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Adding Value Prior to Pulping: Bioproducts from Hemicellulose

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1. Introduction

The global trend for production of biofuels and bioproducts from renewable resources is currently steered by three important drivers: 1) increasing demand and prices of petroleum-derived fuel; 2) increasing food needs; and 3) increasing greenhouse gas emissions. Biomass is the single renewable resource that has the potential to supplant the use of liquid transportation fuels now and help create a more stable energy future.

As recently reported by the US Department of Energy (US DOE), nearly 1.3 billion dry tons of biomass could be available for large-scale bioenergy and biorefinery industries, enough to displace 30% or more of the nation's current consumption of liquid transportation (Perlack et al., 2005). About a third of the biomass resources in US are wood-based and two-thirds are of agricultural origin. However, the biomass share of the US energy supply in 2004 was less than 3% of the total, compared to 40% and 23% derived from petroleum and coal, respectively. In 2009, the US produced 10.75 billion gallons of ethanol (mainly corn-based), and together with Brazil, both countries accounted for 89% of the world's production. The 2007 Energy Independence and Security Act and the new US Renewable Fuels Standard of 2008 call for the production of 36 billion gallons of biofuels, mainly ethanol and biodiesel, annually by 2022, with 21 billion gallons coming from "advanced biofuels" of which 16 billion gallons is expected as biofuels derived from lignocellulosic biomass.

Breakthrough technologies are needed to make cellulosic ethanol cost-competitive with corn-based ethanol by 2012. Plant-derived biofuels as a carbon-neutral technology have to achieve at least 60% lower emissions than petroleum fuel based on lifecycle studies that include all emissions resulting from making the fuel from the field to the tank. Meeting these goals will require significant and rapid advances in biomass feedstock and conversion technologies; availability of large volumes of sustainable biomass feedstock; demonstration and deployment of large scale, integrated biofuels production facilities; and development of an adequate biofuels infrastructure. Although significant progress has been recently made towards commercialization of cellulosic ethanol, there are still economic, social and environmental challenges that need to be addressed. A minimum profitable ethanol selling price of $2.50/gallon can compete on an energy-adjusted basis with gasoline derived from

oil costing $75-$80/barrel. At the lower oil prices ($45 - $50/barrel), cellulosic technology may not be as competitive and could require policy supports and regulatory mandates to drive the market. The biofuels and bioproducts strategies need to be based on a thorough assessment of opportunities and costs associated with the upward pressure on food prices, intensified competition for land and water, and deforestation. As the feedstock costs comprise more than 20% of the production costs, it has now been recognized that biomass waste such as agricultural and forest waste can provide a cost-effective alternative to improve the economic viability of bioethanol production (Zheng et al., 2009).

Due to the increasing off-shore competition, global movement and incentives for green fuels and chemicals, the North American pulp and paper and other fiber processing industries need to create additional revenues and diversify their products and markets to remain competitive. To achieve this, the forest-based industries, and in particular the pulp and paper industry, need to evolve into integrated forest biorefineries (IFBR). IFBR is defined as a processing and conversion facility that fully integrates forest biomass and other biomass waste for simultaneous production of marketplace products, including fibers for pulp and paper products, fuels, chemicals and materials (Fig. 1).

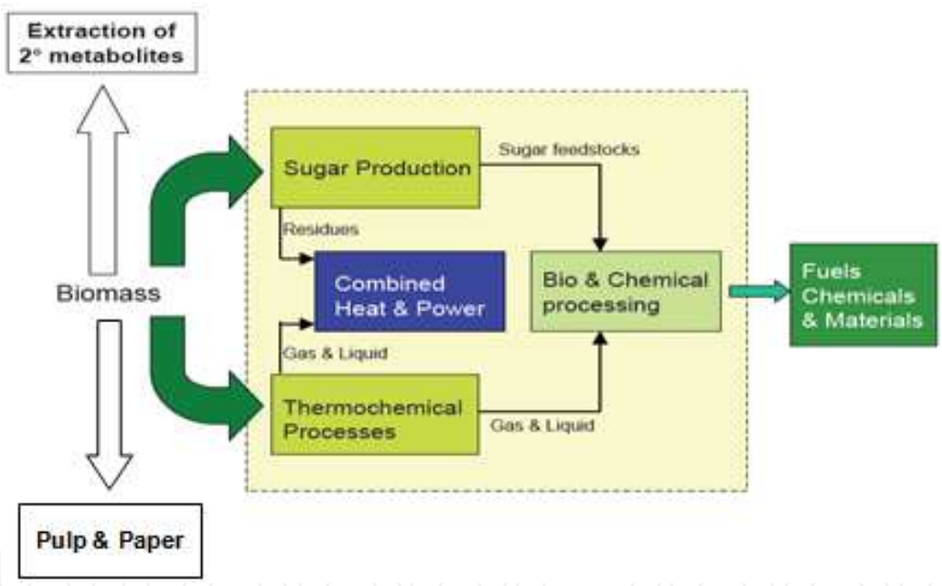


Fig. 1. The Integrated Forest Biorefinery (IFBR) concept

The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Co-products of biofuels production, such as corn gluten feed and meal, corn oil, glycerin, natural plastics, fibers, cosmetics, liquid detergents and other bioproducts, also increase with biofuel production. Currently, however, of the 100 million metric tons of chemicals produced annually in the US, only about 10% are biobased (National Academy Press, 2000).

Based on the billion ton vision of the US DOE, nearly 400 million tons of hemicellulose are available in US per annum for bioprocessing to fuels and chemicals. In addition, every year approximately 15 million tons of hemicellulose are produced by the pulp and paper industry alone, and according to preliminary results, this can yield in excess of 2 billion

gallons of ethanol and 600 million gallons of acetic acid, with a net cash flow of $3.3 billion. Unfortunately, during the current fiber processing of woody feedstocks such as pulping and bleaching, hemicellulose is not efficiently utilized and often discarded as industrial waste with limited usage. However, a number of bioproducts such as biochemicals and biomaterials can be produced from biomass hemicellulose to enhance the value extracted from wood fiber and improve the process economics in a forest-based biorefinery. The aim of this paper was to review the potential of hemicellulose and its monomers derived from pulp and paper processing of wood for production of biofuels and value-added bioproducts.

2. Hemicellulose

The lignocellulosic biomass has an estimated annual production on earth of about 60 billion tons. Biomass is composed of three major polymers – cellulose, hemicelluloses and lignin - and their ratio, composition and structure determine biomass properties. Hemicellulose forms an interface in the cell wall matrix with binding properties mediated by covalent and non-covalent interactions with lignin, cellulose and other polysaccharides (Kato, 1981). The close association between the biopolymers in plant biomass is realized via chemical bonds, predominantly between lignin and hemicelluloses, in lignin-carbohydrate complexes (LCCs) that include benzyl-ether, benzyl-ester and phenyl-glycoside types of linkages. The cellulose and hemicelluloses form the carbohydrate composition of lignocelluloses (Fig. 2).

