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REVIEW PAPER

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Hemicellulose bioconversion

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Abstract Various agricultural residues, such as corn fiber, corn stover, wheat straw, rice straw, and sugarcane bagasse, contain about 20–40% hemicellulose, the second most abundant polysaccharide in nature. The conversion of hemicellulose to fuels and chemicals is problematic. In this paper, various pretreatment options as well as enzymatic saccharification of lignocellulosic biomass to fermentable sugars is reviewed. Our research dealing with the pretreatment and enzymatic saccharification of corn fiber and development of novel and improved enzymes such as endo-xylanase, *β*-xylosidase, and α-L-arabinofuranosidase for hemicellulose bioconversion is described. The barriers, progress, and prospects of developing an environmentally benign bioprocess for large-scale conversion of hemicellulose to fuel ethanol, xylitol, 2,3-butanediol, and other value-added fermentation products are highlighted.

Keywords Hemicellulose · Arabinoxylan · Bioconversion · Hemicellulase · Xylanolytic enzymes

Introduction

Hemicelluloses, the second most common polysaccharides in nature, represent about 20–35% of lignocellulosic biomass. Xylans are the most abundant hemicelluloses. In recent years, bioconversion of hemicellulose has received much attention because of its practical applications in various agro-industrial processes, such as efficient conversion of hemicellulosic biomass to fuels and chemicals, delignification of paper pulp, digestibility enhancement of animal feedstock, clarification of juices, and improvement in the consistency of beer [134, 139, 144]. Enzymes that degrade, or help to degrade, hemicellulose are of great interest to the paper and pulp industry due to their bleach-boosting properties (biobleaching of pulp), which reduces environmentally unfriendly chlorine consumption [91, 135]. Cellulase-free xylanase can facilitate lignin removal from paper pulp without any harmful effect. The utilization of hemicellulosic sugars is essential for efficient conversion of lignocellulosic materials to fuel ethanol and other value-added fermentation products. Xylan-degrading enzymes hold great promise in saccharifying various pretreated agricultural and forestry residues to fermentable sugars. Other potential applications of hemicellulases include biopulping of wood, coffee processing, fruit and vegetable maceration, and preparation of high fiber baked goods [19]. In addition, xylan-degrading enzymes play a great role in elucidating the structures of complex xylans. In this article, a brief review on the bioconversion of hemicellulose—particularly arabinoxylans present in various agricultural residues—to fuel ethanol, xylitol and 2,3-butanediol, is presented.

Structure of hemicellulose

Hemicelluloses are heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids. Unlike cellulose, hemicelluloses are not chemically homogeneous. Hardwood hemicelluloses contain mostly xylans, whereas softwood hemicelluloses contain mostly glucomannans [84]. Xylans of many plant materials are heteropolysaccharides with homopolymeric backbone chains of 1,4-linked *β*-D-xylopyranose units. Besides xylose, xylans may contain arabinose, glucuronic acid or its 4-*O*-methyl ether, and acetic, ferulic, and *p*-coumaric acids. The frequency and composition of branches are dependent on the source of xylan [1]. The backbone consists of *O*-acetyl, α-L-

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arabinofuranosyl, α-1,2-linked glucuronic or 4-*O*-methylglucuronic acid substituents. However, unsubstituted linear xylans have also been isolated from guar seed husk, esparto grass, and tobacco stalks [35]. Xylans can thus be categorized as linear homoxylan, arabinoxylan, glucuronoxylan, and glucuronoarabinoxylan.

Xylans from different sources, such as grasses, cereals, softwood, and hardwood, differ in composition. Birch wood (Roth) xylan contains 89.3% xylose, 1% arabinose, 1.4% glucose, and 8.3% anhydrouronic acid [68]. Rice bran neutral xylan contains 46% xylose, 44.9% arabinose, 6.1% galactose, 1.9% glucose, and 1.1% anhydrouronic acid [126]. Wheat arabinoxylan contains 65.8% xylose, 33.5% arabinose, 0.1% mannose, 0.1% galactose, and 0.3% glucose [51]. Corn fiber xylan is one of the complex heteroxylans containing β-(1,4)-linked xylose residues [117]. It contains 48–54% xylose, 33–35% arabinose, 5–11% galactose, and 3–6% glucuronic acid [31]. About 80% of the xylan backbone is highly substituted with monomeric side-chains of arabinose or glucuronic acid linked to *O*-2 and/or *O*-3 of xylose residues, and also by oligomeric side chains containing arabinose, xylose, and sometimes galactose residues (Fig. 1) [122]. A model for the corn fiber cell wall is shown in Fig. 2 [121]. The heteroxylans, which are highly cross-linked by diferulic bridges, constitute a network in which the cellulose microfibrils may be imbedded. Structural wall proteins might be cross-linked together by isodityrosine bridges and with feruloylated heteroxylans, thus forming an insoluble network [60]. In softwood heteroxylans, arabinofuranosyl residues are esterified with *p*-coumaric acids and ferulic acids [88]. In hardwood xylans, 60–70% of the xylose residues are acetylated [131]. The degree of polymerization of hardwood xylans (150–200) is higher than that of softwoods (70–130).

