Industrial Applications And Production of Cold Active Xylanase: A Review

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ABSTRACT *Xylanase is responsible for hydrolysis of xylan, a major hemicellulose of plant cell wall. A diversity of microorganisms have the capability to produce xylanases, including bacteria, yeasts and filamentous fungi. But it has been estimated that xylanase in fungal culture is typically much higher than those from yeasts or bacteria. Solid state fermentation shows advancement over submerged fermentation especially for fungal cultivars. At present there is an increasing demand for cost effective microbial xylanolytic enzyme which payback the industrial applications and are produced commercially. Cold-active enzymes comprise an attractive source for biotechnological applications. Their high catalytic activity at temperatures below 25°C makes them excellent biocatalysts that eradicate the need of heating processes hampering the quality, sustainability, and cost-effectiveness of industrial production. The major uses of xylanases are bio pulping, bio bleaching, clarifying fruit juices, beer manufacturing industries, improving animal feed, production of bio fuels, in baking industries and textiles. Here we provide a review on production of xylanase enzymes from microorganisms found in different environments, including a revision of the latest techniques that have been used for accomplishing these vital tasks and of the successful use of cold-adapted enzymes in biotechnological and industrial applications.*

Keywords: *Xylan, Xylanases, Microorganisms, cold-adapted enzymes, solid state fermentation, submerged fermentation; Applications:*

INTRODUCTION:

There has been rising interest in xylanase production and its application because, xylanase is important in the bioconversion of hemicellulose, which is a major component of lignocellulosic material. Xylanase is a class of enzymes and is being produced by microorganisms to breakdown a component of plant cell walls known as hemicellulose. Microorganisms have colonized cold places on earth, despite harsh conditions and cold environments present for human life, depending on their optimal growth temperature, these organisms can be psychrophilic or psychrotrophic. Psychrophilic organisms are able to grow at low temperatures, between −20 and 10°C, and are unable to grow at temperatures higher than 15°C. Unlike psychrophiles, psychrotrophic organisms grow and survive optimally at 20–25°C and also these organisms have a high metabolic activity and growth capacity at temperatures below 0°C (Pikuta *et al*., 2007). Typically, psychrotolerant microorganisms are able to survive and are being found in terrestrial cold environments and psychrophiles in marine ecosystems. Microorganisms living on these cold-adapted places are mainly bacteria, yeasts, fungi and algae, and this vast variety has been extensively reviewed by (Cowan *et al*., 2007; Yumoto, 2013). Constantly cold environments (<5°C) cover 80% of the Earth's biosphere and comprise mainly the polar regions, deep water and marine sediments of the oceans, and glaciers of high mountains (Pikuta *et al*., 2007; Huston, 2008).

ENZYMES:

In the context of worldwide needs for sustainability and clean manufacturing technologies, biocatalysts are an attractive alternative for the achievement of chemical transformations (Wohlgemuth, 2010; Bornscheuer *et al*., 2012). Enzymes are biological catalysts that speed up chemical reactions making them compatible with life. Often and hence show important advantages with respect to non-natural catalysts such as their chemo-, regio- and stereo selectivity and the ability to work under mild conditions of temperature and pressure. These are non toxic, biodegradable and efficient biocatalysts with wonderful catalytic properties, offering high levels of safety, low energy consumption and an overall ecofriendly production procedure (Saha and Demirjian, 2001; Dunn, 2012; Wang *et al*., 2012). Though the knowledge about the origin of enzymatic efficiency to catalyse chemical reactions is still not complete and there have been numerous studies that have provided a solid understanding about some of the key factors in bio catalysis (Warshel *et al*., 2006; Benkovic & Hammes, 2003; Garcia *et al*., 2004; Marti *et al*., 2004). Enzymes from cold-adapted species are considerably more active at low temperatures, but the rationale of this adaptation is complex

and relatively difficult to understand. It is usually stated that there is a affiliation between the flexibility of an enzyme and its catalytic activity at low temperature. Filamentous fungi are particularly interesting in this regard, because they secrete significantly higher levels of these enzymes into the medium than yeasts and bacteria.

XYLANASE ENZYME:

Xylanase is the name given to a class of enzymes which degrade the linear polysaccharide β-1,4-xylan into xylose, thus breaking down hemicellulose, which is a chief component of the cell wall of plants (Lee *et al*., 2003). It plays an important physiological role in plant tissue, because they are involved in fruit softening, seed germination and plant defence mechanisms (Turner *et al*., 2007). The complex structure of xylan needs various kinds of enzymes for its complete hydrolysis. Endo-1, 4-ß- xylanases (1, 4-ß-D-xylanxylanohydrolase, E.C.3.2.1.8) depolymerise xylan by the random hydrolysis of xylan backbone and 1, 4-ß-D-xylosidases (1,4-ß-D-xylan xylohydrolase E.C.3.2.1.37) split off small oligosaccharides. The side groups which are present in xylan are liberated by α -L- arabinofuranosidase, α –D-glucuronidase, galactosidase and acetyl xylan esterase. Xylanases show a great diversity and are commonly distributed in xylanolytic microorganisms in nature (Collins *et al*., 2005). Xylans are present in large quantity in hard wood from angiosperm (the cell content 15-30% of the cell wall content) and soft wood from gymnosperms (7-10% as well as in annual plans less than 30% (singh *et al*., 2003).

XYLAN:

Xylan is the polysaccharide with major structures in plant cells and is most abundant polysaccharide in nature, accounting for about one third of renewable organic carbon sources on the earth. Being major component of hemicellulose, these polysaccharides comprise a complex of carbonate hydrolase including xylan, xyloglycan, glucomannan, galactoglucomannan and arabinogalactan. Plant cell wall comprises of three layers, which include primary cell wall, middle lamella and secondary cell wall. Xylan is present in secondary cell wall, at the interface between lignin and cellulose via covalent and non covalent bonds to provide cell wall integrity and fibre cohesion (Motta *et al*., 2013; Corral and Ortega, 2006; Butt *et al*., 2008). Xylan is the second most prevalent in nature after cellulose, representing up to 30-35 percent of plants total dry weight. It is the major structural polysaccharide constituent of hard and soft wood and is the second most abundant renewable resource. This complex hetero polysaccharide is composed of b-(1,4)-linked D-xylopyranosyl residues with substitutions of L-arabinofuranose, D-glucuronic acid, and 4-O-methyl-D-glucuronic acid. The degradation of xylzn requires different xylanolytic enzymes, like xylanase (EC 3.2.1.8), b-xylosidase (EC 3.2.1.37), a-L-arabinofuranosidase (EC 3.2.1.55), a-D-glucuronidase (EC 3.2.1.139), and acetyl xylan esterase (EC 3.1.1.72) (Beg *et al.,* 2001).

