Biomass Conversion and Biorefinery (2024) 14:2959–2981
https://doi.org/10.1007/s13399-022-02746-0

REVIEW ARTICLE

Biotechnological advances in biomass pretreatment for bio-renewable production through nanotechnological intervention

Heena Chandel[1] · **Prateek Kumar**[1] · **Anuj K. Chandel**[2] · **Madan L. Verma**[1]

Received: 23 December 2021 / Revised: 10 April 2022 / Accepted: 25 April 2022 / Published online: 4 May 2022

Abstract

Globally, the fossil fuel reserves are depleting rapidly and the escalating fuel prices as well as plethora of the pollutants released from the emission of burning fossil fuels cause global warming that massively disturb the ecological balance. Moreover, the unnecessary utilization of non-renewable energy sources is a genuine hazard to nature and economic stability, which demands an alternative renewable source of energy. The lignocellulosic biomass is the pillar of renewable sources of energy. Different conventional pretreatment methods of lignocellulosic feedstocks have employed for biofuel production. However, these pretreatments are associated with disadvantages such as high cost of chemical substances, high load of organic catalysts or mechanical equipment, time consuming, and production of toxic inhibitors causing the environmental pollution. Nanotechnology has shown the promised biorefinery results by overcoming the disadvantages associated with the conventional pretreatments. Recyclability of nanomaterials offers cost effective and economically viable biorefineries processes. Lignolytic and saccharolytic enzymes have immobilized onto/into the nanomaterials for the higher biocatalyst loading due to their inherent properties of high surface area to volume ratios. Nanobiocatalyst enhance the hydrolyzing process of pretreated biomass by their high penetration into the cell wall to disintegrate the complex carbohydrates for the release of high amounts of sugars towards biofuel and various by-products production. Different nanotechnological routes provide cost-effective bioenergy production from the rich repertoires of the forest and agricultural-based lignocellulosic biomass. In this article, a critical survey of diverse biomass pretreatment methods and the nanotechnological interventions for opening up the biomass structure has been carried out.

Keywords Forest waste · Biomass pretreatment · Biomass hydrolysis · Bioethanol · Nanomaterials

1 Introduction

In the world, the need for fossil fuels is about 84 million barrels (Mb) per day, and in 2019, it was about less than 16 Mb per day due to the restrictions on transportation to contain the outbreak of COVID-19. Over the years of 2019–2025, the demand for fossil fuels increased by 5.7 Mb per day at an average yearly rate of 950 kilo barrels per day [1]. Globally, the consumption trend of fossil fuel is in danger all over the world [2]. It is evident from the recent survey that the reserves of crude petroleum may be depleted soon. Hence, there is an urgent need to foster a sustainable source of renewable energy [3, 4]. Annually, the worldwide demand of biofuels is set to increase by 28% in the upcoming year of 2026. In Asia, around 30% of the biofuel production will be increased by 2026, beating the European biofuel production. India will become the third largest market of biofuel production in near future. The consumption of renewable sources for energy needs is meagre 23.7%; that warrants making use of maximum energy derived from the sustainable and renewable sources on the priority basis. Now, the primary focus is to use the bio-based raw materials rather than the conventional for the production of renewable energy. Approximately 93% of all renewable energy is provided by biofuels and the remaining being renewable electricity. The biofuel output grows 24% over the time period of 2019–2024 (IEA, 2019) [5].

✉ Madan L. Verma
madanverma@iiitu.ac.in; madanverma@gmail.com

[1] Department of Biotechnology, School of Basic Sciences, Indian Institute of Information Technology Una, Himachal Pradesh 177209, India

[2] Department of Biotechnology, Engineering School of Lorena, University of São, Paulo-12.602.810, Brazil

Biofuels produced from residues, wastes, and dedicated crops account for around 45% of biofuels consumed in the year 2030 in the net zero scenario, and it was high from an examination of approximately 7% in 2020. Presently, animal fats and cooking oil are primarily used for biofuel production as non-food-crop feedstocks. But these feedstocks are present in very limited amounts. Thus, there is a demand for new and advanced technologies to be commercialized to expand the production of biofuel. For example, biomass-to-liquids and cellulosic ethanol technologies use lignocellulosic biomass (LB) residues and waste feedstocks to produce low-carbon biofuels for use in the transportation sector. The utilization of biofuels instead of fossil fuels is one of the primary ways to limit carbon emission. As a matter of fact, biofuels make up 64% of the renewable energy consumption in the year 2030 in the net zero emissions by 2050 scenario [6]. Different renewable technologies are available for energy production by using different energy sources such as biomass, water, wind, geothermal, and solar. All these energy sources are called renewable energy by the International Energy Agency (IEA) [5].

Now, the primary focus is to use the bio-based raw materials rather than the conventional for the production of renewable energy. Biofuel production is one of the feasible choices for sustainable nature [7]. It is predicted that biofuel is outstanding amongst other promising contenders to conquer the energy emergency and deal with this disturbing circumstance, since it has the capacity to limit a large portion of the natural issues [8]. LB is one of the most significant bio-based raw materials for the production of renewable energy. It shows significant advantages such as being eco-friendly, cost effective, easily available, and contains a high amount of carbohydrates which gives high yield of biofuels. In addition, the utilization of these lignocellulose wastes limits the environmental pollution links with its disposal [9]. The lignocellulose biomass has proven a pillar for the biofuel industries [10]. The LB mainly consists of three components: cellulose (30–50%), hemicellulose (20–35%), and lignin (5–30%). Their composition concentration varies depending on the type of raw material. The chemical composition of various feedstocks is described in Table 1. In this regard, different types of edible crops which contain high sugar content, oils, and starch have been used for the production of first-generation biofuels such as biohydrogen, biogas, bioethanol, biodiesel, and bio-oil [11].

Currently, only 2% of the biofuels are used for transport services. But it is assumed that about 27% of the vehicle fuel demand will be fulfilled by biofuels in 2050 [12]. Gao and his co-workers assessed that the residuals of farming (66%) and timberland (34%) forms a sum of 12,693 petajoule biomass which was utilized for producing the energy. All these studies revealed that forest waste and agricultural waste are the best sources for biofuel production. Therefore, there is huge demand for innovative techniques for the production of biofuels by utilizing the waste materials [13, 14]. Agricultural (sugarcane bagasse, corn stover, rice husk) and forest (wood pellets, pine needles) residues can be used for the production of biofuels. The complex structure of the LB is the major challenge in biofuel production. Sugarcane is the most common LB used in Brazil and India [15, 16]. Different types of LB containing raw materials are utilized for the commercial production of biofuels and their chemical composition are described in Table 2.

Table 1 Composition of various lignocellulosic biomass

Lignocellulose biomass	Cellulose	Hemicellulose	Lignin	Reference
Cassia fistula	56.67	7.12	6.22	[144]
Sugarcane bagasse	42.00	20.00	25.00	[145]
Corn stalk	34.85	29.87	8.16	[146]
Corn stovers	32.70	20.90	25.40	[147]
Miscanthus	52.10	21.30	18.60	[148]
Cocoa pods	32.30	27.70	21.44	[149]
Sago palm bark	42.60	24.30	19.20	[150]
Waste cotton	36.00	18.00	16.70	[151]
Neem wood bark	17.58	42.56	39.86	[152]
Sugarcane straw	36.90	19.70	13.70	[153]

Various pretreatment methods were used such as physical, chemical, and biological. They disintegrate the lignin from hemicellulose and cellulose present in the complex structure of biomass. These carbohydrates (holocellulose) are further converted into the renewable mix of sugars by enzymatic hydrolysis [17]. These conventional pretreatment methods have certain drawbacks such as costly chemical substances, catalysts, process complexity, and causing pollution in the environment. The suitable biomass pretreatment methods should have certain properties such as preservation of hemicellulosic and cellulosic parts, limited release of toxic inhibitors, low cost, less demand of energy, and reutilization of chemicals. Most of the conventional pretreatment methods have certain drawbacks such as high processing cost, process complexity, production of degradation products, low processing efficiency, lack of selectivity, limited release of sugar molecules, and causing pollution in the environment [18].

