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REVIEW

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Industrial significance and economics of hemicellulose bioconversion for sustainable ecofriendly development: A state-of-art review

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ABSTRACT

Numerous naturally available biological products including metabolites are synthesised that have valuable and significant applications in numerous important sectors integrated into human life. Biologically-sourced enzymes from plants, animals and microbes are capable of degrading complex biological polysaccharides like cellulose, hemicellulose, lignin, pectin etc. Hemicellulose is an important plant cell wall component synthesised through pentose/hexose pathways. The pentose sugars, the monomeric form of it, could further be transformed to valuable metabolites like clean energy, organic acids, alcohols, single-cell protein and pigments, as also useful enzymes. *Clostridium stercorarium*, for instance, contains 50 dedicated genes to produce thermostable hemicellulose-degrading enzymes like glycoside hydrolase. Arabinoxylooligosaccharides degrading GH10 xylanases, xylanases Xyn105F and β-D-xylosidase Bxl31D are also reported. While *Phanerochaete chrysosporium* possesses cellobiohydrolase, filamentous fungi like *Aspergillus* and *Trichoderma* reportedly can degrade hemicellulose. This review attempts at detailed insights into the natural sources of hemicellulose, its extraction approaches and the responsible hemicellulose-degrading bioenzymes. Their numerous applications in various sectors are also discussed.

KEYWORDS

Bioconversion; Biomass; Cellulose; Circular bioeconomy; Hemicellulose; Microbes

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Introduction

The rising global energy demand is expected to rise further, thus making it difficult to meet the demand through conventional means. The depleting fossil fuel reserve concerns the non-renewable fuel-driven world economy. The current global geopolitical scenario and the climate change issues strongly indicate the necessity of renewable and sustainable fuels, alternatives to fossil fuels as major players in the world economy [1]. Numerous hemicellulose-degrading enzymes in glycoside hydrolase category in microbial systems are reported, and successfully recombined and characterised in bacterial cells like *Clostridium stercorarium* (cultured on cellobiose) as a case instance. There are evidence of xylanases (Xyn11A, Xyn10B/ Xyn10C) and cellulase Cel9Z protein secretome in microbial cell system [2].

Clostridium stercorarium secretome was active on xylan, β-glucan, xyloglucan, galactan and glucomannan as hemicellulose polysaccharides. Nearly 20 recombinant enzymes could breakdown these hemicellulose polysaccharides into simple sugars and have been explored for their degradation ability. Mechelke and Broeker [4] determined three non-classified glycosides hydrolases (GH) family enzymes, but did not include xylanases Xyn105F and *β*-D-xylosidases in the family [2-4]. Filamentous fungi *Aspergillus nidulans* CreA and *Trichoderma* are well known for breaking down plant cell wall components like cellulose, lignin and hemicellulose by cellulases, hemicellulases, ligninases and pectinases. These enzymes are regulated at transcriptional levels in filamentous fungi [5,6].

The responsible genes for these enzymes are activated in presence of the polymer molecules. These enzymes are not needed in presence of glucose sugars and so are not synthesised, and thus the genes express or repress under specific growth conditions. Further, expression from the encoding genes is regulated by various prevailing physicochemical and cellular factors. Some fungi are unique enzyme producers. *Phanerochaete chrysosporium* expresses ligninases enzymes like manganese peroxidase (mnp) and lignin peroxidase (lip/LIG); up to 15 ligninolytic peroxidase genes (10 lips and 5 mnps) are identified in *P. chrysosporium* genome [7]. Most ligninolytic fungi are capable of

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synthesising more enzymes that are closely regulated by lip and mnp genes. Cellobiohydrolase enzyme degrades hemicellulose [5,8].

Of the numerous options being scoped as source of alternate renewable energy, lignocellulose is the most important one, constituting the earth's largest renewable biofuel resource [9]. It is the most underutilised feedstock and its abundance could create storage and disposal issues, as it usually ends up in landfills or incineration chamber thereby affecting the land use pattern and the air quality. It could serve as a reliable feedstock for renewable energy and other high-value products like volatile fatty acids, polyols and 5-hydroxymethylfurfural (HMF), an important platform chemical.

