




Review

Recent Developments in Lignocellulosic Biofuel Production with Nanotechnological Intervention: An Emphasis on Ethanol

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Abstract: Biofuel, an inexhaustible fuel source, plays a pivotal role in the contemporary era by diminishing the dependence on non-renewable energy sources and facilitating the mitigation of CO₂ emissions. Due to the many constraints in existing technology and the resulting increased costs, the production of biofuels on a large scale is a laborious process. Furthermore, the methods used to convert varied feedstock into the intended biofuel may vary based on the specific techniques and materials involved. The demand for bioethanol is increasing worldwide due to the implementation of regulations by world nations that mandates the blending of bioethanol with petrol. In this regard, second-generation bioethanol made from lignocellulosic biomass is emerging at a rapid rate. Pre-treatment, hydrolysis, and fermentation are some of the technical, practical, and economic hurdles that the biochemical conversion method must overcome. Nanoparticles (NPs) provide a very effective approach to address the present obstacles in using biomass, due to their selectivity, energy efficiency, and time management capabilities, while also reducing costs. NPs smaller dimensions allow them to be more effective at interacting with lignocellulosic components at low concentrations to release carbohydrates that can be utilized to produce bioethanol. This article provides a concise overview of various biofuels and the nanotechnological advancements in producing it, with a particular emphasis on ethanol. It provides a detailed discussion on the application of nanotechnology at each stage of ethanol production, with a particular emphasis on understanding the mechanism of how nanoparticles interact with lignocellulose.

Keywords: biofuels; nanomaterials; nanoparticle interaction; agricultural residues; fermentation



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1. Introduction

In view of the severity of the threat posed by catastrophic climate change, typically caused by the burning of fossil fuels, it is becoming increasingly apparent that civilizations must modify the way they generate and utilize energy. Increasing the stream of safe, clean, and benign energy will be challenging and needs adequate inventiveness and capital. There are several resource and technological choices that might reduce emissions in the transportation, shipping, electricity generation, and boiler/heating industries while strengthening energy security [1]. A crucial strategy for guiding the transition from an oil-based economy to a novel bioeconomy—a bioeconomy that seeks to achieve a more productive and sustainable global development by achieving a BCG economy—is the biorefinery approach. This approach aims to produce biofuels, platform chemicals, and bioproducts from insatiable biomass sources. As a result, this a strategy emphasizes safe

and green chemical processes, aims to reduce waste discharges, creates new opportunities for markets, and makes better use of available resources. The bioethanol production from waste agricultural residues aligns with SDG-7 (Affordable and Clean Energy) and SDG-12 (Responsible Consumption and Production) by utilizing agricultural residues and non-food crops. This approach reduces waste and promotes efficient resource utilization for energy production and contributes to the global goal of achieving net zero emissions by 2050 [2,3]. However, in order to compete with petroleum in the long run and maintain economic viability, it is crucial to concentrate on producing bioethanol at a low cost with the integration of advanced technologies and multidisciplinary approach.

The market for bioethanol was estimated at USD 33.61 billion in 2021 and is anticipated to grow at a CAGR of 14.1% in the coming years, with revenues expected to reach USD 101.64 billion in 2030 [4]. Molasses from sugar cane, starchy crops, agricultural remains, and other discarded crops can all be used to make bioethanol. Manufacturers are concentrating on miscanthus, switch grass, and sugarcane bagasse as energy crops for production, with Europe, North America, Asia Pacific, Middle East, Latin America, and Africa included in the regional scope. Government regulatory agencies promoting production are the main factors driving the global bioethanol industry [5]. The industry is expanding due to rising government initiatives to generate and utilize cleaner fuels such as bio-ethanol as well as the rising demand for blending in petrol. Some of the key market players in the bioethanol industry are Archer Daniels Midland, Abengoa Bioenergy, BlueFire Ethanol Fuels Inc., Bioethanol Japan Kansai Co Ltd., CropEnergies AG, Cremer Oleo GmbH & Co., Green Plains, Green Future Innovations Inc., Petrobras Biocombustíveis, Nordzucker AG, Royal Dutch Shell PLC, RaizenEnergia, Tereos, Soufflet Group, and Valero Energy Corporation. To increase their consumer base and firmly establish their position in the market, these businesses are extending their reach across a variety of geographies and are breaking into new markets in emerging nations [6].

The introduction of lignocellulosic biomass (LB) resources as a replacement source of green renewable energy has drawn significant recognition in regard to the rising demand for biofuels due to their abundance, absence of competition with food, and ability to produce sustainable value-added compounds, including biofuels [7]. LB feedstocks provide a plentiful source of organic carbon that may be extensively used for their transformation into bio-based chemicals and biofuels with added value. LB is made up of primarily both polar and non-polar polymeric materials such as cellulose, hemicellulose, and lignin [8]. Cellulose (40–60%), hemicellulose (20–40%), and lignin (10–25%) make up the majority of the components in LB products [9]. Due to its abundance and low cost as a feedstock, LB can provide around 40% of the world's energy demands [10]. As of now, a variety of lignocellulose biomass including rice straw [11], elephant grass [12], switch grass [13], palm wood [14], agricultural waste [15], algal biomass residues [16], and textile mill waste including cotton spinning waste [17] are utilized as bioethanol feedstocks. The cell wall's composition, level of lignification, and cellulose's crystallinity, are the major causes of the structural recalcitrance, enabling lignocellulose to resist chemical and biological deconstruction [18]. It is challenging to convert LB into simple sugars because cellulose, a key component of LB, is bound to lignin and hemicellulose through different bonds. A known robust component of LB called lignin prevents the use of biocatalysts and enzymes to hydrolyze polymeric constituents such as cellulose and hemicellulose. Due to this, LB pre-treatment is the only method that can completely remove lignin and allow polysaccharide components to be fully utilized. After pre-treatment, the separated cellulose/hemicellulose-rich elements can be used for enzymatic hydrolysis and subsequent fermentation, while the segregated fractions can be further used to synthesize biochemicals. At the commercial level, for the pretreatment process employed by LB biorefineries, principal cost investment, energy consumption, and whole process efficiency are often taken into account. There are now a number of pretreatment techniques broadly classified as physical, chemical, and physicochemical procedures. The chemical pretreatment uses a variety of chemicals, including acid, alkaline, organosolv, and/or ionic liquids [19]. Pretreatment frequently involves the use of acids in

particular sulphuric acid and alkalies such as NaOH and CaO [20]. These techniques can effectively extract lignin or digest hemicellulose to break down lignocellulose's structural stubbornness [21]. Their use is constrained, however, mainly due to the high-energy need and production of toxic harmful chemicals (hydroxymethyl furfural and furfural) that can impede the activity of biocatalysts employed in fermentation. Nonetheless, the acid and alkali treatment are the most widely used method for the pretreatment of biomass due to its low cost and ambient operating conditions. Additionally, the used acid/alkali in the pretreatment process must be recycled from the hydrolysate after completion of the process to minimize its hazardous impact to the environment, and reusing recycled acid/alkali can improve the process economy [22]. Furthermore, scientists are looking for the best solution that can efficiently saccharize biomass by enzymatic approaches using hydrolases (cellulases and xylanases), oxidoreductases (laccases), recombinant feruloyl esterase, etc. [23,24], and in some cases genetic lignocellulose modification [21,24]. Contrarily, using biological techniques for LB pretreatment has a number of drawbacks, including the need for a catalyst that meets the stringent constraints, a lack of stability, and expensive manufacturing and purifying procedures.

These barriers restrict the use of current techniques and demand for the advancement of a quick, efficient, cost-effective, and environmentally friendly approach for LB pretreatment. As a result, it is preferable to look for better options that include sustainable and energy-efficient methods for pretreating LB materials. As a result, several techniques have recently been developed by researchers, and one of them is nanoparticles (NPs) assisted pretreatment of LB. Nanomaterials are extensively explored in a variety of applications in medicine, pollutant removal, biosensing, biomass conversion, and the production of biofuels due to their numerous advantages, including higher stability, low-cost production, recyclability, and better catalytic ability [25]. Utilizing nanobiocatalytic substances in bioprocesses is aimed at enhancing process efficiency by improving heat and mass transfer, as well as enzymatic and cellular metabolic processes. This is achieved through their vast surface areas, catalytic characteristics, and enzyme cofactor activity [26].

The worldwide application of second-generation (2G) ethanol in commercial production has gradually increased, but it had not yet achieved universal adoption. The production of microbial ethanol on a commercial or pilot scale is not promising due to the huge difficulties in the pretreatment and production processes. This review therefore focuses on the involvement of NPs at various stages of LB derived ethanol production. The breakthroughs in nanobiotechnology that have been achieved in the production of lignocellulosic ethanol are the primary focus of discussion in this review.

2. Lignocellulosic Biofuel

The initial step in the institution of sustainable biofuel production is the capability to use suitable lignocellulosic biomass as feedstock for the selected product, which is otherwise considered trash and is often simply burned, leading to environmental pollution. Lignocellulosic biomass is a plentiful, affordable, renewable, and carbon-neutral resource that can be exploited to make second-generation biofuels without affecting the food security of the world. Its production is enormous on a global scale and accounts for 181.5 billion tons per year [27,28]. Depending on the type, to varying degrees and proportions, these polymers are structured in an intricate, non-uniform, three-dimensional spatial configuration. The hydrophobic property of lignin, the crystalline structure of cellulose, and the encasement of cellulose by the lignin-hemicellulose matrix, which is firmly bound by hydrogen and covalent bonds, all have an impact on the resilience of lignocellulose [29].

