

Ligninolysis Potential of Ligninolytic Enzymes: A Green and Sustainable Approach to Bio-transform Lignocellulosic Biomass into High-Value Entities



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Abstract The replacement of non-renewable fossil resources with a renewable organic carbon source is a grand challenge in terms of economic, ecological, and environmental motives. Among various renewable sources, the gainful utilization of lignocellulosic biomass seems a perfect choice both to the public and industrial domains for the eco-friendly production of industrially relevant chemicals, biofuels, and functional materials. Nevertheless, minimal processes have been recognized so far in the chemical industry for effective biomass consumption because of the

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complex and recalcitrant nature of lignocellulosic biomass. This scenario re-directed the researcher's attention to develop highly selective and promising bio-catalytic systems and green reaction bioprocesses to realize the biosynthesis of fuels and bio-chemicals from sustainable lignocellulosic materials. Ligninolytic enzymes assisted bio-delignification of lignocelluloses seems a new, environmentally responsive, and sustainable approach for effective processing of complex lignocellulosic-rich agricultural biomasses. This chapter spotlights the significance of agro-industrial waste biomasses and their gainful utilization for the synthesis of eco-friendly and economical products. Particular focus has been given on the ligninolysis potential of ligninolytic enzymes and bioconversion of lignocellulose biomass into high-value biofuels, specialty chemicals, designer composites, and functional materials. In addition to conclusive remarks, potential challenges and future perspectives in this promising field are also directed.

Keywords Biofuels, Delignification, Green chemistry, Ligninolytic enzymes, Lignocellulosic biomass, Sustainable environment, Value-added chemicals

1 Introduction

An increase in population size and the intensified consumer's necessities are expected to diminish fossil carbon resources in the coming years. In addition, environmental pollution, global warming, and ecological imbalance are the major problems of fossil fuel-based sources that pose a serious risk to the ecosystem [1]. Likewise, the extensive consumption of toxic chemicals and polluting non-degradable materials lead to severe ecological, health, and environmental problems. Therefore, mandatory factors, such as economic feasibility, ecological compatibility, and sustainability, should be taken into consideration in an interdisciplinary way to circumvent negative impacts before the formulation of alternative routes for chemicals, fuels, and materials synthesis [2]. Low cost, affordability, and good quality are the desired traits for the production of innovative platform products. Furthermore, it should be synthesized using bio-renewable and highly abundant carbon resources without having an adverse effect on the ecosystem, society, and wildlife. Being a renewable organic carbon source, lignocellulosic biomass can fulfill all the aforementioned criteria and is a potential solution to address the greenhouse gases and environmental pollution problems [3, 4].

Plant biomasses are renewable carbon sources that can be significantly used for the production of industrially relevant chemicals, biofuels, and valuable functional materials. Figure 1 shows various key steps involved in the processing of biomass to high-value entities. Lignocellulose principally containing three biopolymers (lignin, cellulose, and hemicellulose) indicates the most plentiful form of biomass. From the last several years, considerable progress has been made, across the globe, in utilizing

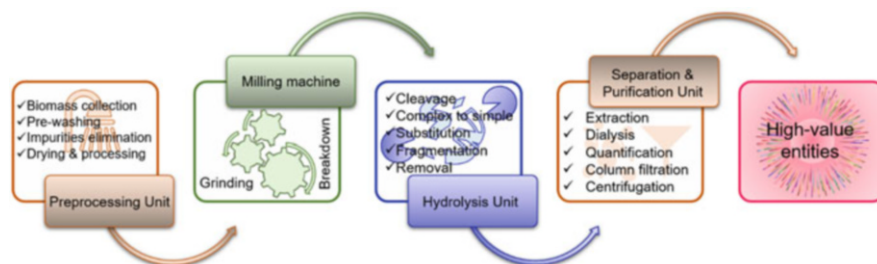


Fig. 1 Various key steps involved in the processing of biomass to high-value entities

biomass to synthesize chemicals and fuels. Beneficial consumption of lignocellulosic biomass appears an effective approach to save natural resources, global food production, and to avoid the environment from continual deterioration [5]. Nevertheless, the complexity and recalcitrant nature of lignocellulosic biomass caused a huge challenge for its efficient consumption and intensified the inevitability to develop highly selective and promising bio-catalytic systems and green reaction bioprocesses. With increasing consciousness and research experience, any product competing with the food supply, or interfering with the environment will be evaded in the future. In this respect, the exploitation of lignocellulosic waste biomass is an ideal option and thus strappingly advocated. This chapter discussed a green and sustainable approach to bio-transform lignocellulosic biomass into high-value entities by ligninolytic enzymes.