XYLANASE PRODUCTION:

A diversity of microorganisms have the capability to produce xylanases, including bacteria, yeasts and filamentous fungi (Kumar *et al.,* 2013. 2014; Lombard *et al.,* 2014). From industrial point of view, xylanase is the most important enzyme in the bioconversion of hemicellulose, which is an important component of lignocellulosic material. Enzymes are commercialy obtained from microbes due to their ease of growth, nutritional requirement and downstream processing (Prakash *et al*., 2013). Biocatalysts have been widely studied and increasingly applied in the industrial production of bulk chemicals and pharmaceuticals (de Carvalho, 2011; Du *et al*., 2011; Patel, 2011; Rubin-Pitel & Zhao, 2006; Schoemaker *et al*., 2003; Wen *et al*., 2009a; Zhao, 2011). Enzymatic hydrolysis using immobilized enzymes has been demonstrated to produce xylooligosaccharides (Aragon *et al*., 2013b). Xylanase has been reported from microbial sources like *Aspergillus sp*. and *Trichoderma sp*., as well as from many bacterial isolates (Sapag *et al*., 2002). However, a smaller amount of work on xylanase from *Penicillium citrinum* isolate has been reported. Moreover, cellulase-free xylanases are of considerable research interests due to their industrial significance (Walia *et al*., 2014). Xylanases are being produced either by solid state or submerged fermentation. Production of these enzymes in solid state fermentation (SSF) is usually much higher than that of submerged fermentation. Therefore, solid state fermentation has gained interest from researchers in recent years and has often been employed for the production of xylanases because of its economic advantages (Sonia *et al*., 2005).The technique of Solid state fermentation can be performed on a variety of ligno-cellulosic materials, such as rice bran, wheat bran, ragi bran, corn cob, soya bran etc. which proved to be most efficient in the production of xylanase (Pandey *et al*., 1999).For production of xylanase, solid state fermentation (SSF) is an attractive method especially for fungal cultivations, because it shows many advantages such as- the higher productivity per reactor volume as well as the lower operation and capital cost. The cost of carbon source plays another key role in the economics of xylanase production. Hence, an approach to reduce the increasing

cost of xylanase production is the use of lignocellulosic materials as substrates rather than opting for the high-priced pure xylans (Senthilkumar *et al*., 2005).

Producing Microorganisms:

Microorganisms, in general have been regarded as a good source of beneficial enzymes because they multiply at extremely high rates and synthesize biologically active products that can be controlled by humans. An increase in the use of enzymes as industrial catalysts has been tremendously increased in recent years. These enzymes put forward advantages over the use of conventional chemical catalysts for numerous reasons, they exhibit high catalytic activity and a much higher degree of substrate specificity, they can be produced in large amounts, they are highly biodegradable, they pose no threat to the environment and they are economically viable (Gote, 2004). Microbial xylanases are the preferred catalysts for xylan hydrolysis, due to their negligible substrate loss, high specificity, mild reaction conditions, and side product generation. Complete xylanolytic enzyme systems, which including all of these activities and have been found to be widespread among fungi (Sunna and Antranikian, 1997; Belancic *et al*., 1995), actinomycetes (Elegir *et al*., 1994) and bacteria (Kulkarni *et al*., 1999). Producers of some most important xylanolytic enzymes include *Aspergillus, Trichoderma, Streptomyces, Phanerochaetes, Chytridiomycetes, Ruminococcus, Fibrobacteres, Clostridia and Bacillus* (Kulkarni *et al*., 1999; Qinnghe *et al*., 2004; Wubah *et al*., 1993; Matte and Forsberg, 1992).

The ecological niches of these organisms is of great diversity and typically include environments where plant materials accumulate and deteriorate, as well as in the rumen of ruminants (Qinnghe *et al*., 2004; Prade, 1996; Krause *et al*., 2003). Although, since 1960, there have been many reports on microbial xylanases and the prime focus has been on plant pathology related studies (Lebeda *et al*., 2001). During the 1980's it was made possible to use xylanases for bioleaching and was tested (Viikari *et al*., 1996). Since 1982, it has been reported that several microorganisms, including fungi and bacteria readily hydrolyze xylans by synthesizing 1,4-β-D endoxylanases (E.C. 3.2.18) and β-xylosidases (EC.3.2.1.37) (Esteban *et al*., 1982). Therefore, production of xylanases must be improved by finding more potent fungal or bacterial strains or by inducing mutant strains to excrete larger amounts of enzymes. Moreover, the level of production of microbial enzymes is influenced by a variety of nutritional and physiological factors, such as the supply of carbon, nitrogen , physical circumstances and chemical conditions (Nagar *et al*., 2010). *Trichoderma, Aspergillus, Fusarium*, and *Pichia* of fungal genera are considered great producers of xylanases (Adsul *et al*., 2005). White-rot fungi have also shown best results to produce extracellular xylanases that act on a wide range of hemicellulosic materials these include, *Phanerochaete chrysosporium* which produces high levels of α- glucuronidase (Castanares *et al*., 1995) and *Coriolus versicolor* that produces a complex xylanolytic combination of enzymes (Abd El-Nasser *et al*, 1997). Although xylanases from eubacteria and archaebacteria show significantly higher temperature optima and stability than those of fungi, but the amount of enzyme produced by these bacteria is comparatively lower than that of produced by fungi. In general, the level of xylanase in fungal cultures is naturally much higher than those from yeasts or bacteria (Singh *et al*., 2003).

SOURCES OF XYLANASE:

Xylanases are the xylosidic hydrolase enzymes generally found in microorganisms like insects, protozoons, marine algae, intestine of termites, , crustaceans, snails, actinomycetes bacteria and fungi which break the glycosidic bonds of xylans forming hemi-acetyls and glycans (Motta *et al*., 2013; Corral and Ortega, 2006; Butt *et al*., 2008; Sharma and Kumar, 2013). However, xylans have been isolated from unsubstituted linear froms of guar seed husk, esparto grass and tobacco stalks (Eda *et al.,* 1976). Microorganisms are the effective producers of xylanase and a list of xylanase producing microorganisms is given below.