Biochemical or thermochemical processes are typically used for transforming lignocellulosic biomass into bioenergy. The biochemical approach uses microorganisms and/or a variety of enzymes to reduce the feedstock into fermentable sugars, which are then fermented to make biofuels, such as bioethanol, biogas, biobutanol, biohydrogen, biodiesel, and so on. Biochemical procedures typically include very mild reaction conditions. The inclusion of a pretreatment step (chemical, physical, or biological), prior to hydrolysis

improves the overall procedure and makes it commercially feasible. The thermochemical route, on the other hand, includes pyrolysis, liquefaction, and gasification to produce a variety of fuels, such as, ethanol, renewable diesel, and aviation fuel. The presence of moisture has a detrimental impact on product yields and emissions, but the thermochemical conversion can employ a wider variety of feedstock and is unaffected by lignin in the biomass.

Alcohol-based biofuels currently make up the majority of the portfolio of liquid biofuels in the traditional bioenergy sector. This mostly consists of so-called “second generation” biofuels such as ethanol and n-butanol, along with natural fermentation products such as iso-butanol and n- and branched isomers of pentanol. There are a variety of biofuels produced out of LB and some of them are mentioned in Table 1 [30–39].

Table 1. Varieties of biofuel produced from lignocellulosic biomass.

Biofuel	Treatment Conditions	Yield	References
Bioethanol	Alkali-pretreated sugarcane bagasse fermented with <i>Clostridium thermocellum</i> DSM 1237	Ethanol: 0.86 g/L (83.3% of theoretical yield)	[30]
	Lignocellulosic biomass-based syngas by freshly cultured <i>Clostridium butyricum</i>	Yield of bioethanol: 29.94 mmol/L of syngas	[31]
Biobutanol	Surfactant pretreatment PEG6000 of apple pomace (100 °C, 5 min), enzymatic hydrolysis followed by fermentation by <i>Clostridium beijerinckii</i> CECT 508 in 96 h.	42 g/L sugars, 3.55 g/L acetone, 9.11 g/L butanol, 0.26 g/L ethanol, 0.276 gB/gS yield; 91% sugar consumption	[32]
	Microwave-assisted alkali pretreated cocoa pod husk, hydrolyzed enzymatically fermentation by <i>Clostridium saccharoperbutylacetonicum</i> N1–4.	Maximum butanol of 54.4 g/L	[33]
Biodiesel	Hydrolysates from steam pretreated sugarcane bagasse and rice husk, used <i>Meyerozyma guilliermondii</i> and <i>Pichia kudriavzevii</i> , respectively.	Maximum lipid concentration: 37.99 +/− 0.003% from <i>Meyerozyma guilliermondii</i> lipid accumulation of 2.39 +/− 0.003 g/L in <i>Pichia kudriavzevii</i>	[34]
	Culturing of <i>Yarrowia lipolytica</i> on hydrolysate of lignocellulosic biomass	12.01 g/L lipids with a maximum yield of 0.16 g/g	[35]
Biohydrogen	Napier grass alkaline hydrolysate at pH 5.5; dark fermentation for 48 h at mesophilic temperature	Maximum amount of hydrogen −763.34 mL	[36]
	Chemically pretreated sugarcane bagasse subjected to bacterial hydrolysis followed by dark fermentation with <i>Clostridium butyricum</i> CGS5	Maximum hydrogen yield: 6.01 mmol H ₂ /g reducing sugar for bagasse	[37]
Biogas	Enzymatic pretreatment by mixed enzymes secreted by <i>Trichoderma viride</i> and <i>Aspergillus</i> sp. in 2:3 ratio	Methane yield: 512.64 mL/g TS added; 31.74% higher than the control	[38]
	Fungal pretreatment of cereal crop materials (rye, wheat, barley, triticale)	Increase in methane yield: 10–18%; 80% cellulose degradation	[39]

2.1. Bioethanol

Separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), Pre-saccharification and simultaneous saccharification and fermentation (PSSF) and consolidated bioprocessing (CBP) are the primary adopted techniques for bioethanol production [40]. Considering bioethanol, the saccharification-fermentation process is the main biological mechanism for converting lignocellulosic biomass into bioenergy. According to this method [41], biomass is hydrolyzed to create monosaccha-

rides, which are subsequently fermented to generate ethanol. An alternative to this is gasification-fermentation, which eliminates the intricate saccharification stage, addressing a key downside of saccharification-fermentation. LB is thermally gasified to create synthetic gas (syngas), which is made of CO, H₂, CO₂, and N₂, and is subsequently fermented to create biomaterials, such as bioethanol [42]. Despite decades of development and research targeted at raising the market value of biomass, commercialized bioenergy production from lignocellulose biomass still needs technological and financial advancement [9].

2.2. Biobutanol

Biobutanol (C₄H₁₀O), also known as butyl alcohol, is a renewable biofuel that has an advantage over bioethanol due to its higher energy density, immiscibility in water, lower Reid vapor pressure, low toxicity, and compatibility with existing infrastructure [43]. It is primarily generated by the acetone-butanol-ethanol (ABE) fermentation process, which entails the microbial fermentation of sugars from biomass feedstocks into butanol using particular bacterial strains, such as *Clostridium* species. Butanol's toxicity to microorganisms, problems with butanol recovery later on, the choice of biomass, and pretreatment, which have an impact on large-scale synthesis, are the main obstacles of the ABE process [44]. The biobutanol industries create a variety of high-value byproducts, including plastics, fibers, solvents, and coatings. They also serve as an important precursor for many chemicals with added value including butyl acetate, acrylic acid, adhesives, and glycol ethers in addition to producing the primary transportation fuel, all of which have the potential to boost economic growth through a variety of product alternates [45].

2.3. Biodiesel

Biodiesel is a clean energy source that reduces greenhouse gas emissions, maintains ecological balance, and is compatible with existing infrastructure. It is derived from biological sources such as edible and non-edible oils, animal fats, and waste cooking oils [46]. Traditional physicochemical processes include transesterification, esterification, pyrolysis, and micro-emulsion, among which transesterification, wherein triglycerides and alcohol react in the presence of a catalyst to yield fatty acids alkyl ester and glycerol at low temperature and pressure, is cost-effective and yields high-quality products. However, conventional production methods have reached their maximum efficiency, making biodiesel less competitive than petroleum-based diesel [47]. In recent years, there has been a growing demand for innovative, clean, and enhanced technology to accelerate the reaction times, use less energy and catalysts, and maintain excellent biodiesel quality. To that end, a variety of techniques, including microwave, ultrasonic, supercritical, hydrodynamic cavitation, reactive distillation, membrane, plasma, cosolvent, rotatory, and plug flow reactors, have been investigated for biodiesel production [48].

2.4. Biohydrogen

Hydrogen, with its high energy density, is used in industries as a fuel and renewable energy source. However, traditional techniques such as water electrolysis and auto-thermal processes are economically unviable due to their high-power requirements. Biohydrogen, a carbon-neutral process, offers potential benefits over thermochemical and electrochemical methods [49]. It can be produced using pure sugars or waste substrates such as lignocellulosic biomass and microalgae. It is produced by dark fermentation, photofermentation, or a combination of these methods. However, the generation and output of biohydrogen are influenced by substrate availability, inoculum origin, and operational factors. A study by Patel et al. established a low-cost biohydrogen manufacturing technique using agricultural waste. H₂ production peaked at 37 °C and pH 8.5. The highest H₂ yield was measured in wheat straw pre-hydrolysate (WSPH) at 2.54 ± 0.2 mol-H₂/mol-reducing sugar and in pre-treated wheat straw enzymatic-hydrolysate (WSEH) at 2.61 ± 0.1 mol-H₂/mol-reducing

sugar [50]. Advancements in technology and renewable energy sources make biohydrogen a promising option for a cleaner and more sustainable future [51].

2.5. Biogas

Biogas is one of the most important renewable energy sources to solve the environmental and energy challenges and serves as a substitute to natural gas or transportation fuel. Biogas refers to a mixture of gases produced by anaerobic organisms via the fermentation of organic materials such as plant materials, agricultural waste, food waste, sewage, municipal waste, and compost without the presence of oxygen [52]. This process is known as bio-methanation, and it primarily produces methane and carbon dioxide with minute amounts of hydrogen sulphides and siloxanes. The main variables affecting the effectiveness of biogas production procedures include organic loading rate, pH, carbon to nitrogen ratio, temperature, retention duration, and mixing rate. According to their sensitivity to temperature, the microorganisms utilized in the bioreactor are divided into three main groups: psychrophilic (15–25 °C), mesophilic (35–40 °C), and thermophilic (55–60 °C) [53]. However, the actual use of lignocellulose-based material in the anaerobic digestion process is limited because of the biomass's resistant nature, which results in poor digestion efficiency and biodegradation. Further developments, such as the use of several pretreatment techniques, microbial inoculum, and the application of chemical (NaOH and CaO) and biological (white-rot and brown-rot fungi) additives, are being prioritized in order to speed up microbial growth and the rate of biogas production [54]. In an investigation, researchers have studied the biogas production from pineapple waste, in which both the biogas and methane production showed significant increases (mL/day) from longer to shorter HRT. The maximal values (HRT 5 days, OLR 5 g/COD/day with recirculation) were 55,130 and 30,322 mL/day, respectively [55]. Its ability to harness methane from organic waste, its various applications in energy generation, cooking, and transportation, as well as its role in fertilizer production, make biogas a valuable asset in our transition towards a cleaner and more sustainable energy system.