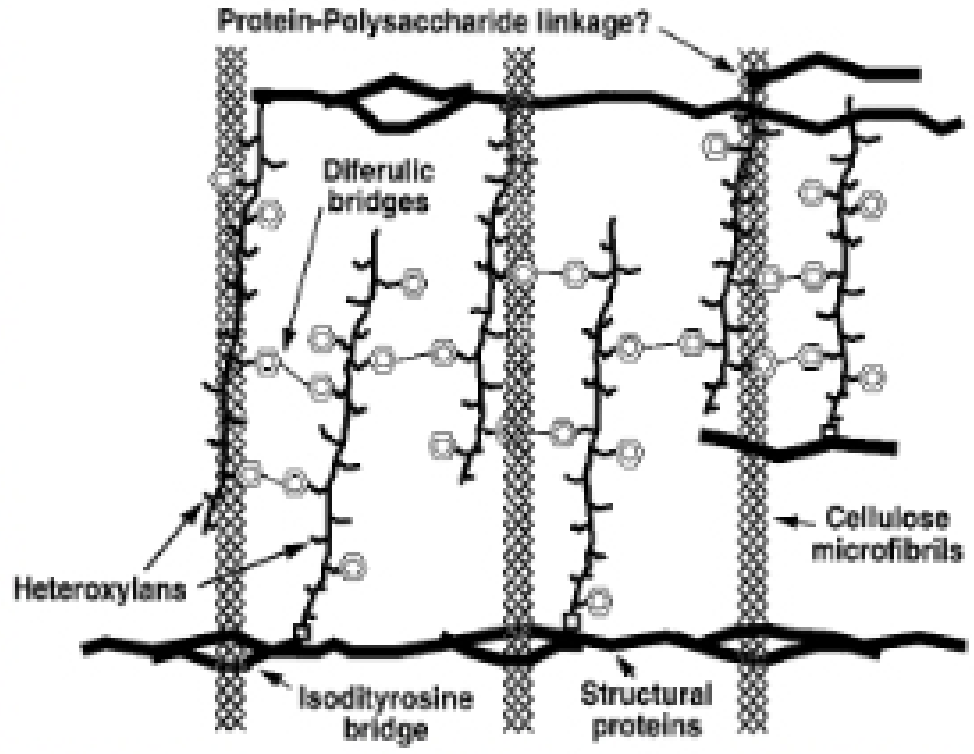

Fig. 2 Model for corn fiber cell walls. Reprinted from [121], with permission from John Wiley & Sons on behalf of SCI

Pretreatment of hemicellulose

Lignocellulosic biomass includes various agricultural residues (straws, hulls, stems, stalks), deciduous and coniferous woods, municipal solid wastes, waste from the pulp and paper industry, and herbaceous energy crops. The compositions of these materials vary. The major component is cellulose (35–50%), followed by hemicellulose (20–35%) and lignin (10–25%). Table 1 gives the composition of some lignocellulosics. Proteins, oils, and ash make up the remaining fraction of lignocellulosic biomass [140]. The structure of these materials is very complex, and native biomass is generally resistant to an enzymatic hydrolysis. In the current model of the structure of lignocellulose, cellulose fibers are embedded in a lignin-polysaccharide matrix.