List of some xylanase producing microbes (* = poor producer, ** = good producer, * = best producers):**

Organisms	References
Fungi	
***Aspergillus foetidus	Shah, *et al*., (2005)
***Aspergillus niger SL-05	Liu *et al*., (2008)
* Fusarium oxysporum VTT-D-80134	Poutanen (1987)
***Melanocarpus albomyces	Gupta *et al*., (2013)

*Penicilium sp. ZH-30	Li, *et al.,* (2008)
*Piromyces sp. E 2	Tenuissen *et al*., (1992)
***Schizophyllum commune	Steiner *et al.,* (1987)
**Talaromyces emersonii CBS 814.70	Tuohy *et al.,* (1990)
***Thermomyces lanuginosus	Singh (2000)
**Trichoderma longibrachiatum	Azin, *et al.,* (2007)
**Trichoderma reesei SAF3	Kar *et al*., (2006)
Yeast	
**Aureobasidium pullulans Y-12311-1	Li *et al*., (1993)
*Cryptococcus albidus	Morosoli *et al*., (1986)
Bacteria	
***Bacillus sp. NCL 87-6-10	Balakrishnan *et al*., (2000)
*Bacillus circulans AB 16	Dhillon *et al*., (2000)
*Bacillus cereus BSA1	Mandal *et al*., (2008)
*Bacillus megatorium	Sindhu *et al*., (2006)
***Bacillus pumilus.	Batton *et al.,* (2006)
***Clostridium absonum CFR – 702	Rani, (1996)
*Pseudonomas sp. WLUN 024	Xu *et al.,* (2005)
**Streptomyces sp. QG-11-3	Beg *et al*., (2000)
**Streptomyces cuspidosporus	Maheswari *et al.,* (2000)
*Streptomyces roseiscleroticus NRRL-B-11019	Grabski and Jeffries, (1991)
*Thermoactinomyces thalophilus sub group C	Kohli *et al.,* (2001)

PROPERTIES OF XYLANASES:

Pertaining to the properties of xylanases, extensive reports are available from different microbial sources. Microbial xylanases are single subunit proteins with molecular masses ranging from 8-145 kDa (Sunna and Antranikian, 1997). Endo-xylanases from various sources have isoelectric points ranging from 3 to 10. Bacteria generally produce two xylanases having high molecular mass (acidic) and low molecular mass (basic) respectively. This phenomena is not observed in fungi, where low molecular mass basic xylanases are more common. In amino acid compositions of xylanases aspartic acid, glutamic acid, glycine, serine and threonine are dominant which has been reported from various sources. The heterogeneity and complexity of xylan has resulted in a plethora of different xylanases with varying specificities and primary sequences and folds.

On the basis of physicochemical properties, xylanases were classified into two groups, one containing low molecular weight (<30 kDa) xylanases with basic pI, and second group containing high molecular weight (>30 kDa) xylanases with acidic pI (Wong *et al.,* 1988). But exceptions to this pattern have been found in fungal xylanases (approximately 30%), due to which they cannot be classified in this system.(Matte & Forsberg, 1992; Sunna & Antranikian, 1997). Generally, xylanases and glycosidases (EC 3.2.1.x) have been classified by a system which is based on primary structure, comparisons of the catalytic domains and grouping enzymes of related sequences (Henrissat *et al.,* 1989; Collins *et al.,* 2005). D-xylose is the main component of xylan a five-carbon sugar that can be converted to single cell protein and chemical fuels by the cheapest "chemical factories" microbial cells (Biely, 1985). Therefore it is not surprising for xylan-degrading cells to produce an arsenal of polymer-degrading proteins. The xylanolytic enzyme system carrying hydrolysis of xylan is usually composed of a repertoire of hydrolytic enzymes including, β-1,4-endoxylanase, β-xylosidase, α-L-arabinofuranosidase, α-glucuronidase, acetyl xylan esterase, and phenolic acid (ferulic and p-coumaric acid) esterase. All these enzymes act cooperatively to convert xylan into its constituent sugars (Beg, *et al.,* 2001).

APPLICATION OF XYLANASES:

Xylanases comprise vital applications including paper and pulp industry, animal feed processing, clarification of beverages and recent application involves biofuel production from agro residues and great attention has been drawn to cold-active xylanases because of their high catalytic activity at low temperatures and their inherently broad substrate specificity relative to their thermophilic counterparts (Georlette *et al*., 2002). These properties allow to make use of of cold-active xylanase in different applications of food industries, textiles like rayon, cellophane, manufacture of certain chemicals such as cellulose ethers and cellulose esters, bioremediation and investigation of proteins, "cold-active mechanisms" (Collins *et al*., 2005; Collins *et al*., 2006; Georlette *et al*., 2002; Shallom & Shoham, 2003). Xylanases are capable to hydrolyise xylan, lignocellulosic materials and agro wastes into useful products for industrial applications and of commercial importance. Highly purified xylanase shows specific applications in food and cosmetic industries, synthetic chemistry, medical diagnostics (Rodriguez Couto and Toca Herrera, 2006) and also acts as inhibitory agent towards human HIV-1 reverse transcriptase (Xiao *et al*., 2003). Xylanases derived from microorganisms have many potential applications in the food, feed, and paper pulp industries (Collins *et al*., 2005; Kulkarni *et al*., 1999; Qinnghe *et al*., 2004).

1. Bio bleaching paper pulp:

An eco-friendly alternative is available for bleaching of pulps by using microbial enzymes such as xylanases and laccases (Maalej-Achouri *et al.*, 2012). Property of bio bleaching of xylanase was reported in 1980 (Viikari *et al*,1986). Bio bleaching paper pulp with xylanase hydrolyze the hemicellulosic chain among the cellulose and lignin thus removing the loosen lignin from the required cellulose. In this method, it reduces the release of organochlorine pollutants like dioxin leading to a chlorine free bleaching without adversely affecting the strength of the paper and hence helps in maintaining good quality of paper.

2. Improving animal feed:

Addition of xylanase to the animal feed helps in reducing the viscosity of the fodder, which makes the fodder easily digestible by the animal gut. It increases the diffusion of pancreatic enzymes into the food and at the same time improves the absorption of the nutrients.It also helps in reducing the unwanted wastes in the animal feed, thus lowering the environmental pollutions.