3. Nanoparticle Application in Biofuel Generation

Lignocellulosic biofuels, obtained from plentiful organic sources provide a hopeful pathway for sustainable energy. Nevertheless, the conversion of these substances into biofuels encounters obstacles as a result of intricate compositions and ineffective decomposition mechanisms. Nanoparticle or nanomaterial application plays a transformative role by acting as a catalyst in the conversion of lignocellulosic materials into biofuels. NMs are defined as materials that have components or particles with at least one dimension in the nanometer scale, typically ranging from one nanometer to a few hundred nanometers. Furthermore, NMs where all dimensions are at the nanoscale are called NPs. Nanoparticles are essential for speeding up the decomposition of the resistant components in lignocellulose, which improves the overall effectiveness of biofuel manufacturing. Their catalytic characteristics greatly enhance the efficiency and standard of biofuels obtained from these renewable raw materials, representing a crucial breakthrough in sustainable energy generation. The application of nanomaterial at different process stages for improving the biofuel quality and yield is represented in Figure 1.

NP application during the synthesis of biofuels plays a role in improving procedural effectiveness by boosting pretreatment, hydrolysis, and reaction rate throughout the fermentation process. The key determining factors for the development of the desired product include reaction time, size, surface area, shape, nature, and type of biomass [56].

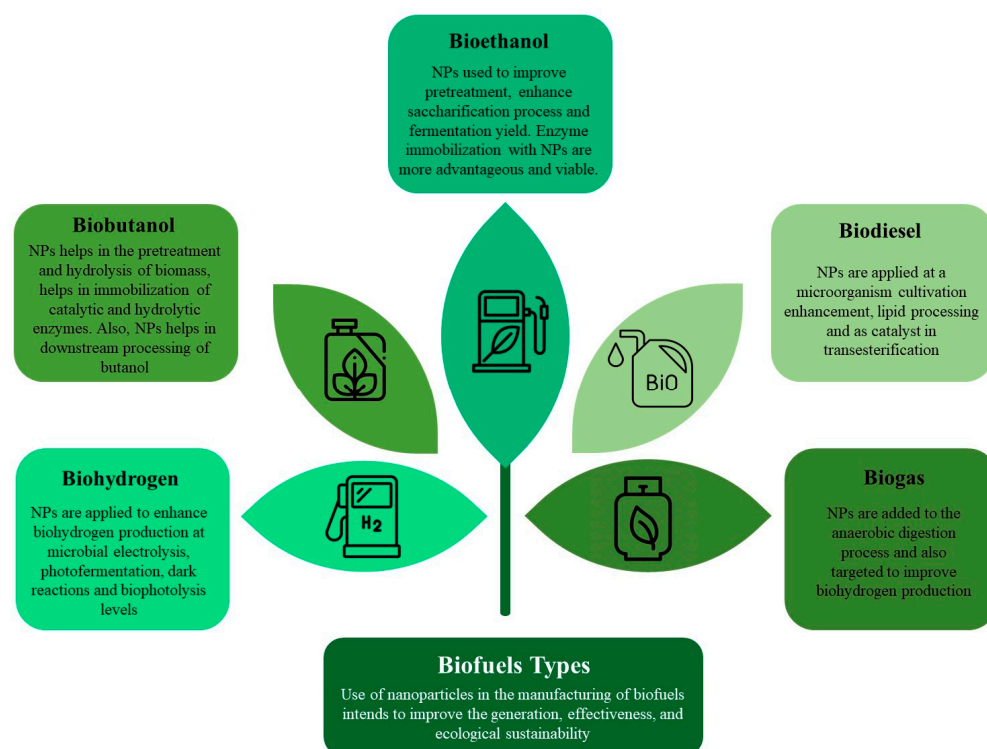


Figure 1. Possible avenues for the utilization of nanoparticles for various biofuel production.

3.1. Bioethanol

Application of nanomaterials in bioethanol production is numerous and encompasses all stages of the lignocellulose to bioethanol process, ranging from pretreatment to fermentation. For example, Kim et al. (2023) explored the use of cerium-doped iron oxide nanoparticles for the simultaneous pretreatment and saccharification of raw corn cob biomass [57]. These modified nanoparticles exhibit laccase and cellulase/hemicellulase mimicking properties, which further aids in the pretreatment. The synthesized NPs are of spherical shape with a size ranging from 40 to 70 nm. During simultaneous pretreatment and saccharification, a small amount of cellulose/hemicellulose enzymes are used. During the pretreatment process, approximately 44% of delignification was achieved due to the laccase mimicking properties of NPs. Further, the hydrolysate resulted in a maximum ethanol production of 21.7 g/L. In another study, Iron oxide NPs of size 70–100 nm synthesized with the *Spinacia oleracea* leaves extract for bioethanol production from Corn cob yielded 53.7% ethanol [58]. The following sections will go into further details about the application of NPs at various stages of the ethanol production process.

3.2. Biohydrogen

Anaerobic bacteria used in dark fermentation break down carbohydrate-rich substrate and create hydrogen. With an energy density of 140 MJ/kg, which is higher than that of coal (24 MJ/kg) and petrol (44 MJ/kg), biohydrogen (H_2) has a lot of promise as a cheap, renewable, carbon-free, and ecologically friendly fuel [59]. The kind of raw materials used, the nutrients that are accessible (such as C, N_2 , PO_4^{3-} , and SO_4^{2-}), and other operational circumstances all have an impact on the synthesis of biohydrogen. To boost microbial development and enhance the activity of enzymes involved in producing H_2 , researchers are proposing novel strategies, such as the use of mixed substrates, mixed microbial culture, and usage of nanomaterials and carbon-based biomaterials [60]. An important way to produce bio- H_2 is nanotechnology-based pretreatment on lignocellulosic biomass structures. The cost of the procedure is decreased since the chemicals are readily recyclable and usable again [61]. Titanium NPs produced 127% more biohydrogen when combined with sugarcane bagasse and anaerobic sludge [62]. In a comparable

manner, using palladium NP in a mixed culture also included with glucose produced 9% H₂ [63].

3.3. Biobutanol

A sustainable, environmentally friendly and perhaps practical alternative fuel to conventional petrol is biobutanol. Zinc oxide (ZnO) NPs were utilized as a catalyst in fermentation from coffee bean husk, a byproduct of farm waste chosen as raw material, and biobutanol was effectively produced by ABE fermentation. High butanol production and 0.36 g/L alcohol, 70.5% sugars were observed with 10 g of ZnO NPs utilized as catalyst [64]. In another study by Gandarias et al. [65], employing distinct bimetallic and trimetallic catalysts made by sol-immobilization under reaction conditions of 100 °C, 6 h, at 3 bar O₂, n-butanol solution yielded butyraldehyde, butyl butyrate, and butyric acid as a conversion product. In a case, Pt/C metal(s)/support NP have a 91.8% conversion rate of n-butanol with a yield of 23.2% butyraldehyde, 67.9% butyric acid, and 8.8% butyl-butyrate.

3.4. Biogas

Research is ongoing to determine the effect of nanoadditives on the anaerobic digestion (AD) process and, as a result, the output of biogas. The study examined the effects of titanium dioxide, zinc oxide, and silver nanoparticles (with an average size of at least 1 dimension <100 nm) on the process of methanogenesis in mesophilic batch anaerobic digestion of primary sludge. The findings indicated that none of the NPs used had a significant impact on methane generation. The methane production rates, measured in m³ of CH₄ per kilogram of volatile solids, ranged from 0.08 to 0.13. There was no statistically significant difference observed between the control groups and experimental sets for the examined NPs [66]. The majority of previous studies have suggested that methane production is decreased by increased NP concentrations. The results on several conductive materials, including graphene oxide (GO), carbon fibers, activated carbon, iron oxides, and biochar, support direct interspecies electron transfer, which is a state-of-the-art method to increase biomethane output. Mixed anaerobic culture with graphene oxide on the anaerobic fermentation process of assam lemon showed 219.64 mL/g VS fed improvement of biomethane yield [67].

3.5. Biodiesel

The process of producing biodiesel can be done in a number of ways, including transesterification, pyrolysis or cracking, and micro-emulsion. The most widely used technique for producing biodiesel among them is triglyceride transesterification of methanol or ethanol in the presence of a chemical or biological catalyst. This may be done by immobilizing lipase on magnetic nanoparticles (MNPs), which will increase the triacylglycerol (TAG) conversion in the presence of a catalyst. Another way of biodiesel production is through whole cell immobilization of recombinant *Aspergillus oryzae*, which was engineered for the generation of biodiesel and expressed the *Candida antarctica* lipase B gene (r-CALB), according to a study by Adachi et al. [68]. In another study, solid catalyst NPs derived from oil-palm empty fruit bunches were used as a renewable catalyst for biodiesel production. The study observed the highest palm-oil to biodiesel conversion of up to 97.90% when using 1% palm bunch ash nanocatalyst, which was produced by heating empty fruit bunches at 600 °C, and a 3 h reaction time. [69].

A summary on the application of NPs in the biofuel production process is given in Table 2 [70–89].

Table 2. Utilization of various nanoparticles in the production process of different forms of biofuels.