Recently, nanotechnology has shown tangible results in the biomass based biorefinery by minimizing the limitations associated with the conventional pretreatment methods [19]. Nano-dimensional materials possess unique properties such as high surface area to volume ratios for high saccharolytic enzyme loading for the efficient biomass processing [20]. However, the utilization of nanomaterials for improving the biofuel production comes under the scope of nanobiotechnology. Different metal oxide nano-catalysts like titanium dioxide, calcium oxide, magnesium oxide, and strontium

Table 2 Detailed composition of biomass used commercially throughout the world

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Glucan (%)	Xylan (%)	Lipids (%)	Carbohydrates (%)	Proteins (%)	Extractives (%)	References
Corn stover	38.00	26.00	17.00	-	-	-	-	-	-	-	[154]
Sugarcane tops	23.59	18.58	-	-	-	-	-	-	-	-	[155]
Sugarcane bagasse	39.84	17.19	22.25	-	-	-	-	-	-	-	[156]
Wood chips	27.60	35.20	21.20	0.50	-	-				15.50	[157]
Sorghum	-	-	22.00	4.00	34.00	18.00	-	-	-	18.00	[158]
Rice straw	74.09	46.62	73.17	-	-	-	-	-	-	-	[159]
Microalgae (*Chlorella* sp.)	-	-	-	04.54	-	-	08.20	23.90	55.20	-	[160]

have been made with a significant amount of catalytic action for manufacturing the biodiesel [21, 22]. Nanotechnology can possibly accomplish the economical and well-organized methods of biofuel industries [23]. Nanomaterials can be used to immobilize the enzymes which were used for hydrolyzing the biomass [24]. Nanomaterials likewise have a high potential for recovery, and reusability of enzymes in the scale up of biofuel production. One example is magnetic nanoparticles which have the ability to enhance the chemistry of lignocellulose biomass at molecular level. Their magnetic nature helps in the recycling process by applying the magnetic field which makes this process cost-effective [25, 26]. The primary focus of the pretreatment process is the complete digestibility of the LB with the limited use of harsh chemicals, limited generation of inhibitory compounds and least amount of pollution in the environment. All these goals are fulfilled by utilizing the nanotechnological intervention for biomass pretreatment and hyper production of biofuel in a cost-effective manner. Here, we review the lignocellulose biomass material availability and its potential application to enhance the biofuel production through nanotechnological interventions.

2 Past and present status of forest and waste materials

Forests are very important for our life. Forests play an important role in managing climatic conditions on the earth. The waste produced from forest is also a source of lignocellulose biomass which is further used for biofuel production, which is the best source of renewable energy. The main materials of the forest's wastes are the logging residues and forest thinning used for the production of biofuel [27]. In the past several generations, the manufacturing of wood chips has been extended by using forest, with the help of industry experts assessing that about 24 million metric tons of overall modern pellet creation will arrive in the year 2019, and this is similar to the raw material of approximately 50 million m^3 of wood. Significantly, most of the modern pellet creation for the power generation and the International Renewable Energy Agency (IRENA) documented all the information under the group of strong biofuels and the balanced wastes. Now, the worldwide producing limit has rose via 52,146 MW in 2009 to 95,687 MW in the year 2018, along the fastest additions happening in the European Union from 15,912 to 24,081 MW and 14,140 to 34,845 MW from Asian countries [28]. There are very few pros of forest residues. Forest resources and manure might be accessible throughout the year and biomass stockpiling may not be necessary. The maintenance of economic charges is the major hurdle to produce energy from the forest debris. Forest residues are scattered across enormous regions, and in this way cause high harvesting charges during collection. Besides, biomass transport and taking care of expenses are high because of low mass thickness, low energy thickness, and high dampness content [29].

The waste of forest biomass consists of various types of chemical groups and components which rely on the inception of their by-product [30]. The food crops significantly select the forests and energy producing crops which further can be utilized for the production of second-generation biofuels. Hydrogen fuel could be delivered naturally just as through chemical routes. Basically, two processes are utilized for the production of hydrogen gas from the timberland and agricultural waste biomass. The first process is gasification in which the biomass converts into combustible gas and the other process is pyrolysis similar to gasification. The forest wastes are basically separated into mass and elective forest wastes which includes the stubbles, humus, wood and dead seeds, spores, and leaf litter, respectively [31].

Carbon-to-nitrogen (C/N) substances of various woodland wastes assume a significant part in different sectors. Forest waste has a diverse proportion of C/N and various supplements that can be utilized as manure crude materials. Both carbon and nitrogen are important for microbial cell development and metabolic processing. The working of anaerobic absorption is significantly influenced by the C/N proportion of the influent substrate [32].

At the world level, the USA, Brazil, India, and China are the nations with the maximum number of studies, which are centered around the utilization and abuse of farming deposits, derived from cereal harvests, fundamentally wheat and corn, as they are the primary makers of this kind of yields [33]. Many scientists, essentially from government and academic organizations, have contributed extensively to this examination and concluded that the dominant part of cellulose remains unused. It comprises gigantic resources of energy production, along with an astonishingly enormous manufacturing of lignocellulose biomass at 1×10^{10} metric tons around the world [34]. It is surveyed in India that about 915 million metric tons of biomass availability involves both agricultural and forestry land wastes which includes 657 and 260 million metric tons per year, respectively. The collective potential power from both the assets is evaluated, i.e., 33,292 MW electric in which the agricultural assets is 18,730 MW electric and the woodland and the waste land includes 14,562 MW electric [27, 35].

3 Conventional approaches of biomass pretreatment

Lignocellulosic biomass (LB) is considered as a dormant source of biofuel because of its plentiful worldwide accessibility. The basic constituents of LB are lignin, cellulose, and hemicellulose. Lignin links with cellulose and hemicelluloses by joining with ester and ether bonds. LB produced from woodlands wastes or their debris contains a high amount of dampness, which may have complexed the handling of biomass, size decrease, and densification, just as expanding the susceptibility of biomass to spoilage and a subsequent quick decline in quality. Drying methods might be common (for example on account of grasses) or directed through traditional heating or microwaves [36, 37]. The principle objectives of pretreatment incorporate relaxing and expanding the surface region, structural adjustment and removal of lignin, incomplete hydrolysis and release of hemicelluloses, and primary structural alterations. Lignocellulosic materials additionally have been broadly used as intermediate fluid fuel or chemical compounds like furfural, levulinic acid, and γ-valerolactone. Lignocellulose biomass materials are produced naturally from incorporation of CO_2 and water through the photosynthetic process. Mostly, LB is considered as sustainable biomass on the planet earth [38].

The lignocellulose biomass composition of softwood and the hardwood are different. In softwood, it consists of 40–44% of cellulose, 30–32% of hemicellulose, 25–32% of lignin, and 5% of extractives. It mainly contains the guaiacyl units (G) [39]. In hardwood, it consists of 40–44% of cellulose, 15–35% of hemicellulose, 18–25% of lignin, and 2% of extractives. The hardwood contains a mixture of guaiacyl (G) and syringyl (S) units [40]. Different pretreatment methods were utilized for disintegration of LB in the softwood and hardwood such as ball milling, UV irradiation [41], alkali or dilute acid pretreatment [42], combined pretreatment (organosolv and steam explosion) [43], among others.

Mattonai and co-workers pretreated the softwood and hardwood with ball milling and UV irradiation method. The cellulose crystallinity was disintegrated by the ball milling process not with UV irradiation. The UV irradiation increases the holocellulose content in woody species. The hardwoods are less affected than hardwood [41]. The LB of softwood and hardwood were treated with the peracetic acid at 95 ℃ for 5 h. After the treatment, around 23% of softwood and 32% of hardwood LB digestibility were determined [42].