Lignocellulose has significant advantages over the first-generation biomass feedstock as it has no other use for the sustenance of living world unlike the first-generation biomass. Lignocellulosic plant biomass like poplar, sunflower and jatropha are cultivated largely as feedstock for biofuel. Biofuel from lignocellulosic feedstock, while serving as an alternative for the declining petroleum reserves thus decreasing the pressure on fossil fuels, seems also to be ecofriendly [6]. Apart from the fuel, the accrued economic benefits also serve numerous socio-economic purposes by providing decentralised employment and improving the earning capacity and livelihoods of the rural poor. Lignocellulose, the major component of plant mass, makes up about half of the photosynthesis product. It contains three intensely intermeshed polymers – cellulose, hemicellulose and lignin – chemically bonded by non-covalent forces and covalent cross-linkages. Lignocellulose is a complex carbohydrate with about 40–50% cellulose [$(C_6H_{10}O_5)n$], 20–40% hemicellulose [$(C_5H_8O_4)m$], 18–25% lignin [$(C_9H_{10}O_3(OCH_3)0.9–1.7)x$] on dry matter bases, and other components. Lignocellulose-rich plant biomass is recalcitrant owing to the prevailing complex intermeshed polymeric structures. Because of such structural complexities, cost effective, high yield, and high throughput production of biofuels and other value-added products from lignocellulose remains a major challenge despite its abundance in nature.

The complex polysaccharide cross-linking and tight packing coupled with the recalcitrant lignin scaffolding inside out lignocellulose is recalcitrant to biotransformation. To enhance the enzymatic digestibility of lignocellulose and improve bioconversion competency, pretreatment strategies depend on the properties of the lignocellulose biomass that have been tried in labs and applied successfully in the field. The three major steps to convert lignocellulose to value-added products are pretreatment, saccharification and fermentation, and distillation. Lignocellulose is subjected to numerous pretreatments, either alone or combined, before the complex structure is enzymatically converted to value-added products. Depolymerisation of polysaccharides catalysed by the action of specialised enzymes is usually a prerequisite in most lignocellulose bioconversion strategies.

The most common pretreatment approaches are grinding/milling, acid-alkali, organo-solve, ionic liquid, steam, steam explosion, autohydrolysis, and biological pretreatments [10]. Many microbes (fungi, yeast and bacteria) could degrade lignocellulose macromolecules using several hydrolytic or oxidative enzymes. Engaging genetically engineered (improved) microbial strains and validating the process to qualitatively and quantitatively enhance the synthesis of the target enzyme form the backbone of translational research. Apart from microbes, cellulolytic enzymes could also be obtained from insects. Wood-eating termite is a valuable source of cellulolytic enzymes, typically useful in the biofuel production process.

After the preliminary physical, chemical, and biological pretreatments the substrate is enzymatically treated. Lignocellulose degrading enzymes like cellulases, hemicellulases, pectinases, ligases and polysaccharide oxygenase are done in order to synthesise value-added products. These hydrolytic enzymes loosen plant cell wall component by decreasing the size and viscosity of matrix polymers, allegedly by augmenting the action of the cell wall loosening agents. Most of the lignocellulose and other polysaccharide-degrading enzymes are grouped together in the O-glycoside hydrolases family by the International Union of Biochemistry and Molecular Biology (IUBMB). They are classified under O-glycoside hydrolases (GH) family also, that classifies the enzymes that cleave glycosidic bonds.

A key hindrance in developing an economically feasible lignocellulose-based circular bioeconomy is the cost of enzymes. Using lignocellulose or derivatives for high-value products and the necessity to eliminate the residual artefacts for particularly the food, beverage, medical and textile industrial applications, has encouraged the use of lignocellulose-degrading enzymes in industrial applications that has grown rapidly in the last few decades. Few industries integrate numerous strategies in line with the biorefinery concept to maximise the percent yield. The first end-to-end cellulosic ethanol industrial production from wood chip in a biorefinery plant was achieved in 2009 in Burnaby, British Columbia. Another company Lignol Innovations Inc. has developed a biorefinery technology to utilise an ethanol-based organosolv process to segregate and extract the cellulose components from the cellulosic fraction of woody biomass [9]. However, due to high operating costs and low efficiency the socioeconomic impact remains largely limited. Biofactories could try improve the cell wall degrading enzyme blends and reduce the enzymatic process cost for economic feasibility of scaled-up operations. This review overviews the recent literature update on particularly enzymatic degradation of hemicellulose, their industrial significance and the economic feasibility in biofactory.

Microbes in Hemicellulose Conversion (Various Potential Microbial Candidates)

Hemicelluloses from natural plants

Plants are good natural source of hemicellulosic polymer. Hemicellulose units are β-(1–4) linked and function as an equatorial configured backbone. The polymer has xyloglucans, xylans, mannans, glucomannans, and β-(1-->3, 1-->4)-glucans. The differentially structured natural hemicelluloses are found in different types of plants in their cell wall, and β-(1-->3, 1-->4)-glucans is restricted to pulses and few others. Literature report the detailed structures of hemicelluloses found in varying quantities in various plants [11]. Its major biological function is to strengthen the cell wall with intimate interactions with cellulose and lignin [11]. These interactions are discussed through accepted primary cell wall models. Hemicellulose synthesis with the help of glycosyltransferases enzyme in golgi

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bodies are reported [12]. To synthesise the polymers like xyloglucans and mannans, many glycosyltransferases are required. Glucomannans and β-(1-->3, 1-->4)-glucans biosynthesis are critically studies in recent times opposed to the above-mentioned polymers [13]. For instance, raw hemp fibre having 67-78% cellulose, 5.5–16.1% hemicelluloses, 3.7–4.3% lignin and 0.9–4.3% pectin is explored. The fat and wax contents in hemp has potential of sustainable use in textile industries [11,13].