Biofuel Type	Nanoparticles	Raw Materials	Yield/Concentration of Biofuel (Specified Units)	Reference
Bioethanol	Novel nano-magnetic catalyst prepared from carbonaceous tailings (dolomite) from cupriferous mineral processing	Edible oil wastewater sludge	3.54 g/L	[70]
	Nickel oxide nanocatalyst of 29 nm size	lignocellulosic weeds	Bioethanol yield of 0.26 g/g, enhanced to >65%	[71]
	Reduced graphene oxide supported Platinum ruthenium used on derived bioethanol	<i>Chlorococcum minutum</i> alga	Bioethanol yield of 32.6g/L	[72]
	Fe ₃ O ₄ and NiO NPs	Potato peel	Bioethanol yield of 50% with NiO and 93% with Fe ₃ O ₄	[73]
	NiO NP for delignification	Elephant grass	Bioethanol production using <i>Kluyveromyces marxianus</i> with 14.65 ± 1.75 g/L yield	[74]
Biodiesel	ZnO nanorods for biodiesel	Olive oil	94.8% conversions at 150 °C, 8 h	[75]
	Dolomite NP	Oil wastewater sludge	Maximum biodiesel yield of 94% at oil to ethanol ratio of 1:9	[70]
	KF–CaO solid base nanocatalyst	Chinese tallow seed oil	Biodiesel yield was 96.8%	[76]
	Magnetic nanocatalysts of NiO.5ZnO.5Fe ₂ O ₄ doped with Cu	Soybean oil	Increase in biodiesel yield by 5.5–85%	[77]
	CZO nanocatalyst—copper-doped zinc oxide nanocatalyst for biodiesel production	Neem oil	Biodiesel yield of 97.18%	[78]
	Zinc oxide with manganese	Mahua oil	Biodiesel yield 97%	[79]
	Fe ₂ O ₃ NPs	Algae <i>Neochloris oleoabundans</i> UTEX 1185	Biodiesel yield of 81%	[80]
Biohydrogen	Anaerobic sludge as the inoculum for a nickel-doped magnetic carbon material	Glucose as the substrate	Yielded 260 mL/g glucose of hydrogen	[81]
	Fe ⁰ and Ni ⁰ NPs	Cotton stalk	90 mL/g substrate yield, hydrogen is produced by <i>Klebsiella</i> sp. WL1316	[82]
	Fe ₃ O ₄ @SiO ₂ -chitosan	Sweet sorghum stover	2.8 mol H ₂ /mol reducing sugar	[83]
	Ferric oxide/carbon NPs	Sewage sludge	218.63 mL/g glucose of hydrogen	[84]
	CoNPs-assisted <i>Clostridial</i> fermentation	Glucose	2.89 mol H ₂ /mol glucose was produced, a 1.6-fold increase	[85]
Biobutanol	Porous silica (SiO ₂)-entrapped FeO NP	Glucose	2.2 mol H ₂ /mol glucose of hydrogen	[86]
	ZnO NP in Sugarcane molasses using <i>Clostridium saccharoperbutylacetonicum</i>	Sugarcane molasses	Biobutanol yield of 0.39 g/L with 0.12 g/Lh productivity	[87]
	ZnO NP in Sugarcane using <i>Clostridium saccharoperbutylacetonicum</i>	Sugarcane extract	Biobutanol yield of 0.39 g/L with 0.07 g/L.h productivity	[87]
	ZnO NP in Sweet sorghum using <i>Clostridium saccharoperbutylacetonicum</i>	Sugary sorghum extract	Biobutanol yield of 0.2 g/L with 0.02 g/Lh productivity	[87]
	CoNPs-assisted <i>Clostridial</i> fermentation	Glucose	Biobutanol yield of 975 ± 2.5 mg/L (1.27 fold higher production)	[85]
Biogas	Nickel and Cobalt NPs	<i>Carthamus oxyacantha</i> , <i>Chenopodium album</i> and <i>Asphodelus tenuifolius</i>	23.75% of biogas	[88]
	Nickel and Cobalt NPs in	<i>Parthenium hysterophorus</i> L. and <i>Cannabis sativa</i> L.	Biogas yield of 17.66% (<i>P. hysterophorus</i>) and 12% (<i>C. sativa</i>)	[89]

4. Nanobiotechnology in Lignocellulosic Ethanol Production

4.1. Nanoparticles and Technology Involved in Biomass Pretreatment

Pre-treatment is the initial stage in converting lignocellulosic biomass into biofuels and involves deconstructing the structure into polymeric fractions such as lignin, hemicellulose, and cellulose (Figure 2). It is crucial for making the biomass more receptive to hydrolysis. Various methods, including physical, chemical, physicochemical, and biological, have been studied, but many involve severe operating conditions and generate toxic inhibitory compounds [19]. Therefore, developing efficient and cost-effective pre-treatment strategies is a critical area of research for LB-based refineries. NPs offer a sustainable solution for pretreatment through enhanced enzymatic catalysis by improving the accessibility of enzymes to cellulose and hemicellulose, enhancing sugar yield, conversion efficiency, and selective removal of lignin. This is due to their high surface area and tunable surface chemistry. It reduces enzyme loading and reaction time due to the recyclability in the case of magnetic nanoparticles, high catalytic activity, stability, and effective storage [90].

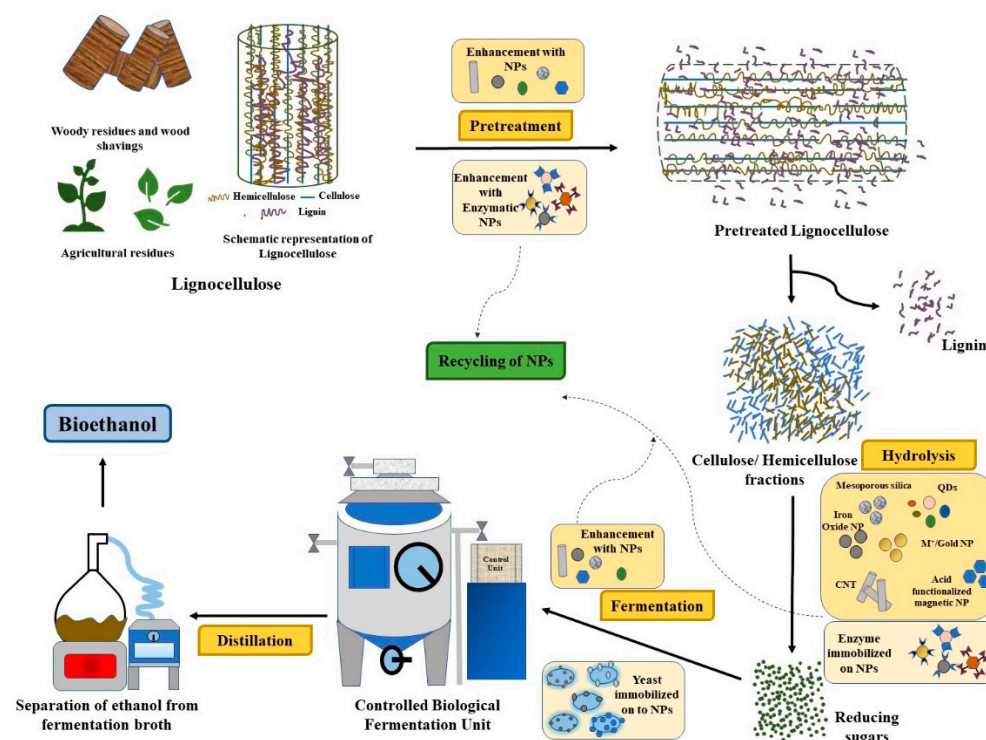


Figure 2. The role of nanobiotechnology in lignocellulosic bioethanol production.

For use in biomass pretreatment, researchers have explored a variety of NPs, including metal, metal oxide, carbon-based NPs, silica NPs, nickel NPs, magnetic NMs, etc. Metal NPs have shown promise in delignification, lignin catalysis, and increasing the effectiveness of enzymatic hydrolysis. Additionally, metal NPs, at an appropriate concentration, increases the electron transfer rate, thereby enhancing the enzyme activity. Huang et al. [91] studied *Phanerochaete chrysosporium* degradation performance using Fe_3O_4 NMs, which increased lipase enzyme activity and promoted CMCase and xylanase production. Metal oxide NPs have shown promise in enhancing the efficiency of enzymatic hydrolysis and promoting the release of fermentable sugars. To specifically depolymerize lignin from corn cob biomass, NP mediated pretreatment was developed. In this method, magnetic iron oxide NPs doped with cerium ($\text{Ce-Fe}_2\text{O}_3$) were used to produce value-added industrial products including aldehydes, alcohols, esters, and other lignin-decomposition products [92].

Carbon-based NPs, such as carbon nanotubes (CNT) and graphene, possess a high surface area and mechanical strength, enabling them to serve as solid support for enzyme immobilization, enhancing enzymatic hydrolysis of biomass. Magnetic carbonaceous acid NPs, produced by pyrolysis of a homogenous mixture of magnetic Fe_3O_4 NPs and glucose, were tested for the pretreatment of tropical biomass with total reducing sugar yields of 79.8% for bagasse, 47.2% for *Jatropha* hulls, and 54.4% for *Plukentia* hulls. The results suggested that acid-functionalized NPs can be used as promising catalysts for the pretreatment of various LBs [93]. According to Qi et al. [94], the carbon-based solid catalyst with sulfonic acid demonstrated high catalytic activity even after five re-uses to give a high yield of xylose (78.1%) during the pre-treatment of corncobs.

In contrast to other NPs, MNPs have multiple benefits, such as easy recoverability utilizing an external magnetic field, reusability in the following pretreatment cycles, high biodegradability, low cytotoxicity to biomass cells, the ability to bind to various target molecules, and simplicity of synthesis [95].