3. Bakery:

Xylanase improves the quality of bakery products by improving the strength of gluten networks and improves the dough characteristics by hydrolyzing the arabinoxylan and starch, thus untying and isolating the gluten from the starch in the wheat flour, making it more elastic, machinable and stable with a more loaf volume and crumb structure. Thus, it increases the durability of bread storage and keeps it fresh for a long period.

4. production and clarification of fruit juice:

By adding xylanase to the fruits increases the increased production of fruit juices and help in maceration. Xylanase also has a great role in stabilization of fruit pulp, liquefaction of fruits and vegetables, recovery of aromas, essential oils, edible dyes, vitamins, mineral salts and pigments etc. It plays a vital role viscosity reduction, hydrolysis of substances that hinder the physical or chemical clearing of the juice or that may cause cloudiness in the concentrate. Hence, it helps in juice clarification and its filteration.

5. Beer manufacturing industries:

Xylanase is capable to hydrolyze the hemicelluloses present in the barley thus helping in production of more reducing sugar for making beer. It also reduces the viscous nature of the fermented liquid making it more clear and much easy to filter. Xylanase plays a great role in the processing of spent barley into animal fodders.

6.Thermostability of xylanases:

Thermostable and alkaline stable xylanases are most desirable for pulp pre-bleaching and can also be beneficial for other industrial processes, since high temperatures speed up transformation rates, increase substrate and product solubility, and decrease the possibility of microbial contamination (Kumar *et al.,* 2013).Moreover, structural basis of the improved stability of S80T and S149T was attributed to new hydrogen bonding and a packing effect, respectively (Ayadi *et al.,* 2015). Xylanase variants with superior thermal resistance have also been obtained by directed evolution strategies, involving techniques such as mutagenic PCR, DNA shuffling and site-saturation mutagenesis. Some examples are xylanases from *T. reesei* (Hokanson *et al.,* 2011), *B. circulans* (Miyazaki *et al.,* 2006), *Thermomyces lanuginosus* (Stephens *et al.,* 2014), or Xyl7 from a metagenomic library (*Qian et al*., 2015). Screening measures have been facilitated by the use of combinatorial libraries (Hokanson *et al.,* 2011). The stabilization of the protein through an improved packing of the enzyme was accomplished by filling hydrophobic cavities, introducing additional

hydrogen bonds or aromatic interactions (Xie *et al.,* 2006; Song *et al.,* 2015; Gallardo *et al.,* 2010). Structural analysis have shown that increased number of interactions around E82 may explain the stabilization of the mutant enzyme (Chen *et al.,* 2014; Wang *et al.,* 2014).

7. Nanotechnology:

The immobilization of enzymes shows some of great advantages for industrial applications, facilitating their re-usability (Shrivastava *et al.,* 2012). In particular, enzyme adsorption of nanomaterials can develop enzyme activity and thermal stability to a great extent (Liu *et al.,* 2014). Nanoparticles reveal a number of unique characteristics as immobilization supports because of their prominent reaction surface. Silica-coated nanoparticles of xylanases also showed increased activity and stability compared to their free versions, and retained more than 80 % of initial activity after 6 cycles (Dhiman *et al.,* 2013; Soozanipour *et al.,* 2015). Xylanase from *Thermomyces lanuginosus* was immobilized on magnetic nanoparticles which were coated with hyper-branched polyglycerol and a derivative conjugated with citric acid (Landarani-Isfahani *et al.,* 2015).

8. Miscellaneous:

Xylanases also improves the silage, which acts as a good manure in agricultures. They also produce nutrients, which are useful for the ruminal microflora. Xylanases enhance the cleaning property of washing detergents to clean different types of stains. Xylanases improves the procedure of retting of flax fibers before they are processed to form linen. These enzymes also help in degradability of disposable plant organic wastes. Xylanases are also used in removal of oil from plant materials like corn oil from corn embryos. Xylooligosaccharides formed from the hydrolysis of xylan have got much periodic effects as they cannot be further hydrolysed, thus stimulating the growth of some beneficial microbes in the colon. They also help in decline of cholesterol, maintenance of health of gastrointestinal tract (GIT) and improve the availability of calcium to our body. They also inhibit the reterogradation of starch. Xylitol is another important product of xylanase which is used to sweeten food products such as, candy, soft drinks, chewing gum and ice creams. In toothpaste and various pharmaceutical products, xylanase acts as a natural sweetener (Motta *et al*., 2013; Corral and Ortega, 2006; Butt *et al*., 2008; Sharma and Kumar, 2013).

CONCLUSION:

Xylan being a hemicellulose with diverse structures due to the presence of many side chains and bonds need a complex enzyme called as xylanase for its hydrolysis to form monomeric subunits. Xylanase is abundantly found in fungi, and in other microorganisms like bacteria, gut of termites, algae, gut of rumens etc. Xylan on hydrolysis with the action of xylanases gets converted into xylose residues which on fermentation with yeasts gets converted into ethanol. Not only in the production of bioethanol but also in many other industries xylanase has got its abundant applications, such as in bakeries, paper bleaching, oil extraction, juice clarification etc. which are based on the partial hydrolysis of xylan. The long term applications of xylanases such as conversion of renewable biomass into liquid fuels, where xylanases play an important role in the conjunction with the celluloses, is not yet economically feasible. However, stringent environmental regulations and awareness to overcome the emission of greenhouse gases have added a new reason for future research developments in the study of xylanases. In order to make the application of xylanases realistic the enhancement in enzyme yields is important. Xylanase enzyme should be promoted in the food processing industry which in turn will replace the chemical emulsifiers and additives. It can provide best results in combination with other enzymes. Considerable progress has been made in the last few years in identifying the process parameters which are important for obtaining high xylanase yields and productivities and thus influencing the economics of xylanase production, These processes has lead to broader applications of biocatalysts in pharmaceutical, agriculture, food, chemical, and energy industries. Therefore, in future, new methods will be developed for easier and cheaper production of these enzymes to fulfil the demands of various industries.