Developments in hemp fibre processing in fibre extraction and comprehensive fibre characterisation in the hemicellulose-rich component are explored. Increased interest in *Cannabis sativa L* and raw hemp-based products as good sources of hemicellulose and the challenges and opportunities have been detailed [14]. Literature discuss the effect of retting process on the chemical composition of hemp fibres that can have specific properties of economic values after cellulose segregation [11]. Along with the retting process to extract fibre from hemp, osmotic degumming, enzymatic retting, steam explosion and mechanical decortication could decompose pectin, lignin and hemicellulose also [15]. Thus, specific approaches are needed to obtain hemicellulose plant source. The extracted hemp fibre could be diverse in nature that is also dependent on the spinning system, such as linen, cotton and wool spinning technologies, with or without decertification [14,15]. The global market size for industrial use of hemp fibre was estimated at US$ 4.71 billion in 2019 with an expected 15.8% annual growth. Table 1 details the hemicellulose quantities in various plant biomass.

Table 1. Proximate of various biomass as against the hemicelluloses content as a good substrate to synthesise fermentable sugars for industrial fuel and specialty chemical processes.

Biomass	Hemicellulose (%)	% cellulose/lignin/arabinose	Reference
Corn stove	21	36/17.2/3.5	[16]
Olive tree	15	25/19/2.4	[17]
Rice straw	15	41/10/5	[18]
Switchgrass	20	32/23/4	[19]
Wheat straw	37	32/15/4–8	[20]
Conifers	5–10	43–46/27–32/0.5–2	[21]
Barley hall	36	34/16.5/-	[22]
Barley straw	28	39/8/-	[23]
Rice husk	20.5	32/18/-	[24]
Sorghum straw	25.5	33.5/18/-	[25]
Poplar wood	15	40/29/1	[26]

The interest in hemp-based products (like oil, food, beverage and pure hemicellulose) application is increasing. Some of the products are biocomposites for automotives and construction with increased use in textile sector in the Asia Pacific [11]. The European hemp industry is also growing fast and thus its cultivation in this region increased by 70% between 2013 and 2018 [11,13]. Figure 1 shows the various hemicellulose structures.

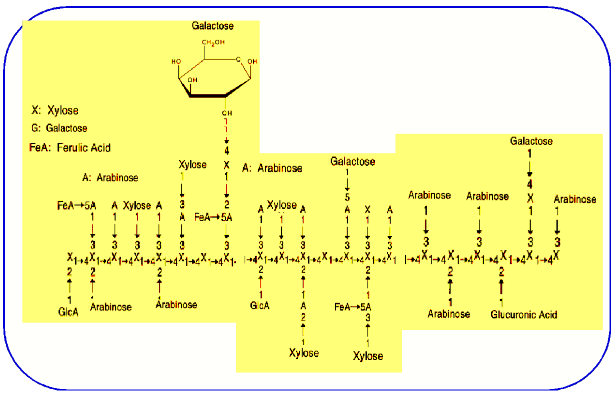

Figure 1. Common structure of hemicelluloses with pentose sugar chain that can be a base substrate for synthesising numerous microbially fermented specialty chemicals, fuels and value-added products.

Microbial conversion of hemicellulose

Figure 1 shows that hemicelluloses are polymers containing different types of pentoses (like xylose and arabinose) and hexoses (like mannose, glucose and galactose) with some quantity of sugar acids. The composition may vary depending on the nature of the plant, like hardwood hennicel and luloses are rich in xylans and softwood hemicellulose is glucomannans rich. The monomers are effectively released after physical, chemical and biological hydrolyses. Biological hydrolysis of hemicellulose by using effective microbial species seems to be a good eco-strategy [27]. Xylan from plants is a heteropolysaccharide with homopolymeric 1,4-linked-β-D-xylopyranose backbone chain. It is a good source of xylose, arabinose, glucuronic acid or its O-methyl ethers, acetic, ferulic and p-coumaric acids [28].