2.1 Hemicellulose composition of wood

Overall, hardwoods contain on average less lignin and extractives and more hemicellulose than softwoods (Table 1). In hardwoods, the major hemicellulose component is the *O*-acetyl-4-*O*-methylglucuronoxylan, whereas in the softwood species, the *O*-acetyl-galactoglucomannan is the predominant one (Fengel & Wegener, 1984). The building blocks of hemicelluloses are hexoses (glucose, mannose and galactose) and pentoses (xylose and arabinose) which exist in a pyranose (*p*) and furansose (*f*) forms (α and β).

Due to the lower degree of polymerization (DP), the chemical and thermal stability of hemicelluloses is lower and their alkali solubility – higher than that of cellulose. Whereas cellulose is present in all plants as a ß-1,4-glucose polymer with a non-branching structure, xylan is composed of ß-1,4-linked xylose units forming a xylan backbone with a DP of 150-200 and of side chains connected to the backbone (Table 2).

Wood components	**Hardwoods**	**Softwoods**
Cellulose	40-50	45-50
Hemicellulose	22-35	20-30
(Galacto)glucomannan	2-5	15-20
Glucuronoxylan	20-30	5-10
Lignin	20-30	25-35
Extractives	1-5	3-8

Table 1. Chemical composition of wood

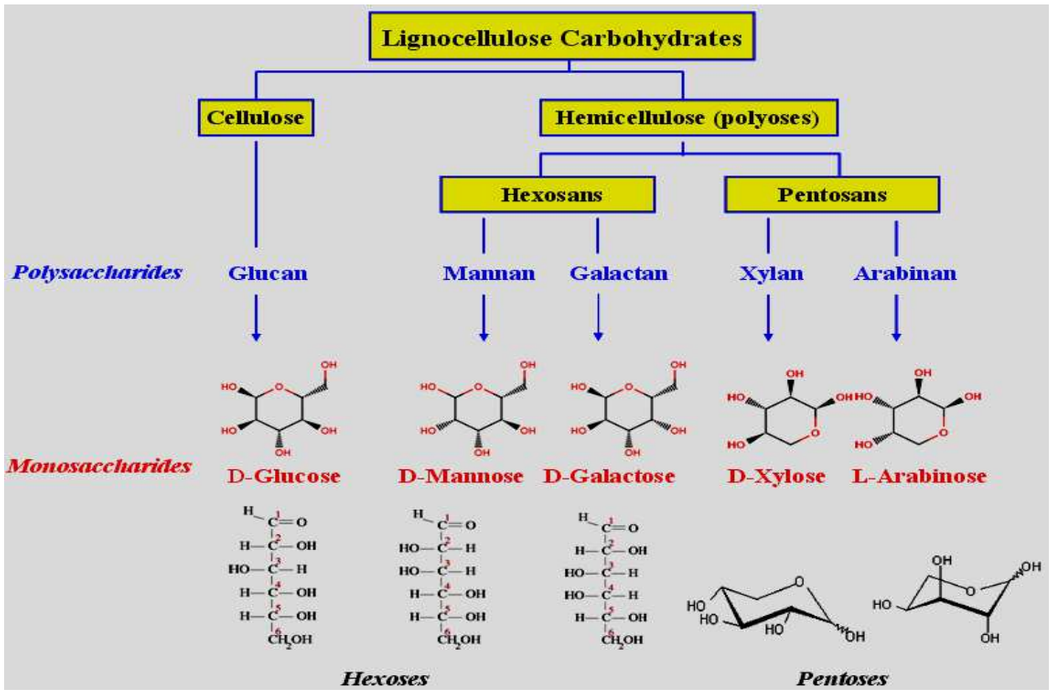


Fig. 2. Chemical structure of lignocellulose carbohydrates

2.2 Hemicellulose structure in wood

The composition and structure of hemicellulose are more complicated than that of cellulose and can vary quantitatively and qualitatively in various woody species (Fengel & Wegener, 1984). Typically, softwoods have more mannose and galactose and less xylose and acetyl groups than hardwoods (Table 2). The side-chain groups in xylan differ depending on the plant origin. The hardwood xylans as complex heteropolysaccharides comprising β-1,4-linked D-xylopyranose units are highly substituted (Sjöstrom, 1993). The xylopyranose unit of the xylan main chain can be substituted at the C2 and/or C3 positions with acetic acid (at both C2 and C3 position in hardwoods), 4-O-methylglucuronic acid (at C2 position in both hardwoods and softwoods), and arabinose (at C3 position in softwoods). The latter may be further esterified by phenolic acids which crosslink xylan and lignin in LCCs in the cell wall matrix.

In hardwoods, *O*-acetyl-4-*O*-methylglucuronoxylan is the main hemicellulose component constituting 20-30% of the wood material. The uronic acid groups in hardwood xylans are not evenly distributed, with 2-3 substituents per one xylose unit. In softwoods, every eight xylose residues are substituted with arabinose by α-1,3-glycosidic linkages whereas the ratio of xylose to glucuronic acid is 4:1.

The galactoglucomannans can be classified into two fractions with different galactose contents – galactose-poor fraction and galactose-rich fraction with a corresponding galactose/glucose/mannose ratio of 0.1/1/3, and 1/1/3, respectively, and acetyl content of 6% in both fractions. The softwood xylan is a linear polymer of D-xylopyranose units slightly branched with 1-2 side chains of arabinofuranose and glucoronic acid per molecule. The degree of substitution of hardwood xylan with acetyl groups can vary from 8 to 17%

corresponding to 3.5-7 acetyl groups per 10 xylose units, and on average every second xylose unit is acetylated.

Hemicellulose	Amount (%)	Units	Bond	Molar ratios	Solubility	DP
Hardwood						
Acetylglucuronoxylan	15-30	β-D-Xyl*p* 4-*O*-Me-α-D-Glc*p*A Acetyl	1-4 1-2	10 1 7	Alkali DMSO*	200
Glucomannan	2-5	β-D-Man*p* β-D-Glc*p*	1-4 1-4	1-2 1	Alkaline borate	200
Softwood						
Acetylgalactoglucomannan	15-23	β-D-Man*p* β-D-Glc*p* α-D-Gal*p* Acetyl	1-4 1-4 1-6	3 1 1 1	Alkali Water*	100
Arabinogalactan	2-5	β-D-Gal*p* α-L-Ara*f* β-L-Ara*p* β -D-Glc*p*A	1-3 1-6 2/3 1/3 Little	6 1-6 1-3 1-6	Water	200
Arabinoglucuronoxylan	5-10	β-D-Xyl*p* 4-O-Me-α-D-Glc*p*A α-L-Ara*f*	1-4 1-2 1-3	10 2 1.3	Alkali DMSO* Water*	100

*Partially soluble

Table 2. Hemicellulose structure in wood

2.3 Hemicellulose behavior during pulping

During kraft pulping of wood chips, xylan and mannan are partially depolymerized, debranched and solubilized in the cooking liquor (Casebier & Hamilton, 1965). Subsequent losses of hemicellulose occur during the heating period of the kraft cook thereby about 40% of xylan is lost and glucuronic acid is converted to hexenuronic acid by ß-elimination reactions. By the end of the cook, 60-70% of the glucuronosyl and 10% of the arabinosyl substituents in softwood xylan are removed. Due to a pH drop in the pulping liquor caused by debranched acetyl residues towards the end of pulping, part of dissolved xylan, lignin and lignin-xylan complexes are reprecipitated back onto the fiber surface. The extent of this readsorption depends on the alkaline cooking conditions and wood species, however, the reprecipitated xylan has a low molecular weight without side-chain groups and a high degree of crystallinity (Gustavsson & Al-Dajani, 2000). For instance, half the xylan content of pine kraft pulp is estimated as relocated xylan whereas up to 14% of birchwood xylan can be reprecipitated during kraft pulping.