3.1 Different pretreatment methods of lignocellulose biomass

There are a few techniques accessible for the pretreatment of lignocellulose biomass (Fig. 1) [33, 44–46]. Their advantages and disadvantages are described in Table 3.

3.1.1 Physical pretreatment

These methods include mechanical operation and different types of irradiation and ultrasonic pretreatments [47, 48].

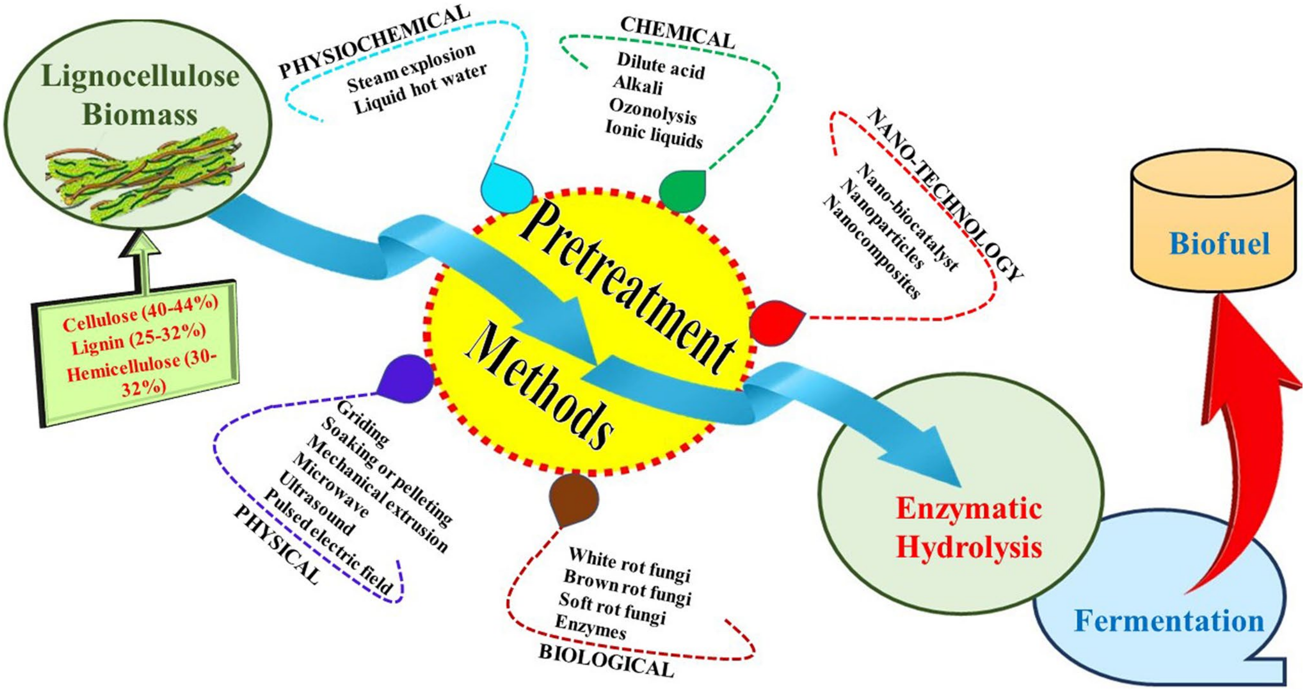

Fig. 1 Different pretreatment methods applied to the lignocellulose biomass

Various physical pretreatment methods are described in the following:

3.1.1.1 Grinding The grinding of biomass feedstock is a significant cycle to accomplish maximum yield of high valued pyrolysis products [49]. Reduction in size of raw material increases the warmth stream between the substrates. During pyrolysis, reduction in polymerization and crystallinity of biomass was noticed which further influenced production of bio-crude/bio-oil compounds [50]. Brandt and co-workers studied a three-stage processing strategy for pretreatment of residuals of softwood. The forest residues were converted into the fuel pellets and sugar molecules [51].

3.1.1.2 Soaking or pelleting It improves the biomass digestibility that can reduce cellulose crystallinity [52]. Huo and co-workers pretreated the eucalyptus residues by utilizing the ammonia-based soaking method to upgrade the proficiency of enzymatic hydrolysis, and 64.96% of sugar yield was obtained. The enzymatic digestibility and delignification rate were increased to 73.85% and 64.49%, respectively [53].

3.1.1.3 Mechanical extrusion In this method, the LB is warmed over 300 °C under the shear blending step. It requires high shearing power and energy which makes this process costly. The type of the screws, pressure proportion, and speed of the screw impacts the pretreatment process [54]. Gu and co-workers treated the forest waste residuals by extrusion process to enhance the yield of fermentable sugars. Enzymatic hydrolysis and sugar production were also enhanced via this process [55].

3.1.1.4 Microwave In this process, microwaves at low energy along with the irradiation gives the high warmth in long duration which disintegrates the structure of lignocellulose with minimum production of inhibitors. In this method, dielectric polarization is responsible for the atomic collision and thermal power production helps in the interruption of the lignocellulosic biomass [56]. Camani and co-workers treated the eucalyptus waste by microwave assisted method and the lignin content was reduced from 26.6 to 4.8% [57].

3.1.1.5 Ultrasound In this method, the ultrasound waves affect both physically as well as chemically. Formation of small bubble cavities bursts the hemicellulose and cellulose content present in the biomass. Researchers treated LB by the ultrasound waves in the range of 10–100 kHz [58]. The pine saw-dust was pretreated with ultrasonication, and it leads to 19% high yield of reducing sugars [59].

3.1.1.6 Pulsed electric field In this method, the lignocellulosic biomass is treated at high voltage in the range of 5–20 kV/cm for a shorter time period [59]. During this process, the pores present in the plasma membrane are opened which expose the cellulose and then the catalysts start hydrolyzing it [60]. Significant increases in sugar content in wood

Table 3 Advantages and disadvantages of various pretreatment methods

Pretreatment method	Advantage	Disadvantage	References
Physical pretreatment			
Grinding	Reduces the size of biomass and cellulose crystallinity	Costly method	[34]
Mechanical extrusion	It decreases the size and does not release the inhibitory compounds	Costly process and also requires high amount of energy	[161]
Microwave	Degrades the lignocellulosic biomass in a short duration of time with minimum production of inhibitors	Expensive method	[162]
Ultrasound	High-frequency ultrasound waves disrupt the lignocellulose biomass which increases the pore volume and thus decreases the crystallinity of cellulose	Expensive method	[163]
Pulsed electric field	Requires very little amount of energy, this exposure on biomass increases the permeability disintegrates the plant tissues	This technique is in their initial stage, more research is required	[164]
Freezing	Utilize minimal amount of hazardous chemicals which reduces the negative impacts on environment and also enhance the productiveness	Costly method	[65]
Pyrolysis	Utilize broad range of raw material, produce char on decomposition of cellulose and gaseous products	Required high temperature	[165]
Physiochemical pretreatment			
Steam explosion	Require minimal amount of energy than mechanical extrusion, limits the extent of pollution, recycling process is highly cost efficient	Incompletely disrupts the lignin and releases the inhibitory compounds	[166]
Liquid hot water	Cost efficient process does not require any type chemicals and also no need of neutralization	Production of inhibitory compounds increases with the rise of temperature	[118]
Ammonia pretreatment	About 90% of cellulose and hemicellulose are hydrolyzed by this method and does not release the inhibitory compounds	Biomass contains high amount of lignin does not disintegrate completely and its cost is depending on the utilization of ammonia	[71]
Carbon dioxide explosion	Require low temperature, cheap cost of carbon dioxide and also does not produce the toxins	High cost of reactor which suffer with different pressure conditions. Due to low temperature, it does not degrade the sugar	[165]
Wet oxidation	Highly efficient for the hydrolysis, solubilization and fractionation of hemicelluloses along with the process of delignification	Require high price of catalyst, oxygen, and also releases the inhibitors by the degradation lignin	[65]
Chemical pretreatment			
Dilute acid	It produces the xylose from the hemicellulose and also changes the lignin	Highly expensive process, release the toxic substances that causes corrosion	[90]
Alkaline	Remove the lignin content from biomass and also enhances the surface area	Downstream processing is costly, require long duration of residence time and high amount of water requires for salt removal	[167]
Ozonolysis	Requires normal pressure and temperature and does not release the toxic residuals	Highly expensive process due to the requirement of ozone	[168]
Ionic liquid	Requires low amount of energy, efficiently solubilized the large amount of cellulose at moderate conditions	Costly process due to the high price of ionic liquids, release inhibitors, face difficulty in reutilization and recycling process	[169]
Organosolv	Breakage of bonds present in the cellulose and hemicellulose	The removal of solvent is essential and it is also expensive method	[91]
Deep eutectic solvents	Cost-efficient, easily produced, biodegradable, harmless, and biocompatible process	Recyclability and reuse of these chemicals is necessary to make the process economically viable	[170, 171]
Biological pretreatment	Requires minimal amount of energy, disintegrates cellulose and lignin	Biodegradation rate is low	[49]

