INDUSTRIAL AND BIOTECHOLOGICAL USES OF β MANNANASE ENZYME

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ABSTRACT

Enzymes are organic molecules involved in the realization of chemical reactions in all living cells. The importance of enzymes, which are involved in almost every aspect of our lives, is increasing day by day. Enzymes are involved in almost all stages of the biosynthesis and biodegradation process (coding, folding, and functionality) faster than expected and with high precision. In every process from a single-celled organism to a complex living organism, protein enzymes produced by living cells are involved in the decomposition of organic and inorganic substances, as well as in the formation or destruction of biomass. Ecological and efficient alternatives to industrial processes increase interest in the use of microorganisms and enzymes as biocatalysts. In addition, enzymes are more environmentally friendly by reducing the use of other chemicals and have advantages such as higher product quality, energy saving, and biodiversity conservation, making their use indispensable in many areas of industry. Mannans are essential components of hemicellulosic fragments of softwoods such as chestnut, tulip poplar, and cypress and are found in plant tissue. The degradation of heteromannan polysaccharide, which is included in the structure of the plant cell wall, is carried out through synergistic activation of enzymes that hydrolyze mannans. There are two enzymes of major importance that degrade heteromannan polysaccharide. These enzymes are endo-β 1,4 Mannanase (EC.3.2.1.78) and exo-β 1,4 Mannosidase (EC.3.2.1.25). β Mannanase enzyme facilitates the digestion of plant material by breaking down the mannan in plant cell walls. In this way, the nutrients contained in plant-based foods are absorbed more effectively by the human or animal digestive system. β mannanases can be synthesized by actinomycetes, animals, plants, bacteria and fungi. Used as an industrial enzyme, mannanases are involved in many industrial fields because they are active in a wide pH and temperature range. The application areas of β-mannanases include animal feed, food, bio-refinery, textile, detergent, paper and pulp. The aim of this study is to provide information about the use of β-mannanase enzyme in industrial and biotechnology fields and to provide a resource for future studies.

Keywords: Enzyme, β Mannanase, Mannanase, Industrial Enzymes, Heteromannan

INTRODUCTION

Enzymes are protein molecules that catalyze biochemical reactions in cells. Enzymes, which have many important metabolic functions in cells, have entered our lives for different purposes (Wiseman 1987). Chemical molecules catalyzed by enzymes and participating in the

reaction with enzymes are called substrates. The enzyme reacts only with the substrate compatible with the three-dimensional structure of its active site. Therefore, an enzyme acts only on a certain type of substrate (Erkaya 2006). Enzymes, which have important metabolic functions in the cell, are proteins that catalyze biochemical reactions.

Enzymes used as industrial enzymes are expected to have some capabilities. These are longevity and high resistance, the ability to use the substrate involved in the reaction correctly even if the environment in which it will show activity is different from the intracellular conditions, and the ability to work without degradation in high temperature, low temperature, acidic or basic conditions used in the industrial environment. Considering these demands, enzymes need to be regulated to meet the needs (Gray et al., 2000). Generally used enzymes: Constant kinetics, optimum pH and temperature, resistance of the enzyme to solvents, reaction and substrate specificity, cofactor requirement, molecular weight and subunit structure.

Due to the gradual development of enzyme technology, the diversity of the usage areas of the products, and the high economic value of the products, various research in the field of biotechnology related to industrial enzymes is becoming more important (Solomon El et al., 1996).

Products produced for biotechnological purposes include lactic acid, insulin, antibiotics, bioethanol, and enzymes. Although all of these products have important areas of use, enzymes are the most important biotechnological product groups in food and other industries. Enzymes were previously isolated from plant and animal sources by various extraction methods. However, due to the increasing need for enzymes, new production techniques have emerged. One of these methods is the production of enzymes with natural or recombinant strains. One of the enzymes that can be produced by this method is β-mannanases. β-mannanases are used in different fields such as animal feed improvement, cleaning products, the paper industry, and coffee production. β-mannanases, which have a wide range of applications, are produced by yeasts, molds, and bacteria. (Koç, C. Y. 2021).

In recent years, there has been a growing interest in the development of biorefinery processes for the conversion of lignocellulosic wastes into second-generation biofuels and value-added products with potential industrial applications (Menon and Rao 2012; Paone et al., 2020). Lignocellulose is the primary structural component of woody and non-woody (e.g. grass) plants and is composed of cellulose, hemicellulose, and lignin (Ragauskas et al., 2006; Sanderson 2011). Lignocellulosic wastes are used in pulp and paper, food, and agriculture (Moreira et al., 2008; Saini et al., 2015). Among lignocellulosic wastes, agro-industrial residues have received special attention as sustainable feedstocks for biorefinery due to their abundance and cost-effectiveness (Anwar et al., 2014; Rodrigues et al., 2020). Reports indicate that cellulose and hemicellulose account for more than 50% of the dry weight of agro-industrial wastes (Sanchez et al., 2009; Rodrigues et al., 2020).

Hemicellulose, the second most abundant carbohydrate biopolymer on earth, is a member of various types and structural polysaccharides found in plant cell walls (Scheller et al., 2010; Van Dyk et al., 2012). These structural polysaccharides are generally composed of monomer sugar compounds: d-xylose, d-mannose, d-glucose, d-galactose, l-arabinose, 4-O-methyl-d-glucuronic acid (Scheller et al., 2010; Yamabhai et al., 2016). Xylan and mannan are the most abundant structural polysaccharides of heteropolymeric hemicellulose content in hardwood and softwood, respectively (Moreira et al., 2008; Malgas et al., 2015; Chauhan et al., 2017). Mannan is also found in the endosperm wall of seeds (coconut, coffee, and locust bean) and as a non-starch replacement component in the coffers (konjac, ivory nut, and guar) (Yamabhai et al., 2016; Saittagaroon et al., 1983; Rodrıguez-Gacio et al., 2012). Mannan has been reported as a cell wall component of several seaweed species belonging to the Chlorophyta and Rhodophyta phyla (Stiger-Pouvreau et al., 2016).

Mannans

Mannans are a series of non-crystalline hemicelluloses found in many living organisms such as bacteria, yeast, fungi, and plants. Mannans are found in the cell walls of different cell and tissue types in plants. (Meier and Reid, 1982) Currently, mannans have gained increasing interest in both academic and industrial research based on the growing demand for efficient use of renewable resources for sustainable development. This is not only because of the important role of these polysaccharides in plant cell wall formation (Whitney et al., 1998; Handford et al., 2003) but also because they are abundant sources of untapped raw materials that can be used in many fields. Thanks to this advantage, they are preferred in many industrial fields such as biofuel production, food and feed industries, cleaning, and many more (Yamabhai et al., 2014).

Function and classification of mannans

β-mannans

They have backbones composed of β-1,4-linked mannose residues, and β-1,4-linked mannosyl and glucosyl residues are likely to be randomly distributed in the backbones of heterogeneous mannans (McCleary et al., 1985). In addition, mannose residues in the main chain may be grafted by α-1,6-linked galactoses forming branched mannans. According to the main chain composition and side chain reaction, these mannans are classified into four main groups: pure mannans, glucomannans, galactomannans, and galactoglucomannans.

These mannan species mainly function as seed storage and/or structural components (Matheson 1990). In legumes, galactomannan as a seed storage component occupies about 30% of the dry weight of the seed (Buckerridge 2010). In the Type III primary cell wall of many ferns, structural mannans function as cellulose cross-linked hemicelluloses, a role that xyloglucans and glucuronoarabinoxylans have in other plants (Rodriguez-Gacio et al., 2012). In conifers, galactoglucomannan is the main structural mannan found in the secondary cell wall (Rowell et al., 2005). In addition to their function as storage and structural saccharides, mannans have an important role as signaling molecules in plant cell differentiation (Benova-Kakosova et al., 2006).

Pure mannan

It is usually found in the seed endosperm of non-legume plants such as ivory walnut (Phytelephas macrocarpa) and tomato (Solanum lycopersicum) (Toorop et al., 1998; Moreira, 2008). This type of mannan is also found in the seeds of pinho cuiabano (Schizolobium amazonicum) belonging to the Leguminosae family (de O Petkowicz et al., 2001). In pure mannan, the linear chain contains only β-1,4-linked D-mannosyl residues (Figure 1). This mannan is insoluble in water and therefore acts mainly as a structural hemicellulose in these plant tissues and plays an important role in resistance to mechanical damage (Toorop et al., 1998; Moreira, 2008). Pure mannan extracted from ivory nuts can form two different types of crystals: mannan I (also called mannan A) and mannan II (also called mannan B). The main differences between the two fractions are solubility, degree of polymerization (DP) (Aspinall et al., 1953; Meier, 1958), and morphology (Meier, 1958; Charrier and Rouland, 2001). Mannan I is highly crystalline with a low molecular weight. This mannan polymer is soluble in 6% (wt/wt) sodium hydroxide solution (Chanzy et al., 1984; Chanzy et al., 1987). In contrast, mannan II is less dense and crystalline and is characterized by a high molecular weight (Mackie and Sellen, 1969). It is insoluble even in high concentrations of sodium hydroxide solution (Chanzy et al., 1984; Millane and Hendrixson, 1994).