During acid sulfite pulping, redeposition of xylans onto the fiber surface has not been observed. The possible reasons for this would be that the harsh cooking conditions and presence of acid-resistant residual acetyl and 4-*O*-methylglucuronic acid groups act as

barriers against the adsorption and intercrystallization of xylan onto the cellulose micromolecules. Significant amounts of xylans are hydrolyzed and solubilized in the sulfite pulping process. For instance, in sulfite cooking of birch only 45% of the original xylan remains in pulp after 20 min and its original DP of 200 is reduced to less than 100.

The bonds between the pentose units (arabinose and xylose) are hydrolyzed much more rapidly than the glycopyranosidic bonds. However, the glucuronic acid-xylose and xylose-acetic acid linkages are relatively more resistant to the acid hydrolysis conditions and little cellulose is lost in the sulfite cook (Kerr & Goring, 1975). The degradation products of the hemicellulose acid hydrolysis appear in the cooking liquor in the following approximate order: arabinose> galactose> xylose> mannose> glucose> acetic acid> glucuronic acid. In the above order, glucose is derived mostly from the glucomannan rather than cellulose polymer. Thus, the residual xylan in sulfite pulps is less accessible since it is localized mainly in the secondary cell walls, although the xylan distribution across the cell wall is more uniform than in kraft pulps.

3. Hemicellulose-degrading enzymes

Due to its complex structure, the complete breakdown of naturally occurring branched hemicelluloses requires the action of several enzymes with different functions. These are classified in two groups, hydrolases and esterases, based on the nature of linkages that they can cleave. The glycosyl hydrolases are involved in the enzymatic hydrolysis of the glycosidic bonds of hemicellulose. Due to the complex nature of hemicelluloses and their enzymatic hydrolysis, only xylan-degrading enzymes will be presented and discussed in this paper.

3.1 Enzymatic hydrolysis of xylan

Of major importance are the endo-β-1,4-xylanases or 1,4-β-D-xylan xylanohydrolases (3.2.1.8) that can randomly hydrolyze internal xylosidic linkages on the backbone of xylan polysaccharide. The main products formed from xylan hydrolysis by xylanase are xylobiose, xylotriose and substituted xylooligosaccharides depending on the mode of action of the particular enzyme (Table 3). The xylooligomers liberated by xylanase are converted to xylose by 1,4-ß-D-xylosidase (EC 3.2.1.37). The so-called accessory enzymes such as acetyl xylan esterases, phenolic acid esterases, arabinofuranosidases and glucuronidases cleave side groups from the xylan backbone. All xylanolytic enzymes act synergistically in xylan hydrolysis (Fig. 3).

Xylanases can be classified structurally into two major groups, family 10 and family 11. Family 10 enzymes have a relatively high molecular weight whereas family 11 xylanases are relatively low molecular weight with low or high pI values. The release of reducing sugars from xylan however has not been shown to correlate to the family belonging of enzyme. The enzyme-substrate interaction is dependent on substrate specificity and kinetic properties of enzyme and can be influenced by pH, presence of xylan binding domain and ionic strength of protein and xylan molecule. Since xylan is negatively charged due to the presence of glucuronic acid side-chain groups, the efficiency of binding of enzyme to xylan is affected by the pH of reaction and pI of protein. For instance, if pH is below the pI value, the enzyme can be completely bound to the polysaccharide. The xylanolytic enzyme system of a variety

of microorganisms have been extensively investigated and several exhaustive reviews have appeared (Coughlan & Hazelwood, 1993; Viikari et al., 1993; Wong et al., 1988).

Enzyme	Mode of action
Endo-xylanase	Hydrolyses interior β-1,4-xylose bonds of xylan backbone
Exo-xylanase	Releases xylobiose from xylan backbone
β-Xylosidase	Releases xylose from xylobiose
α-Arabinofuranosidase	Hydrolyses α-arabino-furanose from xylan
α-Glucurosidase	Releases glucuronic acid from glucuronoxylans
Acetyl xylan esterase	Hydrolyses acetyl ester bonds in acetyl xylans
Ferulic acid esterase	Hydrolyses feruloyl ester bonds in xylans
ρ-Coumaric acid esterase	Hydrolyses ρ-coumaryl ester bonds in xylans

Table 3. Xylan-degrading enzymes

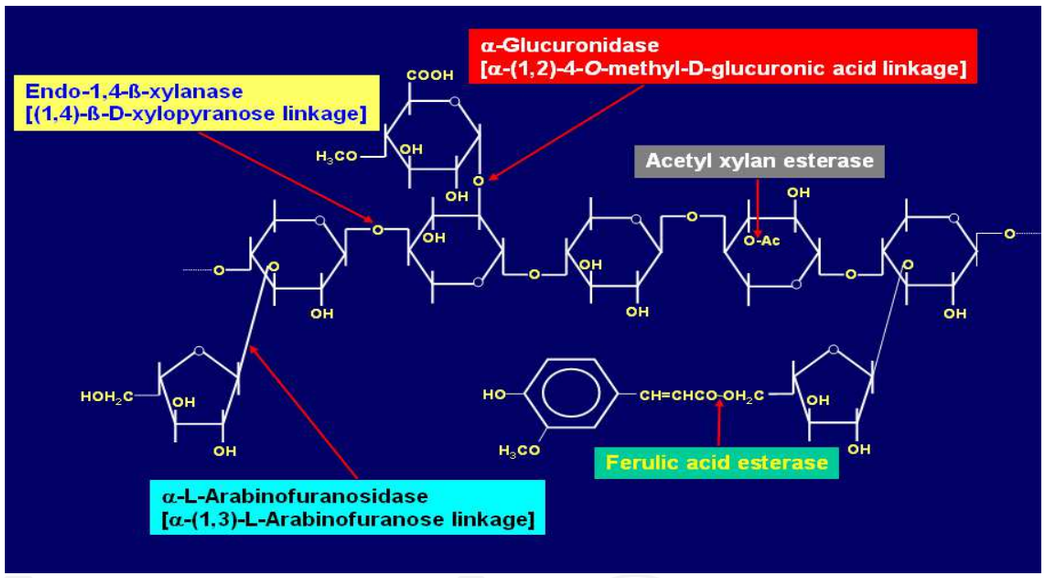


Fig. 3. Enzymatic hydrolysis of xylan

3.2 Production of xylan-degrading enzymes

The optimization of fermentation techniques and isolation of more efficient microbial strains has led to a significant increase in the production rates of xylanase. Fungal systems are excellent xylanase producers, but often co-secrete cellulases which can adversely affect pulp quality. One way of overcoming this is by using suitable separation methods to purify xylanases from contaminating cellulase activity. This approach however is expensive and impractical. By applying appropriate screening methods and selection of growth conditions, it is possible to isolate naturally occurring microorganisms which produce totally cellulase-free xylanases or contain negligible cellulase activity. Alternatively, genetically engineered organisms could be used to produce exclusively xylanase. Most xylanases studied are active in slightly acidic conditions (pH 4-6) and temperatures between 40 and 60°C. The current trend is however to produce enzymes with improved thermostability and activity in

alkaline conditions to fit operations at harsh industrial conditions. ß-Xylanases are produced by many microorganisms on xylan-rich substrates (Wong et al., 1988).