chips and switchgrass were observed after the pretreatment process [61].

3.1.1.7 Freezing In this method, the LB was first merged in the water and then iced at – 18 °C for a certain period of time. After that, the treated biomass was deforested at room temperature [62, 63]. Zhu and co-workers investigated the freeze–thaw pretreatment strategy on poplar chips for the extraction of hemicellulose. The maximum production of hemicellulose content was reported as 85.87 mg/g [64].

3.1.1.8 Pyrolysis During this process, the LB converts into various gaseous products such as H_2, char, and CO. The char residues were formed which were further treated with dilute acid and filtered with water. The water filtrate contains the glucose molecules which is a major source of carbon utilized in the production of biofuels [65]. Dhanalakshmi and co-worker pretreated the wooden bark of *Azadirachta indica* and maximum 49.5 wt% production of bio-oil under 450 °C temperature was observed [66].

3.2 Physicochemical pretreatment methods

It is found that physicochemical methods are effective for forest biomass pretreatment. For example, milling and grinding of biomass prior to treating with any chemicals, expulsion in combination with ammonium fiber explosion (AFEX) and under intense temperature and pressure of acid or alkali treatment or assisted with microwave [67]. Therefore, main physicochemical methods used are AFEX, and carbon dioxide explosion [68].

3.2.1 Steam explosion

It is more economical than other methods such as grinding and soaking [68]. This method incorporates the soaking of dried biomass with vapors at raised pressure and temperature, continued by sudden discharge of pressure while compelling the lignocellulosic biomass via a little hole, during which the flash vaporizing water applies a thermal–mechanical energy which destructs the biomass [69]. Dai and co-workers pretreated the bamboo wood (*Bambusa stenostachya*) by the combination of hydrothermal and steam explosion method and observed reduction in lignin content from 21.7 to 14.7% [70].

3.2.2 Liquid hot water

This method operates under elevated pressure and temperature. The significant range of temperature and pressure, i.e., 125–320 °C and 5–200 bar, is respectively used for the pretreatment of LB [68]. Yang and co-workers pretreated the bamboo chips with liquid hot water for bioethanol

Table 3 (continued)

Pretreatment method	Advantage	Disadvantage	References
Nanoscale pretreatment	It is an inexpensive process because of the reutilization and the easy recovery of immobilized enzymes for the pretreatment of LB	More research is needed	[34]
Combined pretreatment	More effective and advantageous than other pretreatment methods	Costly process as it is required different chemicals	[65]

production. After the pretreatment, xylan and lignin content were reduced from 18.2%, 14.6% to 14.7% and 12.9%, respectively. The highest production yield of glucose, ethanol and xylose were recorded as 53.3%, 4.8 g/L, and 57.3%, respectively [70].

3.2.3 Ammonia pretreatment

Several pretreatment methods are utilized in which the ammonia is used as a major component such as the ammonia fiber explosion method, aqueous ammonia soaking method, and the ammonia recycle percolation method [71]. The ammonia fiber explosion technique is a kind of alkaline thermal pretreatment which reduces the quantity of lignin but also removes the hemicellulose content and decreases the crystallinity of cellulose [71–73]. Their certain advantages are minimum production of inhibitors, release of waste water, high storing of solid material about 18% or higher, and low alteration in the native structure of lignin [74]. In a study, Zhang and co-worker utilized the ammonia sulfate with enzymes by efficiently hydrolyzing the biomass of bamboo. The lignin content was reduced significantly from 22.94 to 1.21% and obtained glucose with maximum yield of 100% in 48 h [75].

3.2.4 Carbon dioxide explosion pretreatment

This method is harmless, inexpensive, incombustible, and also requires a low temperature. The release of fully pressurized explosive CO_2 directly penetrates the substrate of LB which improves the hydrolysis process by enhancing the surface area [76]. The supercritical CO_2 (sCO_2) acquires the liquid density and shows the gaseous attributes at absolute temperature (31 °C) and pressure (7.4 MPa) [68]. Sohni and co-workers pretreated the palm oil biomass by utilizing the sCO_2. The enzymatic hydrolysis reaction was employed to achieve a more cellulose content of 61% as compared to an untreated sample [77].

3.2.5 Wet oxidation

It is a nonspecific process which is commonly carried out at elevated temperature and pressure, respectively [68]. During this process, various oxidation reactions exist which release the organic acids that solubilize, delignify, and hydrolyze the hemicellulose content [78]. Biswas and co-workers utilized the wet oxidation method with enzymes for efficiently hydrolyzing the LB of poplar sawdust and the digestibility of hemicellulose (75%) and cellulose (83%) were enhanced [79].

3.3 Chemical pretreatment methods

The chemically based pretreatment techniques are more convenient to facilitate the degradation of complex biomass [80]. The various methods of chemical pretreatment were described as follows:

3.3.1 Dilute acid

Sulfuric acid is mostly utilized for the pretreatment of agricultural residues such as corn stover, poplar, tidy, and switchgrass [81, 82]. Slathia and co-workers utilized the dilute HCl for the enzymatic hydrolysis of pine needles (*Pinus roxburghii*) and maximum yield of sugars (0.43 g/g biomass) was observed [83].

3.3.2 Alkaline

This method utilizes alkalies such as potassium hydroxide, calcium hydroxide, ammonium salts, and sodium hydroxide for the pretreatment of LB [84, 85]. Bay and co-workers utilized sodium hydroxide for the hydrolysis of softwood pine and hardwood poplar and obtained the enhanced bioethanol yield (109.83 g/kg initial pinewood and 101.44 g/kg initial poplar wood). [86].

3.3.3 Ozonolysis

The lignin content was significantly degraded when treated with this process [87]. The different forest residues such as softwood sawdust and hardwood sawdust were treated to reduce their lignin content. After the ozone pretreatment, the release of these monolignol compounds were enhanced which signifies the delignification of forest residues [88].

3.3.4 Ionic liquids

The solvents utilized in this method have significant properties such as low level of vapor pressure, low liquefying point, high level of heat energies which are stable and also high level of polarization [0]. It disrupts the complex structure of LB by competing with the hydrogen bonds which are existing in the complex. Ionic liquids separated the cellulose from lignocellulose present in forest waste: poplar, softwood pine, sawdust and also recycled the costly ionic liquids for further process [89].

3.3.5 Organosolv pretreatment

In this method, solvents are used for disintegrating the lignin or hemicellulose along with the use of acid catalysts such as hydrogen chloride or sulfuric acid [89, 90]. Different organic acids and solvents are utilized in this process such as salicylic acid, oxalic acid, acetylsalicylic acid, acetone, ethanol, tetrahydrofurfuryl alcohol, ethylene glycol, triethylene glycol, and methanol [91, 92]. Alio and co-workers pretreated the softwood species such as pine, fir, spruce, douglas fir, and scots pine, and approximately 80% of cellulose content was recovered with 70% of purity [93].