Magnetic NPs with acid-functionalization are strong acid nanocatalysts, which have the same catalytic effect as mineral acids in decomposing the lignocellulosic biomass during pretreatment, and an external magnetic field can be used to recover and re-use in subsequent hydrolysis cycles, which in turn minimizes downstream processing and reduces the process

cost [96]. Using two different acid-functionalized magnetic NPs (MNPs), perfluoroalkyl-sulfonic (PFS) acid and alkylsulfonic acid functionalized, Wang et al. [97] demonstrated the effective catalytic degradation of wheat straw. At 80 °C, PFS NPs significantly increased the hydrolysis of hemicelluloses ($24.0 \pm 1.1\%$) compared to their alkylsulfonic counterparts ($9.1 \pm 1.7\%$), while the hydrothermolysis control only hydrolyzed $7.7 \pm 0.8\%$ of the original hemicelluloses in the sample [97]. In a different study, two different acid-functionalized MNPs, alkylsulfonic acid ($\text{Fe}_3\text{O}_4\text{-MNPs@Si@AS}$) and butylcarboxylic acid ($\text{Fe}_3\text{O}_4\text{-MNPs@Si@BCOOH}$), were developed and their efficacy in treating sugarcane bagasse was assessed. Both $\text{Fe}_3\text{O}_4\text{-MNPs@Si@AS}$ and $\text{Fe}_3\text{O}_4\text{-MNPs@Si@BCOOH}$ released the most sugar at 500 mg/g of bagasse, with rates of 18.83 and 18.67 g/L, respectively. There was a substantial difference between the value obtained and a typical acid-treated sample (15.40 g/L) and an untreated sample (0.28 g/L), demonstrating the importance of acid-functionalized magnetic particles in the process [98].

NP-enzyme combination enhances catalytic activity, reaction scope, and enzyme stability compared to free enzymes [99]. Immobilization protects enzymes from harsh operating conditions including high temperatures, pH variations, or the inhibitor concentration, ensuring stability and an increased lifespan of enzymes. Immobilized enzymes can be easily recovered and reused, using simple physical methods, simplifying downstream processing and minimizing enzyme contamination in the final product. Immobilization techniques enable higher enzyme loading, enhancing the reaction rates and efficiency. It also prevents enzyme leaching, allowing for controlled reactions, reducing enzyme costs, and improving the overall process stability. For the pretreatment of corn stover, Gou et al. [100] used laccase immobilized on Cu^{2+} modified reusable magnetite NPs— $\text{Fe}_3\text{O}_4\text{-NH}_2$. The rate of lignin degradation was about 40.76% when immobilized laccase was used, which was higher than the control. This immobilized enzyme was recycled for 6 cycles, with about 50% of the reutilization activity [100]. For improved delignification of olive pomace biowaste, Amin et al. [101] immobilized laccase, isolated from *Trametes versicolor*, by covalent attachment to modified $\text{Fe}_3\text{O}_4\text{@SiO}_2\text{@Kit-6}$ magnetite NPs in the presence of IL. After 6 h of incubating the biomass with immobilized laccase and [Bmim][PF₆] as an ionic liquid without the use of a mediator, they saw a reduction in kappa number of up to 77.3% [101]. Another study used copper ferrite magnetic NPs (CuMNPs) and ferrite magnetic NPs (MNPs) to immobilize laccase produced from *Trametes versicolor* for pretreatment of lignocellulosic biomass. The laccase immobilized on CuMNPs (13.2 U/mL) recovered more activity than that immobilized on MNPs (10.93 U/mL). Additionally, laccase immobilized NPs maintained more than 70% of their initial activity after 20 days of storage at 4 °C and reuse up to 6 cycles. In comparison to laccase immobilized MNPs and free enzyme, the delignification of the laccase immobilized CuMNPs on *Ipomoea carnea* was greater (~43%) [102].

A completely new and developing technique for nano-based pretreatment of lignocellulosic biomass is the nano-shear hybrid alkaline (NSHA) method. This method combines a milder heat action with high-speed shearing and chemical reagent synergy and is frequently carried out in the Taylore Couette reactor. By moving the high shearing work axis to the biomass nanostructure, lignin may be removed effectively while cellulose and hemicellulose are exposed in a short amount of time. For corn stover processed with sodium hydroxide at room temperature for 2 min in a modified reactor, Wang et al. [103] devised a pretreatment method by employing the NSHA approach. When compared to untreated corn stover, they were able to acquire an 82% higher cellulose content. The NSHA pretreatment's production of nanoscale polysaccharide agglomerations and the recalcitrant degraded biomass, combined with the synergistic action of the cellulase enzyme during hydrolysis, can be readily converted to fermentable sugars. Enzymatic conversion of cellulose and hemicellulose increased by 4- and 5-folds, respectively, when immobilized cellulase was used along with the NSHA pretreatment approach [103]. Another study employed Poly (diallyldimethylammonium chloride, or PDAC), a positively charged polyelectrolyte, as an addition in the NSHA pretreatment of corn stover. By framing a globular complex

of cationic polyelectrolytes with lignin, the cell wall underwent a major morphological alteration. PDAC may be employed in pretreatment processes to significantly reduce the amount of chemicals and enzymes needed, stabilize lignin, and increase the availability of polysaccharides to enzymes [104].

4.2. Biomass Hydrolysis through Nanobiotechnology

An essential stage in determining the overall efficiency of ethanol production is the hydrolysis of lignocellulosic biomass into readily fermentable sugars. Hydrolysis, either chemical or enzymatic, is typically used to accomplish this. Chemical degradation employs various acids, such as hydrochloric acid, sulfuric acid, phosphoric acid, etc., at high temperatures and pressures. This method is marked by less specificity, lower efficacy, the generation of toxic inhibitors such as hydroxymethyl furfural (HMF) and furfural, and the necessity to neutralize or remove unreacted acids. However, the high specificity, selectivity, and catalytic activity of enzymes at ambient conditions provide an effective, eco-friendly, and sustainable approach for the breakdown of carbohydrate polymers. A schematic representation of the process is shown in Figure 3.

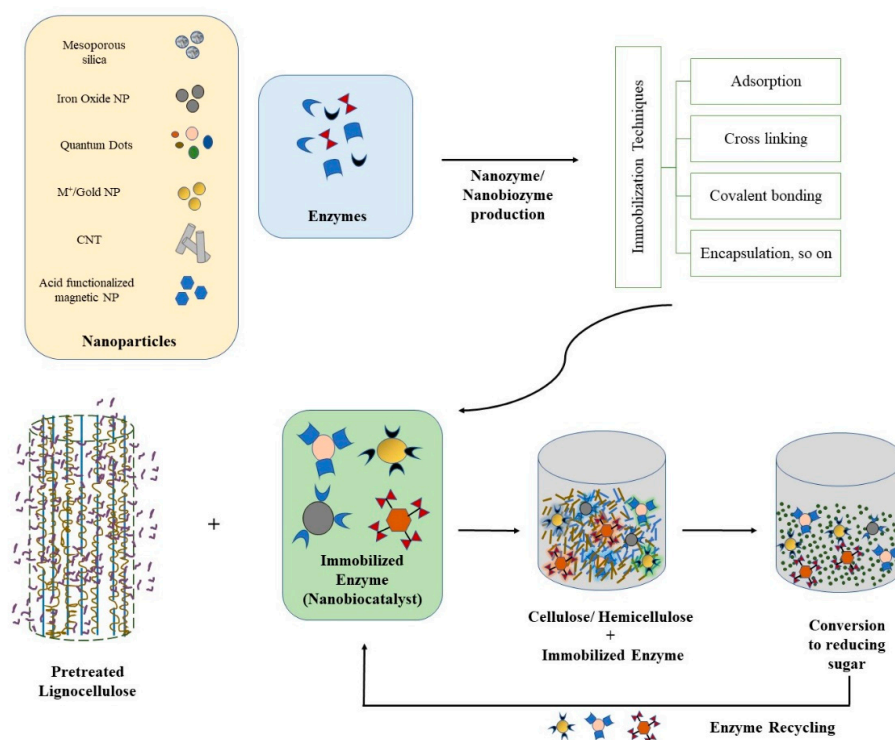


Figure 3. Different immobilization techniques for nanobiocatalyst production and its role in hydrolysis of biomass.

Enzymatic hydrolysis at room temperature (45–50 °C) has some drawbacks despite the above-mentioned benefits, such as a relatively slow reaction rate, vulnerability to microbial contamination, and partial hydrolysis. Due to this, the yield of fermentable sugars is often low, and the enzyme's lack of reusability necessitates additional enzyme loading, which also raises the cost of production [105]. Several reports suggest that the thermophilic or thermostable enzyme can be a useful strategy to get rid of the aforementioned bottlenecks [106]. Preliminary research indicates that the stability and catalytic efficiency of enzymes are increased by immobilizing various biocatalysts, such as laccase, β -glucosidase, cellulase, xylanase, and cellobiase, on support materials such as nanomaterials. According to some investigations, enzyme immobilization on firm support increases its resistance to structural changes that may arise due to an increase in temperature during the course of the reaction, thus conferring thermal stability and also guaranteeing efficient catalyst dispersion with

minimal agglomeration, which in turn increases the enzyme activity. Immobilization provides an opportunity to combine multiple enzymes with complementary functions onto the same support material. This allows for synergistic enzyme actions, where different enzymes work together to enhance the efficiency of lignocellulosic biomass treatment. The spatial proximity of the enzymes within the immobilized system facilitates better enzyme cooperation and improves overall process performance. Ionic bonding, covalent binding, entrapment, adsorption, and encapsulation are several strategies employed for immobilizing enzymes. The addition of calcium hydroxyapatite NPs at 80 °C enhanced the thermal stability of cellulase in one of the investigations by Dutta et al. [107], which led to increased sugar production. Furthermore, the researchers observed that the presence of hydroxyapatite NPs increased the hydrolysis of hemicellulose and cellulose to yield a 5.71-fold raise in D-xylose and other reducing sugars by 15-fold.