2 Lignocellulosic Biomass Resource and Compositional Analysis

At present, lignocelluloses are generally considered the most promising substrates for growing microorganisms as they related to low cost and relatively abundant availability. Figure 2 illustrates several requisite features that justify the potentialities of lignocellulosic biomass as a valuable source. Lignocellulose is the principal constituent in agricultural residues and a rigid structural complex in plants. Lignin (15–30%), hemicellulose (25–35%), and cellulose (25–50%) are the three essential organizational constituents of woody plants and agro-wastes accompanied by minor quantities of other constituents like minerals, acetyl groups, and phenolic compounds as shown in Fig. 3 [6–8]. Lignocellulosic biomass on average has 50–80% (on dry basis) carbohydrates, which are polymers of pentose and hexose sugar units. The cellulose and hemicelluloses are polysaccharides, which could be bio-transformed into sugars and eventually to ethanol by fermentation [9]. Cellulose is a polysaccharide that consists of several hundred to tens of thousands of D-glucose monomers connected via β -(1,4)-glycosidic linkages with amorphous and crystal-like structure. It is a water-insoluble, non-branched, and the most abundant naturally



Fig. 2 Several requisite features that justify the potentialities of lignocellulosic biomass as a valuable source

occurring biopolymer on earth [10]. The individual chains of cellulose polymer are bundled together generating the independent cellulose fibrils, which are feebly joined through van der Waals forces and hydrogen bonding. Hemicellulose is a multifarious heterogeneous polymeric material composed of various monosaccharide units such as hexoses, pentoses, and sugar acids. These polysaccharides are vulnerable to hydrolysis because of the low molecular weight, amorphous, and branched structure with short adjacent chains [11]. After cellulose, lignin is the second most plenteous bio-renewable polymer with a natural occurrence on earth. From a chemical point of view, it is a complex three-dimensional structure of phenylpropane inter-units, which are extremely resistant to microbial attack, and decreases its biodegradability. It is a bulky polymer composite of non-carbohydrate polyphenolics, i.e., phenylpropane and methoxy groups, which make it difficult to break. Lignin makes approximately 20–30% of the dry-basis weight of wood; this shows that it is the most copious organic substance present on the earth [12]. Lignin is linked with hemicelluloses and cellulose and form physical seals around these two components preventing the enzymes and solutions to penetrate [13]. The weakening

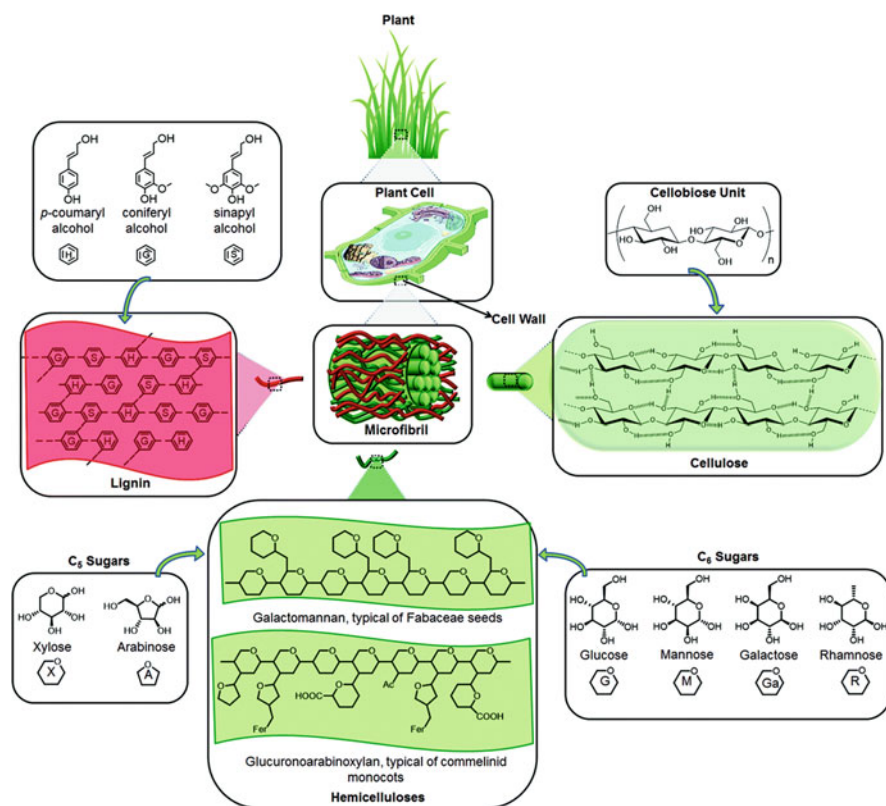


Fig. 3 The main components and structure of lignocellulose (adopted with permission from [6])

of the recalcitrant nature of renewable lignocellulosic biomass is a major obstacle for their bioconversion into useful and worthwhile products. Therefore, pretreatment is a mandatory step to modify the structural organization of lignocellulosic biomass, which enables enzymes accessibility to cellulose polymer and convert it into fermentable sugars [14]. Ligninolysis pretreatment seems a potential approach to hasten its bioconversion is highly important to harness the lignocellulosic biomasses entirely.

Despite numerous palpable advantages, the utilization of natural enzymes faces several practical difficulties like high-cost isolation and purification, activity inhibition, operational unsteadiness in organic media, and repeatability. Currently, enzyme immobilization is conceived as one of the most successful innovations in green biotechnology that could provide multiple benefits over the use of soluble enzymes such as recovery and separation, reusability of costly enzymes with less degradation rate, and durable shelf lives, and protection from proteolytic activity. Besides, enzymes in an immobilized form are more resilient to perturbed environmental conditions like pH, temperature, and acquaintance to toxic chemicals.