3.3.6 Deep eutectic solvents

This method employed a eutectic mixture which is composed of two or three cost-effective components [94]. Choline chloride is frequently utilized and shows significant advantages such as it acts as a receiver of hydrogen bond, biodegradable, easily recovered, and also has the ability to form the deep eutectic solvents (DESs) by associating with the hydrogen donors such as carboxylic acid, polyols, and urea [95]. Lin and co-workers observed maximum yield of glucose (76.9%) and xylose (81.3%) from the hydrolysis of bamboo residuals by using DESs [96].

3.4 Biological pretreatment

In contrast with traditional physical and chemical pretreatment strategies, the biotic/biological pretreatment method is recognized as an effective, eco-friendly, and very low energy consumption process [97]. These treatments are accomplished by microbes like soft-rot fungi, earthy brown fungi, and white fungi which mostly disintegrates the hemicellulose, lignin, and very little amount of cellulose [98, 130]. Suhara and co-workers pretreated the bundles of bamboo with fungi such as *Punctularia* sp. After pretreatment, the total sugar yield (60.3%) was enhanced and the lignin content was reduced [99].

3.5 Combined pretreatment

The combination of pretreatments shows significant advantages such as enhancing the sugar production efficiency, limiting the production of inhibitors and reduction in processing time. The combined process is easily scalable and highly efficient to recover the lignin and hemicellulose [100]. Mahajan and co-workers investigated the impact of consecutive physicochemical pretreatment viz. steam explosion, grinding, and acid base-acid pretreatment on the pine spikes. Approximately 65.92% of cellulose content and 21.34% reduction of total lignin content were observed [101]. The combination of alkali and ionic liquids increase the disintegration of sugarcane bagasse biomass. After 24 h, maximum production of xylanase (833 IU L^{-1} h^{-1}) and high content of cellulose were observed [102].

3.6 Nanoscale pretreatment methods

The conventional pretreatment methods have limitations to minimize the rate of polymerization and crystallinity of cellulose. The production of inhibitory compounds, incomplete digestibility of LB, and the production of monomer compounds of lignin remains the hurdles for enzymatic hydrolysis of LB. The main challenge is how to eliminate the lignin compounds completely, cost-effectively while maintaining the purity of sugars which are further utilized in the production of biofuels [103]. To overcome all these issues, the introduction of nanotechnology greatly impacts the biorefinery industries with their significant properties. Recently, pretreatment methods based on nanotechnology are being explored at broad level [21]. This technique basically depends upon the penetrating ability of nanoparticles which helps to penetrate the cell membrane of LB. The interaction of nanoparticles with the other chief components to release the targeted molecules like hemicellulose or lignin under the severe conditions. To enhance the functioning of the chemical catalyst, this technique produces a high level of shearing in the reactor which disintegrates the LB recalcitrance [104]. The use of magnetic nanoparticles is a favorable methodology for the pretreatment of LB and it also possibly gives us different benefits. Easy retrieval and reusability of the immobilized enzyme make this technique a cost-effective methodology. Nanoparticles have gained the attention of the researchers due to their significant properties such as nanoscale size, high surface area to volume ratio and forms a large number of active sites that participates in different reactions, high reactivity, thermal stability, chemically stability, high specificity, high catalytic efficiency, high rate of crystallinity, and high adsorption capacity. All these novel properties of the nanoparticles play a significant role in the production of biofuels [67].

3.6.1.1 Acid-functionalized magnetic nanoparticle (AFMAN) Acid-functionalized magnetic nanoparticles are the strong acid nanocatalysts, for example nanoscale magnetic particles (NMN). Such nanoparticles act like acid (as in the event of acid pretreatment) in decomposing the LB during pretreatment (Fig. 2), yet their magnetic behavior empowers their retrieval with the recycle of magnet to employ them [105]. Examples of the acid functionalized magnetic nanoparticles incorporate alkyl-sulfonic acid functionalized nanoparticles, silica-protected cobalt bearing spinel ferrite nanoparticles, and silica-propyl sulphonic functionalized nanoparticles. Silica-covered nanoparticles that function with the carboxylic acid, and propyl-sulfonic acid, and perfluoropropyl-sulfonic acid to fully catalyze the decomposition of disaccharide sugar such as cellobiose and essentially solubilize wheat straw hemicelluloses brought about 58–90% dextrose yield of the hemicellulose. The

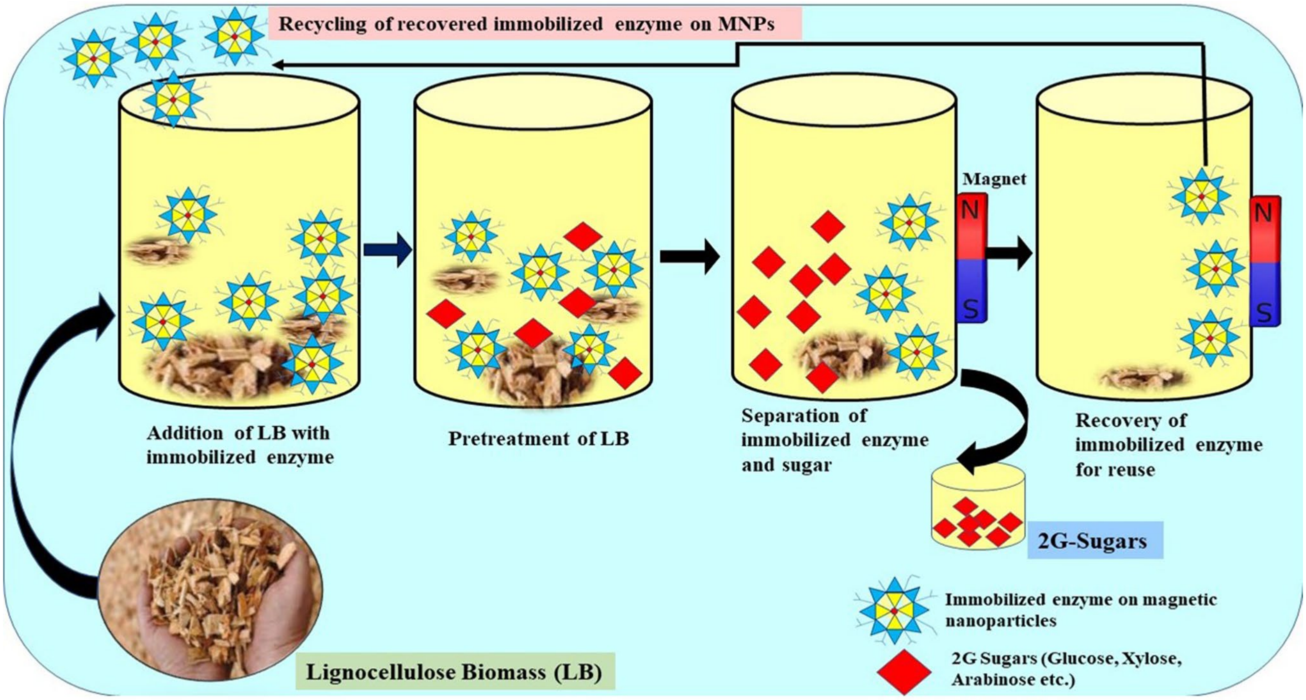

Fig. 2 Hydrolysis of lignocellulosic biomass using cellulase immobilized on magnetic nanoparticles (MNPs)