Bioconversion of hemicellulose to fuels and chemicals is challenging. Various physicochemical (to loosen cell components), and biological (through enzymatic or microbial hydrolysis) pretreatments are adopted to obtain monomers. Each step contributes to the monomer generation which is later subjected to further microbial fermentation to synthesise value-added products. Hemicellulose-rich agri-residues like corn fibre, wheat/rice straw and sugarcane bagasse contain up to 20–40% hemicellulose [27,28]. An effective pretreatment to

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separate hemicellulose from lignocellulosic biomass is enzymatic saccharification which helps in generating fermentable sugars. Corn fibre hemicellulose was bioconverted through enzymatic saccharification using endo-xylanase, β-xylosidase and α-l-arabinofuranosidase [29]. Benign bioprocessing of hemicellulose through such ecofriendly microbial fermentation approaches at commercial level can be utilised to synthesise bioethanol, xylitol, 2,3-butanediol and other value-added products [27-29].

Monomers Dependent Biomass Pretreatment/ Saccharification

Reports discuss the composition and frequency of occurrence of branched structures in various hemicellulose-rich biomass that is typically dependent on the xylan content in biomass [30]. The xylan backbone contains units like O-acetyl, a-L-arabinofuranosyl, a-1,2-linked glucuronic and 4-O-methylflucuronic acids. Various forms of xylan are found in grass, cereal, softwood and hardwood biomass. Guar seed husk, esparto grass and tobacco stalks contain unsubstituted linear xylans [31]. Xylan is present as linear homoxylan, arabinoxylan, glucuronoxylan and glucuronoarabinoxylan. Birchwood (Roth) xylans reportedly contain xylose (89.3%), arabinose (1%), glucose (1.4%) and anhydrouronic acid (8.3%) monomers in vaying percentage. Rice bran contains neutral xylans in the form of xylose (46%), arabinose (44.9%), glucose (1.9%), galactose (6.1%) and anhydrouronic acid (1.1%) [31]. Wheat arabinoxylans contain xylose (65.8%), arabinose (33.5%), glucose (0.3%), galactose (0.1%) and mannose (0.1%). The complex corn fibre heteroxylans has xylose (33–35.8%), arabinose (5–11%), glucuronic acid (3–6%) xylose monomers with β-(1,4)-linkage [32]. Xylan backbone is highly substituted with monomeric arabinose or glucuronic acid side-chains linked to O-2 and/or O-3 of xylose residue. Oligomeric side chain contains arabinose, xylose and galactose monomers. Figure 2 illustrates the hydrolysed monomers to synthesise value-added products [31,32].

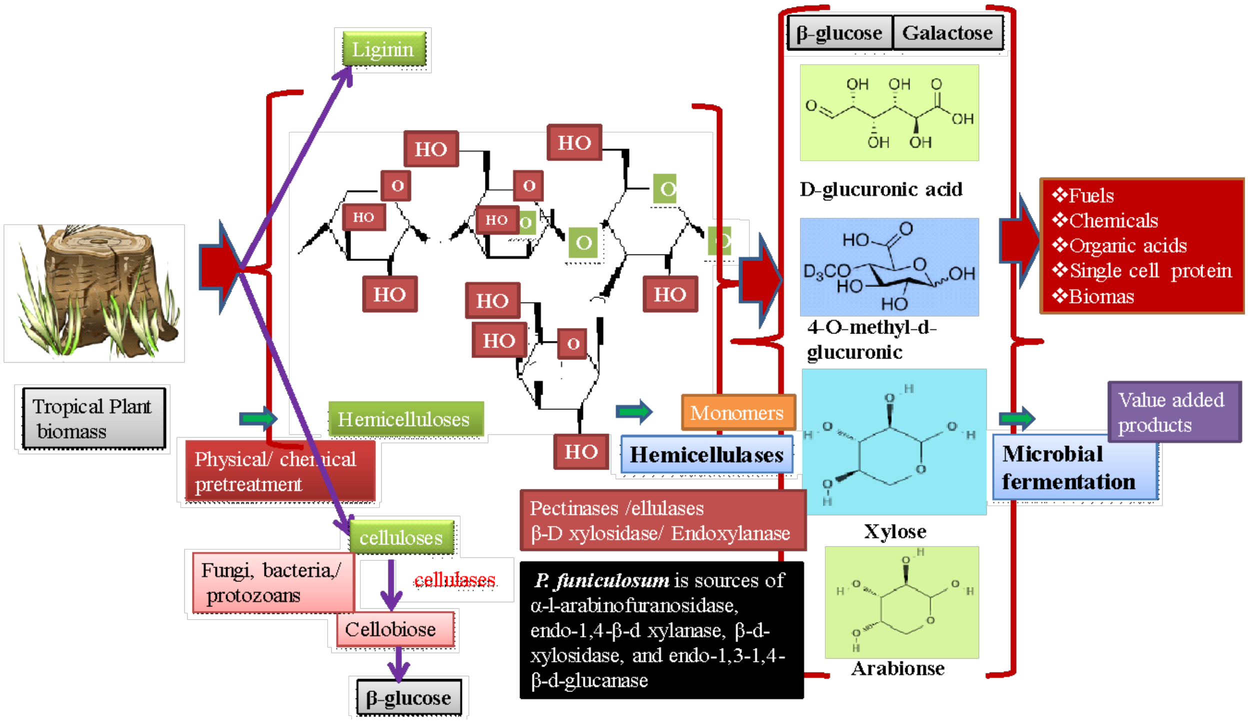

Figure 2. Hemicelluloses of plant biomass are pretreated by physical and chemical processes to loosen the cellulose, hemicellulose, lignin and/or pectin, after removing cellulose, lignin and pectin, the hemicelluloses are treated by hemicellulases (from, say, *Penicillium funiculosum*) to biotransform to monomers, to finally convert to value-added products.