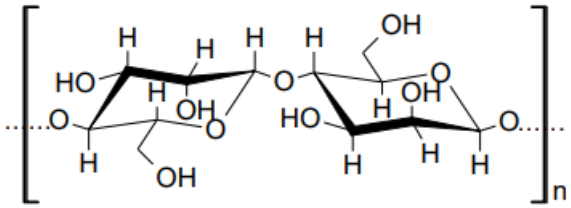


Figure 1. Pure mannan structure

Galactomannan

It is a water-soluble polysaccharide and the main hemicellulose in the seeds of legume plants but is also found in the seeds of several non-legume plants such as Cocos nucifera and Elaies guineensis (Nishinari et al., 2007). In these plant seeds, galactomannan not only provides energy for seed germination but also has the function of preventing seeds from drying out by retaining water, preventing denaturation of proteins important for germination (Dey, 1978; Moreira, 2008). In galactomannan, the backbone is formed by β-1,4-linked D-mannosyl substituted by α-1,6-linked galactosyl as a side group (Figure 2). This mannan is water soluble and its solubility is affected by the number of hydrophilic galactoses attached to the main chain. Three of the most commercially important galactomannans are carob galactomannan from the carob or locust bean tree (Ceratoniasiliqua), guar gum extracted from guar beans (Cyamopsistetragonoloba or Cyamopsispsoraloides) and tar gum isolated from the tara tree (Caesalpiniaspinosa). Carob galactomannan, known as carob gum (E-number: 410), is extracted mainly from the seed endosperm of the carob tree, which is native to the Mediterranean region. Normally, 100 g/kg seed (pod weight) contains roughly 320-400 g/kg of highly purified carob galactomannan. Carob gums are used in the food industry, e.g. in ice cream and ketchup. Typical carob galactomannan has a mannose/galactose substitution level of 4:1 (McCleary and Matheson, 1975) and is viscous and relatively stable in different pH solutions. Guar gum (E-number: E412), the main alternative to carob galactomannan, is isolated from the seeds of the guar tree, a tree grown in abundance in northwest India, Pakistan, and the USA. World production of guar is about 150,000 tons per year, with about two-thirds originating in Pakistan. Commercial guar is widely used for coating/hardening paper in cattle feed and gum production, as it is cheaper than carob. More recently, this gum has found use in hydraulic fracturing of oil (fracking). Guar gum has a mannose: galactose substitution level of 2:1 (McCleary and Matheson, 1975). Tara gum (E-number: E417) is obtained from the tara bush, which grows mainly in Ecuador, Peru, and East Africa. This mannan is widely used in the food industry to control ice crystal growth in frozen desserts and to improve the gel structure of meat-based products. The viscosity of tara gum is similar to that of locust bean and guar gum in cold solution but has higher viscosity in heated solution compared to these two types of galactomannan. Typically, the mannose: galactose ratio of tara gum is 3:1 (Dea, 1993).

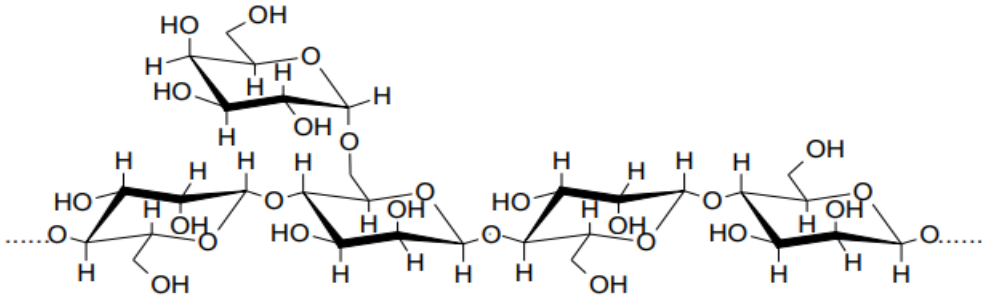


Figure 2. Galactomannan structure

Glucomannan

It is found as a minor structural hemicellulose in hardwoods and grasses (Scheller and Ulvskov, 2010). Glucomannan and xylan have been proposed to form a polysaccharide network closely related to cellulose. Glucomannan is a linear chain of D-mannosyl and D-glucosyl residues linked by β-1,4-bonds and frequently acetylated (Figure 3). These polysaccharides are soluble in water with a mannose: glucose ratio ranging from 4:1 to 1:1 (Meier and Reid, 1982) and a DP value higher than 200. In the konjac plant, about 60-80% of the tuber consists of glucomannan, which acts as the main storage carbohydrate. As Konjac glucomannan is water soluble and abundant, it is widely used in the food industry and pharmaceutical research. Konjac glucomannan (E number: 425) has a mannose: glucose ratio of approximately 1.5:1 (Dey and Dixon, 1985). Generally, 5-10% of the backbone residues of konjac glucomannan are linked to acetyl groups by ester bonds (Maekaji, 1978). These extra chemical modifications significantly affect konjac glucomannan properties such as solubility and gelation. For example, at high temperatures, the higher degree of acetylation weakens the network structure of konjac glucomannan gel (Penroj et al., 2005).

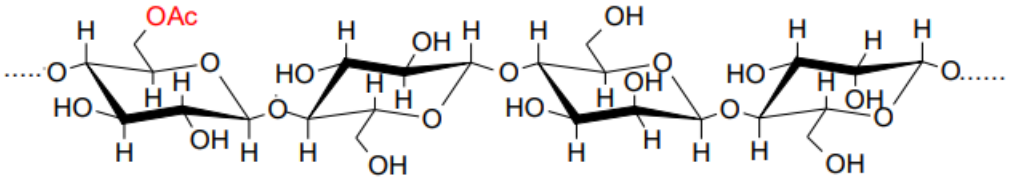


Figure 3. Acetylated glucomannan structure

Galactoglucomannan

It is the most complex mannan. Its backbone consists of β-1,4-linked D-mannosyl and D-glycosyl residues decorated with α-1,6-linked galactosyl side chains (Figure 4). Usually, backbone mannopyranose residues are acetylated at the hydroxyl groups of the C2 or C3 positions and the acetylation ratio is estimated to be 1:3-4. In general, acetylated galactoglucomannan extracted from the lignified secondary wall has a DP range between 100 and 150 and two groups can be distinguished. The first group is rich in galactose (5-8% w/w dry weight) and water-soluble, with a ratio of mannose:glucose: galactose residues of 3:1:1. The second group is poor in galactose (10-15% w/w dry weight) and aqueous alkali-soluble with a ratio of mannose:glucose: galactose residues of 3:1:0.1 (Timell, 1967). Galactoglucomannan is an abundant hemicellulose in many softwood species such as Norway spruce (Picea abies), which contains about 10-20% O-acetylated galactoglucomannan (Timell, 1967; Willför et al., 2005). Economically important Norway spruce is grown in the Scandinavian countries and is mainly used for timber or in the pulp and paper industry. Spruce galactoglucomannan, one of the most characterized and extensively studied galactoglucomannans, has a mannose:glucose: galactose ratio of 3.5-4.5:1:0.5-1 (Sundberg et al., 2000; Hannuksela and du Penhoat, 2004; Hannuksela et al., 2004). In addition to softwoods, it is found in other tree species, e.g. Populus monilifera, and also in club moss (Willför et al., 2008), blackberries (Cartier et al., 1988) and ferns (Bailey and Pain, 1971).

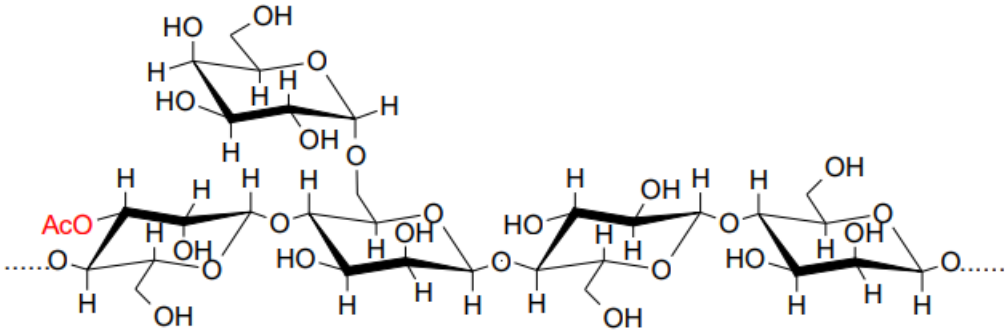


Figure 4. Acetylated galactoglucomannan structure

Mannan's biosynthesis and degradation

Mannan and other hemicelluloses are synthesized in the Golgi complex and then deposited in secretory vesicles and transferred to the plasma membrane for eventual delivery to the cell wall (Buchanan et al., 2000). Mannan synthesis can be divided into two main steps: backbone elongation and side-chain substitution. In the first step, elongation of the β-1,4-linked backbone of pure mannans, glucomannans, and galactoglucomannans is mediated by the cellulose synthase-like A (CSLA) family (Liepman et al., 2005; Goubet et al., 2009; Liepman and Cavalier, 2012; De Caroli et al., 2014). Recently, CSLD gene products have also been reported to be involved in pure mannan synthesis in Arabidopsis (Verhertbruggen et al., 2011; Yin et al., 2011). While glycosyl residues are believed to be iteratively attached to the non-reducing end of the elongating polysaccharide chain, an alternative route suggested that the reducing end of the elongating chain may also accept the addition of glycosyl residues (York and O'Neill, 2008). In the second step, galactosyltransferases add single α-1,6-galactopyranosyl residues to the backbone residues of β-1,4-mannans or β-1,4-glucomannans (Edwards et al., 2002).

Mannans are known to be involved in various biological processes involving cell wall degradation (Buckerridge, 2010). For complete digestion of mannans, the degrading enzyme system usually includes endo-β-1,4-mannanases (EC 3.2.1.78), endo-β-1,4-mannosidases (EC 3.2.1.130), exo-β-1 4-mannosidases (EC 3.2.1.25), β-glucosidases (EC 3.2.1.21), α-galactosidases (EC 3.2.1.22) and acetyl-mannan esterases. Endo-β-1,4-mannanases, exo-β-1,4-mannosidases, and β-glucosidases are mainly involved in the hydrolysis of the mannan backbone into oligosaccharides and monosaccharides. Other enzymes, such as acetyl-mannan esterases and α-galactosidases, endo-β-1,4-mannanases (del Carmen Rodríguez-Gacio et al., 2012), as exemplified in the degradation of O-acetyl-galactoglucomannan (Figure 5).