Fig. 1 Schematic structure of corn fiber heteroxylan. Reprinted from [122], with permission from Elsevier, Amsterdam

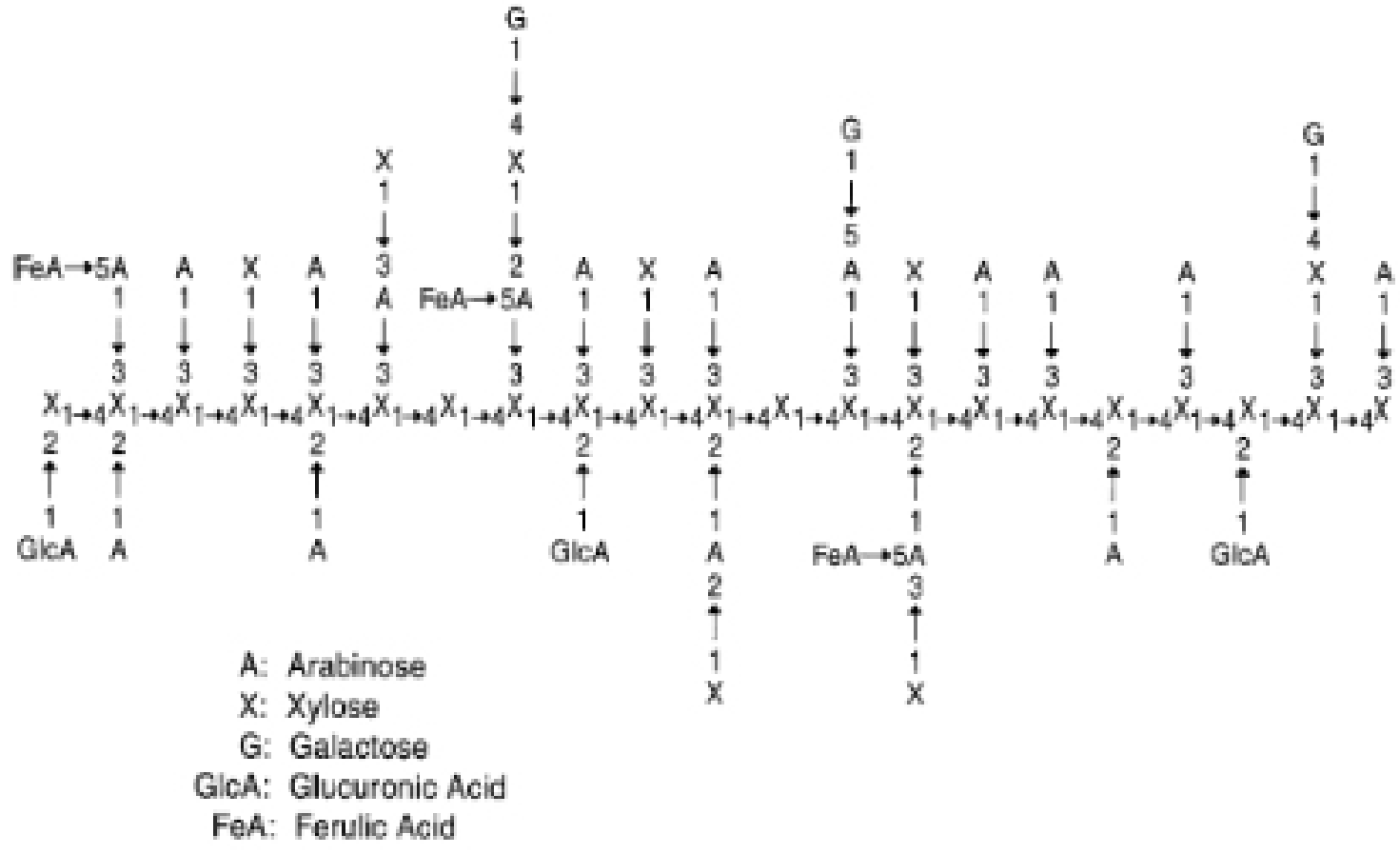

Table 1 Composition of some agricultural lignocellulosic biomass

	Composition (%, dry basis)		
	Cellulose	Hemicellulose	Lignin
Corn fiber[a]	15	35	8
Corn cob	45	35	15
Corn stover	40	25	17
Rice straw	35	25	12
Wheat straw	30	50	20
Sugarcane bagasse	40	24	25
Switchgrass	45	30	12
Coastal bermuda grass	25	35	6

[a] Contains20% starch

Xylan may play a significant role in the structural integrity of cell walls by both covalent and non-covalent associations [130].