REFERENCES

1. Abd El-Nasser, N.H., Helmy, S.M., and El-Gammal, A.A. (1997). Formation of enzymes by biodegradation of agricultural wastes with white rot fungi. Polymer Degradation and Stability, 55: 249–255.
2. Adsul, M.G., Ghule, J.E., Shaikh, H., Singh, R., Bastawde, K.B., and Gokhale, D,V. (2005). Enzymatic hydrolysis of delignified bagasse polysaccharides. Carbohydrate Polymers, 62: 6–10.
3. Aragon, C., Santos, A., Ruiz-Matute, A., Corzo, N., Guisan, J., Monti, R., and Mateo, C. (2013b). Continuous production of xylooligosaccharides in a packed bed reactor with immobilized–stabilized biocatalysts of xylanase from Aspergillus versicolor. J Mol Catal B Enzym 98:8–14.
4. Ayadi, D.Z., Sayari, A.H., and Hlima, H.B. (2015). Improvement of Trichoderma reesei xylanase II thermal stability by serine to threonine surface mutations. Int J Biol Macromol 72:163–170.

5. Azin, M., Moravej, R., and Zareh, D. (2007). Production of xylanase by Trichoderma longibrachiatum on a mixture of wheat bran and wheat straw: optimization of culture condition by Taguchi method. Enzyme Micrb Technol 40:801-805.
6. Balakrishnan, H., Srinivasan, M.C., Choudhury, K., Rele, M.V., and Chsndwadkar, A.J. (2000). Effect of syntheticzeoites on xylanase production from an alkalophilic Bacillus sp. Current Sci 79:95-97.
7. Battan, B., Sharma, J., and Kuhad, R.C. (2006). High level xylanase production by alkaliphilic Bacillus pumilus ASH under solid state fermentation. World J Microbiol Biotechnol 22: 1281-1287.
8. Beg, Q.K., Bhushan, B., Kapoor, M., and Hoondal, G.S. (2000). Production and characterization of thermostable xylanase and pectinase from a Streptomyces sp. QG-11-3. J Ind Microbiol Biotechnol 24:396–402.
9. Beg, Q.K., Kapoor, M., Mahajan, L., and Hoondal, G.S. (2001). Microbial xylanases and their industrial applications: a review. Applied Microbiology and Biotechnology;56: 326–338.
10. Belancic, A., Scarpa, J., Peirano, A., Diaz, R., Steiner, J., and Eyzayuirre, J. (1995). Penicillium purpuro- genum produces several xylanases: purification and properties of two of the enzymes. Journal of Biotechnology;41: 71–79.
11. Benkovic, S.J., and Hammes-Schiffer, S. (2003). Science.; 301:1196–1202. [PubMed: 12947189].
12. Biely, P. (1985). Microbial xylanolytic systems. Trends Biotechnol.3, 286–290.
13. Bornscheuer, U.T., Huisman, G.W., Kazlauskas, R.J., Lutz, S., Moore, J.C., and Robins, K. (2012). Engineering the third wave of biocatalysis. Nature 485, 185–194. doi: 10.1038/nature11117.
14. Butt, M.S., Nadeem, M.T., Ahmad, Z., and Sultan, M.T. (2008). Xylanases and their Applications in Baking Industry. Food Technol.Biotechnol; 46(1) 22-31.
15. Castanares, A., Hay, A.J., Gordon, A.H., McCrae, S.I., and Wood, T.M. (1995). D-Xylan-degrading enzyme system from the fungus Phanerochaetechrysosporium: Isolation and partial characterisation of an α-(4-O-methyl)-D-glucuronidase. Journal of Biotechnology 43: 183-194.
16. Chen, C.C., Luo, H., and Han, X. (2014). Structural perspectives of an engineered b-1,4-xylanase with enhanced thermostability. J Biotechnol 189:175–182
17. Collins, T., Gerday, C., and Feller, G. (2005). Xylanases, xylanase families and extremophilic xylanases.FEMS Microbiology Reviews 29: 3–23. [PubMed: 15652973].
18. Collins., T., Hoyoux, A., Dutron, A., Georis, J., Genot, B., Dauvrin, T., Arnaut, F., Gerday, C., and Feller, G. (2006). Use of glycoside hydrolase family 8 xylanases in baking. J. Cereal Sci.; 43(1):79–84.
19. Corral, O.L., and Ortega, F.V. (2006). Xylanases. Advances in Agricultural and Food Biotechnology,;305-322.
20. Cowan, D.A., Casanueva, A., and Stafford, W. (2007). "Ecology and biodiversity of cold- adapted microorganisms," in Physiology and Biochemistry of Extremophiles, eds C.Gerdayand N.Glansdorff (Washington, DC: American Society of Microbiology), 119–132.
21. DeCarvalho, C.C. (2011). Enzymatic and whole cell catalysis: finding new strategies for old processes. Biotechnol. Adv.; 29:75–83. [PubMed: 20837129].
22. Dhillon, A., and Khanna, S. (2000). Production of a thermostable alkali-tolerant xylanase from Bacillus circulans AB 16 on wheat straw. World J Microbiol Biotechnol 16:325-327.
23. Dhiman, S.S., Kalyani, D., and Jagtap, S.S. (2013). Characterization of a novel xylanase from Armillaria gemina and its immobilization onto SiO2 nanoparticles. Appl Microbiol Biotechnol 97:1081–1091.
24. Du, J., Shao, Z., and Zhao, H.M. (2011). Engineering microbial factories for synthesis of value-added products. J. Ind. Microbiol. Biotechnol.; 38:873–890. [PubMed: 21526386].
25. Dunn, P. J. (2012). The importance of green chemistry in process research and development. Chem. Soc. Rev. 41, 1452–1461. doi: 10.1039/C1CS15041C.
26. Eda, S., Ohnishi, A. and Kato, K. (1976). Xylan isolated from the stalk of Nicotiana tabacum. Agric. Biol. Chem. 40, 359–364.
27. Elegir, G., Szakács, G., and Jeffries, T.W. (1994). Purification, Characterization, and Substrate Specif- icities of Multiple Xylanases from Streptomyces sp. Strain B-12-2. Applied and Envi- ronmental Microbiology;60: 2609–2615.
28. Esteban, R., Villanueva, I.R., and Villa, T.G. (1982). β-D-Xylanases of Bacillus circulans WL-12, Can. J. Microbiol;28: 733–739.
29. Gallardo, O., Pastor, F.I., Polaina, J., Diaz, P., Łysek, R., Vogel, P., Isorna, P., Gonza, ´lez, B., and Sanz-Aparicio, J. (2010). Structural insights into the specificity of Xyn10B from Paenibacillus barcinonensis and its improved stability by forced protein evolution. J Biol Chem 285:2721–2733.
30. Garcia-Viloca, M., Gao, J., Karplus, M., and Truhlar, D.G. (2004). Science.; 303:186–195. [PubMed: 14716003] .
31. Georlette, D., Bentahir, M., Claverie, P., Collins, T., D'amico, S., Delille, D., Feller, G., Gratia, E., Hoyoux, A., Lonhienne, T., Meuwis, M.a., Zecchinon, L., Gerday, C., Cuyper, M., and Bulte, J.W.M. (2002). Cold-adapted enzymes: physics and chemistry basis of biotechnology. Hofman, M., Anné, J., Cuyper, M., Bulte, J.W.M., editors. Vol. 7. Springer; Netherlands:. p. 177-196.
32. Gote, M. (2004). Isolation, purification and characterization of thermostable-galactosidase from Bacillus stearothermophilus (NCIM-5146). University of Pune.
33. Grabski, A.C., and Jeffries, T.W. (1991). Production, purification and characterization of β-(1-4)-endoxylanase of Streptomyces roseiscleroticus. Appl Environ Microbiol 57:987-992.