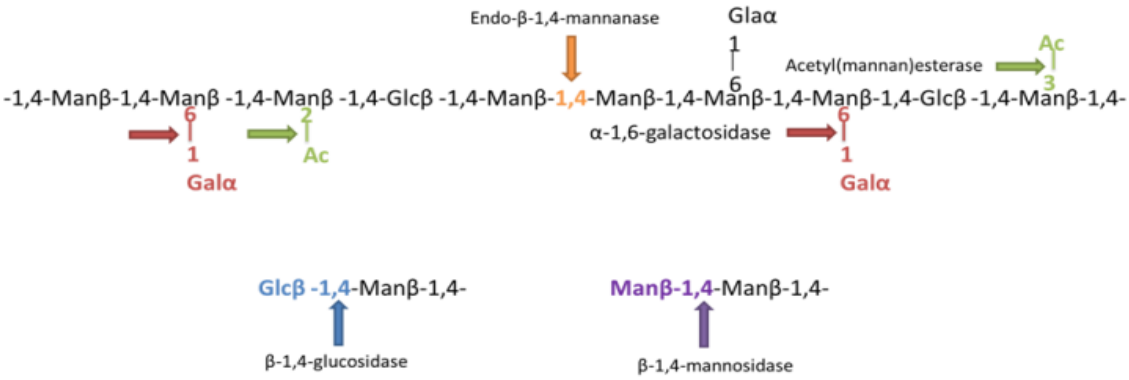


Figure 5. Overview of the enzyme portfolio required for the complete degradation of O-acetyl-galactoglucomannan.

β-Mannanase

In many biotechnological applications of mannan, the aim is to completely degrade polymers to monosaccharides. This degradation can be accomplished by chemical methods or by enzymatic hydrolysis. During the enzymatic hydrolysis process, endo-β mannanases (E.C. 3.1.2.78) play a crucial role in the digestion of mannan backbones. Mannanases from various organisms, including bacteria, fungi, plants, and animals (Larsson et al., 2006; Jagtap et al., 2012; Liu et al., 2012; Wang et al., 2014), have been classified into three GH families: GH5, GH26, and GH113 in the CAZy database (Cantarel et al., 2009). These families are categorized into clan A, and as a result, all mannases share one (β/α)8 barrel-folding structure and two Glu residues. Moreover, they all retain GHs, and therefore all could potentially function as transglycosylases. To date, GH mannanases with transglycosylation activity were found in GH5 and GH113, but not in GH26 (Couturier et al., 2013). Some mannanases show exo-acting activity in addition to endo-acting activity (Setati et al., 2001; Katrolia et al., 2013).

β-Mannanase Function

Mannan is composed of β-1,4-linked D-mannose (and/or glucose) and α-1,6-linked galactose as a backbone and side chain, respectively. Figure 6 shows the effect of B mannanase on various mannan species (Chauhan et al. 2017; Chauhan et al., 2012). Due to the complexity of the structure of mannan, complete hydrolysis of this biopolymer is achieved by the synergistic action of four enzymes: β-mannanase (EC3.2.1.78), β-mannosidase (EC3.2.1.25), β-glucosidase (EC 3.2.1.21) and α-galactosidase (EC3.2.1.22) (Yamabhai et al., 2016; Malgas et al., 2015). Among these enzymes, β-mannanase has received significant industrial interest as it catalyzes the cleavage of β-1,4 linkages in mannan into biologically active mannooligosaccharides. These mannooligosaccharides are then hydrolyzed by three other mannan deconstruction enzymes. Potential industrial applications of β-mannanase are listed in Table 1.

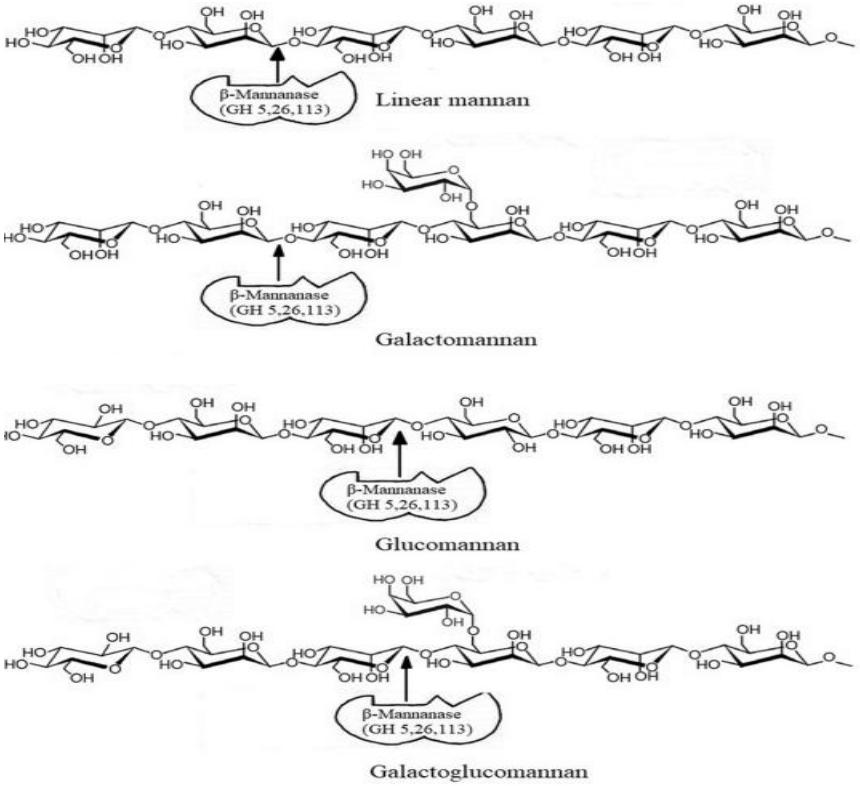


Figure 6. Effect of mannanase enzyme on various mannan species Yeoman et al. (2010).

Table 1. Industrial uses and applications of β-mannanase Mohapatra, B. R. (2021).

Endüstri	**Potansiyel Uygulama Alanları**
Biorafinery	Facilitating efficient enzymatic degradation of lignocellulosic waste into sustainable products
Detergent	Application as an additive for the effective removal of sticky gum stains from fabrics
Feed	Improving the palatability and digestibility of animal feed
Food processing	Reducing the viscosity of coffee extract during instant coffee production n oil extraction, softening and clarification of fruits and vegetables
Oil and gas	Increasing the recovery of oil and gas during the drilling process
Medicines	Use as a therapeutic agent for irritable bowel syndrome, acute diarrhea in children and as a prebiotic
Pulp and paper	To enable biological bleaching of paper and softwood pulp
Textile	Reducing the viscosity of printing paste used in textile processing
Waste water treatment	Control slime and biofilm formation by preventing bacterial adhesion to surfaces

Table 2. Some sources of mannanase

Organism	**Source**
Bacillus subtilis HM7	(Leerawatthanakun, et al., 2022)
Klebsiella pneumoniae SS11	(Singh et al., 2019)
Streptomyces species Alg-S25	(Mohapatra 2021)
Lactobacillus casei HDS-01	(Zhao et al., 2020)
Rhizopus microsporus	(Li et al., 2020)
Penicillium aculeatum APS1	(Bangoria et al., 2021)
Lichtheimia ramosa	(Xie et al., 2019)
Aspergillus sulphureus	(Chen et al., 2007)
Aspergillus terrus	(Huang et al., 2007)
Aspergillus kawachii IFO 4308	(Liu et al., 2020)

Aspergillus niger CBS 513.88	(Tang et al., 2019)
Trichoderma longibrachiatum RS1	(Ismail et al., 2019)
Bacillus sp. R2AL2A	(Kim et al., 2018)
Paenibacillus curdlanolyticus,	(Pason and Ratanakhanokchai, 2006)
Paenibacillus polymyxa,	(Han et al., 2006)

Utilization of β-Mannanase Enzyme in Industrial and Biotechnology Fields
Utilization of Mannanase in the Biorefinery Industry

The efficient use of renewable lignocellulosic biomass as second-generation biofuels has become a global endeavor for sustainable energy systems and environmental reasons (Lin et al., 2013). In addition, more research is also focusing on increasing the value of waste or residual materials through the biorefinery concept (FitzPatrick et al., 2010). Various biorefinery techniques are estimated to greatly reduce the amount of biowaste generated worldwide, as many of them have the potential to be converted into a wide range of value-added products.

Different lignocellulosic plants have a variable composition of macromolecules, but the main components average in the following order: glucan > lignin > xylan > mannan >arabinan > galactan. The mannan content is about 5% (Lavoie et al., 2011; Wolf et al., 2012), except in conifers or softwoods, which contain more mannan (~10%) than xylan. Lignocellulosic biomass is therefore the most suitable feedstock for biofuel production. After cellulose, mannans from softwood are important sugar sources for biofuel production.
The application of mannan-degrading enzymes in biotechnology has gained significant interest over the last decade based on the growing demand for efficient utilization of renewable bio-resources for sustainable development (Do et al., 2009).

Bioconversion of biomass to monomeric sugars and subsequent fermentation to products such as ethanol can be efficiently achieved through hydrolysis using multiple enzymes (Van Dyk and Pletschke, 2012). For softwood, mannan-degrading enzymes constitute an important group of enzymes that can be used both in the pretreatment step and for the production of second-generation biofuels for the complete release of all sugars and potentially for health production. Endo-β1,4-mannanases or β-mannanases are the main enzymes for the complete degradation of mannan (Rodriguez-Gacio et al., 2012).

In a 2015 study by Yoo, H. Y. et al. 2015, an extracellular endo-β-1,4-D-mannanase was produced by Streptomyces sp. It was purified 8.5-fold in 43.4% yield using CS147 (Mn147) and Sephadex G-50 column. The production of sugars such as mannose, mannobiose, and other oligosaccharides shows a clear pathway for the utilization of cellulosic biomass, and fermentable sugars can be converted into bioethanol or biopolymers by biorefinery. The study has shown that Mn147 is attractive in the search for potential bioindustrial applications.