3 Gainful Harnessing of Lignocellulosic Waste

The rising energy crisis in the 1970s rekindled increasing interest in producing chemicals, biomaterials, and biofuels from biomass resources [15]. Recent years have witnessed a significant momentum in the effective utilization of lignocellulosic agro-waste because of the dismissing of fossil resources, economic crises, and environmental burden. Traditionally, the agricultural waste was usually burnt in crop fields besides its utilization as cooking fuel or cattle feed. This practice can still be observed in several countries. The burning of agricultural waste is uneconomical and imparts undesirable consequences on the ecosystem and health because of the generation of smoke, fumes, and gases. Some reports have demonstrated that the atmospheric smoke, in some countries, is partially due to the open crops burning in neighboring regions. Recently, the inclination in biomass exploitation has been shifting toward fossil fuel replacement with the harnessing of biomass resources. Current research impetus related to biomass utilization is focused predominantly on the production of chemicals and fuel additives, many of which possess similar properties as petroleum-based products. Valorization of biomass into fuels and chemicals is an active area of research European Union and the USA [5, 16]. In comparison to fossil carbon sources, biomass possesses an elevated O/H ratio and therefore necessitates fewer reaction steps to manufacture commodity chemicals following an easier synthetic method. Figures 4 and 5 show a simplified selective and non-selective transformation of lignocellulosic biomass, respectively.

4 Physico-chemical vs. Enzyme-Oriented Strategies

Despite an immense potential of biomass, the deconstruction and separation of primary lignocellulosic components (cellulose and lignin) is a major bottleneck step in the process of biomass bioconversion to fuels and specialty chemicals owing to their intricate chemical and rigid structural arrangement. Processing of lignocellulosic materials by conventional physico-chemical strategies received less attention because these are cumbersome, suffer from elevated production costs, and result in the generation of by-products similar to the petroleum-originated products that consequently may impart ecological, environmental, and health-related complications. In contrast to fossil carbon sources, it is easy to produce economic and eco-sustainable products from the processing of biomass resources. Hence, it is meaningful to design new, environmentally responsive, and sustainable approaches for the effective processing of complex lignocellulosic-rich agricultural biomasses. Ligninolytic enzymes assisted bio-delignification of lignocelluloses is of paramount interest and has renewed the researcher's attention due to associated drawbacks and limitations of existing pretreatments techniques.

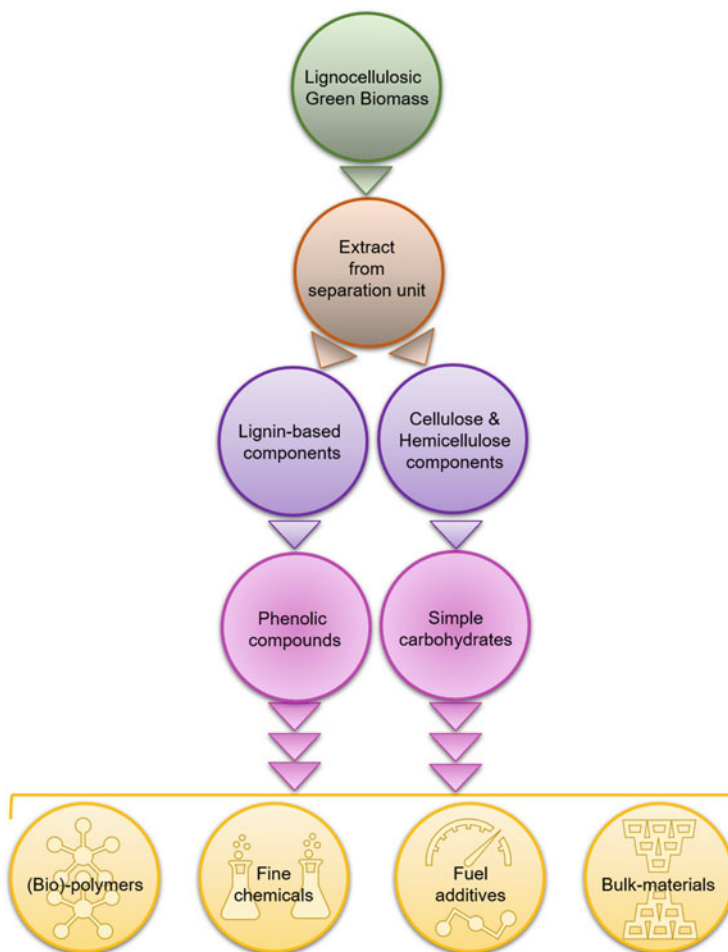


Fig. 4 A simplified selective (bio)-transformation of lignocellulosic biomass

5 White-Rot Fungi and Lignin-Modifying Enzymatic System

During the last few decades, a tremendous effort has been made on fungal biotechnology to produce a vast array of various commodities and high-value bioproducts such as liquid biofuel, chemicals, enzymes, secondary metabolites, etc. Among various wood-inhabiting microorganisms, white-rot basidiomycetous fungi are the prime microorganisms for depolymerization and deconstruction of wood lignocellulose with an incredible capability to secreting an irreplaceable set of non-specific extracellular oxidases and peroxidases including manganese peroxidase (MnP, E.C. 1.11.1.13), lignin peroxidase (LiP, E.C. 1.11.1.14), and laccase