Steam-mediated pretreatment for saccharification of woody biomass

Physical factors (pressure, temperature, and retention time) are critical during steam explosion, and thus they need to be critically monitored. Steam explosion pretreatment of biomass enhances the hydrolysis with a potential of high saccharification. The sugars obtained through such treatments are glucose, xylose, galactose, mannose, and arabinose. Pinewood of <200μm was steam exploded at 190°C for 10 min with biomass loading, N_2 pressure, and release time as variable parameters were studied [33]. The steam-exploded material reported the best glucose yield when enzymatically saccharified for 72h by *Trichoderma reesei* at ~0.44MPa N_2 pressure and ~22s release time [34].

Such treatment conditions generated good (97.72%) glucose, xylose (85.6%), mannose (87.8%), galactose (86.4%) and arabinose (90.3%) yields from pinewood pulp [33,34]. The solid-liquid phase and the particle size (maximum up to 200μm) influenced the treatment. Chemical characterisation of the resultant monomers in the solid phase was done [35]. The xylose yield in the liquid fraction with 0MPa N2 pressure, ~4g biomass loading and ~0.22s release time was high (89.6%). Low (<4g) biomass loading and shorter (<22s) release time yielded higher glucose and xylose than higher biomass loading (8g) and longer release time (46s). N2 pressure increased glucose yield in the solid phase and reduced the xylose yield in the liquid phase [34,35]. Table 2 details some reported enzymatic bioconversion of hemicellulose-rich biomass.

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Table 2. Bioprocesses to enzymatically treat hemicellulose-rich biomass to value-added products.

Hemicellulose biomass	Microbial process	Value-added product(s)	References
Liquid hydrolysate fraction of cocksfoot grass	*Pichia stipitis* CBS 6054 fermentation	Ethanol (89–158 mL/kg DM), with high (92%) theoretical yield	[36]
Plant biomass with heterogeneous polymeric nature	Low industrial fermentability by the commonly employed microbial strains	Cellulosic ethanol enzymatically at pilot scale after pretreatment and hydrolysis	[37]
Wheat straw as an abundant agroresidue	Biofermentation by recombinant bacteria and yeasts	74–99.6% sugar yield and 65–99% ethanol yield (theoretical values)	[38]
Efficient, sustainable and harmonised use of various biomass feedstock (biorefinery model)	Integrating 1G & 2G bioethanol production technologies	Efficient and sustainable bioethanol production	[39]
Hemicellulose from wood and kraft pulping process	SSF of concentrated (46.6 g/L) southern pine prehydrolysate	43.3 g/L sugar produced 10.8 g/L ABE with 0.25 g solvent yield /g sugar	[40]
Acetone from hemicellulose biomass	Combined acetone-calcium carbide (CaC_2) treatment at 200-350°C	Single-pot synthesis of methyl-substituted benzenes and methyl-substituted naphthalenes	[41]
Plant biomass glucose and hemicellulose	*Clostridium* sp. strain NJP7 with ABE fermentation; large-scale biobutanol synthesis hindered	Butanol (12.21 g/L) and isopropanol (0.92 g/L); enhanced buffering capacity and alcohol dehydrogenase activities	[42]
Readily available and inexpensive agro-industrial waste products	*Aspergillus niger* fermentation	High yield; effects of fermentation conditions, citric acid recovery options discussed	[43]
Sulphuric acid pretreated and biodetoxified corn stover feedstock	*Aspergillus niger* SIIM M288 fermentation	100.04 g/L citric acid at 94.11% yield	[9]
Acid pretreated and biodetoxified biorefining of distillation stillage	Oxidative fermentation of xylose to xylonic acid by *Gluconobacter oxydans*	75.22 g/L of xylonic acid and 59.80 g/L of ethanol from xylose in hemiccellulosic mass	[44]

Industrial Significance of Hemicellulose Conversion

Integrated biorefinery approach to convert lignocellulose biomass to value-added products increases economic value. Lignocellulose could be fractionated to bioenergy, biomaterials and specialty chemicals in a biorefinery following a combined pretreatment and processing [45].