Utilization of Mannanase in the Detergent Industry

The applications of microbial enzymes in the detergent industry are well known. The most commonly used enzymes are proteinases, lipases, amylases, and cellulases (Srivastava and Kapoor, 2014). Recently, alkaline β-mannanases, which show stability against detergent components, have been increasingly used as stain-removal enhancers in certain laundry

departments. β-mannanase hydrolyzes different mannan-based materials such as guar gum, glucomannans, galactomannans, and others (Liao et al., 2014). Available as thickeners and due to their gel texture, guar gums are found in an increasing number of consumer products, including barbecue sauce, ice cream, salad dressing, makeup, and hair styling (Mudgil et al., 2014). These gums act as glue, adhering to soil particles and making it difficult to remove dirt. β-mannanases effectively hydrolyze these gums and remove them from the fabric, thus preventing dirt from sticking to the fabric.

ManSS11, a β-mannanase enzyme isolated from a novel Klebsiella pneumoniae strain SS11, was used to perform washing performance experiments (Singh et al., 2019). Analysis of the hydrolyzed products at the end of the washing process shows that β-mannanase has 80.5 ± 1.07% better cleaning power (cleaning power) in removing the strain fixed with locust bean gum + powder compared to the case where detergent alone was used alone, which shows only 30.6 ± 0.86% detergent. Similarly, another study investigated the cleaning power of β-mannanase from Bacillus sp. CFR1601 was tested on a cotton cloth stained with chocolate ice cream and tomato sauce (Srivastava and Kapoor, 2014). The detergent combined with β-mannanase shows greater stain removal than the detergent alone. We also checked the stability and compatibility of the isolated β-mannanase with different commercially available laundry detergents. The enzyme retains 89.0-100% of its original activity for up to 1 hour at 37°C in the presence of different detergents in the following order: Wheel > Surf > Excel> Ariel > Tide > Rin. This suggests that enzyme performance is influenced by the components present in the detergent, as enzyme stability varies with the different detergents tested. David et al. (2018) investigate the optimization of the co-production of protease and β-mannanase from a Bacillus nealsonii strain PN-11, along with the potential of both of these enzymes as additives to detergents. The enzymes show good compatibility with detergents and detergent performance improves on different types of stains when β-mannanase or protease is used. However, dye removal is much more efficient when both β-mannanase and protease are used in combination.

There are opportunities for geographical and quantitative expansion of the use of β-mannanases in detergents. In developing countries, β-mannanases have not found widespread use, even though these countries are dusty and hot and therefore require frequent laundry. In the West, especially in the United States, β-mannanase has found its way into commercial household detergent preparations. Novozymes, a Danish company, markets Mannaway, a laundry detergent containing β-mannanase. This can be used effectively to remove mannan-based stains. Adding β-mannanase to detergents improves the stain-removal ability of the detergent and prevents other particles from sticking to the fabric during the washing process.

Purabrite is another commercial β-mannanase marketed by another United States company, Genencor. For decades, detergent formulators have faced the fundamental challenge of developing products with superior cleaning performance at competitive prices. Genencor claims that Purabrite meets these requirements. Purabrite is available in both liquid and granular form. The granular form, incorporating the patented Enzoguard® coating, is a proprietary technology of Genencor. These granules are safer to handle than poly powders and have enhanced properties for easy mixing and storage.

Use of Mannanase in Feed Industry

Poultry nutritionists are continuously striving to improve the production performance of bird species, which is essential for successful farming. Several strategies have been implemented to increase commercial poultry production over the last two decades, such as introducing environmentally controlled shaping, improving feed formulation (Saeed et al., 2019; Saeed et al., 2018 a, b; Yatao et al., 2018), the application of probiotics (Sun et al., 2016) and the use of herbal medicinal plants as an alternative source of antibiotics. Dietary

enzymes are biologically active proteins that facilitate the breakdown of complex nutrients into smaller molecules for further digestion and absorption (Thacker, 2013). There are a large number of enzymes derived by fermentation from microbes such as fungi and bacteria and used in poultry and their benefits in improving feed efficiency and growth. There are different classes of enzymes commonly used in poultry diets, including phytase, carbohydrases (β-mannanase, xylanase, α-galactosidase, cellulase, pectinase, and α-amylase), and proteases. The biological activities of various in-feed enzymes in promoting growth and improving feed efficiency in poultry have been well reported (Bedford and Schulze, 1998; Choct, 2007).

For successful commercial poultry production, it is imperative to identify factors that inhibit nutrient digestibility. Non-starch polysaccharides (NSPs) such as hemicellulose, cellulose, and pectin can reduce nutrient digestibility in poultry (Choct, 2007). Among NSPs, β-mannanes are a group of hemicelluloses found in many ingredients used in poultry feed such as soybeans and other legume seeds. It is found in the plant's cell walls in the form of galactomannans and glucomannans. β-mannan is found in many feedstuffs including palm kernel meal, soybean meal, copra meal sesame meal, and other legume feeds (Dierick, 1989). As protein sources, soybean meal, and whole soybeans are the most important feed ingredients in poultry diets, and most poultry feed contains β-mannan. However, β-mannan has been found to have detrimental effects on animal performance and health. The negative effects of β-mannans on poultry performance were attributed to the low digestibility of the nutrients and high intestinal viscosity, which negatively affects the immune response and microbial proliferation in the gut, as well as growth and carcass characteristics (Alagawany et al. al., 2015, 2017). In an early study, Patel & McGinnis (1985) found that egg weight, egg production, and feed intake were significantly reduced by β-mannan in laying hen diets. Previously published literature has shown that the enzyme β-mannanase can improve innate immunity and promote a non-productive energy depletion response of the innate immune system (Zhang & Tizzard, 1996; Duncan et al., 2002).

Hydrolysis of Coffee Extract

Instant coffee offers consumers a combination of convenience and high-added value. The main residue produced during instant coffee production is used coffee grind (SCG), which consists mainly of polysaccharides such as galactomannan and cellulose. These polysaccharides do not dissolve during the extraction process and therefore remain as insoluble solids (Figure 4). In this context, the application of β-mannanase seems to be a suitable strategy to solubilize/hydrolyze the remaining solids, thus increasing the yield of soluble solids of instant coffee. Jooste et al. (2013) applied different carbohydrase enzymes to increase the solubility of residual solids produced during coffee production. Among the enzymes tested for the hydrolysis of SCG, the highest increase in soluble solids yield was obtained with the use of β-mannanase (Man 1). Combining β-mannanase (Man1) with other enzymes shows an additive rather than synergistic effect, indicating that β-mannanase is mainly responsible for the highest soluble solids yield. Similarly, Favaro et al. (2020) also show that a large amount of carbohydrates in SCG can be hydrolyzed by β-mannanase. When a commercial cellulase cocktail is added to β-mannanase, the hydrolysis yield is further increased (56%), showing the promise of increasing soluble coffee processing. Baraldi et al. (2016) compared enzymatic and thermal processes during instant coffee production. The roasted coffee is first extracted with water at 125°C and the spent coffee is then processed by enzymatic hydrolysis at 50°C (with the aid of an enzyme cocktail containing β-mannanase) or thermal hydrolysis at 180°C. The yield of enzymatic hydrolysis (18%) is lower than the yield of thermal hydrolysis (28%). However, instant coffee produced through enzymatic hydrolysis has a lower amount of undesirable compounds such as furfural, acetaldehyde, and 5-HMF,

and less energy is consumed in the process. These findings suggest that the enzymatic procedure is a viable alternative to thermal hydrolysis for instant coffee production.

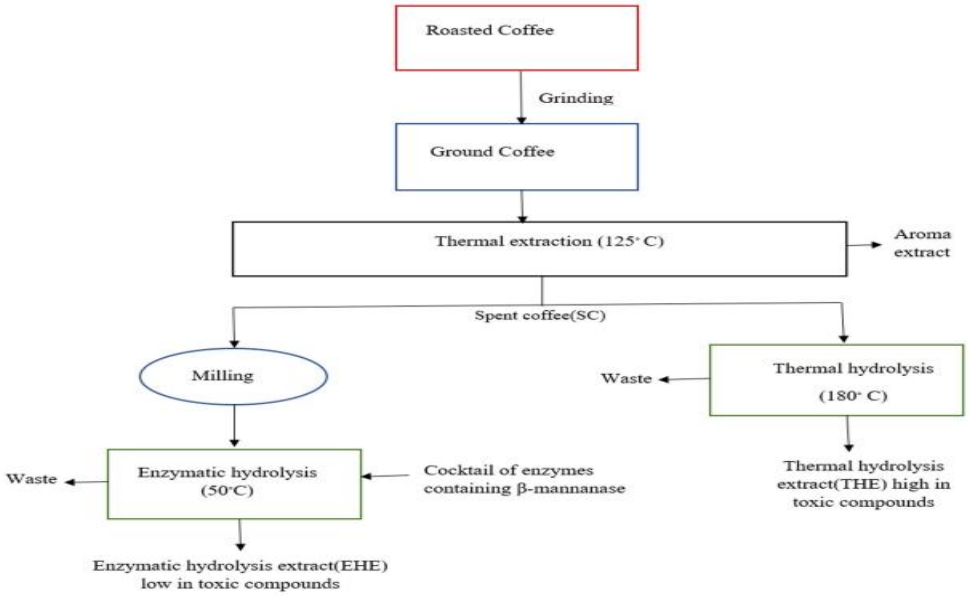


Figure 7. Comparison of soluble coffee production by enzymatic and thermal hydrolysis. Modified from Baraldi et al. (2016).