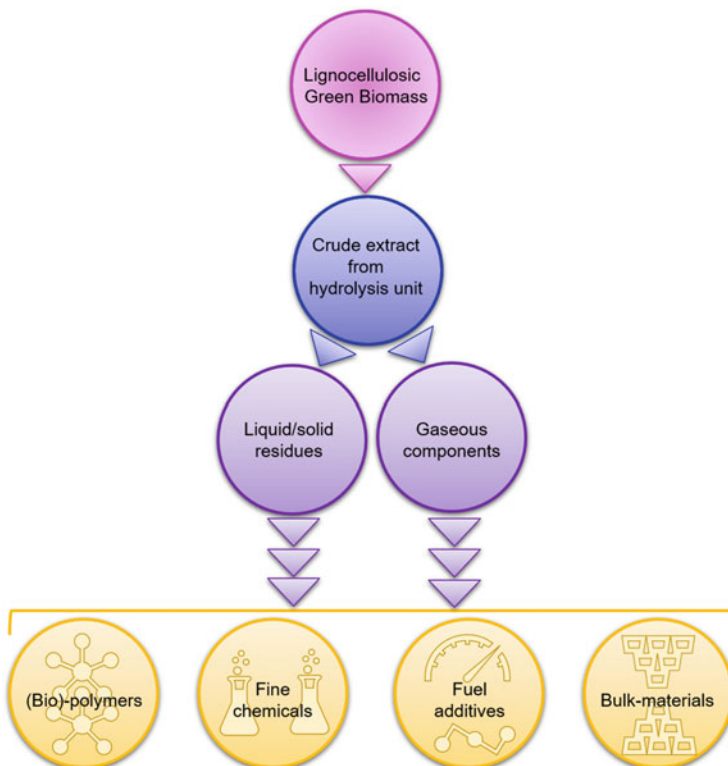


Fig. 5 A simplified non-selective (bio)-transformation of lignocellulosic biomass

(EC 1.10.3.2). Apart from this unique enzyme battery, many auxiliary enzymes such as glyoxal oxidase, aryl alcohol oxidase, versatile peroxidase, P-450 monooxygenase, and oxalate decarboxylase are also involved in lignin deconstruction. The broader substrate specificity allows this enzyme to catalyze depolymerize a wide variety of refractory xenobiotics and organ pollutants that possess structural similarity with the lignin molecule. These fungal oxidative enzymes are efficient biocatalysts, which play a major role, in not only lignin valorization but also are involved in the oxidizing a broad array of inorganic and organic contaminants such as dyes, PAHs, and chlorophenols [17, 18]. During their secondary metabolic phase, some wood-decaying fungal organisms secrete all three major kinds of lignin mineralizing enzymes, whereas only one or two enzymes are produced in the ligninolytic culture of other fungi [19]. Besides these three families of enzymes, some versatile peroxidases (VPs) with combined properties of MnP and LiP are also documented in the literature.

Lignin peroxidase discovered was the first time discovered in carbon- and nitrogen-deficient cultures *P. chrysosporium* culture in 1983 and seems a major component with the principal contribution in the ligninolytic system. It displays low

pH optimum (3–4.5), high redox potential, and excellent potentiality to the catalytic decomposition of numerous compounds with aromatic structures, i.e., methoxybenzenes, and 3,4-dimethoxybenzyl [20]. MnP, a key heme-containing peroxidase associated with ligninolysis, was also first discovered in the extracellular fluid medium of *P. chrysosporium*. MnP belongs to the family of oxidoreductases and is so far one of the most common glycosylated, heme-containing lignin-mineralizing enzyme secreted by nearly all wood-decaying basidiomycetes organisms [21]. In an H_2O_2 -mediated reaction, MnPs catalyzes the oxidative conversion of Mn^{2+} to reactive Mn^{3+} and thereby transform phenolic structures to phenoxy radicals [22]. However, the range of MnPs can be expanded to even non-phenolic molecules by incorporating some low molecular weight redox mediators. Furthermore, many other proteins synergistically functioning with MnPs have also amplified the roles of MnPs in fungal degradation. Laccases (EC 1.10.3.2) are N-glycosylated multicopper-containing oxidases that are versatile mineralizers of lignin and an array of several different recalcitrant compounds. In the past decade, ligninolytic enzymes find a prominent place in various industries such as in biomass debasement for biofuel synthesis, biobleaching, bio-pulping, pollutants mitigation, fruit juices stabilization, construction of biosensors, textile, beverage processing, animal feed, cosmetics, detergent manufacturing, and transformation of steroids and antibiotics.

6 Ligninolytic Enzymes Mediated Delignification

Enzyme delignification is referred to as the utilization of ligninolytic enzymes in crude, semi-purified, or purified form to catalyze lignin deconstruction. Among the ligninolytic enzymes, laccase is advocated as the most widely adopted biocatalyst for this purpose, followed by MnP and LiP. Nonetheless, some pretreatments have also implicated the consortium of two or three enzymes. In such a scenario, the synergetic collaboration among the ligninases led to the augmented debasement of lignocellulosic biomass. In contrast to chemical pretreatment, ligninolytic delignification of plant biomasses is particularly appealing because of several beneficial aspects such as mild processing conditions, pronounced biocatalytic potential, and high reaction specificity [23]. Moreover, the existence of small amounts of other additional enzymes/proteins along with redox mediators in WRF culture extracts may accelerate the lignin depolymerization by cleaving the linkages involved in associating xylan chains and hence exposing the lignin structures [24]. When compared with the chemical pretreatments, the enzyme-based method generates no or negligible inhibitory compounds. It is documented that more than 35 different kinds of toxic by-products are produced during the processing of lignocellulosic biomass by acid or alkali treatments, which exhibit a significant effect on the suppression of enzyme availability and microbial growth [25]. Figure 6 illustrates the schematic representation of ligninolysis and lignin deconstruction potential of ligninolytic enzymes [23].