3.2.1 Solid state fermentation

Currently, most commercial enzymes are mainly produced in a conventional submerged fermentation (SF) process, which is an inherently expensive operation best suited for high value antibiotics and other pharmaceutical products. Solid substrate fermentation (SSF) is an economically viable alternative for enzyme production which offers numerous advantages over the SF systems as many enzymes and other biochemicals can be produced by SSF at a fraction of the cost for SF production (Szakacs et al., 2001).

The SSF allows the direct use of *in-situ* enzymes (i.e. xylanase for pulp pretreatment and bleaching) without their prior downstream processing. The substrate (i.e. paper pulp which contains xylan), which is initially used as a carbon source for enzyme production, subsequently becomes the target substrate of enzyme (xylanase) action. This approach could certainly improve the economics and enhance the efficiency of the biobleaching technology due to the operational simplicity of SSF, high volumetric productivity and concentration of enzyme and production of substrate-specific enzymes in a water-restricted environment (Szendefy et al., 2006). Advantages include high concentration of the product and simple fermentation equipment as well as low effluent generation and low requirements for aeration and agitation during enzyme production (Pandey et al., 1999). Due to the considerably lower production costs, the SSF xylanase has been shown to be more cost-efficient when compared to commercial liquid products.

3.2.2 Spent sulfite liquors

Spent sulfite liquor (SSL) results from the delignification of wood chips in an aqueous solution of acid bisulphites with an excess of SO_2, resulting in the solubilisation of lignin and leaving the wood cellulose largely undegraded (Mueller & Walden, 1970). The resultant black liquor referred to as SSL contains 50 to 65 % lignosulphonates, 15 to 22 % total sugars and 2 to 5 % volatile acids such as acetic acid. The sugars found in the SSL include xylose, mannose, galactose, arabinose and glucose. The SSL is therefore a concentrated waste with high BOD and COD levels and needs treatment prior to disposal. The utilization and recovery of the valuable organics in this effluent would, therefore, be more desirable than its simple discharge. The microbial utilisation of SSL has been studied for production of various metabolites such as lactic acid, single-cell yeast protein (Mueller & Walden, 1970) and ethanol (Kosaric et al., 1981). Recently, the use of this inexpensive carbon source as inducer of xylanase activity has also been demonstrated (Chipeta et al., 1981). Potential advantages include reduced xylanase production costs and development of effluent-free technology that impact positively on the environment.

3.3 Application of xylan-degrading enzymes

Xylan-degrading enzymes, and in particular xylanases, have a great potential in industrial processes such as saccharification of lignocellulosic biomass to fermentable sugars for production of biofuels and biochemicals, bread making, clarification of beer and juices, enzymatic retting of flax, surface softening and smoothing of jute-cotton blended fabrics

(Royer & Nakas, 1989). Nethertheless, the most important application of these enzymes to date is their use in the pulp and paper industry. Xylanases have been reported to enhance inter-fiber bonding through fibrillation without reducing pulp viscosity. Xylanase-treated pulps have shown improved beatability and brightness stability. When applied together with cellulases, xylanases can improve the drainage rates of recycled fibers and can facilitate the release of toners from office waste and the following flotation and washing steps. The xylanase production on large scale constitutes approximately 50% of the total enzyme market and the demand for xylanases grows about 25% per year, with a major application in bleaching of paper pulps.

The use of xylanases at pulp and paper mills to facilitate bleaching (biobleaching) and improve fiber properties is one the most important large-scale biotechnological applications of recent years (Onysko, 1993; Viikari et al., 1994). The enzymatic improvement in pulp bleachability depends on a number of factors such as the wood source, pulping and bleaching processes as well as properties and substrate specificity of the enzyme. Factors such as inhibitory effect of residual pulping and bleaching chemicals in pulp as well as degradation end products on xylanase efficiency, presence of xylan-lignin and xylan-cellulose bonds may as well impact on extent of xylan hydrolysis and pulp bleachability. Restrictions in the enzymatic removal of xylan from pulp have been assigned to retarded accessibility and chemical modification of residual hemicellulose. Accessibility problems arise from the fact that chemical pulping and bleaching apparently remove the more accessible portion of xylan from the cell walls, leaving the remaining part in locations, that are less accessible to xylanase. Xylanases should contain no or very low cellulase activities as cellulases prove detrimental to yield and strength properties of pulp. The bleaching efficiency of xylanase is measured either as the reduction in the amount of chemicals used for bleaching of pulp or the brightness gain induced by the enzyme. As the biobleaching effect is dependent on the amount of enzyme used, the enzyme production costs should be kept as low as possible to ensure a cost-effective bleaching process. The major benefits from the enzyme bleaching are: 1) Reduced bleaching costs; 2) Reduced chemical consumption; 3) Increased pulp throughput; and 4) Reduced pollution (Christopher, 2004). A few hypotheses exist to explain the phenomenon of xylanase-aided bleaching of pulp, although the exact mechanism is not completely understood. It should be noted that the proposed mechanisms for biobleaching are not mutually exclusive and more than one model can be involved depending on pulp type, on one side, and substrate specificity of xylanase to a specific xylan type in pulp, on another (Wong et al., 1997).

- The initial model proposed suggested that xylanases attack and hydrolyze mainly xylan redeposited on the fiber surface thereby enabling the bleaching chemicals a better and smoother access to residual lignin (Kantelinen et al., 1993). During kraft pulping, pulp xylan is first solubilized and later on part of it is redeposited back onto the pulp fibres. Xylanase acts on these reprecipitated xylans by partially hydrolysing them to facilitate extraction of lignin during pulp bleaching (Fig. 4).
- The second hypothesis suggests that xylanases can partly hydrolyze xylan that is involved in lignin-xylan complexes thereby reducing the size of these complexes and improving their mobility and extractability from the cell walls. Indirect evidence does exist that lignin-carbohydrate bonds are formed during biosynthesis and aging of wood as well as during kraft pulping and that xylose is released as the main sugar component

of isolated lignin-carbohydrate complexes. The biobleaching effect appeared to be accompanied by a decrease in the degree of polymerization of xylan and a slight reduction in xylan.

- It has also been reported that xylan-chromophore associations can be generated during alkaline pulping which contribute to pulp color and brightness reversion of pulps. A direct brightening effect has been observed following xylanase pretreatment of pulp. This could be due to a direct removal of lignin fragments involved in lignin-xylan complexes and/or removal of xylan derived chromophore structures. This hypothesis is supported by the recent findings that during the kraft cook the methylglucuronic acid of xylan can be modified to hexenuronic acid giving rise to double bond chromophore-type formations.
- Xylanases may also be able to disrupt to an extent the physical interlinking between xylan and cellulose within the fiber matrix thereby improving the fiber swelling and generating macropores to facilitate lignin removal. The biobleaching effect observed with some hardwood sulfite pulps may also be caused by an improved pulp porosity. This suggestion is based on the fact that in acid sulfite pulps, in contrast to kraft pulps, xylan is not reprecipitated on the fiber surface but is largely entrapped across the fiber the cell walls.