sulfonated magnetic carbonaceous nanoparticles utilized throughout the hydrolysis series of various LB showed a 78% transformation of cellobiose with a better retrieval rate [106]. Researchers pretreated the sugarcane bagasse by utilizing the two types of acid functionalized magnetic nanoparticles, i.e., alkylsulfonic acid and butylcarboxylic acid. About 500 mg/g of sugarcane bagasse biomass was treated with both the acids such as alkyl sulfonic acid and butyl carboxylic acid, and it released high amounts of sugar, i.e., 18.83 g/L and 18.67 g/L, respectively. It was comparatively high as compared to the sugar yield of non-treated biomass. It is also cost-effective due to the magnetic nature of nanoparticles. By applying the magnetic field, the nanoparticles are recovered easily for further use [106]. Guo and co-workers utilized the immobilized enzyme laccase for the hydrolysis of corn stover. They synthesized the magnetic nanoparticles for the immobilization of laccase and utilized them in the pretreatment process. By using the immobilized laccase, the degradation rate of lignin was about 40.76% which was high as compared to control. After the pretreatment process, this immobilized enzyme was recycled for further use. Approximately 50% of reutilization activity were retained after 6 cycles [107]. Khalid and co-workers combined two methods such as alkaline pretreatment method and magnetic nanoparticles for the pretreatment of rice straw. Alone each method gives minimum yield of biogas and methane but in the combination of 2% sodium hydroxide and 100 parts per million of magnetic nanoparticles enhance the yield of biogas and methane by 100 and 120% respectively as compared to the control sample [108].

Nanoscale shear hybrid alkaline (NSHA) method In this method, the combination of chemical catalyst like an acid, volatile solvent, or alkali and the high-speed shear force degrades the recalcitrance of LB [67]. A specific reactor, i.e., Taylor-Couette, is utilized to give the shearing force of around 10,000 s^{-1} LB for a few minutes in the occurrence of a chemical catalyst. The high production of cellulose is recovered in a simpler edible form. NSHA permits effective lignin disposal with cellulose and hemicellulose work in a brief timeframe [109]. Wang and his co-workers used the NSHA method for pretreatment of corn stover biomass for the production of biofuel. Around 12,500 s^{-1} shear rate and sodium hydroxide in 1:1 proportion were used on biomass for one minute at room temperature. After the pretreatment, about 70% of cellulose was converted which impacts positively on the production of biofuel [110]. Various studies on the NSHA pretreatment method indicate that lignin and hemicellulose content were eliminated from the original sample and left approximately 80% of the cellulose content [34]. Researchers used the cellulase enzyme which performs synergistic action like degradation of biomass and formed minute size polysaccharides agglomeration. These molecules are further converted into simple sugar molecules by the NSHA pretreatment method. In fact, the combination of immobilized cellulase and NSHA pretreatment method improves the enzymatic degradation of biomass by 4- to fivefold and converts into the simple forms of sugars which are further utilized in the production of biofuels [109].

3.6.1 Synthesis of nanoparticles

A wide range of methods are available for the synthesis of nanoparticles. It includes the physical, chemical, and biological techniques. All these techniques are broadly categorized into bottom-up and top-up approaches. Each method has its own advantages and disadvantages [110]. Though biological methods are mostly recommended for the nanoparticles synthesis as they are toxic free, eco-friendly, and release a minimum number of inhibitory compounds which affects the functioning of biocatalyst during biofuel production. Biological methods are more favored because they are less expensive and also require a minimum amount of energy for the production of biofuel [111–113]. Different synthesis methods of nanoparticles are described in Table 4.

4 Nanomaterials in the immobilization of enzyme and their role in the pretreatment of LB

The different concerns are related with the conventional pretreatment techniques. Thus, it is necessary to utilize novel, environment-friendly, and cost-effective pretreatment methodologies. It is demonstrated that nanotechnology-based methods can play a significant role to overcome the issues of other methods. The high usage of nanotechnology in various regions, including the production of biofuels, has drawn the attention of various researchers. The forming units of LB are nanometric in dimensions, so the nanotechnological technique can be utilized to improve the characteristics of lignocellulosic material [109]. The nanoscale instrumentation and enzymatic reactions are utilized for analyzing the structure of lignocellulose biomass which helps to improve the conversion process (fermentation, gasification, etc.) of biomass for the production of biofuels. Nanoparticles play an important role in the production of biohydrogen which occurs in the dark fermentation conditions. Specifically, the inorganic nanoparticles like iron, silver, nickel, and titanium oxide have expanded the production efficiency of biohydrogen [114].

Nanomaterials are the smaller size entities that help to penetrate smoothly into the cell membrane of LB to deliver monomeric and oligomeric sugars. It is used in the pretreatment process and also hydrolyzes the LB by using enzymes for the conversion of biomass. The pretreatment of lignocellulose biomass by utilizing the nanomaterial is proven as a cost effective and environment friendly process. Nanotechnology has the capability to enhance the structure of biomass at atomic level. Nanomaterial with magnetic characters are ideally utilized as it helps in their retrieval from reaction mixture and reutilize; in this manner, it makes the procedure economical [115]. Recently, nanomaterials have been used for the immobilization of enzymes that enhance their reusability [116]. Various nanomaterials used for immobilization of enzymes are discussed in Table 5. Cellulase, hemicellulase, and other lignolytic enzymes are immobilized on different nanomaterials. In hydrolysis, various nanomaterials are utilized as a pillar for immobilizing the enzymes which mostly incorporate the different nanomaterials such as magnetic, silica, nickel, and oxide nanoparticles. Nanomaterials can mainly enhance the productivity of immobilized proteins

Table 4 Various methods for synthesis of nanomaterials

Synthesis approach	Advantages	Disadvantages	Techniques for synthesis	References
Bottom-up	Cost-effective, uniformity and large scalability Limited defects in the structure of nanoparticles	Require compatible molecules and surface Has limitation in changing the structure of atoms and molecules	Electrochemical oxidation or reduction, Chemical reduction, sonochemical synthesis, solvothermal synthesis, photochemical synthesis, thermolysis, co-precipitation, microemulsion, sol gel fabrication, microwave-assisted synthesis, atomic layer deposition, arrested precipitation, vapor phase chemical deposition, biological methods which includes bacteria, fungi, yeast and plant extracts	[172–176]
Top-down	Simple method	Requires costly and heavy instruments Defects in surface structure creates hinderance in fabrication of nanoparticles and this applicable for large-scale production not for small scale	Ball milling, micromachining, arc discharge, ion-sputtering, laser excision, inert-gas condensation, lithography which includes electron beam, nanoimprint, scanning probe, block copolymer	[172, 177–180]

Table 5 Different types of nanomaterial used for immobilizing the enzyme and their pros and cons

Type of nanomaterials	Enzyme	Immobilizing method	Activity	Advantages	Disadvantages	References
Chitosan-coated magnetic nanoparticles	Laccase	Cross-linking	High delignification rate, i.e., 84%	Strong binding between the enzyme and nanoparticles Limits the desorption	Changes in the active site occur	[181]
Amino-functionalized magnetic nanoparticles modified with copper ions	Laccase	Physical adsorption	Lignin content up to 41% was degraded and around 38% of cellulose conversion rate	Limits the inactivation of enzyme by combining with copper ions Increases the enzyme desorption	Highly sensitive method to the temperature, pH Sometimes weak bonds cause the biocatalyst desorption, requirement of modification	[107]
Chitosan-coated magnetic nanoparticles	Cellulase	Covalent binding	The maximum sugar yield was noted as 22 g/L	High stability and easily recycle Increase the surface area	Requires further functionalization, matrix cannot regenerate	[182]
Magnetic iron oxide nanoparticles	Cellulase	Covalent binding	The yield of reducing sugar was noted about 457 mg g^{-1}	Easy recyclable due to magnetic nature of nanoparticles	The matrix and support material are non-renewable	[183]
Dextran coated iron oxide magnetic nanoparticles and glyoxyl agarose	Endocellulase and β-glucosidase	Cross linking	The maximum sugar yield was noted as 14 g/L	High stability, biocompatible, high surface area, easily recyclable	Alteration in the active site might be occur	[184]

since it expands the surface region for the enzyme connection, which improves the loading efficiency of enzymes [117].

