christakopoulos P (2016) Hydrolysis and fermentation for cellulosic ethanol production. In: Lund DE, Byrne J, Berndes G, Vasalos LA (eds) Advances in bioenergy: the sustainability challenge. Wiley, New York, pp 11–31

Yang X, Chen H, Gao H, Li Z (2001) Bioconversion of corn straw by coupling ensiling and solid-state fermentation. Bioresour Technol 78(3):277–280

Yang SJ, Kataeva I, Hamilton-Brehm SD, Engle NL, Tschaplinski TJ, Doeppke C, Davis M, Westpheling J, Adams MWW (2009) Efficient degradation of lignocellulosic plant biomass, without pretreatment, by the thermophilic anaerobe *Anaerocellum thermophilum* DSM 6725. Appl Environ Microbiol 75:4762–4769

Yang B, Dai ZY, Ding SY, Wyman CE (2011) Enzymatic hydrolysis of cellulosic biomass. Biofuels 2:421–450

Zhou L, Liu Z, Shi M, Du S, Su Y, Yang X, Xu J (2013) Sulfonated hierarchical H-USY zeolite for efficient hydrolysis of hemicellulose/cellulose. Carbohy Polym 98(1):146–151