Value-added products from hemicellulose biorefinery

The valuable materials derived from hemicellulose hydrolysates with the underlying technology and their industrial applications are detailed in Table 1. Majority of them synthesised/purified from such biorefinery are xylitol, xylooligosaccharides, polyhydroxyalkanoates, furfurals, lactic acid, ethanol, 2,3-butanediol and cellulose nanocrystals.

Commercial production of xylitol is accomplished through biochemical reduction of xylose carried out enzymatically by microbes. Xylitol, a good low-calorie sucrose substitute, is usually industrially synthesised by catalytically reducing D-xylose in presence of Ni at excess pressure and temperature. Xylitol is used in preparing sweets and also helps enhance the shelf-life, colour, texture and taste of food. It is also used in manufacturing candies, toothpaste and chewing gums along with other sugar substitutes. Xylitol consumption is favourable for the diabetic demonstrating non-fermentability and non-carcinogenic properties. Being non-fermentable, xylitol-based pharma products like tonics and syrups help minimise dental caries [46].

Xylooligosaccharides (XOS) could be efficiently synthesised by direct autohydrolysis or combined chemical-enzymatic treatment of xylan residues in hemicellulose feedstock. XOS consumption regulates blood glucose levels in the diabetic when used as a regular sugar substitute. As a prebiotic, XOS can potentially ameliorate gut microflora and diminish gastrointestinal infection. XOS prebiotic could help control cancer and benefit fatty acid metabolism, mineral absorption, immunity boosting and intestinal pH reduction [47].

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Hemicellulose could be used to produce polyhydroxyalkanoate (PHA), the bioplastics. PHA could be commercially produced from hemicellulose-digested sugar by microbially fermenting it. Commonly used in the medical, packaging and tissue engineering industries, it is non-toxic, UV-resistant and acts as a gas-barrier. It is significantly used in food packaging, textiles, adhesives, ear implantation, sutures, bone tissue engineering, plastic films etc. due to its biocompatibility and biodegradability nature [48]. Xylose could be cyclodehydrated to furfural using a heterogeneous catalyst. Conventionally, furfural is a base material to produce chemicals like furoic acid, furfuryl alcohol, tetrahydro-furfuryl amine, methyl-tetrahydrofuran, levulinic acid, 2-methyl tetrahydrofuran, tetrahydrofuran acid, pyrrole, etc. It is also applied as a fungicide, preservative and organic solvent to extract and purify hydrocarbons [49].

Lactic acid (LA) could be generated by microbially fermenting sugar through separate hydrolysis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF) [50]. It can be used in preparing green solvents, polylactic acid (PLA) and acrylic acid. The low-cost biodegradable PLA is increasingly applied in textile and packing industries due to its excellent heat stability and barrier properties [51]. Similarly, ethanol is industrially produced from hemicellulose hydrolysate by a stepwise process of pre-saccharification, biodetoxification and simultaneous saccharification and cofermentation (SSCF) carried out in a single bioreactor. The ethanol is purified by distilling the bioreactor extract. It is a good substitute for fossil and petroleum fuels and is blended with conventional fossil fuel to feed automobiles [52].

2,3-Butanediol is an industrially valuable odourless, colourless and transparent liquid, biologically synthesised by a mixed acid-butanediol pathway in a bacterial cell involving several key enzymes. The process involves two pyruvate molecules transformed into α-acetolactate by α-acetolactate synthase. The α-acetolactate is anaerobically converted to acetoin by acetoin-reductase, and finally, the reduction of acetoin by butanediol dehydrogenase synthesises butanediol. The mixed butanediol pathway generates coproducts like succinic acid, acetic acid, formic acid, ethanol and lactic acid. Butanediol has applications in diverse sectors like chemical, fuel, agriculture, biopolymer, etc. Other B-to-B applications include the synthesis of plasticiser, printing ink, fumigant, resin, pesticide and softening agent [53].

Cellulose nanocrystals (CNCs) have wide application as a sustainable bio-based nanomaterial with potential use in biomedicine, pharmaceuticals, electronics, barrier film, nanocomposites, membranes and supercapacitors. Hemicellulose is reinforced in CNCs through pre-sorption and in situ sorption that enhances the pore structure and mechanical strength for increased applications [54].

Global Hemicellulose Market

This section discusses the size and growth potential of various hemicellulose-derived value-added products, in the global market, especially the specialty chemicals. Global xylitol market was at US$1.04 billion in 2020, expected to increase to US$1.46 billion by 2026 at 6.93% compounded annual growth rate (CAGR) [55]. Its Asia Pacific region market was anticipated to rise between 2019 and 2026 at still higher CAGR. Worldwide, Cargill Inc., Dupont, Mitsubishi Shoji Foodtech Co. Ltd, Novagreen Inc., and Roquette group are some of the key industries in xylitol market [55,56].