34. Gupta, G., Sahani, V., and Gupta, R.K. (2013). Optimization of xylanase production from Melanocarpus albomyces using wheat straw extract and its scale up in stirred tank bioreactor.. Indian J of Chem Technol 20: 282-289.
35. Hokanson, C.A., Cappuccilli, G., and Odineca, T. (2011). Engineering highly thermostable xylanase variants using an enhanced com- binatorial library method. Protein Eng Des Sel 24:597–605.
36. Huston, A.L., Haeggström, J.Z., and Feller, G. (2008). Cold adaptation of enzymes: structural, kinetic and micro calorimetric characterizations of an amino peptidase from the Arctic psychrophile Colwellia psychrerythraea and of human leukotrieneA4 hydrolase.Biochim. Biophys.Acta1784,1865–1872.doi: 10.1016/j.bbapap.2008.06.002
37. Kar, S., Mandal, A., Das, Mohapatra, P.K., Mondal, K.C., and Pati, B.R. (2006). Production of cellulase free xylanase by Trichoderma reesei SAF3. Brazilian J Microbiol 37:462-464.
38. Kohli, U., Nigam, P., Singh, D., and Chaudhary, K. (2001). Thermostable, alkalophilic and cellulase free xylanase production by Thermo actinomyces thalophilus subgroup C. Enzyme Microbial Technol 28:606–610.
39. Krause, D.O., Denman, S.E., Mackie, R.I., Morrison, M., Rae, A.L., and Attwood, G.T. (2003). Opportunities to improve fibre degradation in the rumen: microbiology, ecology, and genomics. FEMS Microbiology Reviews;27: 663–693.
40. Kulkarni, N., Shendye, A., and Rao, M. (1999). Molecular and biotechnological aspects of xylanases. FEMS Microbiology Reviews;23: 411–456.
41. Kumar, V., Pandey, P., Gupta, S., and Shukla, P. (2014). A reviving preliminary evoke on few xylanase producing fungal isolates from different ecological niche. Int J Curr Microbiol App Sci 3(4):501–506.
42. Kumar, V., Verma, D., Archana, A., and Satyanarayana, T. (2013). Thermostable bacterial xylanases. In: Satyanarayana T, Littlechild J, Kawarabayasi Y (eds) Thermophilic microbes in environmental and industrial biotechnology. Springer, New York, pp 813–857.
43. Landarani-Isfahani, A., Taheri-Kafrani, A., and Amini, M. (2015). Xylanase immobilized on novel multifunctional hyper branched polyglycerol-grafted magnetic nanoparticles: an Efficient and Robust Biocatalyst. Langmuir 31:9219–9227.
44. Lebeda, A., Luhova, L., Sedlarova, M., and Jancova, D. (2001). The role of enzymes in plant-fungal pathogens interactions. Zeitschrift Für Pflanzenkrankheiten Und Pflanzenschutz;108: 89–111.
45. Lee, R.C., Hrmova, M., and Burton, R.A. (2003). Bifunctional family 3-glcoside hydrolases from Braley with α-L-Arabino furamosidase and β-D-xylosidase activity characterization, primary structure and COOH terminal processing J. Biol.Chem, 278 : 5377-5388.
46. Li, N., Meng, K., Wang, Y., Shi, P., and Luo, H. (2008). Cloning, expression, and characterization of a new xylanase with broad temperature adaptability from Streptomyces sp. S9. Appl Microbiol Biotechnol online:3 June.
47. Li, X.L., Zhang, Z.Q., Dean, J.F.D., Eriksson, K.E.L., and Ljungdahl, L.G. (1993). Purification and characterization of a new xylanase (APX-II) from the fungus Aureobasidium pullulans Y-2311–1. Appl Environ Microbiol 59:3213–3218.
48. Liu, C., Sun, Z.T., Du, J.H., and Wang, J. (2008). Response surface optimization of fermentation conditions for producing xylanase by Aspergillus niger SL-05. J Ind Microbiol Biotechnol DOI 10.1007/s 10297-008-0330-0.
49. Liu, M., Dai, X., Guan, R., and Xin, X. (2014). Immobilization of Aspergillus niger xylanase A on Fe3O4-coated chitosan magnetic nanopar- ticles for xylooligosaccharide preparation. Catal Commun 55:6–10.
50. Lombard, V., Golaconda Ramulu, H., Drula, E., Coutinho, P.M., and Henrissat, B. (2014). The carbohydrate-active enzymes database (CAZy). Nucleic Acids Res 42:D490–D495.
51. Maalej-Achouri, I., Guerfali, M., Romdhane, I.B.B., Gargouri, A., and Belghith, H. (2012). The effect of Talaromyces thermophilus cellulase-free xylanase and commercial laccase on lignocellulosic components during the bleaching of kraft pulp. Int Biodeterior Biodegrad 75:43–48.
52. Maheshwari, R., Bhardwaj, G., and Bhat, M.K. (2000). Thermophilic fungi: Their physiology and enzymes, Microbiol. Mol. Boil. Rev., 63: 461-488.
53. Maheswari, U., and Chandra, T.S. (2000). Production and potential applications of a xylanase from a new strain of Streptomyces cuspidosporus. World J Microbiol Biotechnol 16:257-263.
54. Mandal, A., Kar, S., Das, Mohapatra, P.K., Maity, C., Mondal, K.C., and Pati, B.R. (2008). Xylanase production under submerged fermentation by newly isolated Bacillus cereus BSA1: parametric optimization of cultural conditions. J Pure Appl Microbiol 2:55-160.
55. Martí, S., Roca, M., Andrés, J., Moliner, V., Silla, E., Tuñón, I., and Bertrán, J. (2004). Chem. Soc. Rev.; 33:98– 107. [PubMed: 14767505].
56. Matte, A., and Forsberg, C.W. (1992). Purification, characterization, and mode of action of endoxylanases 1 and 2 from Fibrobacter succinogenes S85. Appl. Environ. Microbiol. 58,157–168.
57. Miyazaki, K., Takenouchi, M., and Kondo, H. (2006). Thermal stabilization of Bacillus subtilis family-11 xylanase by directed evolution. J Biol Chem 281:10236–10242.
58. Morosoli, R., Roy, C., and Yaguchi, M. (1986). Isolation and partial primary sequence of a xylanase from the Cryptococcus albidus. Biochem Biophys Acta 870:473–478.
59. Motta, F.L., Andrade, C.C.P., and Santana, M.H.A. (2013). A Review of Xylanase Production by the Fermentation of Xylan: Classification, Characterisation and Applications. Intech .