Use of Mannase in the Pharmaceutical Industry

D-Mannose derived from beech and birch hydrolysates is commercially available as an excipient. The production of fast-dissolving tablets using mannose (Parisi et al., 2002) takes advantage of the high solubility of mannose; it contributes to the structure-forming and rapid dissolution properties of the tablets. Ingestion of mannose is a popular remedy for urinary tract infections, but there is little current scientific literature supporting this treatment regimen. However, there are many mannose products on the market and this sector represents a significant demand for sugar. Currently, mannose is obtained from the chromatographic separation of sulfite-spent liquids (Alam et al., 2000). Mannan-rich substrates such as palm kernel and copra bagasse represent low-cost alternative sources of mannose. The mannose enrichment of animal feeds containing these flours using a crude, commercial A. niger enzyme preparation has been described (Fu et al., 2006). The method involves the addition of a combination of mannan-degrading enzymes and cellulases, presumably to carry out hydrolysis. However, aqueous extraction of the hydrolysate and chromatographic purification of mannose or manno-oligosaccharides represent a more cost-effective option for obtaining these compounds.

Depending on the chemical composition of the mannan-containing substrates, a range of mannan-degrading enzymes, cellulases and even proteases would be required to effectively hydrolyze these substrates. However, hydrolysis of palm kernel press cake with different enzyme combinations has provided little evidence of synergism between hydrolytic enzymes (Heikkila, 1986). The combination of cellulase and β-mannanase/p-mannosidase preparations did not increase the mannose yield relative to the β-mannanase/p-mannosidase preparation alone, implying that glucans or cellulose does not block the access of mannan-degrading enzymes to the substrate. Increasing β-mannosidase activity relative to β-mannanase increased mannose yields, especially when high solid loadings were used (Yokomizo, 2009). The addition of an α-galactosidase to the β-mannanase/β-mannosidase cocktail did not significantly increase the mannose yield. Since the addition of a protease preparation did not

increase mannose yield, proteins present in the substrate did not appear to restrict the enzymes' access to polysaccharides (Jorgensen et al., 2010).

Utilization of Mannanase in the Oil and Gas Industry

Another important application of guar gum and subsequently mannanase is the addition of guar gum to increase the viscosity of fracturing fluids used during stimulation of oil/gas wells. Fracturing fluids are pumped into wells and the high pressures cause the bedrock to fracture. Fluid-containing proppant, usually a suspension of sand, flows into the fractures. For the well to start producing, the fluid needs to be pumped out, the viscosity of which needs to be reduced to facilitate pumping. The remaining sand supports open the fractures that allow the oil or gas to flow. -Mannases and galactosidases act as enzyme crackers that hydrolyze galactomannans in the fracturing fluid. Thermostable enzymes are of particular interest in this application due to geothermal gradients in deep oil wells (Comfort et al., 2004). In addition, premature hydrolysis of galactomannanes at the earth's surface is prevented when hyperthermophilic enzymes are used because the environment only reaches optimum temperatures for enzyme activity deep in the well (Kelly et al., 2002). Due to the extreme temperatures in the wells (>80 ◦C), it is unlikely that many wild-type fungal mannan-degrading enzymes will find use in this application. Enzymes capable of operating at high temperatures have been isolated from Thermotoga maritima, Thermotoga neapolitana, and Rhodothermus marinus (Politz et al., 2000; Parker et al., 2001).

Utilization of Mannanase in the Pulp and Paper Industry

Bleaching is an important step to remove the color of pulp for papermaking. In ancient times, methods such as sunlight, soaking in streams, etc. were used to bleach pulp (Toren and Blanc 1997), followed by chemical-based processes. The chemical-based multi-stage bleaching commonly used in industry today involves repeated treatment of the pulp with an alkaline solution and calcium hypochlorite (Hintz 2001). Strict environmental concerns have made it necessary to make industrial processes environmentally friendly. Some alternative bleaching methods such as long-term cooking and hydrogen peroxide/ozone-based delignification are available, but their implementation requires process modifications and is expensive on a large scale (Singh et al., 2016). Several studies have investigated the replacement of chemical-based bleaching processes with enzymatic processes. The most important enzymes in this regard are hemicellulolytic and ligninolytic enzymes (Barneto et al., 2011). Hemicellulolytic enzymes help remove hemicelluloses deposited on the fiber surface, which facilitates the release of lignin with a smaller amount of chemicals (Dawood and Ma 2020). The two main enzymes of this class are xylanases and mannases (Kansoh and Nagieb 2004).

Although enzymes can be used for a variety of purposes in the papermaking process, such as pitch control, de-inking, and crumb removal, their maximum potential lies in the biobleaching of pulp. Several authors have reported that effective pulp biobleaching using microbial enzymes results in a significant reduction in chemical use and better quality paper production (Mahfouz et al., 2020; Saibu et al., 2020). Since crude enzymes can be used for biobleaching of pulp, their application in industries is economically feasible (no need for purification) (Sridevi et al., 2017); moreover, such enzymes are likely to have a longer shelf life than purified enzymes. However, studies are still needed to find stable enzymes or to improve the stability of existing enzymes, to increase their potential, and to make them suitable for commercial application.

Utilization of Mannanase in the Textile Industry

The textile industry uses two-thirds of the dyestuff production (Riu et al., 1998). Large volumes of water and chemicals are consumed during the wet processing of textile products. The chemical agents used in the textile industry are very diverse and range from inorganic compounds to polymers and organic products (Mishra et al., 1993; Juang et al., 1996). The variety of commercial dyes used in the textile industry is more than 100,000 and the annual production of these dyes is over 7 x 105 tons (Zollinger 2022). Due to their chemical structure, textile dyes are highly resistant to discoloration when exposed to light, water, and different chemical oxidizing agents (Poots et al., 1976; McKay 1979). In addition, decolorization of most of these dyes is very difficult to achieve due to their synthetic origin. Moreover, it is not possible to degrade or decolorize all of the different categories of textile dyes using physical or chemical methods. Enzymatic methods are preferred over physico-chemical methods for the treatment of textile dye-containing wastes, as sometimes the breakdown products of these dyes can be much more toxic (Spadaro et al., 1994).

β-mannanases can be used in combination with detergents to clean or prepare fibers in the textile and cellulosic processing industries. To prepare the material for garment manufacturing, cellulosic material is processed in several stages: burning, de-sizing, cleaning, bleaching, dyeing, and finishing (Mojsov, 2011). The application of β-mannanase can be useful in the biological cleaning and desizing of cellulosic fibers, thus preparing the material for good response in subsequent dyeing operations.

Bio-scouring is the process by which the fabric is cleaned of impurities such as pectin, hemicellulose, wax, and mineral salts through enzymatic action (Bristi et al., 2019). These impurities render the raw cotton hydrophobic and thus interfere with aqueous chemical processes such as dyeing and finishing. It is therefore important to remove these impurities so that the fabric can be dyed.

Conclusion

β-mannanases are used in a wide range of industries such as feed, detergents, biorefineries, and textiles. The production and utilization of β-mannanases is increasing due to the growing awareness of their benefits and the incorporation of enzyme engineering and gene manipulation techniques. There is now an urgent need to create β-mannanases at low costs that are more in line with the demands of the industrial sector to replace the use of harmful chemicals in the industrial sector with environmentally friendly biocatalysts. The government and higher levels need to encourage this change to produce cleaner industrial products and reduce the risk of environmental pollution.

REFERENCES

Adiguzel A., Nadaroglu H., Adiguzel G. (2015). Purification and characterization of β-mannanase from Bacillus pumilus (M27) and its applications in some fruit juices. J. Food Sci. Technol. 52 5292–5298.

Adiguzel G., Sonmez Z., Adiguzel A., Nadaroglu H. (2016). Purification and characterization of a thermostable endo-beta-1, 4 mannanase from Weissella viridescens LB37 and its application in fruit juice clarification. Eur. Food Res. Technol. 242 769–776.

Alam NH, Meier R, Schneider H, Sarker SA, Bardhan PK, Mahalanabis D, et al. Partially hydrolyzed guar gum-supplemented oral rehydration solution in the treatment of acute diarrhea in children. J Pediatr Gastr Nutr 2000;31:503–7.

Anwar Z, Gulfraz M, Irshad M. Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: a brief review. J Rad Res Appl Sci. 2014;7(2):163–173

Aspinall G, Hirst E, Percival E, Williamson I (1953) The mannans of ivory nut (Phytelephas macrocarpa). Part I. The methylation of mannan A and mannan B. J. Chem. Soc. 635: 3184-3188.

Bailey R, Pain V (1971) Polysaccharide mannose in New Zealand ferns. Phytochemistry 10: 1065-1073.

Bangoria, P., Divecha, J., & Shah, A. R. (2021). Production of mannooligosaccharides producing β-Mannanase by newly isolated Penicillium aculeatum APS1 using oil seed residues under solid state fermentation. *Biocatalysis and Agricultural Biotechnology*, *34*, 102023.

Baraldi, I., Giordano, R., and Zangirolami, T. (2016). Enzymatic hydrolysis as an environmentally friendly process compared to thermal hydrolysis for instant coffee production. Braz. J. Chem. Eng. 33, 763–771. doi: 10.1590/0104-6632. 20160334s20140028

Barneto, A. G., Valls, C., Ariza, J., & Roncero, M. B. (2011). Thermogravimetry study of xylanase-and laccase/mediator-treated eucalyptus pulp fibres. *Bioresource technology*, *102*(19), 9033-9039.

Bedford M, Schulze H. Exogenous enzymes for pigs and poultry. Nutrition Research Revivews 1998;11:91-114.

Benova-Kakosova A, Digonnet C, Goubet F, Ranocha P, Jauneau A, Pesquet E, Barbier O, Zhang ZN, Capek P, Dupree P, Liskova D, Goffner D (2006) Galactoglucomannans increase cell population density and alter the protoxylem/metaxylem tracheary element ratio in xylogenic cultures of zinnia. Plant Physiology 142: 696-709

Bristi, U., Pias, A., and Lavlu, F. (2019). A Sustainable process by bio-scouring for cotton knitted fabric suitable for next generation. J. Text. Eng. Fash. Technol. 5, 41–48.