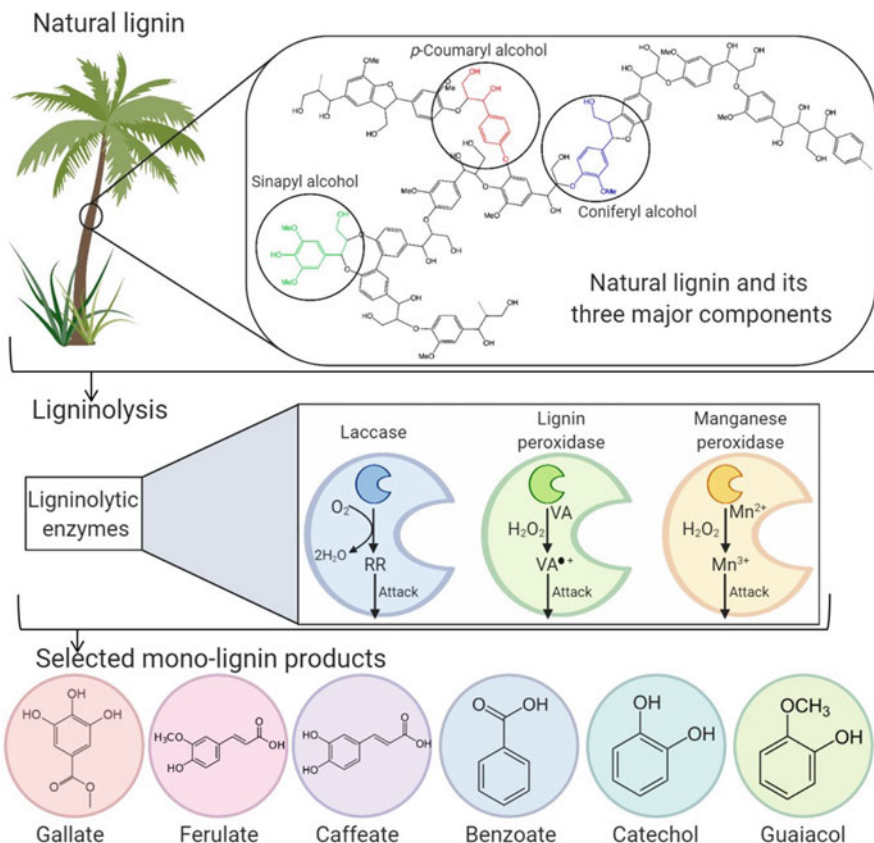


Fig. 6 Schematic representation of ligninolysis and lignin deconstruction potential of ligninolytic enzymes. The upper starting part represents the natural lignin with sinapyl alcohol, *p*-coumaryl alcohol, and coniferyl alcohol units. The middle part represents the unique action mechanisms of ligninolytic enzymes, i.e., laccase, lignin peroxidase, and manganese peroxidase as models. The last part shows various mono-lignin products that can be obtained after multiple steps involved in the ligninolysis process (adopted with permission from [23])

Though enzyme-assisted treatment processes result in an identical percentage of lignin removal as in microbial pretreatment. However, the enzyme exposure accomplishes the target delignification in less time duration of 24–96 h [26]. For example, ligninolytic enzyme extract from *G. lucidum* effectively catalyzed the lignin removal in different agro-industrial based lignocellulosic wastes. After 15 h exposure, it showed a high delignification rate of 57.3% in sorghum Stover [3, 4]. Likewise, ligninolytic consortium produced by *Pleurotus ostreatus* caused 33.6% depolymerization of lignin content in sugarcane bagasse after 48 h of contact time [26]. *P. sapidus* WC 529 derived ligninase extract catalyzed the removal of 51.08, 56.54, 57.4, and 65.81% lignin from sugarcane bagasse, rice straw, wheat straw, and corn cobs, respectively, after 48 h enzyme exposure to these substrates at 35°C

[27]. Despite the significant reduction in time duration, the enzymatic process cannot compare with the physicochemical methods with regard to costs and timespan [28].

Delignification of lignocelluloses by ligninases can be enhanced by modifying the catalytic traits of enzymes following protein-engineering approaches. Ligninolytic enzymes can be modified by using three kinds of engineering strategies including directed evolution, rational, and semi-rational protein engineering. In rational strategies, the sequence of the ligninolytic enzyme is reconstructed or modified at the molecular level by carrying out site-specific mutation. Using these approaches, the degradation ability of the laccase enzyme was remarkably increased toward non-phenolic molecules. It also presented enhanced aptitude to oxidizing large phenolic substances [29, 30]. In semi-rational approaches, saturation mutagenesis was applied for the alteration of functional “hot-spot” residues in the enzymes [31]. This strategy can lead to the production of the enzymes with three- to eightfold greater biocatalytic efficacies [32]. Directed evolution is an incredibly powerful enzyme engineering method that is widely exploited to optimize the catalytic properties of enzymes. This can be achieved by the combinatorial effect of the site-specific mutation, semi-random mutation, gene recombination, and high-throughput expression of the protein. Importantly, directed evolution does not depend on the prior structural information for enzyme engineering. It has been successfully employed to increase solvent tolerance and catalytic activities of numerous enzymes [31].