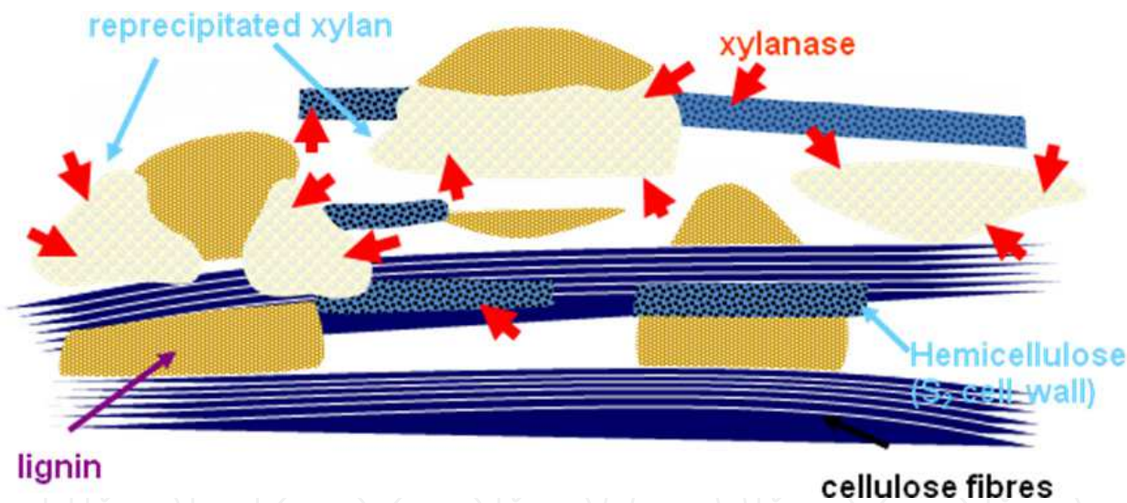


Fig. 4. Mechanism of xylanase-aided bleaching of paper pulps

3.4 Bioproducts from xylan

Hemicelluloses including xylan need to have a certain degree of purity before they can be utilized in various industrial processes. The xylan source and recovery process (extraction) directly impact the physical and chemical properties of the recovered polysaccharide and determine its applicability. Xylans can be extracted from lignocellulosic materials or partially delignified pulps. Fractionation from lignified materials yields polysaccharides with major proportions of lignin, whereas higher purity xylans are obtained when isolated from pulps, especially bleached pulps (Puls & Saake, 2004). Table 4 summarizes the major extraction, fractionation, precipitation and quantification methods and their impact xylan deacetylation and salvation.

Polymer	Extraction	Deacetylation	Solvation	Precipitation	Fractionation	Quantification
Xylan	DMSO KOH NaOH Alkaline peroxide Water (steam)	NaOH KOH Water (partial)	DMSO	Acidification (CH_3COOH) Solvents (C_2H_5OH)	Increasing gradient of alkali	Acid/enzyme hydrolysis Sugar/lignin analysis

Table 4. Xylan extraction methods

However, the properties of xylans have not been fully characterized, defined and exploited. Although annual plants have been proven a rich source of xylan, because of the difficulties in extraction and purification of xylans and hemicellulose in general, an efficient isolation process has never been realized (Ebringerova & Heize, 2000). Table 5 summarizes some of the most important current and potential applications of xylan in the pulp and paper, pharmaceutical, chemical, food and fermentation industries.

3.5 Bioproducts from xylose

3.5.1 Ethanol

For the economic production of ethanol from lignocellulosics, the fermentation of both glucose and xylose is an economic necessity. Unfortunately most yeasts including *Saccharomyces cerevisiae* do not ferment xylose. On the other hand, bacterial fermentations are associated with low ethanol yields, slow fermentation rates, byproduct formation (acids) which requires additional product separation, contamination problems due to the neutral pH requirements for bacterial growth, bacterial sensitivity to inhibitors and intolerance to high ethanol concentrations. To overcome these problems, two major strategies have been developed (Fig. 5).

The first strategy is to introduce pentose-utilizing capability into efficient ethanol producers such as *Saccaromyces* and *Zymomonas* (Matsushika et al., 2009). Genes encoding for xylose reductase, xylose isomerase, xylose isomerise, xylulokinase, transaldolase and transketolase (Fig. 5 - blue print) are inserted to enable the pentose-phosphate pathway which enables xylose to enter the glycolysis pathway of glucose fermentation to ethanol.

Pulp and Paper	**Pharmaceutical**	**Chemical**	**Food**	**Fermentation**
• Beater additive improved swelling, porosity, drainage, strength • Fiber coating • Wood resin stabilizer	• Anticoagulant • Anti-cancer agent • Cholesterol-reducing agent • Wound treatment agent • HIV inhibitor • Tabletting material • Dietary fiber	• Thermoplastic material • Polypropylene filler • Paint formulations • Gel-forming material • Chiral polymer building blocks	• Xylose • Xylitol • Biodegradable polymers – plastics, films, coatings with increased hydrophobility and water resistance (acety xylans)	• Enzymes–xylanase, xylose isomerise • Biopolymers–polyhydroxy-alkanoates

Table 5. Major large-scale applications of xylan

Using this strategy for *Z. mobilis*, Zhang et al. (1995) achieved 85% of the theoretical ethanol yield on xylose. The second strategy targets to divert the carbon flow in *E. coli* from native fermentation products to ethanol by introducing pyruvate decarboxylase and alcohol dehydrogenase (Fig. 5 – red print). On mixed sugars (xylose and glucose), a recombinant *E. coli* produced 103-106% of the theoretical yield of ethanol (Tao et al., 2001). However, the most common problems with recombinant microorganisms that still need to be resolved are their instability, slower production rates and reduced robustness compared to the wild strains (Eliasson et al., 2000).