The marketplace expansion, market share, global market size, product launch and technological innovations of XOS are described [56,57]. Valued at US$66 million in 2020, the market was expected to increase in the next five years at 3.9% CAGR. Companies like Long Live, Kangwei, HFsugar, Henan Shengtai, etc. are the major players in this market segment [57]. Similarly, the PHA market led by Europe was valued at US$62 million in 2020 and expected to grow to US$121 million at 14.2% CAGR between 2020 and 2025. Other players expanding their business in this are RWDC Industries (Singapore), Shenzhen Ecomann Biotechnology Co. Ltd. (China), Danimer Scientific (US) and Kaneka Corporation (Japan) [58]. In similar lines, the furfural market size was about US$1.2 billion in 2019 and forecasted to be US$2.0 billion at 6.9% CAGR by 2027. at 7.1% CAGR, the Asia Pacific market is expected to maximise its revenue in near future. Companies like Hongye Holding Group Corporation, Arcoy Industries Pvt. Ltd., Illovo Group, Central Romana Corporation Ltd., etc. are prominent performers in furfural market [59].

The lactic acid market was valued at US$1.19 billion in 2021, anticipated to reach US$3.55 billion by 2028 at 16.9% CAGR between 2022 and 2028. DuPont (US), Corbion (Netherlands), DOW (US), Galactic (Belgium), Unitika (Japan), Musashino Chemical (Japan), Vigon International (US), COFCO BioChemical (China), Vaishnavi Biotech (India) are major companies such playing a critical role in LA commercialisation [60]. Demand in LA market increased as North America led in its production and usage. The global market of PLA was valued at US$729.1 million in 2020 and could reach US$1.7 billion by 2026 at 15.4% CAGR. Market value of PLA in the US was estimated at US$218.8 million in 2021 with 26.52% share of the global market. Companies like Danimer Scientific, Futerro SA, COFCO Corporation, Evonik Industries AG and Galactic SA are noteworthy players in the PLA global market [61].

The market worth of bioethanol was about US$89.1 billion in 2019, expected to increase at 4.8% CAGR between 2020 and 2027. The key players bioethanol market is Archer Daniels Midland Company, British Petroleum, AB miller and Kirin and are successfully fulfilling its increasing demand [61]. The 2,3-butanediol market size could expand from US$72.43 to 88.99 million by 2025 at 2.88% CAGR. Considering the production, consumption, capacity and market value in regions like the US, Europe, China and Japan, the global market size of BDO has expanded [62]. The CNCs market size is expected to reach US$8.56 billion by 2026 at 12.05% CAGR between 2021 and 2026 [63].

The bioeconomics of hemicellulose conversion

A sustainable circular economy strategy revolves around the reuse and recycling of feedstock that ensures optimal use and restoration of resources with a 'zero-waste' system. A lignocellulose-based biorefinery, a glaring instance of a linear economy, primarily utilises hemicellulose, lignin and cellulose to synthesise value-based products [64]. Such linear economy model follows a ‘take-make-dispose’ scheme that seems not-so-ecofriendly and thus unsustainable. Circular economy

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(CE) approach extends and circularises linear economy (LE) signifying the construction and maintenance of a circular loop of renewable materials. CE principle follows criteria like complete utilisation of the substrate, developing products thus obtained with a high reuse potential, ameliorating the liquid market for economic growth and cascading the use of the feedstock with zero-waste approach. Circular economy in the general focuses on converting renewable biological resources into value-added products and energy, and scoping their time-to-time replacement. Table 3 details the valorisation of hemicellulose to synthesise high-value products.

Table 3. A list of literature on hemicellulose valorisation to high-value industrial products.

Bioproduct	Technology used	Commercial sector	Business value	References
Xylitol	Catalytic reduction of D-xylose	Food and Pharma industries	Low-calorie sweetener for chewing gum, toothpaste, syrups and in food for the diabetic	[43]
Xylooligosaccharides	Combined chemical-enzymatic treatment or autohydrolysis of Xylan	Food and Pharma industries, Agriculture	used as prebiotics, animal feed, growth stimulants in plants	[44]
Polyhydroxyalkanoate	Microbial fermentation of sugar	Packing industry	Biodegradable plastic	[45]
Furfural	Cyclodehydration of xylose	Coating and construction industries	Used for preparation of inks, plastics, adhesives, antacids, fertilisers, fungicides and flavouring compounds	[46]
Lactic acid	Separate hydrolysis and fermentation or simultaneous saccharification and fermentation	Food, Pharma, Packaging, Biomedical and Cosmetic industries	Biodegradable plastic by polymerising LA (polylactic acid), for packaging and wound healing	[47,48]
Ethanol	Pre-saccharification, biodetoxification and simultaneous saccharification and co-fermentation	Fuel industry	Biofuel	[49]
2,3-butanediol	Mixed acid-butanediol pathway	Transport, Food and Polymer industries	Liquid solvent, fuel, flavouring agent and precursor of many polymers and resins	[50]
CNCs	Incorporating hemicellulose into nanocellulose	Biomedical industry	Wound healing and tissue engineering	[51]