7 Conversion of Lignocellulosic Materials to Valuable Chemicals

Bioconversion of biomass is important to produce chemicals for sensitive or special application purposes like cosmetics, pharmaceuticals, and commodity products. The fundamental constituents of lignocellulosic biomass, including lignin, cellulose, and hemicellulose exhibit immense untapped potential to produce an array of various specialty chemicals [33, 34]. These polymers could be transformed into their monomeric forms. For example, hemicellulose and cellulose can be converted to sugars, while lignin is transformed into phenols [35, 36]. Additional modification of the resultant monomers enables their use in diverse applications. A wide variety of aromatic compounds can be synthesized by the effective utilization of lignin, whereas cellulose can be used to produce a list of specialty chemicals that possess various functional moieties like carboxylic acids, furans, and lactones [37, 38]. It is worth noting that the biomass processes implicate reducing the oxygen content as compared to classical chemical processes, where oxygen atoms were inserted or the O/C ratio was increased in fossil carbon sources [15]. The utilization of biomass can markedly decrease the number of chemical reaction steps and reagents used to make value-added compounds. In this way, this route can circumvent the discharge of environmental polluting agents such as acids, sulfur, metals, chlorine, and peroxides.

Increasing efforts have been directed on the bioconversion for biomass components into various industrial compounds and applications. Overall, it is not surprising to illustrate that biomass exhibit a great potential to swap the entire fossil fuel industry.

7.1 Formation of Sugars (C_5 and C_6) from Lignocellulosic Biomass

Sugar compounds are the first and important platform chemicals that can be achieved from the utilization of non-food lignocellulosic biomasses. The efficient formation of pentoses and hexoses with minimum energy consumption has profound significance in the bio-refinery because this step is critical to generate subsequent depolymerization products. The depolymerization of cellulose gives rise to glucose sugar, whereas both glucose and other six- (galactose, rhamnose, mannose,) and five (arabinose, xylose)-membered sugar monomers are formed as the degradation products of hemicellulose. Currently, concentrated acid (HCl)-driven hydrolysis constitutes the industrially proven and most potent method for lignocelluloses transformation into inexpensive fermentable sugars [39]. Nevertheless, this technology is mainly hindered due to the challenging recovery of acid recovery that is a major drawback of an acid hydrolysis reaction. Continuous research investigations are required to overcome the limitations of mineral acid separation and to improve the recovery and yield of target products.

7.2 Development of Sugar-Containing Polymers from Lignocellulosic Biomass

Lignocellulosic biomass can appear as the promising feedstock for the development of polymers by providing carbon five and carbon six monosaccharides and their derived compounds such as glucuronic acid, methyl glucoside, and glucaro- δ -lactone. The sugars and their modified derivatives either can serve as pendant moieties or can be integrated into the polymeric backbone. The polymer-incorporated derivatives are known as glycopolymers that garnered particular interest due to promising applications in emulating functional and structural properties of glycoproteins [40]. Hence, extensive efforts have been made to design glycopolymer with various architectures to develop novel gene/drug delivery systems. The contemporary investigation related to glycopolymeric drugs largely emphasis the treatment of patients with different diseases such as Alzheimer's disease, influenza, and HIV. Nonetheless, these studies are at their infancy level and thus necessitating continuous research to execute the clinical trials of the drugs [41, 42]. In addition to serving as a source of direct monosaccharides, lignocellulosic biomass-derived alditols (sorbitol, erythritol, xylitol, isosorbide, mannitol, arabinitol), aldonic acids

(2-ketogluconic acid, gluconic acid), and aldaric acids (α -ketoglutarate, xylaric acid, glucaric acid) can provide huge feedstock to synthesize numerous biopolymers. These linear carbohydrates-based biopolymers are non-toxic and biodegradable and possess improved hydrophilicity. Thus, they are useful in medical devices and food packaging related applications [6].

7.3 Synthesis of Commodity Chemicals from Lignocellulosic Biomass

A large number of platform chemicals or high-value materials such as 1,4-diacids (malic acid, fumaric acid, succinic acid), sorbitol, glycerol, aspartic acid, levulinic acid, glutamic acid, itaconic acid, 3-hydroxy propionic acid, glucaric acid, 3-hydroxybutyrolactone, xylitol/arabinitol, and 2,5-furan dicarboxylic acid can be potentially produced from lignocellulosic derived C₅ and C₆ sugars [6, 43]. Figure 7 shows a generalized scheme of lignocellulose-based integrated approach for the production of various biochemicals [44].

The US Department of Energy (DOE) recognized and listed all the high-value specialty chemicals that can be formed from lignocellulosic biomass and could be used as initial feedstocks to synthesize a wide range of bio-products through biochemical or bio-based processes [43]. Ethanol is among the most popular and well-known illustration of a bio-based fine chemical synthesized, around the world;