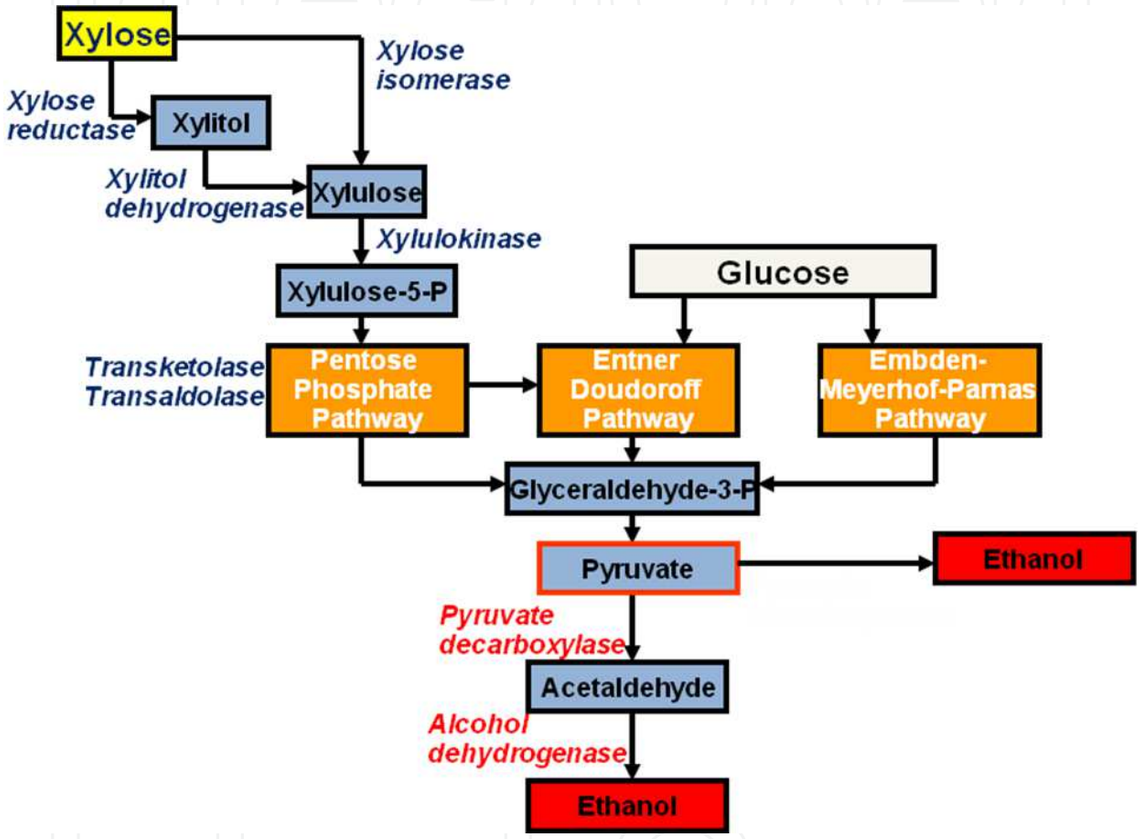


Fig. 5. Fermentation pathways of xylose to ethanol

3.5.2 Organic acids

In the last decade, microbially-produced organic acids (Mattey, 1992) find increased use in the food industry and as raw materials for manufacture of biodegradable polymers (Magnusson & Lasure, 2004). For instance, the production of D-lactic acid as well as L-lactic acid is of significant importance for the practical application of polylactic acid, which is an important raw material for bioplastics that can be produced from biomas (Okano et al., 2009) Organic acids are used in food preservation because of their effects on bacteria (Dibner & Butin, 2002). The non-dissociated (non-ionized) organic acids can penetrate the bacteria cell wall and disrupt the normal physiology of certain types of bacteria such as *E. coli*, *Salmonella* and *Campylobacter* species that are pH-sensitive and cannot tolerate a wide internal and external pH gradient. Upon passive diffusion of organic acids into the bacteria,

where the pH is near or above neutrality, the acids dissociate and the cations lower the bacteria internal pH, leading to situations that impair or stop the growth of bacteria. Furthermore, the anions of the dissociated organic acids accumulate within the bacteria and disrupt their metabolic functions leading to osmotic pressure increase that is incompatible with the bacterial survival. For example, lactic acid and its sodium and potassium salts are widely used as antimicrobials in food products, in particular, meat and poultry such as ham and sausages. Tables 6 and 7 summarize the major production organisms, substrates and uses of organic acids.

3.5.3 Xylitol

Xylitol is produced chemically by hydrogenation of xylose, which converts the sugar aldehyde into a primary alcohol (Karimkulova et al., 1989). Hydrogenation is carried out at high pressures (up to 50 atm), high temperature (80-140°C) using expensive catalysts (Nickel Raney) and expensive purification processes (Mikkola et al., 2000). The xylitol yields are low – on average 50-60% from xylan. The drawbacks of the chemical process can be overcome by using a biological route of xylitol production that is carried out by microorganisms at low temperature (30-35°C). The microbial conversion employs naturally fermenting yeasts (*Candida*) such as *C. tropicalis and C. guillermondi* that yield of 65-90% from xylan.

Organic acid	**Production organism**	**Substrate**	**State**
Citric	*A. niger*	Sugar cane molasses, corn syrups, lignocellulose, agri- and food waste	Commercial
Gluconic	*A. niger*	Glucose, glucose corn syrups	Commercial
Lactic	*L. delbrueckii* *A. oryzae*	Xylose, glucose, starch, cellulose, newspaper, MSW (xylose, mannose)	Commercial
Itaconic	*A. terreus*	Sugar cane molasses, corn syrups, xylose	Commercial
Fumaric	*Rhyzopus* spp.	glucose, sucrose, sugar cane molasses, corn syrups, starch, xylose	Experimental
Malic	*Brevibacterium*	Fumaric acid	Commercial
Aspartic	*E. coli*	Fumaric acid + NH_3	Commercial
Succinic	*A. succiniciproducens* *A. succinogenes* *E. coli* (recombinant)	Glucose, sugar cane molasses Glucose, xylose	Experimental

Table 6. Production of organic acids from xylose

Alternatively, recombinant strains containing a xylose reductase gene (i.e. recombinant *S. cerevisiae*) can be used with a very high production yield of 95% from the theoretical maximum. The microbially produced xylitol requires less purification than the chemical process (Prakasham et al., 2009). Due to its anti-cariogenic and anti-plaque action (Trahan, 1995), xylitol is used around the world as a sweetener in chewing gums, pastilles, and oral hygiene products such as toothpaste, fluoride tablets and mouthwashes. More than 10% of its use in sugar-free chewing gums which have a world market of more than $12 million per annum. Due to its structure, xylitol is a non-fermentable sugar alcohol with dental health

benefits in caries prevention, showing superior performance to other polyols (polyalcohols). Its plaque-reducing effect is manifested by attracting and starving harmful micro-organisms because cariogenic bacteria prefer fermentable six-carbon sugars as opposed to the nonfermentable xylitol (Milgrom et al., 2006).

Possessing approximately 40% less food energy, xylitol is a low-calorie alternative to table sugar. Absorbed more slowly than sugar, it does not contribute to high blood sugar levels or the resulting hyperglycemia caused by insufficient insulin response. Its glycemic index is approximately 10-fold lower than that of sucrose (Fig. 6). This characteristic has also proven beneficial for people suffering from metabolic syndrome, a common disorder that includes insulin resistance, hypertension, hypercholesterolemia, and an increased risk for blood clots.