Magnetic NPs are increasingly sought after as support carriers in enzyme immobilization due to their large surface-area-to-volume ratio, the possibility of loading numerous enzymes, increasing catalytic activity, and easy recoverability. Enzymes can be immobilized using a variety of approaches on the MNP support. For instance, silicon-functionalized MNPs, amino-functionalized MNPs, composite-functionalized MNPs, chitosan-functionalized MNPs, or carrier-free functionalized MNPs can be used for cellulase immobilization. Goh et al. [108] used magnetic single-walled carbon nanotubes for enzyme immobilization in biofuel production, reducing costs and maintaining activity for a month in an acetate buffer at 4 °C. In the work of Srivastava et al. [109], it was discovered that cellulase with Fe₃O₄/alginate nanocomposite had higher heat stability and sugar production. In another study, functionalized magnetic NPs immobilized with β -glucosidase from fungus produced a nanobiocatalyst system with 93% binding efficiency and 50% activity retention after 16 cycles [110].

Immobilization techniques are compatible with various reactor configurations and can be easily integrated into large-scale processes. This scalability enables the efficient handling of larger volumes of lignocellulosic biomass and facilitates the transition from lab-scale to industrial-scale operations.

The utilization of various nanobiocatalysts in the hydrolysis process of different lignocellulosic biomass is summarized in Table 3 [95,111–118].

Table 3. Utilization of various nanobiocatalysts in the hydrolysis process of different lignocellulosic biomass.

Pre-Treated Lignocellulosic Biomass	Nanoparticle	Enzyme	Result	References
Acid autoclave + alkali pre-treated rice straw	Glutaraldehyde crosslinking on magnetic iron oxide nanoparticles	Cellulase produced from <i>Aspergillus fumigatus</i>	Enhanced saccharification efficiency; 50.34% activity retention after 4 saccharification cycles	[111]
Agave atrovirens leaves	Chitosan-coated magnetic NPs	<i>Trichoderma reesei</i> cellulase using glutaraldehyde as a coupling agent	Reused for four cycles with 50% of activity	[95]
Ultrasound-assisted alkaline-pretreated <i>Crotalaria juncea</i>	Zinc ferrite NPs	Cellulase enzyme immobilized using glutaraldehyde as the cross-linker	Improved thermal stability at a temperature of 60 °C compared to free enzyme; retained activity for three cycles	[112]
Alkali-pretreated paddy straw	Iron oxide (Fe ₂ O ₃) NPs	Holocellulase from <i>Aspergillus niger</i>	Holocellulase from <i>Aspergillus niger</i>	[113]
<i>Allamanda schottii</i> L.	Iron oxide (Fe ₂ O ₃) NPs	Cellulase	Retained 60% activity after 5 cycles	[114]
Hydrothermally pretreated corn cob	Chitosan coated magnetic NPs	Cellulase	Reused up to 13 cycles with 44.8% of its initial activity and produced 8.2-fold glucose compared to free enzyme	[115]
Waste textile	Chitosan-coated Fe ₃ O ₄ NPs	Cellulase	Glucose yield of 51.5 g/L and cellulase retained 51.5% of its initial activity after three times reuses	[116]

Table 3. Cont.

Pre-Treated Lignocellulosic Biomass	Nanoparticle	Enzyme	Result	References
Avicel PH101	Magnetic hierarchical porous carbon (MHPC) nanomaterials	Cellulase from <i>Trichoderma reesei</i>	Thermal, storage, and operational stability of the immobilized cellulase improved compared to the free enzyme; enzyme activity: 1.35 U mg^{-1}	[117]
Rice straw and sugar beet pulp	Carbon Nano-Carriers functionalized with magnetite nanoparticles and dopamine (DA/Fe ₃ O ₄ NPs@CNC)	Enzyme cocktails including 3 cellulases, 2 hemicellulases, and their combinations	Increase in 20–76% of fermentable sugars in contrast to free enzyme cocktails. Recovery/reuse of the nano-biocatalyst up to 10 cycles, with >50% of initial activity	[118]

4.3. Application of Nanotechnology in the Fermentation Process

Nanotechnology has the potential to significantly impact the ethanol fermentation process, offering several advantages and opportunities for improvement. Many substances such as Furan derivatives, aliphatic acids, phenolic compounds, ketones, and alcohols have been found to adversely affect the processes of fermentation and enzymatic hydrolysis. Supplemental NPs or nanocatalysts can increase fermentative ethanol production and alter the microorganism's metabolic pathway thus stimulating ethanol generation. According to an investigation, the interaction between the NPs (Fe₃O₄) and the sugar facilitated the uptake of glucose by *S. cerevisiae* BY4743, increasing the generation of bioethanol. Fe₃O₄ NPs considerably boosted the synthesis of ethanol, with the greatest bioethanol output being 0.26 g/g, hexose sugar consumption being 99.95%, ethanol productivity being 0.22 g/L/h, and fermentation efficiency being 51% at 0.01 wt% [119].

Saeed et al. [120] reported increased bioethanol production from potato waste using laser irradiation and graphitic carbon nitride (g-C₃N₄) nanomaterials. According to the authors, the bioethanol yield in the presence of g-C₃N₄ and laser irradiation was 56.8%, compared to only 4% in the control [120]. In another study, zinc oxide NPs were utilized to enhance bioethanol from rice straw to give a maximum ethanol yield of 0.0359 g/g dry weight-based rice straw at a ZnO NP concentration of 200 mg/L [121]. Kim et al. [122] reported 0.3060 g/L bioethanol production using methyl-functionalized silica NPs in syngas fermentation, compared to a control (0.1150 g/L) without NPs, as mentioned earlier.

Additionally, immobilizing the yeast cells onto NPs enhances yeast cell stability, substrate utilization, stress resistance, and nutrient delivery, leading to increased viability and efficiency during fermentation (Figure 4). They provide a protective layer, allowing yeast cells to adapt to environmental stresses and maintain their metabolic activity. NP coatings also confer increased tolerance to inhibitory compounds, preventing their diffusion and neutralizing their effects. They also enhance yeast resistance to stress conditions by maintaining cell membrane integrity and protecting cellular components. NP-coated yeast can be easily recovered from the broth, reducing the need for new inoculum in subsequent fermentations.

Nanotechnology-based sensors can be utilized for real-time monitoring of key parameters during ethanol fermentation, such as glucose concentration, ethanol production, pH levels, or temperature. Nanosensors offer high sensitivity, selectivity, and rapid response times. They enable precise monitoring of fermentation conditions, allowing for better process control and optimization, and facilitating early detection of fermentation issues. For instance, Lin et al. [123] synthesized ultrathin ZnO nanosheets with Ag NPs for ethanol detection using a two-step hydrothermal method. Silver NPs showed excellent gas sensitivity and could function even at an ultralow ethanol vapor concentration.

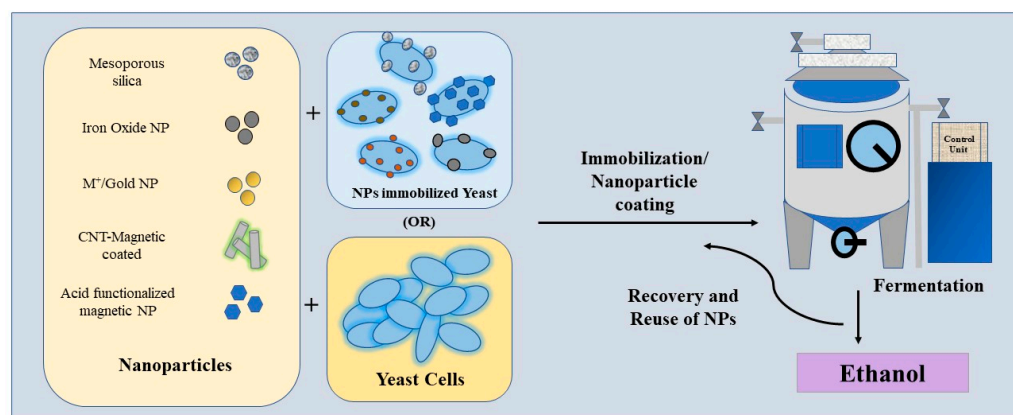


Figure 4. Encapsulation of fermentation organisms for its increased stability, viability, and efficiency during fermentation and its easy recovery for use in subsequent cycles.

5. The Mechanism Underlying the Interaction of Nanoparticles

Nanotechnology has emerged as a promising tool for enhancing the efficiency of lignocellulosic pretreatment, hydrolysis, and fermentation processes. By leveraging the unique characteristics of nanomaterials, researchers have successfully developed novel approaches for breaking down lignocellulosic biomass. Such strategies involve the penetration of nanomaterials into the cellular membrane and interaction with its components by enhancing the surface area of biomass, thereby promoting enzymatic hydrolysis and resulting in the release of significant quantities of saccharides. Indeed, the decreased dimensions of nanomaterials facilitate the interactions at the molecular level with LB, thereby enhancing the molecular chemistry of biomass and leading to the breakdown of intricate structures into simpler components such as glucose and other sugars [124]. The utilization of NPs in various phases of the conversion of LB-to-bioethanol process has been discussed in the subsequent sections.

5.1. Interactions of Nanoparticles during Pretreatment of Biomass

The degradation of lignin in lignocellulosic biomass encompasses various processes, such as biomass swelling, structural modifications, increased internal surface area, and enhanced penetrability of hydrolytic enzymes in cellulose [125]. The degree of the pretreatment process plays a crucial role in determining the level of lignin removal or modification in its structure. Although the extracted lignin may be low in amount, the pretreatment of biomass enhances its digestibility by enzymes in comparison to untreated biomass. The degradation of lignin is facilitated by NPs through the process of inducing swelling and penetration into lignocellulosic biomass. During pretreatment, the introduction of NPs has the potential to disturb the lignocellulosic framework, enhance the enzymatic or catalytic accessibility, and expedite the subsequent hydrolysis or conversion procedures and diminish the energy utilization.