In various hydrolytic responses, the nanobiocatalysts are retrieved and reutilized frequently. Lignocellulose material can be hydrolyzed using nanomaterials and can be attained by two main approaches such as covalent cross-linking or physical adsorption and utilizing the functionalized nanomaterial [34]. Recovering and reutilization of the pretreated nanocatalysts will be useful in limiting the cycle value because of the least demand of downstream handling. The acid functionalized magnetic nanoparticles also play a significant part in cost reduction. They are also considered as solid acid nanocatalysts having solid potential to catalyze hydrolysis response. These nanoparticles have the advantage that they can be recycled due to their magnetic nature [118]. It can also increase the production of sugars. At 175 °C, by using the 0.8% of sulfuric acid, the LB of yellow poplar saw changed into the 96% of hemicellulose. At 160 °C, sulfuric acid along with nanoparticles changed hemicellulose content to 66% and 61% with 50- and 400-fold, respectively [119].

Different techniques and nanomaterials were used such as magnetic nanocatalyst, nanofibers, nanofiltration, nanotubes, nanosensors, and nanoshear hybrid alkaline procedure (NSHA). Different nanomaterials in pretreatment of LB are depicted in Table 6. Nanoreactor empowered with high speed shear is used for removal of lignin in NSHA at mild temperature [120]. Nanocatalysts, i.e., particles of very small size, are undergoing an explosive development to enhance the hydrolysis of LB. Nanocatalyst designs the catalyst with high performance, great sensibility, and high steadiness, and all these properties can be effortlessly acquired by shortening the dimensions, heat or chemical steadiness, and morphological and electronic structures of specific nanomaterial [121]. At 95 °C, around 6.18-fold of amino acid creation and about 18-fold deletion of lignin content was done by utilizing the nanoparticles of magnesium oxide with functional protease as compared with unprocessed enzymes. By contrasting with the samples of preprocessed cellulase, it was observed that about 30-fold of reducing sugars are produced, when the preprocessed samples of MgN-pro were exposed to xylanase-initiated magnesium oxide nanoparticles at 8 °C. Sugarcane bagasse were treated with xylanase along with magnesium oxide nanoparticles that produced 1.82-fold reducing sugars at 8 °C as contrast with the unprocessed samples [122].

Magnetic nanocatalysts, i.e., magnetically recovered gold nanocatalysis, was assessed in various responses, for example, manufacturing of propargylamines and couplet response [123]. Nanoimmobilization of hydrolytic compounds, for example, cellulase, xylanase, and laccase, that react on lignocellulose compounds is reported to enhance long-run steadiness of catalysts under severe conditions

Table 6 Significant functions of nanomaterials in pretreating the lignocellulose biomass

Substratum	Nanomaterial	Pretreatment conditions	Properties	References
Wheat straw	Nickle oxide nanoparticles (NiOx)	Four different concentrations of NiOx (1 to 4%) were used at varied duration of radiation exposure time (0 to 4 h) for the pre-treatment of wheat straw	More than 40% of methane was produced with 3% of NiOx in 4 h	[185]
Sugarcane bagasse	Magnesium oxide nanoparticles	The sugarcane bagasse pretreated with MgN-pro and MgN-xyl, which increases the amino acid production by sixfold and more than 30-fold at temperature of 90 and 8 ℃, respectively	After 24 h, the substrate changes rate of treated xylanase and MgN-xyl was 58 and 77, respectively	[122]
Sugarcane bagasse	Iron oxide magnetic nanoparticles	Pretreated slurry of sugarcane bagasse powder was further treated with immobilized cellulase, both incubated for 24 h at varied range of temperature (27–60 °C)	Glucose yield was 72% after 24 h	[186]
Rice straw	Magnetic nanoparticles (β-cyclodextrin conjugated Fe_3O_4)	Cellulase immobilized on magnetic nanoparticles and then the reducing sugars were determined	The sample (sodium cyanohydride-containing) maintained 85% of the initial activity and the control maintained only 40% of the activity, in 192 h	[187]
Hemp hurd	Magnetic nanoparticles	Biomass was treated with immobilized cellulase at 60 °C, and the samples were removed at every 12 h of intervals	About 98% of biomass was hydrolyzed in 48 h	[188]
Agave atrovirens leaves	Cellulase immobilized on Fe_3O_4-chitosan coated magnetic nanoparticles	Agave leaves pretreated with immobilized cellulase for a period of 20 h at 50 °C temperature	5 g L^{-1} of glucose released. By increasing the concentration of biomass, the concentration of glucose also increasing	[189]
Corn stover	Laccase immobilized on magnetic nanoparticles	Pre-cleaned corn stover treated with immobilized laccase with sodium acetate solution for about 72 h	Lignin up to 41% was hydrolyzed	[107]

[124]. Shaheen and his co-workers used nanomaterials to produce useful materials from futile squanders, predominantly sawdust. Researchers utilized the wood sawdust for extracting the cellulose nanocrystal by utilizing the technique of acid hydrolysis through execution of ultrasonication strategy. The magnetic nanoparticles are utilized for the breakdown of cellulose and their production is done by chemical precipitation technique [125]. These nanoparticles were utilized for immobilizing the cellulase which improved the hydrolytic viability of biomass than the free form of cellulose. The researchers observed the activity of immobilized cellulase, and it showed that after 48 h, the initial run of hydrolysis response released more amount of glucose (20 g/L) than the free form of cellulose (14 g/L). After the pretreatment of 48 h, the immobilized catalyst maintained its steadiness in the second and third cycles and released glucose of about 6.15 g/L and 3.03 g/L, respectively [126–131].

On the other hand, the carbon nanotubes (CNTs) have drawn much consideration for biomass pretreatment because of their outstanding design and high ability to offer significant properties like high tensile durability, high thermal characters, and the electrical strength [131, 132]. They are formed of graphite sheets which are organized in a round and hollow shape and depending on the number of layers such as single-walled CNTs or multi-walled CNTs. Multi-walled CNTs seem to be more favorable for immobilizing the cellulase as they enhance the electronic characters, high physical and chemical steadiness, economic, easily prepared, and safe as contrast with the single-walled CNTs [133]. The immobilization of enzymes on carbon nanotubes shows consistent and dynamic nature at elevated temperature, high surface region, high protein value, and prevalent distribution in combination with the other supportive qualities, for example, reciprocal of the mass transfer coefficient also reutilizing the enzyme.

The utilization of carbon-based nanomaterials for immobilizing the cellulase was studied by different researchers. Ahmad and co-worker immobilized cellulase on multi-walled CNTs through carbodiimide mixing which were isolated from *Aspergillus niger*. At significant pH and stable temperature, the immobilized cellulase maintained 85% of enzyme activity and also reused multiple times for hydrolyzing the cellulose [132]. Azahari and his co-workers isolated the cellulase from *Trichoderma reesei* was additionally immobilized onto multi-walled CNTs by using the physical adsorption strategy. Despite its usage for 3 cycles, it maintained its enzymatic activity up to 60% [134]. Consequently, the utilization of nanoparticles enhanced the catalytic proficiency of enzymes which plays a significant part in enhancement of pretreatment of lignocellulosic biomass.