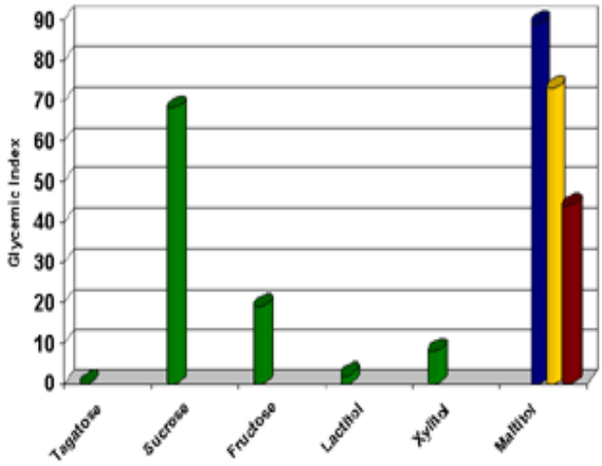


Fig. 6. Glycemic index of xylitol in comparison to other sweeteners

Xylitol also has potential as a treatment for osteoporosis - it prevents weakening of bones and improves bone density (Mattilla et al., 2002). Studies have shown xylitol chewing gum can help prevent ear infections (Uhari et al., 1998). When bacteria enter the body, they adhere to the tissues using a variety of sugar complexes. The open nature of xylitol and its ability to form many different sugar-like structures appears to interfere with the ability of many bacteria to adhere. Xylitol is also one of the building block chemicals that can be used in production of ethylene glycol, propylene glycol, lactic acid, xylaric acid, and for synthesis of unsaturated polyester resins, antifreeze, etc.

3.5.4 Enzymes

As discussed in 3.2, xylan-containing substrates, and in some instances xylose, can serve as inducers for production of xylan-degrading enzymes including xylanase. Another enzyme of importance that can be produced on these substrates is xylose isomerise (EC 5.3.1.5). This enzyme is used industrially to convert glucose to fructose in the manufacture of high-fructose corn syrups, HFCS (Bhosale et al., 1996). HFCS is produced by milling corn to produce corn starch which is first treated with alpha-amylase to produce shorter chains oligosaccharides and then with glucoamylase to produce glucose. Finally, xylose isomerase (also known as glucose isomerase) converts glucose to a mixture of about 42% fructose and

Organic acid	Application
Citric (Kubicek et al., 1980)	70% in food, confectionary and beverage products, 30% pharmaceuticals (anticoagulant blood preservative, antioxidant) & metal cleaning. Selling price decreased with market shift from pharmaceuticals to food applications (879,000 metric tons produced in 2002)
Lactic (Yang et al., 1995)	Acidulant, flavor enhancer, food preservative, feedstock for calcium stearoyl-2-lactylates (baking), ethyl lactate (biodegradable solvent) and polylactic acid plastics (100% biodegradable) for packaging, consumer goods, biopolymers (approved by FDA). Estimated US consumption 30 million lb with 6% growth pa. Potential demand 5.5 billion lb as very large volume-commodity chemical
Itaconic (Kautola et al., 1985)	Feedstock for syntheses of polymers for use in carpet backing and paper coating N-substituted pyrrolidinones for use in detergents and shampoos. Cements comprising copolymers of acrylic and itaconic acid
Aspartic (Dunn & Smart, 1950)	For synthesis of aspartame, monomer for manufacture of polyesters, polyamides, polyaspartic acid as a substitute for EDTA with potential market of $450 million per year
Fumaric (Overman & Romano, 1969)	For manufacture of synthetic resins, biodegradable polymers, intermediate in chemical and biological synthesis
Malic (Peleg et al., 1989)	Acidulant in food products, citric acid replacement, raw material for manufacture of biodegradable polymers, for treatment of hyperammoemia, liver dysfunction, component for aminoacid infusions
Succinic (Zeikus et al., 1999)	Acidulant, pH modifier, flavoring and antimicrobial agent, ion chelator in electroplating to prevent metal corrosion, surfactant, detergent, foaming agent, for production of antibiotics, amino acids, pharmaceuticals. Market potential of 270,000 t in 2004, US domestic market estimated at $1.3 billion per year with 6-10% annual growth

Table 7. Applications of organic acids

50–52% glucose (HFCS-42) with some other sugars mixed in. This 42–43% fructose-glucose mixture is then subjected to a liquid chromatography step, where the fructose is enriched to about 90% and then back-blended with 42% fructose to achieve a 55% fructose final product (HFCS-55). While the relatively inexpensive alpha-amylase and glucoamylase enzymes are added directly to the slurry and used only once, the more costly xylose isomerase is packed into columns and used repeatedly until it loses its activity. Thus, production of HFCS using xylose isomerase is the major application of immobilized enzyme technology (Parker et al., 2010).

The most widely used varieties of high-fructose corn syrup are HFCS-55 (mostly used in soft drinks) and HFCS-42 (used in many foods and baked goods). In the US, HFCS is among the sweeteners that have primarily replaced sucrose. Factors for this include governmental production quotas of domestic sugar, subsidies of US corn, and an import tariff on foreign sugar, all of which combine to raise the price of sucrose to levels above those of the rest of the world, making HFCS less costly for many sweetener applications. Pure fructose is the sweetest of all naturally occurring carbohydrates and 1.73 times as sweet as sucrose (Hyvonen & Koivistoinen, 1982). Fructose has the lowest glycemic index (GI = 19) of all the natural sugars and may be used in moderation by diabetics. In comparison, ordinary table sugar (sucrose) has a GI of 65 and honey has a GI of 55. Per relative sweetness, HFCS-55 is

comparable to sucrose. Currently, HFCS dominate industrial sugar market in the US. The average American consumed approximately 17.1 kg of HFCS in 2008 versus 21.2 kg of sucrose. In Japan, HFCS consumption accounts for one quarter of total sweetener consumption. The world market for HFCS was 5 million tons in 2004.