The pretreatment of lignocellulosic biomass is crucial before enzymatic hydrolysis. Various pre-treatment options are available now to fractionate, solubilize, hydrolyze and separate cellulose, hemicellulose, and lignin components [8, 21, 137, 141]. These include concentrated acid [45], dilute acid [117], alkaline [71], SO_2 [17], hydrogen peroxide [48], steam explosion (autohydrolysis) [40], ammonia fiber explosion (AFEX) [22], wet-oxidation [123], lime [64], liquid hot water [73], CO_2 explosion [21], and organic solvent treatments [15]. In each option, the biomass is reduced in size and its physical structure is opened. Two categories of dilute acid pretreatments are used: high temperature (>160°C) continuous-flow for low solids loading (5–10%, w/w) and low temperature (<160°C) batch process for high solids loading (10–40%, w/w) [128]. Dilute acid pretreatment at high temperature usually hydrolyzes hemicellulose to its sugars (xylose, arabinose and other sugars), which are water soluble [8]. The residue contains cellulose and often much of the lignin. The lignin can be extracted with solvents such as ethanol, butanol, or formic acid. Alternatively, hydrolysis of cellulose with lignin present produces water-soluble sugars and insoluble residues, which are lignin plus unreacted materials. The use of SO_2 as a catalyst during steam pretreatment results in the enzymatic accessibility of cellulose and enhanced recovery of the hemicellulose-derived sugars [7]. Steam pretreatment at 200–210°C with the addition of 1% SO_2 (w/w) was superior to other forms of pretreatment of willow [36]. A glucose yield of 95%, based on the glycan available in the raw material, was achieved. By steam explosion, optimal solubilization, and degradation of hemicellulose can generally be achieved by either high temperature and short residence time (270°C, 1 min) or lower temperature and longer residence time (190°C, 10 min) [33]. Morjanoff and Gray [87] reported that enzymatic saccharification of 100 g sugarcane bagasse after steam explosion with 1% H_2SO_4 at 220°C for 30 s at a water:solid ratio of 2:1 yielded 65.1 g sugar.

Super critical carbon dioxide explosion was effective for pretreatment of cellulosic materials before enzymatic hydrolysis [65, 147]. Zheng et al. [148] compared CO_2 explosion with steam and ammonia explosion for pretreatment of sugarcane bagasse and found that CO_2 explosion was more cost-effective than ammonia explosion and did not cause the formation of inhibitory compounds, which could occur in steam explosion. Cao et al. [9] reported a pretreatment method that involves steeping of the lignocellulosic biomass (using corn cob as a model feedstock) in dilute NH_4OH at ambient temperature to remove lignin, acetate, and extractives. This is followed by a dilute acid treatment that readily hydrolyzes the hemicellulose fraction to simple sugars, primarily xylose. The residual cellulose fraction of biomass can then be enzymatically hydrolyzed to glucose. Kurakake et al. [72] pretreated sugarcane bagasse, corn husk, and switchgrass with ammonia water to enhance enzymatic hydrolysis. Garrote et al. [43] treated *Eucalyptus* wood substrates with water under selected operational conditions (autohydrolysis reaction) to obtain a liquid phase containing hemicellulose decomposition products (mainly acetylated xylooligosaccharides, xylose, and acetic acid). In a further acid-catalyzed step (posthydrolysis reaction), xylooligosaccharides were converted to xylose. The wet oxidation method can be used for fractionation of lignocellulosics into solubilized hemicellulose fraction and a solid cellulose fraction susceptible to enzymatic saccharification. Bjerre et al. [3] found that a combination of alkali and wet oxidation did not generate furfural and 5-hydroxymethyl furfural (HMF). Klinke et al. [67] characterized the degradation products from alkaline wet oxidation (water, sodium carbonate, oxygen, high temperature, and pressure) of wheat straw. Apart from CO_2 and water, carboxylic acids were the main degradation products from hemicellulose and lignin. Aromatic aldehyde formation was minimized by temperature control and the addition of alkali. Draude et al. [32] reported that oxygen delignification of kraft pulp removed up to 67% of the lignin from softwood pulp and improved the rate of, and yield from, enzymatic hydrolysis by up to 111% and 174%, respectively.

Phenolic compounds from lignin degradation, furan derivatives (furfural and HMF) from sugar degradation, and aliphatic acids (acetic acid, formic acid and levulinic acid) are considered to be fermentation inhibitors generated from pretreated lignocellulosic biomass [94]. Various methods for detoxification of the hydrolyzates have been developed [93]. These include treatment with ion-exchange resins, charcoal or the ligninolytic enzyme laccase, pre-fermentation with the filamentous fungus *Trichoderma reesei*, removal of non-volatile compounds, extraction with ether or ethyl acetate, and treatment with alkali (lime) or sulfite. Persson et al. [97] employed countercurrent flow supercritical fluid extraction to detoxify a dilute acid hydrolyzate of spruce prior to ethanol fermentation with baker's yeast. A summary of various pretreatment options is given in Table 2. Each pretreatment method offers distinct advantages and disadvantages.