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Review

# Biotransformation of lignocellulosic materials into value-added products—A review

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ABSTRACT

In the past decade, with the key biotechnological advancements, lignocellulosic materials have gained a particular importance. In serious consideration of global economic, environmental and energy issues, research scientists have been re-directing their interests in (re)-valorizing naturally occurring lignocellulosic-based materials. In this context, lignin-modifying enzymes (LMEs) have gained considerable attention in numerous industrial and biotechnological processes. However, their lower catalytic efficiencies and operational stabilities limit their practical and multipurpose applications in various sectors. Therefore, to expand the range of natural industrial biocatalysts e.g. LMEs, significant progress related to the enzyme biotechnology has appeared. Owing to the abundant lignocellulose availability along with LMEs in combination with the scientific advances in the biotechnological era, solid-phase biocatalysts can be economically tailored on a large scale. This review article outlines first briefly on the lignocellulose materials as a potential source for biotransformation into value-added products including composites, fine chemicals, nutraceutical, delignification, and enzymes. Comprehensive information is also given on the purification and characterization of LMEs to present their potential for the industrial and biotechnological sector.

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## 1. Introduction

Lignocellulose that refers to the plant biomass accounts for more than 60% of the total biomass. This includes but not limited to the wood residues (sawdust and paper mill discards), grasses, waste paper, agricultural residues (straw, stover, peelings, cobs, stalks, nutshells, nonfood seeds and bagasse), domestic wastes (lignocellulose garbage and sewage), food industry residues and municipal solid wastes [1,2]. In agricultural countries like Pakistan, tons of agricultural, forests and agro-industrial residues are generated annually as a waste which can be harnessed for the biosynthesis of a variety of industrially commodity products through enzymatic degradation by microbial ligninases and cellulases. Lignocellulosic materials (LCMs) are among the most abundant, naturally available renewable resources for the cultivation of WRF [3]. At contemporary, the most extensively used LCMs for the production of lignin-modifying enzymes are wheat straw, rice straw, sugarcane bagasse, banana stalk, sawdust, soft and hard wood chips, cottonseed hulls, corn cobs, and rice bran. Other green biomaterials, such as cotton stalk and soybean straw, coffee pulp, etc. have also been studied for growing edible mushrooms [4]. Fig. 1 illustrates main components and structure of lignocellulose materials [5].

## 2. Physiochemical characteristics of LCMs

A detailed compositional profile of various previously reported LCMs is summarized in Table 1. Regarding compositional analysis, LCMs comprises lignin, cellulose, and hemicellulose [31]. Lignin is an abundant polymer in plant cell walls, conferring marked rigidity and thus protecting cellulose polymer from the hydrolytic attack by pathogenic microbes. Chemically, it has been described as hydrophobic three-dimensional phenylpropanoid precursor derived from the random coupling of lignin monomers; coniferyl, sinapyl and *p*-coumaryl alcohols. Owing to its complex molecular texture, it is highly resistant to both chemical as well as microbial degradation and its tight association with cellulose and hemicelluloses also contributes degradation resisting support to these polymers [36–38].

Explicitly, many significant efforts have been devoted to converting these lignocellulosic to value-added products including composite, fine chemical, animal feed, pulp and paper, biofuels and enzymes (Fig. 2) [39]. The most crucial step in the effective utilization of these lignocellulosic feedstocks is delignification, which expedites the separation of the main biomass components (i.e., cellulose, hemicellulose, and lignin). Nevertheless, the bioconversion is hindered by the structural complexity of substrate making these materials a challenge to be used [40].

## 3. Biotransformation of LCMs

Biotransformation of LCMs to useful products requires multi-step processes including pre-treatment, enzymatic digestibility, and fermentation. Pretreatment process depolymerizes lignin in the LCMs, so the resulted biomass becomes more amenable to consequent cellulolytic enzymes attack for improved saccharification. It is worth mentioning that following suitable de-lignification; the cellulose conversion to glucose becomes easier, resulting in higher ethanol yield due to greater bio-digestibility and approachability of the cellulase enzymes to cellulose [39].

In the scientific literature, a large variety of pretreatment procedures have been experimented in the past decades and are generally distinguished as mechanical (e.g., grinding, milling), physicochemical (e.g., autohydrolysis, liquid hot water, steam, supercritical fluids), chemical (e.g., alkali, acid, organic solvents, oxidizing agents), and biological (e.g., fungi) processes and/or combinations of these methods [41]. Chemical pretreatment is deliberated as the current leading de-lignification approach; however, scaling up of the treatment proves to be uneconomical and impractical, since chemical routes rely on the appliance of expensive equipment and toxic/corrosive chemicals that are eventually narrowing its scope [42].