5 Role of nanotechnology in the production of bio-renewables and energy

The nanotechnology field is emerging very rapidly. Their significant applications are widely spread all over the world. Nanotechnology shows high potential in various sectors such as healthcare, food, agriculture, and biofuels [34, 135]. The demand for fossil fuels is increasing day by day. These non-renewable energies are very harmful for the environment, so there is a need for an alternative source of energy, i.e., renewable energy. Renewable and sustainable energy has limited the environment pollution and also meets the demand of energy globally. The utilization of LB feedstocks make this process more economical, sustainable, and eco-friendly [136]. Different conventional pretreatment methods were used for the production of biofuels but they showed certain disadvantages such as environmental pollution, time consumption, and high cost of chemical substance/catalysts. To overcome all these drawbacks, the utilization of nanomaterials in the pretreatment of LB makes this process cost-effective, sustainable and environment friendly [113]. Various nanomaterial such as nanoparticle, nanobiocatalyst, magnetic based nanomaterial has been utilized in the production of different renewable bioenergy (biogas, bioethanol, biodiesel, bio-oil, biohydrogen) with utilizing the lignocellulosic raw material. The production of various renewable energy by utilizing the nanotechniques are discussed in Table 7. The nanoscale dimensions of nanoparticles play a major role in the disintegration of LB. As they easily penetrate the cell wall of LB and interact with the constituents of LB, they release a high amount of sugars. These released constituents are further treated with the nanomaterial immobilized enzyme for the enzymatic hydrolysis process and improves the production of renewable energy [137]. Utilization of immobilized enzymes in the hydrolysis makes this process economical by recovery and reutilization of highly costly enzymes.

Acid-functionalized magnetic nanoparticles are used for immobilizing the enzyme for the hydrolysis of lignocellulose biomass. Magnetic nanoparticles have certain important characteristics such as high surface area, thermal stability, and high specificity. Their magnetic nature shows high potential in recovering the enzyme by applying the magnetic field [138]. Ali and his co-workers utilized the nickel and cobalt nanoparticles as a nanocatalyst for the production of biodiesel, biogas, and bio-oil by hydrolyzing the mixed weed lignocellulose biomass through gasification process. This whole reaction was carried out at 400 °C temperature. These bioproducts were analyzed by GC–MS technique, and it was observed that about 65.47% of esters were present in biodiesel, and it

Table 7 Various nanotechnological approaches used in the production of biorenewable energy

Nanomaterial	Bioenergy production	Application	Reference
Magnetic nanoparticles	Biogas	Enhance the lignocellulosic biomass degradation, increase surface-volume ration and adsorption rate for the rapid production of biogas	[19]
Nanomaterials	Biohydrogen	Increase the catalytic efficiency, improves stability, reusability and proficiency of enzyme	[190]
Nanocoating on microbial fuel cells	Bioelectricity	Shows high electrical conductivity and voltage stability	[191]
Magnesium oxide nanocatalyst	Biodiesel	Widely used base catalyst, high rate of esterification	[140]
Graphite carbon nitride nanosheets	Bioethanol	Improves the laser irradiation which directly increases the yield of bioethanol	[192]
Iron nanoparticles (zero valent)	Biohydrogen	Increases the transfer of electrons between hydrogenase and ferredoxin which directly enhance the enzymatic activity	[139]
Nickel nanoparticles and graphitic carbon nitride nanosheets	Biohydrogen	Increases the biostimulation of purple non-sulfur bacteria that enhance the yield of biohydrogen	[141]
Bio-iron nanoparticles	Biodiesel	Improves the transesterification reaction due to its high catalytic activity, high surface area and small size of particles	[142]
Graphene oxide and platinum-ruthenium nanocomposites	Bioethanol	Enhances the chlorophyll content in biomass of *C. minutum* and also improves the production of bioethanol	[193]
Zinc oxide nanoparticles	Biogas	Improves the anaerobic digestion process that directly improves the production of biogas	[143]

is higher than the routinely produced biodiesel. The ester concentration shows that its quality is higher than the normally produced biodiesel. The GC–MS analysis showed that the biogas consists of various components such as methanol (34.64%), propane (8.32%), methane (3.76%), ethene (50.16%), and propylene (3.12%). The utilization of nanocatalyst makes this process economically feasible [121].

For the production of clean and sustainable bioenergy, different types of nanomaterials were used. The zero valent iron nanomaterial is one of them which shows significant properties for the production of biohydrogen via dark fermentation of grass. It removes the undesirable amount of oxygen from the system which improves the activity of oxygen sensitive hydrogenase and also decreases the oxidation–reduction potential that favors the growth of fermentative microbes. The zero valent iron nanoparticles also enhance the microbial communities which directly enhance the metabolic reaction for the hyper production of biohydrogen. Maximum production of biohydrogen was observed as 64.7 ml per gram of dry grass [139]. Ashok and co-workers utilized the magnetic oxide nanoparticles for the production of biodiesel. The magnetic oxide nanoparticles were synthesized by co-precipitation method which was further used for the transesterification of cooking oil for the production of biodiesel. The transesterification reaction was carried out at a temperature range of between 25 and 75 °C for 1 h with continuous stirring. The maximal yield of biodiesel was about 93.3% with 2 weight% of magnetic oxide nanoparticles [140].

Attia and co-workers utilized the graphitic carbon nitride nanosheets and nickel nanoparticles for enhancing the production of biohydrogen from biomass. The laser-photoactivated nanomaterials biostimulates the purple non-sulfur bacteria growth and activity which directly increases the yield of biohydrogen. The graphitic carbon nitride nanosheets show maximum production of biohydrogen than nickel nanoparticles [141]. For the sustainable production of biofuels, researchers utilized bio-iron nanoparticles for the production of biodiesel in which micro-algal biomass has been used. Bio-nanocatalyst (bio-iron nanoparticles) enhances the transesterification reaction due to its high catalytic activity, high surface area, and small size of particles. Bio-nanocatalyst converts the lipid extraction into the fatty-acid methyl esters which was a very suitable choice for enhancing the biodiesel production [142]. Hassaan and his co-workers used zinc oxide nanoparticles for the production of biogas. Five different crops such as barley, abyssinian cabbage, rapeseed, durum wheat, and triticale have been used as a biomass for biogas production. These nanoparticles improve the conversion efficiency in anaerobic digestion process. Out of five biomasses, durum wheat treated with zinc oxide nanoparticles shows the maximum production of biogas such as 457 mL/g volatile solids which was higher than the control [143].

6 Conclusion

The utilization of lignocellulose biomass for the production of cost-effective bioenergy and mitigation of environmental pollution is the need of the moment. Different conventional pretreatment methods such as physical, chemical, and biological have certain disadvantages which makes the process inconvenient, costly, and also cause environmental pollution. Therefore, there is an urgent need for an economically feasible and eco-friendly method for the pretreatment of LB. Currently, the various applications of nanotechnology make this process convenient, cost-effective, and eco-friendly. On the other side, it is responsible for the minimum production of toxic inhibitors as compared to the conventional pretreatment methods. Hence, the use of magnetic nanoparticles in biomass pretreatment or immobilizing the enzyme used in the saccharolytic process is considered as the most favorable process. It shows the high reusability and recovery of immobilized enzymes due to their magnetic nature. The small size of nanomaterials easily penetrates into the cell wall of lignocellulosic biomass matrix (cellulose, hemicellulose, and lignin). These components of biomass will be further utilized for the cellulose conversion via enzymatic hydrolysis. Nevertheless, the detailed mechanism of the pretreatment process by using nanotechnological routes is not well understood. In the future, the detailed study of their mechanism should be done to enhance the potential of nanotechnology approaches for large-scale production of biofuels or biochemicals.

Acknowledgements One of the authors, Dr. Madan L. Verma, is grateful to the Director, Indian Institute of Information Technology Una, Himachal Pradesh, India, for providing the necessary facility to accomplish the research work.

Author contribution Madan L. Verma had the idea for the article. All authors contributed to the literature search and data analysis. The first draft of the manuscript was written by Madan L. Verma and Heena Chandel and all authors commented and critically revised the work. All authors read and approved the final manuscript.

Funding One of the authors, Dr. Madan L. Verma, gratefully acknowledges the financial support of Himachal Pradesh Council for Science, Technology and Environment (HIMCOSTE Sanction Order: No. STC/F(8)-6/2019(R&D 2019-20)-377) for the present work.

Declarations

Conflict of interest The authors declare no competing interests.

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