60. Nagar, S., Gupta, V.K., Kumar, D., Kumar, L., and Kuhad, R.C. (2010). Production and optimization of cellulase-free, alkali-stable xylanase by Bacillus pumilus SV-85S in submerged fermentation. Journal of Industrial Microbiology & Biotechnology;37: 71–83.
61. Pandey, A.P., Selvakumar, C.R., Soccol and Nigam, P. (1999). Solid state fermentation for the production of industrial enzymes.Curr. Sci. Vol 77, 1999, pp 149-162.
62. Patel, R.N. (2011). Biocatalysis: synthesis of key intermediates for development of pharmaceuticals. ACS Cata.; 1:1056–1074.
63. Pikuta, E.V., Hoover, R.B., and Tang, J. (2007). Microbial extremophiles at the limits of life. Crit. Rev. Microbiol. 33, 183–209. doi: 10.1080/104 08410701451948.
64. Poutanen, K., Ratto, M., Puls, J., and Viikari, L. (1987). Evaluation of different microbial xylanolytic systems. J Biotechnol 6:49-60.
65. Prade, R.A. (1996). Xylanases: from biology to biotechnology. Biotechnology & Genetic Engi- neering Reviews;13: 101–131.
66. Prakash, D., Nawani, N., Prakash, M., Bodas., M., Mandal, A., Khetmalas, M., and Kapadnis, B. (2013). Actinomycetes: a repertory of green catalysts with a potential revenueresource. Biomed. Res. Int. 2013:1–8. http://dx.doi.org/10.1155/2013/264020.
67. Qian, C., Liu, N., and Yan, X. (2015). Engineering a high-performance, metagenomic-derived novel xylanase with improved soluble protein yield and thermostability. Enzyme Microb Technol 70:35–41.
68. Qinnghe, C., Xiaoyu, Y., Tiangui, N., Cheng, J., and Qiugang, M. (2004). The screening of culture con- dition and properties of xylanase by white-rot fungus Pleurotus ostreatus. Process Bio- chemistry;39: 1561–1566.
69. Rani, S., and Nand, K. (1996). Development of cellulase free xylanase producing anaerobic consortia for the use of lignocellulosic wastes. Enzyme Microbial Technol 18:23-28.
70. Rodriguez., Couto, S., Toca., and Herrera, J.L. (2006). Industrial and biotech- nological applications of laccases: a review. Biotechnol Adv 24(5):500–513.
71. Rubin-Pitel, S.B., and Zhao, H.M. (2006). Recent advances in biocatalysis by directed enzyme evolution. Comb. Chem. High Throughput Screen.; 9:247–257. [PubMed: 16724916].
72. Saha, B.C., and Demirjian, D.C. (2001)."Advances in enzyme development and applied industrial biocatalysis," in ACS Symposium Series (Washington, DC: American Chemical Society), 2–12.
73. Sapag, A., Wouters, J., Lambert, C., de Ioannes, P., Eyzaguirre, J., and Depiereux, E. (2002). The endoxylanases from family 11: computer analysis of protein sequences reveals important structural and phylogenetic relationships. J Biotechnol 95(2):109–131.
74. Schoemaker, H.E., Mink, D., and Wubbolts, M.G. (2003). Dispelling the myths--biocatalysis in industrial synthesis. Science.; 299:1694–1697. [PubMed: 12637735].
75. Senthilkumar, S.R., Ashokkumar, K., Chandra, R., and Gunasekaran, P. (2005). Optimization of medium composition for alkali-stable xylanase production by Aspergillus fischeri Fxn 1 in solid-state fermentation using central composite rotary design. Bioresour. Technol. 96: 1380-1386.
76. Shah, A.R., and Madamwar, D. (2005). Xylanase production under solid state fermentation and its characterization by an isolated strain of Aspergillus foetidus in India. W J Microbiol Biotechnol 21:235-243.
77. Shallom, D., and Shoham, Y. (2003). Microbial hemicellulases. Curr. Opin. Microbiol.; 6(3):219–28. [PubMed: 12831897].
78. Sharma, M., and Kumar, A. (2013). Xylanases :An Overview. British Biotechnology Journal;3(1) 1-28.
79. Shrivastava, S., Lata, S., and Shukla, P. (2012). An insight on recent advances on immobilization methods for Industrial enzymes and its relevance to xylanases. Dyn Biochem Process Biotech Mol Biol 6(1):57–61.
80. Sindhu, I., Chibber, S., Capalash, N., and Sharma, P. (2006). Production of cellulose free xylanase from Bacillus megatorium by solid state fermentation for biobleaching of pulp. Current Microbiol 53:167-172.
81. Singh, A.M., and Madlala, B.A. (2003). Prior. FEMS Microbial Rev , 27, 3-16.
82. Singh, S., Pillay, B., and Prior, B.A. (2003). Thermal stability of β-xylanases produced by different Thermo myces lanuginosus strains. Enzyme Microb. Technol., 26: 502-508.
83. Singh, S., Reddy, P., Haarhoff, J., Biely, P., Janse, B., Pillay, D., and Prior, B.A. (2000). Relatedness of Thermomyces lanuginosus strain producing a thermostable xylanase. J Biotechnol 81:119-128.
84. Song, L., Tsang, A., and Sylvestre, M. (2015). Engineering a thermostable fun- gal GH10 xylanase, importance of N-terminal amino acids. Biotechnol Bioeng 112:1081–1091.
85. Sonia, K.G., Chadha, H.S., and Saini, B.S. (2005). Sorghum straw for xylanase hyper-production by Thermo myces lanuginosus (D2W3) under solid state fermentation. Bioresour.Technol. 96: 1561-1569.
86. Soozanipour, A., Taheri-Kafrani, A., and Isfahani, A.L. (2015). Covalent attachment of xylanase on functionalized magnetic nanoparticles and determination of its activity and stability. Chem Eng J 270:235–243.
87. Steiner, W., Lafferty, R.M., Gomes, I., and Esterbauer, H. (1987). Studies on a wild strain of Schizophyllum commune: cellulase and xylanase production and formation of the extracellular polysaccharide. Biotechno Bioeng 30:169-178.
88. Stephens, D.E., Khan, F.I., and Singh, P. (2014). Creation of ther- mostable and alkaline stable xylanase variants by DNA shuffling. J Biotechnol 187:139–146.