**Table 1**
Compositional analysis of representative common lignocellulosic feedstocks.

| Lignocellulosic materials | Carbohydrate composition (% dry wt.) | | | References |
|---|---|---|---|---|
| | Lignin | Cellulose | Hemicellulose | |
| Agricultural residues | 5–15 | 37–50 | 25–50 | [6] |
| Banana waste | 14 | 13.2 | 14.8 | [7] |
| Bagasse | 23.33 | 54.87 | 16.52 | [8] |
| Barley hull | 19 | 34 | 36 | [9] |
| Barley straw | 6.3–9.8 | 36–43 | 24–33 | [10] |
| Bamboo | 23 | 49–50 | 18–20 | [11] |
| Corn straw | 8.2 | 42.6 | 21.3 | [12] |
| Corn cobs | 15 | 45 | 35 | [13] |
| Corn stover | 19 | 38 | 26 | [14] |
| Cotton seed hairs | 0 | 85–95 | 5–20 | [15] |
| Coffee pulp | 15.6–19.1 | 33.7–36.9 | 44.2–47.5 | [16] |
| Douglas fir | 15–21 | 35–48 | 20–22 | [17] |
| Eucalyptus | 29 | 45–51 | 11–18 | [18] |
| Grasses | 10–30 | 25–40 | 25–50 | [19] |
| Horticultural waste | 36 | 34.5 | 28.6 | [20] |
| Hardwood | 18–25 | 40–55 | 24–40 | [19] |
| Olive tree biomass | 19.1 | 25.2 | 15.8 | [21] |
| Jute fibers | 21–26 | 45–53 | 18–21 | [22] |
| Leaves | 0 | 15–20 | 80–85 | [15] |
| Nut shells | 30–40 | 25–30 | 25–30 | [23] |
| Newspaper | 18–30 | 40–55 | 25–40 | [24] |
| Oilseed rape | 14.2 | 27.3 | 20.5 | [25] |
| Oat straw | 10–15 | 31–35 | 20–26 | [10] |
| Poplar wood | 10–21 | 45–51 | 25–28 | [26] |
| Pulp and paper sludge | 16 | 23.4 | 8.6 | [27] |
| Pine | 23–29 | 42–49 | 13–25 | [18] |
| Rice Straw | 18 | 32.1 | 24 | [13] |
| Rice husk | 15.4–20 | 28.7–35.6 | 11.96–29.3 | [28,29] |
| Sugar cane bagasse | 20 | 42 | 25 | [30] |
| Sweet sorghum | 21 | 45 | 27 | [30] |
| Softwood | 25–35 | 45–50 | 25–35 | [19] |
| Sponge gourd fibers | 15.46 | 66.59 | 17.44 | [8] |
| Sorted refuse | 20 | 60 | 20 | [15] |
| Solid cattle manure | 2.7–5.7 | 1.6–4.7 | 1.4–3.3 | [15] |
| Swine waste | NA | 6 | 28 | [31] |
| Sugar beet | NA | 5 | 5.5 | [32] |
| Tamarind kernel | NA | 10–15 | 55–65 | [33] |
| Winter rye | 16.1 | 29–30 | 22–26 | [25] |
| Wheat straw | 16–21 | 29–35 | 26–32 | [34] |
| Water-hyacinth | 3.55 | 18.4 | 49.2 | [15] |
| Wheat bran | 8.3–12.5 | 10.5–14.8 | 35.5–39.2 | [35] |

Enzymatic pretreatment approach appears to be encouraging in this scenario to disrupt plant cell wall (lignin) and modify lignocellulosic structures with appreciable benefits like no chemical treatment, optimum product recovery, least by-product generation, low energy input, significant biomass conversion, eco-friendly and mild operating conditions [31,43]. Enzymatic de-lignification exploits crude, purified and semi-purified ligninolytic enzymes to carry out lignin biodegradation. Inarguably, fungal laccase is the most engaged enzyme for this purpose followed by MnP and LiP; however, mixtures of two or three ligninolytic enzymes (crude extract) have also been employed extensively for pretreatments of many substrates. In this respect, the collaborated dependence among the ligninolytic enzymes substantially improves the biomass deconstruction [44]. However, enzyme recycling and re-using could upgrade the rate and yield of hydrolysis and significantly trim down the cost of enzymatic treatment [45–53].

In recent years, several authors achieved high levels of lignin removal rate in different lignocellulosic plant biomasses using LMEs of white-rot basidiomycetes. Under optimized conditions, Silva and coworkers, (2014) produced MnP containing crude