Buchanan BB, Gruissem W, Jones RL (2000) Biochemistry & molecular biology of plants. American Society of Plant Physiologists Waldorf^ eMD MD

Buckeridge MS (2010) Seed cell wall storage polysaccharides: models to understand cell wall biosynthesis and degradation. Plant Physiol 154: 1017-1023

Buckeridge MS (2010) Seed cell wall storage polysaccharides: models to understand cell wall biosynthesis and degradation. Plant Physiol 154: 1017-1023

Cantarel BL, Coutinho PM, Rancurel C, Bernard T, Lombard V, Henrissat B (2009) The Carbohydrate-Active EnZymes database (CAZy): an expert resource for glycogenomics. Nucleic acids research 37: D233-D238

Cartier N, Chambat G, Joseleau JP (1988) Cell-Wall and Extracellular Galactoglucomannans from Suspension-Cultured Rubus-Fruticosus Cells. Phytochemistry 27: 1361-1364

Chanzy H, Perez S, Miller DP, Paradossi G, Winter WT (1987) An Electron-Diffraction Study of Mannan .1. Crystal and Molecular-Structure. Macromolecules 20: 2407-2413

Chanzy HD, Grosrenaud A, Vuong R, Mackie W (1984) The Crystalline Polymorphism of Mannan in Plant-Cell Walls and after Recrystallization. Planta 161: 320-329

Charrier M, Rouland C (2001) Mannan-degrading enzymes purified from the crop of the brown garden snail Helix aspersa Muller (Gastropoda Pulmonata). J Exp Zool 290: 125-135

Chauhan PS, Gupta N. Insight into microbial mannosidases: a review. Crit Rev Biotechnol. 2017;37(2): 190–201.

Chauhan PS, Gupta N. Insight into microbial mannosidases: a review. Crit Rev Biotechnol. 2017;37(2):190–201. [Taylor & Francis Online]

Chauhan PS, Puri N, Sharma P, et al. Mannanases: microbial sources, production, properties and potential biotechnological applications. Appl Microbiol Biotechnol. 2012;93(5):1817–1830.

Chauhan, P. S., Sharma, P., Puri, N., & Gupta, N. (2014). Purification and characterization of an alkali-thermostable β-mannanase from Bacillus nealsonii PN-11 and its application in mannooligosaccharides preparation having prebiotic potential. *European Food Research and Technology*, *238*, 927-936.

Choct M. Enzymes for the feed industry: past, present and future. World's Poultry Science Journal 2007;62:5-16.

Comfort DA, Swapnil R, Chhabra SR, Conners SB, Chou C-J, Epting KL, et al. Strategic biocatalysis with hyperthermophilic enzymes. Green Chem 2004;6:459–65.

Couturier M, Roussel A, Rosengren A, Leone P, Stålbrand H, Berrin J-G (2013) Structural and biochemical analyses of glycoside hydrolase families 5 and 26 β-(1, 4)-mannanases from Podospora anserina reveal differences upon manno-oligosaccharide catalysis. Journal of Biological Chemistry 288: 14624-14635

David A., Chauhan P. S., Kumar A., Angural S., Kumar D., Puri N., et al. (2018). Coproduction of protease and mannanase from Bacillus nealsonii PN-11 in solid state fermentation and their combined application as detergent additives. Int. J. Biol. Macromol. 108 1176–1184. 10.1016/j.ijbiomac.2017.09.037

Dawood A, Ma K (2020) Applications of microbial β-mannanases. Front Bioeng Biotechnol 8:1336. https://doi.org/10.3389/fbioe. 2020.598630

De Caroli M, Lenucci MS, Di Sansebastiano G-P, Tunno M, Montefusco A, Dalessandro G, Piro G (2014) Cellular Localization and Biochemical Characterization of a Chimeric Fluorescent Protein Fusion of Arabidopsis Cellulose Synthase-Like A2 Inserted into Golgi Membrane. The Scientific World Journal 2014

de O Petkowicz C, Reicher F, Chanzy H, Taravel F, Vuong R (2001) Linear mannan in the endosperm of Schizolobium amazonicum. Carbohydrate Polymers 44: 107-112

Dea IC (1993) Conformational origins of polysaccharide solution and gel properties. Industrial Gums: 21-52

del Carmen Rodríguez-Gacio M, Iglesias-Fernández R, Carbonero P, Matilla ÁJ (2012) Softening-up mannan-rich cell walls. Journal of experimental botany 63: 3976-3988

Dey PM (1978) Biochemistry of plant galactomannans. Advances in Carbohydrate Chemistry and Biochemistry

Dey PM, Dixon R (1985) Biochemistry of storage carbohydrates in green plants. Academic Press: London

Dey T. B., Banerjee R. (2014). Application of decolourized and partially purified polygalacturonase and α-amylase in apple juice clarification. Braz. J. Microbiol. 45 97–104. 10.1590/s1517-83822014000100014

Do BC, Dang TT, Berrin JG, et al. (2009). Cloning, expression in Pichia pastoris, and characterization of a thermostable GH5 mannan endo1,4-b-mannosidase from Aspergillus niger BK01. Microb Cell Fact, 8, 59 (1–12)

Edwards ME, Dickson CA, Chengappa S, Sidebottom C, Gidley MJ, Reid J (2002) Molecular characterisation of a membrane-bound galactosyltransferase of plant cell wall matrix polysaccharide biosynthesis. The Plant Journal 19: 691-697

Erkaya E, Çaylıkoca AB, Kalınyaprak F. Enzimatik Kataliz, Kimya Mühendisliği Uygulaması, Konya: Selçuk Üniversitesi, 2006: 78.

Favaro, C. P., Baraldi, I. J., Casciatori, F. P., and Farinas, C. S. (2020). βMannanase production using coffee industry waste for application in soluble coffee processing. Biomolecules 10:227. doi: 10.3390/biom10020227

FitzPatrick M, Champagne P, Cunningham MF, Whitney RA. (2010). A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. Bioresour Technol, 101, 8915–22

Fu Y, Jeong SH, Kim J, Callihan JA, Park K, Pai CM et al. Mannose-based fast dissolving tablets. United States of America patent US20060134195A1 2006.

Goubet F, Barton CJ, Mortimer JC, Yu X, Zhang Z, Miles GP, Richens J, Liepman AH, Seffen K, Dupree P (2009) Cell wall glucomannan in Arabidopsis is synthesised by CSLA glycosyltransferases, and influences the progression of embryogenesis. The Plant Journal 60: 527-538

Gray HB, Malmstrom BG, Williams RJ. Copper coordination in blue proteins. J Biol Inorg Chem, 2000; 5: 551-59

Handford MG, Baldwin TC, Goubet F, Prime TA, Miles J, Yu X, Dupree P (2003) Localisation and characterisation of cell wall mannan polysaccharides in Arabidopsis thaliana. Planta 218: 27-36

Hannuksela T, du Penhoat CH (2004) NMR structural determination of dissolved O-acetylated galactoglucomannan isolated from spruce thermomechanical pulp. Carbohydrate Research 339: 301-312 ,

Hannuksela T, Holmbom B, Mortha G, Lachenal D (2004) Effect of sorbed galactoglucomannans and galactomannans on pulp and paper handsheet properties, especially strength properties. Nordic Pulp & Paper Research Journal 19: 237-244

Heikkila H. Production of pure sugars and lignosulfonates from sulfite spent liquor. United States of America patent US 4631129 1986

Hintz HL (2001) Paper: pulping and bleaching. Enc Mater Sci Technol. 2nd edn., pp 6707–6711

Ismail S. A., Hassan A. A., Emran M. A. (2019). Economic production of thermo-active endo β-mannanase for the removal of food stain and production of antioxidant manno-oligosaccharides. Biocatal. Agric. Biotechnol. 22:101387

Jagtap SS, Dhiman SS, Jeya M, Kang YC, Choi J-H, Lee J-K (2012) Saccharification of poplar biomass by using lignocellulases from Pholiota adiposa. Bioresource Technology 120: 264-272

Jooste, T., García-Aparicio, M., Brienzo, M., Van Zyl, W., and Görgens, J. (2013). Enzymatic hydrolysis of spent coffee ground. Appl. Biochem. Biotechnol. 169, 2248–2262. doi: 10.1007/s12010-013-0134-1

Jorgensen H, Sanadi AR, Felby C, Lange NEK, Fischer M, Ernst S. Production of ethanol and feed by high dry matter hydrolysis and fermentation of palm kernel press cake. Appl Biochem Biotechnol 2010;161:318–32.

Juang RS, Tseng RL, Wu FC, Lin SJ. Use of chitin and chitosan in lobster shell wastes for colour removal from aqueous solutions. J Environ Sci Health Part A Environ Sci Eng, 1996; 31: 325–38.

Kansoh AL, Nagieb ZA (2004) Xylanase and mannanase enzymes from Streptomyces galbus NR and their use in biobleaching of softwood kraft pulp. Antonie Leeuwenhoek 85(2):103–114. https:// doi.org/10.1023/B:ANTO.0000020281.73208.62

Katrolia P, Yan Q, Zhang P, Zhou P, Yang S, Jiang Z (2013) Gene cloning and enzymatic characterization of an alkali-tolerant endo-1, 4-β-mannanase from Rhizomucor miehei. Journal of agricultural and food chemistry 61: 394-401

Kelly RM, Khan SA, Leduc P, Tayal A, Prud'homme RK. Compositions for fracturing subterranean formations. United States of America patent US6428995 2002.