In this light, hemicellulose can be fractionated to obtain products like xylitol, xylooligosaccharides, polyhydroxyalkanoates, furfurals, lactic acid, ethanol and 2,3-butanediol using lignocellulose-based circular bioeconomy green synthesis approach. As against conventional petroleum-based products, this approach is promising if the production cost for specialty industrial chemicals and fuels could be reduced through technology fine-tuning and cost rationalisation. As demand for biobased chemicals like polymers, fuels and fibre increases, Marquez et al. (2021) predicted that the investments on biobased products could intensify to US$5.8 trillion from US$2.6 trillion between 2025 and 2030. They opined that investment on xylooligosaccharides (XOs) in the prebiotic food market could swell to US$130 million dollars by 2023 that shall undoubtedly further propel economic growth [65].

The lignocellulose-based bioethanol production cost includes, not necessarily restricted to, substrate pretreatment, labour, production, bottling, transportation and inflation adjustment. A raw biomass substrates-based bioethanol refinery in Maharashtra, India with a fixed operating cost of Rs.19.11 crore reported Rs.96.79 as production cost, Rs.35.76 variable operating expenses, and Rs.5.08 transportation cost per liter of bioethanol synthesised [66]. The other economically significant B-to-B chemical from hemicellulose is furfural extracted through one-pot fractionation is useful in producing other valuable materials. Banu et al. [46] reduced the furfural production cost by 37.5% through the biorefinery approach comparing the market value, while the revenue increased by 34.7% [65]. The global market value of Xylitol, for food and pharma industries as a cheaper sweetener substitute, is expected to reach US$1.15 billion by 2023. Lactic acid, a useful basic raw

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material for biodegradable PLA, could potentially enhance the economy with 16.2% CAGR [63]. The market value of 2,3-butanediol is expected to reach US$72.43–88.99 million by 2025 as a good substitute in chemical, fuel, agriculture and polymer industries [67]. With a global share estimated to reach US$121 million by 2025, process optimised and cost rationalised polyhydroxyalkanoate (PHA) could potentially replace synthetic plastic, reduce pollution and ensure sustainable growth [67,68].

Successful business ventures - Case studies

A biorefinery, capable of replacing non-renewable feedstock with renewable resources for human economic benefits, is the heart of a linear or a circular bioeconomy. Biorefinery contributes to global sustainable development goals with numerous advantages as mandated by the UN. Biorefineries in Finland and Sweden have set up many CE-compliant companies. Forest-biorefinery in the Nordics (Finland and Sweden) prominently engages in green-strategy advantages, biotechnology-focussed utilisation and commercialisation of resources across, bioresources-inspired biomass feedstock, ecology-enabled sustainability, energy management, eco-process, soil and biodiversity conservation [67,69-70]. Three large Finnish industries UPM, Metsa Group and Stora Enso developed biodiesel from wood biomass. Biofuels Directive (Directive 2003/30/EC) entails biofuel distributors to blend biofuel with gasoline and diesel.

The biomass-fed refineries convert biomaterials like hemicellulose into valuable products and could potentially replace fossil-based economy. A biorefinery supplies chemicals, materials and fuels, and provides higher revenue opportunities, enhanced economic activities and increased employment opportunities at the local and regional levels. Activities dependent on forest produce follow bioeconomy strategies and provide scope for novel value-added products like pharmaceuticals, biofuels, chemicals, etc. from organic feedstock. Biorefinery and bioeconomy extend advantages like providing abundant novel products for extended socioeconomic benefits like rural livelihood opportunities. Lenzing group of Austria used hemicellulose from wood components to manufacture chemicals and cellulose components for textile industry [68,70]. It contemplates diversification to support sustainable development.

Conclusions

The review attempts to compile recent literature of various lignocellulose polysaccharides and their ecofriendly bioconversion utilising microbial systems. The enzymes to bioconvert natural substrates like lignocellulose, cellulose, hemicellulose, lignin and others, primarily bacterial and filamentous fungal microbial forms, are explored. Such enzymes are applied to synthesise various value-added products from the natural polysaccharides by breaking them down. In this context, many approaches to degrade and extract hemicellulose with respective enzymes are discussed. The thermostable hemicellulose degrading enzyme glycoside hydrolases from Clostridium sp. needs to be explored. The review also explores the economic significance and global market importance of the numerous specialty chemicals like xylooligosaccharides, polyhydroxyalkanoates, furfurals, lactic acid, ethanol, and 2,3-butanediol thus obtained from hemicellulose fractionation/breakdown for various industries. Thus, hemicellulose could be valorised for valuable promising applications and economic growth.

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