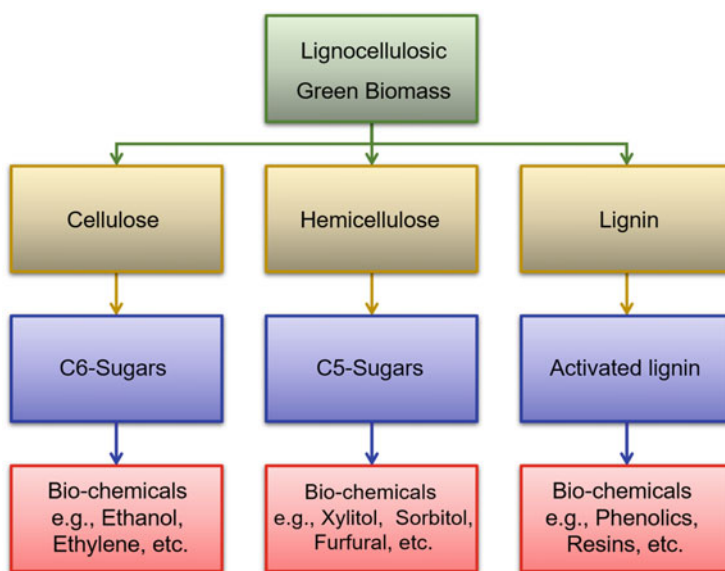


Fig. 7 A generalized scheme of lignocellulose-based integrated approach for the production of various biochemicals (adopted with permission from [44])

however, numerous other bio-based products have widespread commercial applications. The purified form of cellulose is presently employed to manufacture water-soluble gums, textile fibers, cellophane, wood-free paper, explosives, membranes, photographic film, and polymers that are widely used in varnishes and lacquers. Cellulose acetate is a major biodegradable cellulose derivative, which is utilized to form acetate rayon, photographic film, lacquers, and different thermoplastic products [45]. Enzymatic catalysis and fermentation processes are the principal routes for the production of specialty chemicals. A plethora of several different industrially relevant chemicals have already been produced for industrial level by the fermentation process, such as lysine, citric acid, and glutamic acid. Apart from these valuable chemicals, a list of commodity polymers can also be synthesized using bio-synthesized monomers by a combination of chemical and biological polymerization strategies, by either vigorously growing cells or isolated biocatalysts. Lactic acid synthesized by the fermentative processes can be chemically transformed into lactide, methyl lactate, and polylactate. The polylactate available commercially is a completely biodegradable substitution to polyethylene terephthalates [46]. Efficient processes for the synthesis of acrylic acids and methacrylic from bio-based hydroxy propionic and lactic acids are being developed. Genencor and DuPont established a lucrative and cost-efficient fermentation-based technology for the production of a key building block, 1,3-propanediol, which was not available from petro-based building blocks [47]. Succinic acid, a potential replacement to maleic anhydride has now been synthesized from butane using fermentative routes by various microbial strains [48]. In recent years, some chemical companies have commenced utilizing glycerol as an attractive and inexpensive starting feedstock material to produce value-added propylene glycol. Moreover, Solvay and Dow Chemical Company are utilizing the potential of glycerol for epichlorohydrin production, which might be useful in manufacturing epichlorohydrin elastomers and epoxy resins [49]. Owing to its cost-effectiveness, abundant availability, and high versatility, glycerol is speculated to emerge as a promising replacement to many frequently used toxic and polluting petrochemicals [50]. The contemporary scenario emphasizes that the demand for commodity chemicals, food, energy, and materials will enormously increase in the coming years. It is critical to address the problems such as scarcity of raw feedstocks and deficiency of constant supply of raw material for the production of food, biofuels, energy, and materials [51].

7.4 Synthesis of Green Composites from Lignocellulosic Biomass

With the strategic technological innovations together with unique structural and excellent physicochemical properties, a special focus has been put toward the use of lignocellulosic biomass for designing novel functional composites with numerous applications. It is important to mention that biomass-derived composites are

environmentally-friendly, biocompatible, and commercially feasible, thus representing a positive impact on industrial sectors and step toward global economic sustainability [3, 4]. To date, a vast number of designer bio-composites have been synthesized developed by using different polymers as building materials accompanied by various fabrication technologies [52]. Nevertheless, lignocellulosic biomass-based fibers provide a notable aptitude for easy surface functionalization via non-toxic approach with no health hazard risks [53]. Xie et al. [54] developed a new technique for the efficient exploitation of lignocellulosic biomass to synthesize highly bio-compatible thermoplastic composites of poly(propylene) and poly(styrene). Thermal characterization revealed that the as-synthesized thermoplastic wood composites presented enhanced thermal tolerance, improved melting characteristics, and were easily extruded into sheets or filaments. Recently, urea-reinforced calcium phosphate along with sugarcane bagasse and its derivatives (cellulose and lignin) were used to design novel composite materials and employed as a slow-release fertilizer. Notably, the urea release rate was observed slower in water in the case of coated fertilizer as compared with uncoated urea/HAP fertilizer [55]. Kulal et al. [56] engineered lignocellulose (lignin and cellulose)-based graphene reinforced hydrophobic spongy bio-composites for the adsorption of organic solvents and oil from wastewater. Sugarcane waste powder and graphene oxide were used to prepare cellulose-lignin modified graphene sponge by using a highly efficient and robust one-pot hydrothermal technique. The resultant biocomposite showed potential efficiency in the recovery and separation of oil from wastewater. Furthermore, it also exhibited marked sorbent ability to separate organic compounds in several repeated cycles. In addition, an array of lignocellulosic biomass-derived multifunctional composites have recently been prepared for their applications in diverse industrial domains such as environmental remediation, bio-medical, textiles, pharmaceutical, nutraceutical, drug delivery, and food packaging [57–60].