Kim, S., Lee, M.-H., Lee, E.-S., Nam, Y.-D., and Seo, D.-H. (2018). Characterization of mannanase from Bacillus sp., a novel Codium fragile cell wall-degrading bacterium. Food sci. Biotechnol. 27, 115–122. doi: 10.1007/s10068-017-0210-3

Koç, C. Y. (2021). Rekombinant Aspergillus sojae AsT3 kullanılarak katı faz fermantasyonu ile Mannanaz üretimi.
Larsson AM, Anderson L, Xu B, Muñoz IG, Usón I, Janson J-C, Stålbrand H, Ståhlberg J (2006) Three-dimensional Crystal Structure and Enzymic Characterization of β-Mannanase Man5A from Blue Mussel Mytilus edulis. Journal of Molecular Biology 357: 1500-1510
Lavoie J-M, Beauchet R, Berberi Vr, Chornet M. (2011). Biorefining lignocellulosic biomass via the feedstock impregnation rapid and sequential steam treatment. In: Bernardes DMADS, ed. Biofuel's 40 M.
Leerawatthanakun, S., Charoenwongpaiboon, T., Klaewkla, M., Chunsrivirot, S., Sirirak, J., Sriwitool, T. E., ... & Pichyangkura, R. (2022). High surfactant-tolerant β-mannanase isolated from Dynastes hercules larvae excrement, and identification of its hotspot using site-directed mutagenesis and molecular dynamics simulations. Enzyme and Microbial Technology, 154, 109956.
Li Y.-x., Liu H.-j., Shi Y.-q., Yan Q.-j., You X., Jiang Z.-q. (2020). Preparation, characterization, and prebiotic activity of manno-oligosaccharides produced from cassia gum by a glycoside hydrolase family 134 β-mannanase. Food Chem. 309:125709.
Liao H., Li S., Zheng H., Wei Z., Liu D., Raza W., et al. (2014). A new acidophilic thermostable endo-1, 4-β-mannanase from Penicillium oxalicum GZ-2: cloning, characterization and functional expression in Pichia pastoris. BMC Biotechnol. 14:90.
Liepman AH, Cavalier DM (2012) The CELLULOSE SYNTHASE-LIKE A and CELLULOSE SYNTHASE-LIKE C families: recent advances and future perspectives. Frontiers in plant science 3
Liepman, A. H., Wilkerson, C. G., & Keegstra, K. (2005). Expression of cellulose synthase-like (Csl) genes in insect cells reveals that CslA family members encode mannan synthases. *Proceedings of the National Academy of Sciences*, *102*(6), 2221-2226.
Lin CSK, Pfaltzgraff LA, Herrero-Davila L, et al. (2013). Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective. Energy Environ Sci, 6, 426–64.
Liu Q, Yang P, Luo H, Shi P, Huang H, Meng K, Yao B (2012) A Novel endo-1, 4-β-Mannanase from Bispora antennata with Good Adaptation and Stability over a Broad pH Range. Applied biochemistry and biotechnology 166: 1442-1453
Liu Z., Ning C., Yuan M., Yang S., Wei X., Xiao M., et al. (2020). High-level expression of a thermophilic and acidophilic β-mannanase from Aspergillus kawachii IFO 4308 with significant potential in mannooligosaccharide preparation. Bioresour. Technol. 295:122257.
Mackie W, Sellen D (1969) The degree of polymerization and polydispersity of mannan from the cell wall of the green seaweed codium fragile. Polymer 10: 621-632
Maekaji K (1978) Relationship between Degree of Deacetylation and Gelation of Konjac Mannan - Kinetic Study on Gelation of Konjac Mannan .3. Journal of the Agricultural Chemical Society of Japan 52: 513-517
Mahfouz S, Mansour G, Murphy DJ, Hanano A (2020) Dioxin impacts on lipid metabolism of soil microbes: towards efective detection and bioassessment strategies. Bioresour Bioprocess 7(1):1–17
Malgas S, van Dyk JS, Pletschke BI. A review of the enzymatic hydrolysis of mannans and synergistic interactions between b-mannanase, b-mannosidase and a-galactosidase. World J Microbiol Biotechnol. 2015;31(8):1167–1175.
Malgas S, van Dyk JS, Pletschke BI. A review of the enzymatic hydrolysis of mannans and synergistic interactions between β-mannanase, β-mannosidase and α-galactosidase. World J Microbiol Biotechnol. 2015;31(8):1167–1175.

Matheson NK (1990) Mannose-based polysaccharides. Methods in plant biochemistry 2: 371-413
McCleary B, Matheson N (1975) Galactomannan structure and β-mannanase and β-mannosidase activity in germinating legume seeds. Phytochemistry 14: 1187-1194
McCleary BV, Clark AH, Dea I, Rees DA (1985) The fine structures of carob and guar galactomannans. Carbohydrate Research 139: 237-260
McKay G. Waste colour removal from textile effluents. Am Dyest Report, 1979; 68: 29-36.
Meier H (1958) On the structure of cell walls and cell wall mannans from ivory nuts and from dates. Biochimica et biophysica acta 28: 229-240
Meier H, Reid J (1982) Reserve polysaccharides other than starch in higher plants. In Plant Carbohydrates I. Springer, pp 418-471
Meier H, Reid J (1982) Reserve polysaccharides other than starch in higher plants. In Plant Carbohydrates I. Springer, pp 418-471
Menon V, Rao M. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. Prog Energ Combust. 2012;38(4):522–550.
Millane RP, Hendrixson TL (1994) Crystal-Structures of Mannan and Glucomannans. Carbohydrate Polymers 25: 245-251
Mishra G, Tripathy M. A critical review of the treatments for decolourization of textile effluent. Colourage, 1993; 40: 35–8.
Mohapatra, B. R. (2021). Characterization of β-mannanase extracted from a novel Streptomyces species Alg-S25 immobilized on chitosan nanoparticles. *Biotechnology & Biotechnological Equipment*, *35*(1), 150-161.
Mojsov, K. (2011). "Application of enzymes in the textile industry: a review," in Proceedings of the II International Congress "Engineering, Ecology and Materials in the Processing Industry", (Jahorina), 230–239.
Moreira L (2008) An overview of mannan structure and mannan-degrading enzyme systems. Applied microbiology and biotechnology 79: 165-178
Moreira LR, Filho EX. An overview of mannan structure and mannan-degrading enzyme systems. Appl Microbiol Biotechnol. 2008;79(2):165–178.
Mudgil D., Barak S., Khatkar B. S. (2014). Guar gum: processing, properties and food applications—a review. J. Food Sci. Technol. 51 409–418.
Nagar S., Mittal A., Gupta V. K. (2012). Enzymatic clarification of fruit juices (apple, pineapple, and tomato) using purified Bacillus pumilus SV-85S xylanase. Biotechnol. Bioprocess Eng. 17 1165–1175.
Nishinari K, Takemasa M, Zhang H, Takahashi R (2007) Storage plant polysaccharides: xyloglucans, galactomannans, glucomannans. Comprehensive glycoscience: from chemistry to systems biology, 1st edn. Elsevier, Oxford
Paone E, Tabanelli T, Mauriello F. The rise of lignin biorefinery. Curr Opin Green Sustain Chem. 2020;24: 1–6.
Parisi GC, Zilli M, Miani MP, Carrara M, Bottona E, Verdianelli G, et al. Highfiber diet supplementation in patients with Irritable Bowel Syndrome (IBS): A multicenter, randomized, open trial comparison between wheat bran diet and partially hydrolyzed guar gum (PHGG). Digest Dis Sci 2002;47:1697–704
Parker KN, Chhabra SR, Lam D, Callen W, Duffaud GD, Snead MA, et al. Galactomannanases Man2 and Man5 from Thermotoga species: growth physiology on galactomannans, gene sequence analysis, and biochemical properties of recombinant enzymes. Biotechnol Bioeng 2001;75(3):322–33.
Penroj P, Mitchell JR, Hill SE, Ganjanagunchorn W (2005) Effect of konjac glucomannan deacetylation on the properties of gels formed from mixtures of kappa carrageenan and konjac glucomannan. Carbohydrate Polymers 59: 367-376

Politz O, Krah M, Thomsen KK, Borriss R. A highly thermostable endo- (1,4)--mannanase from the marine bacterium Rhodothermus marinus. Appl Microbiol Biotechnol 2000;53(6):715–21.
Poots VJP, McKay JJ. The removal of acid dye from effluent using natural adsorbents- Peat. Water Res, 1976; 10: 1061–66.
Ragauskas AJ, Williams CK, Davison BH, et al. The path forward for biofuels and biomaterials. Science. 2006;311(5760):484–489.
Riu J, Schönsee I, Barcelo D. Determination of sulfonated azo dyes in groundwater and industrial effluents by automated solid-phase extraction followed by capillary electrophoresis/mass spectrometry. J. Mass Spectrom, 1998; 33: 653–63.
Rodrı´guez-Gacio Mdel C, Iglesias-Fernandez R, Carbonero P, Matilla AJ. (2012). Softening-up mannan-rich cell walls. J Exp Bot, 63, 3976–88.
Rodrıguez-Gacio Mdel C, Iglesias-Fernandez R, Carbonero P, et al. Softening-up mannan-rich cell walls. J Exp Bot. 2012;63(11):3976–3988
Rodrigues ISV, Barreto JT, Moutinho BL, et al. Production of xylanases by Bacillus sp. TC-DT13 in solid state fermentation using bran wheat. Prep Biochem Biotechnol. 2020;50(1):91–97
Rodriguez-Gacio Mdel C, Iglesias-Fernandez R, Carbonero P, Matilla AJ (2012) Softening-up mannan-rich cell walls. J Exp Bot 63: 3976-3988
Rowell RM, Pettersen R, Han JS, Rowell JS, Tshabalala MA (2005) Cell wall chemistry. Handbook of wood chemistry and wood composites: 35-74
Saeed M, Yatao X, Hassan FU, Arain MA, Abd El-Hack ME, Noreldin AE, et al. Influence of graded levels of l-theanine dietary supplementation on growth performance, carcass traits, meat quality, organs histomorphometry, blood chemistry and immune response of broiler chickens. International Journal of Molecular Sciences 2018a;19:462.
Saeed M, Yatao X, Tiantian Z, Qian R, Chao S. 16S ribosomal RNA sequencing reveals a modulation of intestinal microbiome and immune response by dietary L-theanine supplementation in broiler chickens. Poultry Science 2019;98:842–854.
Saibu S, Adebusoye SA, Oyetibo GO (2020) Aerobic bacterial transformation and biodegradation of dioxins: a review. Bioresour Bioprocess 7(1):1–21. https://doi.org/10.1186/s40643-020-0294-0
Saini JK, Saini R, Tewari L. Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments. 3 Biotech. 2015;5(4):337–353.
Saittagaroon S, Kawakishi S, Namiki M. Characterisation of polysaccharides of copra meal. J Sci Food Agric. 1983;34(8):855–860.
Sanchez C. Lignocellulosic residues: biodegradation and bioconversion by fungi. Biotechnol Adv. 2009; 27(2):185–194.
Sanderson K. Lignocellulose: a chewy problem. Nature. 2011;474(7352):S12–S14.
Scheller HV, Ulvskov P (2010) Hemicelluloses. Plant Biology 61: 263
Scheller HV, Ulvskov P. Hemicelluloses. Annu Rev Plant Biol. 2010;61:263–289.
Setati M, Ademark P, van Zyl W, Hahn-Hägerdal B, Stålbrand H (2001) Expression of the Aspergillus aculeatus endo-beta-1, 4-mannanase encoding gene (man1) in Saccharomyces cerevisiae and characterization of the recombinant enzyme. Protein expression and purification 21: 105-114
Sharma H. P., Patel H., Sharma S. (2014). Enzymatic extraction and clarification of juice from various fruits–a review. Trends Post Harvest Technol. 2:56.
Singh G, Capalash N, Kaur K, Puri S, Sharma P (2016) Enzymes: applications in pulp and paper industry. Agro-industrial wastes as feedstock for enzyme production, 1st edn. Academic Press, Cambridge, pp 157–172