Nanomaterials can be utilized for pretreatment purposes, either as nanozymes/nanocatalysts, or alternatively as nano-absorbents for enzymes/nanobiocatalysts. The utilization of nanozymes and nanocatalysts has demonstrated significant promise in augmenting the efficacy of biomass pre-treatment. These nanocatalysts have the ability to facilitate the degradation of intricate biomass compounds into less complex forms, thereby enhancing their suitability for subsequent procedures. In contrast, nano-absorbents have the potential to be employed for the purpose of immobilizing enzymes and biocatalysts, consequently enhancing their stability and activity levels. The aforementioned methodology has demonstrated notable efficacy in the preliminary treatment of lignocellulosic biomass, which will be discussed in the upcoming sections.

5.1.1. Nanozymes/Nanocatalysts in Biomass Pretreatment

Researchers have suggested that nanoscale metallic NPs might exhibit enhanced effectiveness in traversing the cellular barrier of lignocellulosic biomass in comparison to unbound enzymes [126]. According to several sources [126–128], it has been reported that this ability is achieved due to their reduced dimensions. In fact, the pretreatment of LB with NPs relies on the inherent capacity of NPs to effectively penetrate the cell membrane of LB to cause disturbance in the cell wall and subsequent liberation of the intracellular constituents [23]. These nanocatalysts employed in the pretreatment method may again be categorized as either acid-functionalized or non-acid-functionalized in nature.

Non-Acid-Functionalized Nanocatalysts in Pretreatment

Several types of NPs, such as zeolite supported nickel, palladium cerium oxide (Pd-CeO₂), and carbon nanotube supported molybdenum oxide (MoOx/CNT), have been examined for their effects on the oxidative/reductive and catalytic hydrogenolysis of lignin compounds. An investigation documented the utilization of a nanozyme catalyst, specifically the Cu/GMP complex, which mimics the behavior of multicopper laccase. This nanozyme catalyst demonstrated exceptional performance in facilitating the biodegradation of organosolv lignin (OL) into oligomers with low molecular weights. Notably, the process took place at room temperature and atmospheric pressure and the study revealed that Cu/GMP exhibits enhanced laccase-like activity, which is advantageous for the degradation of C–O bonds in lignin, resulting in the production of oligomers with a substantial yield of 81.7 wt% [129].

An advanced approach for the pretreatment of lignocellulosic biomass (LCBs) involves the use of nanomaterials-based photocatalysis. A study was conducted in 2019 in which they prepared a TiO₂/polystyrene composite nanostructure and utilized the degradation of lignin through photocatalysis under UV radiation in a batch-recirculated photoreactor. The researchers achieved a lignin degradation efficiency of approximately 93.98% under optimized conditions [130]. Furthermore, the nanocomposite exhibited good stability and efficient photocatalysis even after undergoing five cycles of reuse. In another investigation, the application of a CuFe₂O₄/reduced graphene oxide nanocomposite was explored for the selective cleavage of lignin model compounds under sunlight exposure. This process demonstrated high efficiency and could be effectively employed for value addition purposes [131].

In an attempt to understand the mechanism of NP interaction with LB, various scientists have mentioned electrostatic interactions, van der Waals interactions, hydrophobic interactions, etc., which occur between the NPs and the biomass in their studies. In this context, a group of scientists presented the operational mechanism of Thiocyanate-Gold (TC-Au) NPs in their study (Figure 5). The nanozymatic activity of TC-Au NPs is depicted schematically as follows: (i) the generation of •OH radicals by breaking down H₂O₂ on the surface of TC-Au NPs; (ii) the initiation of TMB oxidation by •OH radicals; and (iii) the formation of a solution with a blue color [132]. Furthermore, NPs carrying surface charges can interact electrostatically with lignocellulosic biomass, which also carries charges. For example, negatively charged NPs, such as silica dioxide, can interact with positively charged functional groups, e.g., amino groups present in the biomass. This electrostatic interaction enhances the attachment of NPs onto the biomass surface. The zeta-potential, which is determined by the surface charge, is commonly employed as an indicator of the strength of electrostatic interactions between NPs. Consequently, it was utilized as a valuable metric to assess the interaction between NiO NPs and glucose. The presence of NiO NPs had a significant impact on both the optical characteristics and stability of glucose [133].

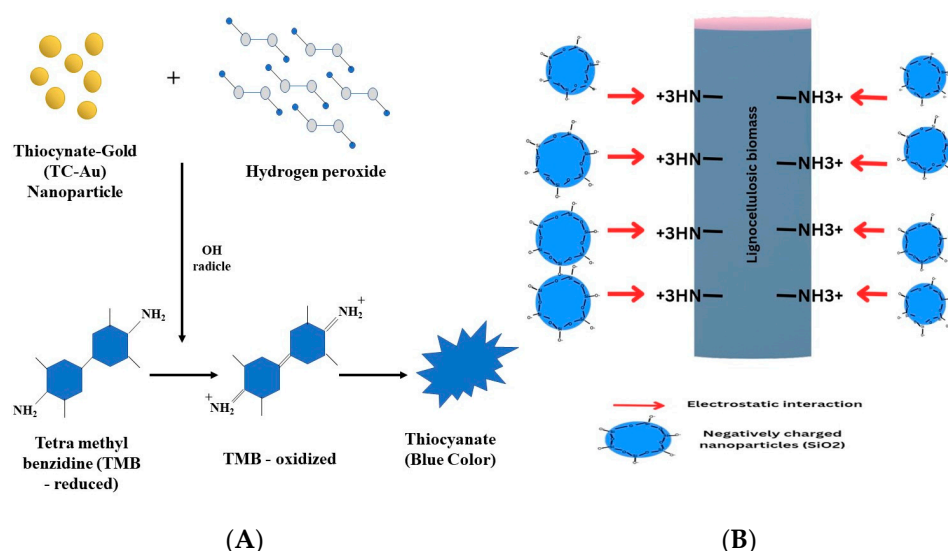


Figure 5. (A) Nanozymatic activity of TC-Au nanoparticles; (B) electrostatic interaction of lignocellulosic biomass carrying surface charges with oppositely charged nanoparticles.

Acid-Functionalized Nanocatalysts in Pretreatment

The use of surface-modified or functionalized NPs to enhance their interaction with lignocellulosic biomass has been observed in various cases. The application of silica-coated NPs in conjunction with carboxylic acid, propyl-sulfonic acid, and perfluoropropyl-sulfonic acid has been found to effectively catalyze the breakdown of disaccharide sugar, specifically cellobiose. This catalytic process also facilitates the solubilization of hemicelluloses derived from wheat straw, resulting in a dextrose yield ranging from 58% to 90% [61]. Additionally, the magnetic nature of the nanocatalyst makes its separation from the reaction mixture easy [93,97,134,135]. The nanocatalyst exhibited enzyme-like properties and removed approximately 44% of lignin from corncob biomass [136]. The glucose-NP electropositive interaction has been observed in nickel oxide NPs, which provides a favorable condition for the contact between the substrate and the nanocatalyst [137]. In addition, NPs exhibit an increased affinity towards electrons as a result of their redox potential and reduced size [138].

A study aimed to investigate the impact of two distinct types of NPs on the augmentation of bioethanol production during syngas fermentation conducted by *Clostridium ljungdahlii*. The utilization of methyl-functionalized silica and methyl-functionalized cobalt ferrite-silica ($\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-CH}_3$) NPs was employed to enhance the mass transfer of syngas and water. Among the NPs considered, it was observed that $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-CH}_3$ NPs exhibited superior enhancement in the mass transfer of syngas [26,122]. The possible phenomenon of increased mass transfer coefficient resulting from the attachment of NPs to the interface between gas and liquid can be elucidated through three mechanisms (as mentioned by Mena [139]): the shuttling or grazing effect, hydrodynamic effects occurring at the boundary layer between gas and liquid, and alterations in the specific interfacial area between gas and liquid [139].

5.1.2. Nanobiocatalyst in Biomass Pretreatment

The term ‘nanobiocatalyst’ refers to a group of immobilized enzymes that are based on NPs. The process of creating a nanobiocatalyst involves the attachment of enzymes onto different nanomaterials through the use of cross-linking molecules. This method improves the intended chemical kinetics and selectivity for specific substrates [140,141]. According to Basso et al. [142], immobilizing an enzyme using a cross-linking molecule provides a spacer that reduces steric hindrance between the enzyme and the solid supports, increasing the flexibility of the immobilized enzyme. According to the available reports, it has been

suggested that nanoscale materials possess significant advantages in terms of their large surface areas. These advantages include the ability to accommodate a higher enzyme loading and to minimize the mass transfer resistance for substrates. This characteristic is considered to be a crucial requirement in the advancement of nanobiocatalysts [140]. Similar to the nanocatalysts, these nanobiocatalysts employed for pretreatment can also be further categorized as acid-functionalized and non-acid-functionalized nanobiocatalysts.

Non-Acid-Functionalized Nanobiocatalysts in Pretreatment

In most cases the nanobiocatalysts are acid-functionalized, and non-acid-functionalized nanobiocatalysts are rarely explored. The amino acid production was increased by a factor of 6.18 when the protease enzyme was used to activate magnesium oxide NPs (MgN-pro) at a temperature of 95 °C, in comparison to the enzyme that was not treated. The samples treated with protease (+MgN) exhibited a significant 18-fold reduction in lignin content compared to the untreated samples [124].