89. Subramanium, S., and Prema, P. (2002). Biotechnology of microbial xylanases: Enzymology, molecular biology and application, Critical Rev. Biotechnol. 22:33-46.
90. Sunna, A., and Antranikian, G. (1997). Xylanolytic enzymes from fungi and bacteria. Crit. Rev. Biotechnol. 17, 39–67.
91. Tenuissen, M.J., deKort, G.V.M., Opden Camp, H.J.M., and Huisint Veld, J.H.J. (1992). Production of cellulolytic and xylanolytic enzymes during growth of the anaerobic fungus Piromyces sp. on different substrates. J Gen Microbiol 138:1657-1664.
92. Tuohy, M., Coughlan, T.L., and Coughlan, M.P. (1990). Solid-state versus liquid cultivation of Talaromyces emersonii on straw and pulps: enzyme productivity, In: Coughlan MP, Amaral Collaco MT (Eds) Advances in biological treatment of lignocellulosic materials. Elsevier Applied Science, London, pp153.
93. Turner, T.S., Mamo and Karlsson, E. (2007). Potential and utilization of thermophiles and thermostable enzymes in biorefining. Microbial Cell Factories, 6 :2859-2869.
94. Viikari, L., Ranua, M., Kantelinen, A., Sundiquist, J., and Linko, M. (1986). Biotechnology in the pulp and paper industry, in: Bleaching with Enzymes, Proc. 3rd Int. Con. Stockholm.
95. Walia, A., Mehta, P., Chauhan, A., Kulshrestha, S., and Shirkot, C.K. (2014). Purification and characterization of cellulase-free low molecular weight endo beta-1,4 xylanase from an alkalophilic Cellulosimi- crobium cellulans CKMX1 isolated from mushroom compost. World J Microbiol Biotechnol 30(10):2597–2608.
96. Walia, A., Mehta, P., Guleria, S., and Shirkot, C.K. (2015). Improvement for enhanced xylanase production by Cellulosimicrobium cellulans CKMX1 using central composite design of response surface methodology. 3 Biotech 5:1053–1066.
97. Wang, K., Luo, H., and Tian, J. (2014). Thermostability improvement of a streptomyces xylanase by introducing proline and glutamic acid residues. Appl Environ Microbiol 80:2158–2165.
98. Wang, M., Si, T., and Zhao, H. (2012). Biocatalyst development by directed evolution. Bioresour. Technol. 115, 117–125. doi: 10.1016/j.biortech.2012.01.054.
99. Wang, S.L., Yen, Y.H., Shih, I.L., Chang, A.C., Chang, W.T., Wu, W.C., and Chai, Y.D. (2003). Production of xylanases from rice bran by Streptomyces actuosus A-151. Enzyme Microbiol Technol 33:917–925.
100. Warshel, A., Sharma, P.K., Kato, M., Xiang, Y., Liu, H., and Olsson, M.H.M. (2006). Chem. Rev.; 106:3210–3235. [PubMed: 16895325].
101. Wen, F., Nair, N.U., and Zhao, H.M. (2009a). Protein engineering in designing tailored enzymes and microorganisms for biofuels production. Curr. Opin. Biotechnol.; 20:412–419. [PubMed: 19660930].
102. Wohlgemuth, R. (2010). Biocatalysis - key to sustainable industrial chemistry. Curr. Opin. Biotechnol. 21, 713–724. doi: 10.1016/j.copbio.2010.09.016.
103. Wong, K.K., Tan, L.U., and Saddler, J.N. (1988). Multiplicity of β-1,4-xylanase in microorganisms: functions and applications. Microbiological Reviews 52: 305–17.
104. Wubah, D.A., Akin, D.E., and Borneman, W.S. (1993). Biology, fiber-degradation, and enzymology of anaerobic zoosporic fungi. Critical Reviews in Microbiology;19: 99–115.
105. Xiao, Y.Z., Tu, X.M., Wang, J., Zhang, M., Cheng, Q., Zeng, W.Y., and Shi, Y.Y. (2003). Purification, molecular characterization and reactivity with aromatic compounds of a laccase from basidiomycete Trametes sp. strain AH28-2. Appl Microbiol Biot 60(6):700–707.
106. Xie, H., Flint, J., and Vardakou, M. (2006). Probing the structural basis for the difference in thermostability displayed by family 10 xylanases. J Mol Biol 360:157–167.
107. Xu, Z.H., Bai, Y.L., Shi, J.S., and Tao, W.Y. (2005). Production of alkali tolerant cellulose free xylanase by Pseudomonas sp. WLUN 024 with wheat bran as the main substrate. World J Microbiol Biotechnol 21:575-581.
108. Yumoto, I. (2013). Cold-Adapted Microorganisms.Norfolk,UK:HorizonScientific Press.
109. Zhao, H.M. (2011). Highlights of biocatalysis and biomimetic catalysis. ACS Catal.; 1:1119–1120.