Singh G., Khatri M., Kaur A., Arya S. K. (2019). Thermo and alkali stable β-mannanase: characterization and application for removal of food (mannans based) stain. Int. J. Biol. Macromol. 134 536–546. [Google Scholar]
Singh, S., Singh, G., Khatri, M., Kaur, A., & Arya, S. K. (2019). Thermo and alkali stable β-mannanase: characterization and application for removal of food (mannans based) stain. *International journal of biological macromolecules*, *134*, 536-546.
Singh, S., Singh, G., Khatri, M., Kaur, A., & Arya, S. K. (2019). Thermo and alkali stable β-mannanase: characterization and application for removal of food (mannans based) stain. *International journal of biological macromolecules*, *134*, 536-546.
Solomon EI, Sundaram UM, Machonkin TE. Multicopper oxidases and oxygenases. Chem Rev, 1996; 96: 2563–605.
Soni, H., Rawat, H. K., Ahirwar, S., & Kango, N. (2017). Screening, statistical optimized production, and application of β-mannanase from some newly isolated fungi. *Engineering in Life Sciences*, *17*(4), 392-401.
Spadaro JT, Lorne I, Renganathan V. Hydroxyl radical mediated degradation of azo dyes: evidence for benzene generation. Environ Sci Technol, 1994; 28: 1389–93.
Sridevi A, Ramanjaneyulu G, Suvarnalatha Devi P (2017) Biobleaching of paper pulp with xylanase produced by Trichoderma asperellum. 3 Biotech 7(4):1–9 https://doi.org/10.1007%2Fs13205-017-0898-z
Srivastava P. K., Kapoor M. (2014). Cost-effective endo-mannanase from Bacillus sp. CFR1601 and its application in generation of oligosaccharides from guar gum and as detergent additive. Preparat. Biochem. Biotechnol. 44 392–417.
Stiger-Pouvreau V, Bourgougnon N, Deslandes E. Carbohydrates from seaweeds. In: Fleurence J, Levine I, editors. Health and disease prevention. San Diego: Academic Press; 2016. p. 223–274.
Sun Y, Rajput IR, Arain MA, Li Y, Baloch DM. Oral administration of Saccharomyces boulardii alters duodenal morphology, enzymatic activity and cytokine production response in broiler chickens. Animal Science Journal 2016;88:1204–1211
Sundberg A, Holmbom B, Willfor S, Pranovich A (2000) Weakening of paper strength by wood resin. Nordic Pulp & Paper Research Journal 15: 46-53, Hannuksela T, du Penhoat CH (2004)
Sundberg A, Holmbom B, Willfor S, Pranovich A (2000) Weakening of paper strength by wood resin. Nordic Pulp & Paper Research Journal 15: 46-53
Tang S.-z., Lin F.-l., Zheng J., Zhou H.-b. (2019). Effect of gene dosage and incubation temperature on production of β-mannanase by recombinant Pichia pastoris. J. Cent. South Univ. 26 184–195.
Thacker PA. Alternatives to antibiotics as growth promoters for use in swine production: a review. Journal of Animal Science and Biotechnology 2013;4:35.
Timell TE (1967) Recent progress in the chemistry of wood hemicelluloses. Wood Science and Technology 1: 45-70
Toorop PE, van Aelst AC, Hilhorst HW (1998) Endosperm cap weakening and endo-β-mannanase activity during priming of tomato (Lycopersicon esculentum cv. Moneymaker) seeds are initiated upon crossing a threshold water potential. Seed Science Research 8: 483-492
Torén K, Blanc PD (1997) The history of pulp and paper bleaching: respiratory-health efects. The Lancet 349(9061):1316–1318 Valls C, Vidal T, Roncero MB (2010) Boosting the efect of a laccase– mediator system by using a xylanase stage in pulp bleaching. J hazard mater 177(1-3):586–592

Van Dyk JS, Pletschke BI. (2012). A review of lignocellulose bioconversion using enzymatic hydrolysis and synergistic cooperation between enzymes – factors affecting enzymes, conversion and synergy. Biotechnol Adv, 30, 1458–80.

Van Dyk JS, Pletschke BI. A review of lignocellulose bioconversion using enzymatic hydrolysis and synergistic cooperation between enzymes-factors affecting enzymes, conversion and synergy. Biotechnol Adv. 2012;30(6):1458–1480.

Verhertbruggen Y, Yin L, Oikawa A, Scheller HV (2011) Mannan synthase activity in the CSLD family. Plant signaling & behavior 6: 1620

Wang Y, Vilaplana F, Brumer H, Aspeborg H (2014) Enzymatic characterization of a glycoside hydrolase family 5 subfamily 7 (GH5_7) mannanase from Arabidopsis thaliana. Planta 239: 653-665

Whitney SEC, Brigham JE, Darke AH, Reid JSG, Gidley MJ (1998) Structural aspects of the interaction of mannan-based polysaccharides with bacterial cellulose. Carbohydrate Research 307: 299-309

Willför S, Sundberg A, Hemming J, Holmbom B (2005) Polysaccharides in some industrially important softwood species. Wood Science and Technology 39: 245-257

Willför S, Sundberg K, Tenkanen M, Holmbom B (2008) Spruce-derived mannans–A potential raw material for hydrocolloids and novel advanced natural materials. Carbohydrate Polymers 72: 197-210

Wiseman A. Handbook of Enzymes Biotechnology. Second Ed. Chapter 3. The Application of Enzymes in Industry, 1987: 274-373.

Wolf S, Hematy K, Hofte H. (2012). Growth control and cell wall signaling in plants. Annu Rev Plant Biol, 63, 381–407.

Xie, J., He, Z., Wang, Z., Wang, B., and Pan, L. (2019). Efficient expression of a novel thermophilic fungal β-mannosidase from Lichtheimia ramosa with broad-range pH stability and its synergistic hydrolysis of locust bean gum. J. Biosci. Bioeng. 128, 416–423. doi: 10.1016/j.jbiosc.2019.04.007

Yamabhai et al. Crit Rev Biotechnol, 2016; 36(1): 32–42 Engineering Process Technology. InTech. Available at: http:// www.intechopen.com/books/biofuel-s-engineering-process-technology/biorefining-lignocellulosic-biomass-via-the-feedstock-impregnation-rapid-and-sequential-steam-treatm [last accessed 27 May 2014].

Yamabhai M, Sak-Ubol S, Srila W, Haltrich D (2014) Mannan biotechnology: from biofuels to health. Critical reviews in biotechnology: 1-11

Yamabhai M, Ubol SS, Srila W, et al. Mannan biotechnology: from biofuels to health. Crit Rev Biotechnol. 2016;36(1):32–42

Yamabhai M, Ubol SS, Srila W, et al. Mannan biotechnology: from biofuels to health. Crit Rev Biotechnol. 2016;36(1):32–42. [Taylor & Francis Online]

Yatao X, Saeed M, Kamboh AA, Arain MA, Ahmad F, Suheryani I, ElHack Ma, et al. The potentially beneficial effects of supplementation with hesperidin in poultry diets. World's Poultry Science Journal 2018;74:265-276.

Yeoman, C. J., Han, Y., Dodd, D., Schroeder, C. M., Mackie, R. I., & Cann, I. K. (2010). Thermostable enzymes as biocatalysts in the biofuel industry. *Advances in applied microbiology*, *70*, 1-55.

Yokomizo F. Mannose-containing palm kernel meal. United States of America patent US20040151804A1 2009.

Yoo, H. Y., Pradeep, G. C., Lee, S. K., Park, D. H., Cho, S. S., Choi, Y. H., ... & Kim, S. W. (2015). Understanding β-mannanase from Streptomyces sp. CS147 and its potential application in lignocellulose based biorefining. *Biotechnology Journal*, *10*(12), 1894-1902.

York WS, O'Neill MA (2008) Biochemical control of xylan biosynthesis—which end is up? Current opinion in plant biology 11: 258-265
Zhao D., Zhang X., Wang Y., Na J., Ping W., Ge J. (2020). Purification, biochemical and secondary structural characterisation of β-mannanase from Lactobacillus casei HDS-01 and juice clarification potential. Int. J. Biol. Macromol. 154 826–834.
Zollinger H. Synthesis, properties and applications of organic dyes and pigments. Colour chemistry. New York: John Wiley-VCH Publishers, 2002; 92- 100