7.5 Bio-fuels from Lignocellulosic Biomass

Bio-fuels are a sustainable solution to substitute costly petroleum fuels and offer numerous economic and environmental benefits. Bio-ethanol is among the most broadly consumed bio-based fuel for transportation across the world. Synthesis of bioethanol from waste biomasses is an attractive way of reducing dependence on crude oil consumption and to alleviating ecological contamination. Production of fuel ethanol from bio-renewable lignocelluloses has immense potential to diminish petroleum dependency by reducing the emanations of greenhouse gas. Nevertheless, it is indispensable to obtain feedstocks from non-edible parts of crops to circumvent intense competition between bio-ethanol and food resources. The second-generation fuels produced from lignocellulosic waste materials such as straw, wood, and switchgrass are increasingly used because of no competition with food productions [61]. In recent years, lignocellulosic materials have, therefore, been a subject of investigation as a renewable resource for ethanol production in Sweden, Canada, and

the USA [62]. Being less expensive and available in large amounts, lignocellulosic materials have great potential for bioethanol production than sucrose- (e.g., sugar-cane) and starch (e.g., corn)-producing crops.

Bio-butanol is an advanced second-generation bio-fuel with lower volatility and greater energy density than that of ethanol. Butanol can be biosynthesized through fermentation technology by processing many domestic crops, including sugar beets, corn, as well as agricultural wastes and rapidly growing grasses [63]. The primary function of bio-butanol is its utilization in industrial products as a biocompatible solvent such as varnishes and lacquers. Owing to its compatibility with ethanol, it can also be employed to increase ethanol blending with gasoline [64]. In combination with fuel cell technology, butanol can be envisioned as a cleaner and safe substitute for batteries in the future. However, the fermentative production of bio-butanol mainly relies on the abundant and inexpensive openness of raw feedstock to swap the chemical process. Solventogenic Acetone Butanol Ethanol (ABE)-synthesizing *Clostridia* exhibit a well-known capacity to assimilate pentoses and hexoses that are obtained agricultural residues and from wood biomass following hydrolytic reactions [65]. There has been an increasing trend on butanol synthesis from agricultural-based lignocellulosic residues including barley straw, switchgrass, and corn stover. Therefore, ABE fermentation was re-examined by various strategies to reduce or eliminate the toxicity effects of butanol to the culture, and the culture was manipulated to realize high product yield and specificity by using lignocellulosic biomass [66, 67].

Similarly, all of the fermentable sugars found in cellulose and hemicellulose hydrolysates, including arabinose, glucose, galactose, mannose, xylose, and cellobiose can also be transformed into 2,3-butanediol, also known as butanediol or 2,3-butylene glycol. 2,3-butanediol is a highly important and industrially pertinent biochemical that possess application as a liquid fuel and biocompatible solvent. It also serves as a building block for synthesizing a range of resins and synthetic polymers [68]. Cheng et al. [69] utilized corncob hydrolysate as a lignocellulosic medium for the synthesis of butanediol in a fed-batch fermentation mode. After 60 h fermentation, butanediol titer reached 35.7 g/L with a corresponding yield and productivity of 0.5 g/g and 0.59 g/h/L reducing sugar. In conclusion, the effective deployment of lignocellulosic biomass as renewable feedstock integrated with advanced processing technologies ensures the socially acceptable and economically feasible production of biofuels to address the ever-increasing demand of the world.

In conclusion, given exponentially rising population growth and accelerated consumer demand, special research attention should be given on economic, ecological, environmental, and food considerations. In this regard, the utilization of agricultural waste might play a leading alternative to fossil resources. Massive research explicitly in chemical sciences and biotechnology is underway to promote structural modification of biomass, and its bioconversion into a variety of specialty chemicals and biomaterials. New or state-of-the-art bioconversion techniques adhering to the circular bio-economy based concept should be developed for effective utilization of agro-waste biomass or transformation to chemicals, materials, or biofuels adopting a multidisciplinary method. Timely and prioritized collaboration

among various sectors like academia, agriculture, scientists, industries, research, and government can lead to quicker developments and improvements in the beneficial use of agricultural waste.

8 Current Challenges and Solutions

This chapter summarized the current progress on the synthesis of liquid fuels and many high-value chemicals from lignocellulosic waste biomass. Tremendous achievements have been made in the past decade in terms of efficient biocatalytic systems, multipurpose bioprocesses, and novel catalytic routes for the decomposition of lignocellulose, enabling the value-added utilization of bio-renewable biomass-based feedstocks a practicable reality. Notwithstanding incredible advancements in this arena, many insufficiencies need to be addressed for industrial exploitability.

1. A highly pure final product is necessary during the synthesis of commodity chemicals, but the complex nature and recalcitrance of lignocellulosic biomass and the poly-functionality of molecules produced from biomass result in the synthesis of a mixture of products, which in turn render the target compounds separation and purification very costly and energy-intensive.
2. Though the catalytic lignocellulose transformation offers considerable advantages of milder reaction conditions and higher selectivity over the thermochemical routes, the majority of the catalytic processes furnish low product yield in batch mode due to the non-soluble nature of lignocellulosic biomass, which makes these processes less appealing.
3. As an eco-friendly and natural bio-solvent, water is generally involved in the conversion of lignocellulose, but only a few catalysts are capable of tolerating the hydrothermal milieu for longer industrial lifespan practice.
4. The majority of the catalysts employed for biomass processing are developed only at a laboratory scale with elevated processing costs; therefore, the amplified preparation of catalysts without compromising their performance remains the biggest issue to solve.

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