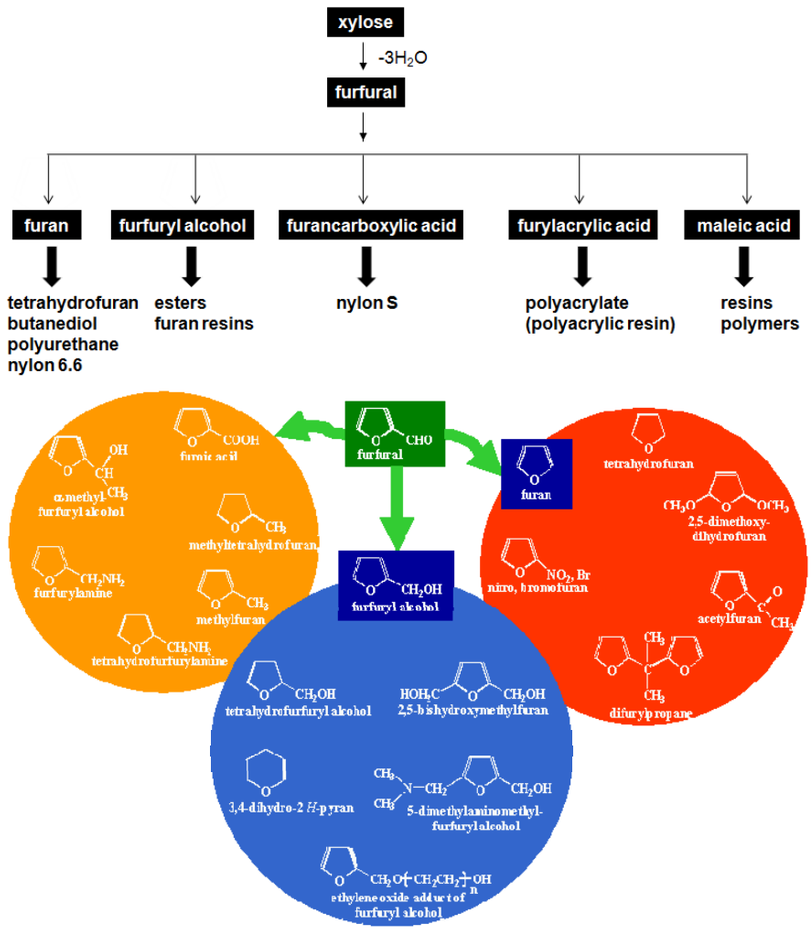


Fig. 7. Furfural-based applications

3.5.5 Furfural

When heated with sulfuric acid, hemicellulose (xylan) undergoes hydrolysis to yield monosugars (xylose). Under the same conditions of heat and acid, xylose and other five carbon sugars undergo dehydration, losing three water molecules to become furfural (Fig 7). Furfural and water evaporate together from the reaction mixture, and separate upon condensation. Biomass agri-wastes like cornstalks, corncobs and the husks of peanuts and oats are rich in xylan and about 10% of the mass these plant residues can be recovered as furfural (Zeitsch, 2000). Furfural represents a renewable building block chemical which is currently regaining attention as a biobased alternative for the production of industrial and household chemicals (Mamman et al., 2008) - from antacids and fertilizers to plastics and paints (Fig. 6). The global production capacity is about 450,000 tons as of 2004. China is the biggest supplier of furfural, and accounts for around half of the global capacity. The

world production of furfural in 2005 was about 250,000 t/a, at a stable price of $1,000/t and it is being projected to 225 thousand metric tons per annum (Win, 2005).

4. Hemicellulose-based biorefinery

A diagram of a biorefinery based on generation of primary and secondary bioproducts from hemicelluloses is presented in Fig. 8. It illustrates the enormous potential that hemicelluloses have to produce high-value products that can enhance the economics of the integrated production of biofuels, biochemicals and biopolymers (Zhang, 2008). There are however technological and socio-economic challenges that still need to be overcome to make these processes viable (Carvalheiro et al., 2008). The technological challenges are related to optimization of process conditions to maximize biorefinery-derived value such as 1) improvements in extraction efficiency of hemicellulose for minimal sugar degradation while preserving the pulp and paper properties; 2) improvements in pentose fermentation and tolerance of microbial producers to inhibitors and ethanol. A further process integration would reduce the number of processing steps, decrease energy needs and reuse process streams. The socio-economic challenges need to address the 1) complex systems of policies and regulations in different countries and make them more compatible; 2) environmental impact of biomass removal; 3) pressure from environmental groups on policy makers; and 4) unstable commodity prices.

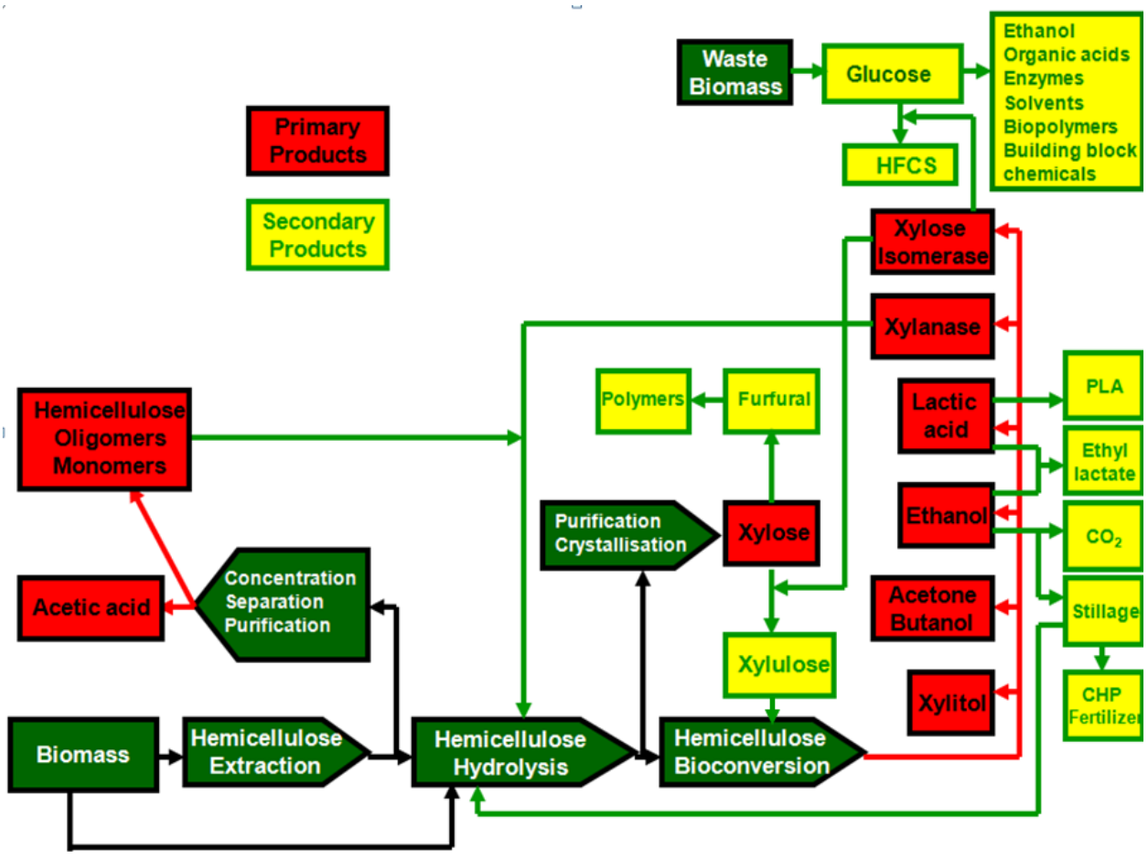


Fig. 8. Schematic of a hemicellulose-based biorefinery

5. Conclusion

Hemicellulose is the second most abundant polysaccharide after cellulose and comprises about 25-30% of the lignocellulosic biomass, which has an estimated annual production on earth of about 60 billion tons. The US Department of Energy has recently projected that annually more than 1.3 billion tons of biomass could be produced on a sustainable basis which could provide about 30% of the country's demand for transportation fuels. About a third of the biomass resources in US are wood-based. Due to the increasing off-shore competition, global movement and incentives for green fuels and chemicals, the North American pulp and paper and other fiber processing industries need to create additional revenues and diversify their products and markets to remain competitive. To achieve this, these forest-based industries need to evolve into integrated forest biorefineries. Based on the billion ton vision, nearly 400 million tons of hemicellulose are available in US per annum for bioprocessing to fuels and chemicals. In addition, every year approximately 15 million tons of hemicellulose are produced by the pulp and paper industry alone, and according to preliminary results, this can yield in excess of 2 billion gallons of ethanol and 600 million gallons of acetic acid, with a net cash flow of $3.3 billion. Unfortunately, during the current fiber processing of woody feedstocks, hemicellulose is not efficiently utilized and often discarded as agri-waste or industrial effluents with limited usage. However, a number of bioproducts including biofuels, biochemicals and biomaterials can be produced from biomass hemicellulose to enhance the value extracted from wood fiber and improve the process economics in a forest-based biorefinery.

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