Acid-Functionalized Nanobiocatalysts in Pretreatment

Acid-functionalized NPs acting as nanobiocatalysts offer the advantage of reducing the severity of the pretreatment process and minimizing acid usage in each cycle [98]. Additionally, their utilization enables the release of a significant quantity of fermentable sugars, owing to their high surface-to-volume ratios and the presence of a smaller amount of acids and/or enzymes coated with NPs. This, in turn, contributes to an increased percentage of hydrolysis and enhanced sugar recovery [23].

Currently, there is a limited amount of research available on the utilization of NPs in biomass pretreatment, despite the potential benefits. This is primarily due to the fact that the use of nanotechnology in biomass refineries is still in its early stages [124].

5.1.3. The Nanoscale Shear Hybrid Alkaline (NSHA) Method

The NSHA pre-treatment involves the utilization of sodium hydroxide to achieve a synergistic effect in the removal of hemicellulose and lignin through a shearing process. The NSHA pre-treatment process also involved the utilization of PDAC cationic polyelectrolyte as an additive, as mentioned previously. In a study, the utilization of immobilized cellulase in conjunction with the NSHA pretreatment method has been shown to enhance the enzymatic degradation of biomass by a factor of 4 to 5, resulting in the conversion of complex sugars into simpler forms that can be utilized for biofuel production [143].

5.2. Interactions of Nanoparticles during the Hydrolysis of Lignocellulosic Biomass

The utilization of NPs or their microemulsion has demonstrated a comparable hydrolytic effect in LB processing to that observed during chemical pretreatment. This characteristic renders them a viable substitute for conventional chemical pretreatment techniques, which incur high costs and pose environmental risks. The hydrolytic effect observed can be attributed to the reduced sizes of the NPs, facilitating their infiltration into the fibers of the LB substance and subsequent degradation of its internal architecture. The utilization of nanomaterials has been found to significantly improve the efficiency of immobilized enzymes by effectively increasing the surface area available for enzyme loading [144]. In the process of hydrolysis of lignocellulosic biomass, nanomaterials can act either as nanobiocatalysts or nanocatalysts.

5.2.1. Nanocatalysts in Biomass Hydrolysis

Nanocatalysts employed in the hydrolysis of lignocellulosic biomass mainly include acid-functionalized nanocatalysts, which may be magnetic or non-magnetic in nature. In a previous study, researchers employed H-form zeolite catalysts, as well as sulfated and sulfonated catalysts, to facilitate the generation of glucose from cellulose. Notably, this study represents the first record of the application of solid catalysts in the conversion of cellulose. The sulfonated activated-carbon catalyst demonstrated better glucose yield

compared to the other catalysts in the study. This can be attributed to its remarkable catalytic property and high hydrothermal stability, which are believed to be a result of strong acid sites and the hydrophobic planes present in them [145]. The hydrolysis mechanism of a water-soluble polysaccharide for an H-form zeolite has been proposed by another group of scientists. The process involves the adsorption of a water molecule onto the acid site of an H-form zeolite through an intermolecular hydrogen bond. Subsequently, the soluble polysaccharide diffuses into the zeolite's internal pores, where it undergoes hydrolysis with the help of the adsorbed water. Finally, the hydrolyzed products dissipate through the pores. They also suggested that to fully utilize Bronsted acid sites within the internal channels of the zeolite, cellulosic materials must be dissolved in a solvent and converted into short sugar chains [146].

Acid-functionalized NPs seem to have a higher affinity to hydrolyze LCB. Their efficiency appears to be on par with mineral acids used in chemical techniques [96]. Moreover, these NPs have the advantage that they can be recycled due to their magnetic nature [147]. In a study involving the utilization of magnetic silica-protected cobalt-spinel ferrite NPs for the acid functionalization process, three types of acids, namely perfluoroalkylsulfonic acid, alkylsulfonic acid, and butylcarboxylic acid, were used for this purpose. These acid-functionalized NPs were then employed for the cleavage of β -(1 \rightarrow 4) glycosidic bonds of cellobiose. The results indicated a 78% conversion rate of cellobiose [148]. A comprehensive understanding of the mechanism by which nanocatalysts operate is crucial for optimizing bioethanol production. Catalysts are essential in facilitating the increase in conversion rates by utilizing distinct active sites and diverse interaction patterns. In a study by Bosu et al. [149], iron oxide NPs possess acid sites that enable the donation of electron pairs to the substrate. The act of donating, in a reciprocal manner, enhances the reactivity of the substrate by virtue of the existence of metal-based Lewis acids. The formed complex demonstrates a phenomenon of partial charge transfer, leading to the emergence of a lone pair donor with increased electronegativity. The occurrence of nucleophilic attack and heterolytic bond cleavage on either the product or reactant is a direct result of the transfer of charge. Moreover, the process of sulfonation applied to iron oxide NPs results in the production of catalysts that exhibit a high level of activity. The utilization of these nanocatalysts facilitates acid-catalyzed reactions, which involve the disruption of both intramolecular and intermolecular hydrogen bonds existing between the hydroxyl groups present in cellulose. The aforementioned disturbance results in the disintegration of cellulose chains, ultimately leading to the hydrolysis of cellulose into glucose [149].

5.2.2. Nanobiocatalysts in Biomass Hydrolysis

Nanobiocatalysts have the ability to interact with cellulase, preventing its aggregation and thereby enhancing the stability of the enzyme. Numerous studies have focused on immobilizing different enzymes, such as cellulase, hemicellulase, and laccase on the NPs for enzymatic hydrolysis of lignocellulosic components [150]. The hydrolysis process may involve various interactions such as covalent cross-linking, electrostatic binding, or physical adsorption between biomass and the nanomaterials along with utilization of the functionalized nanomaterial [124]. In 2019, a research team conducted a comprehensive analysis of the efficacy of multiple nanobiocatalysts in the hydrolysis of biomass. The study focused on the immobilization of various enzymes responsible for polymer degradation, and the investigators stated that these techniques are highly cost-effective approach [151].

Utilization of magnetic nanobiocatalysts with immobilized enzymes enhances efficiency, streamlines enzyme recovery, and contributes to cost-effectiveness within the system. In a previous study, the authors demonstrated a maximum hydrolysis efficiency of 81% for carboxymethyl cellulose (CMC) and 93% for Hemp (*Cannabis sativa*) hurd biomass by using *Trichoderma reesei* cellulase, which was immobilized on activated magnetic NPs. There was a 94% binding of cellulase onto the NPs, and the enzyme activity remained at 50% for up to 5 consecutive cycles [152]. In another study, dur-

ing biofuel generation, enzyme immobilization was achieved through the utilization of TiO₂ NPs via the physical adsorption method. The aforementioned immobilization technique demonstrates notable efficacy in promoting the hydrolysis of lignocellulosic materials [153].

By reductive amidation and silanization, *Aspergillus niger* cellulase was immobilized on β -cyclodextrin-conjugated MNPs [154]. Immobilized cellulase produced more glucose than free cellulase did during the hydrolysis of rice straw. Additionally, immobilized cellulase could be retrieved up to 85% by using a magnetic field, and reused for continuous hydrolysis. Successful immobilization of the enzyme for hydrolysis of lignocellulosic substrates could also be achieved through various means such as physical adsorption, electrostatic adsorption, covalent binding, etc. Research has demonstrated the successful electrostatic adsorption of cellulase onto functionalized Fe₃O₄ magnetic nanospheres [155]. The augmentation of surface charge on the magnetic nanospheres has been found to enhance the capacity for cellulase immobilization compared to non-functionalized magnetic nanospheres. This immobilization process further contributes to increased enzyme stability, resulting in the retention of 87% of its native activity. Moreover, the enzyme displayed consistent performance over 6 successive cycles, retaining 60% of its initial activity. The findings of this study showed similarity to the research conducted by Alftren and Hobbey [156] on the hydrolysis of spruce using covalently immobilized β -glucosidase. The substitution of free cellulase with immobilized β -glucosidase resulted in a significant enhancement in the hydrolysis rate, increasing it from 44% to 65%. Furthermore, it has been observed that the immobilization of the enzyme cellulase can be once again detached from *Aspergillus fumigatus* through the introduction of manganese dioxide NPs, which form a covalent linkage.

In an alternative investigation, a newly developed magnetic cross-linked cellulase aggregate (MCLCA) was produced and utilized for the enzymatic transformation of lignocellulosic biomass. A comparison was made between the performance of immobilized cellulase and free cellulase. The findings of the study revealed that the cellulase that was immobilized displayed enhanced activity and showed notable durability for a maximum of six successive runs during the hydrolysis process of LB. More precisely, it maintained a retention rate of 74% of its original activity [157].

5.3. Interactions of Nanoparticles during the Fermentation Process of Biomass

El-Kemary et al. [133] proposed a potential mechanism for the interaction between NPs (NiO) and lignocellulosic biomass (glucose) during fermentation (Figure 6). Because of negative charge, electrostatic repulsion forces exist between NiO and hydrophilic hydroxyl groups of glucose, which should cause hindrance to their interactions. Yet the glucose molecules interact with the NiO NPs. They suggested that the possible adsorption mode is that the hydrophobic part of glucose is adsorbed onto the surface layers of NiO by Van der Waals interactions, and most likely the hydrophilic part is oriented toward the aqueous phase [133]. Thus, NPs can physically adsorb onto the surface of lignocellulosic biomass due to Van der Waals forces or hydrophobic interactions in a reversible manner and can easily desorb under appropriate conditions. The surface roughness and porosity of the biomass provide binding sites for NPs.

Although various benefits are there for using NPs for the treatment of LB, further investigation is required to optimize their efficacy and comprehend their underlying mechanisms. Despite these obstacles, the outlook for NPs appears promising as they persistently advance the frontiers of nanotechnology and present innovative resolutions to global challenges.

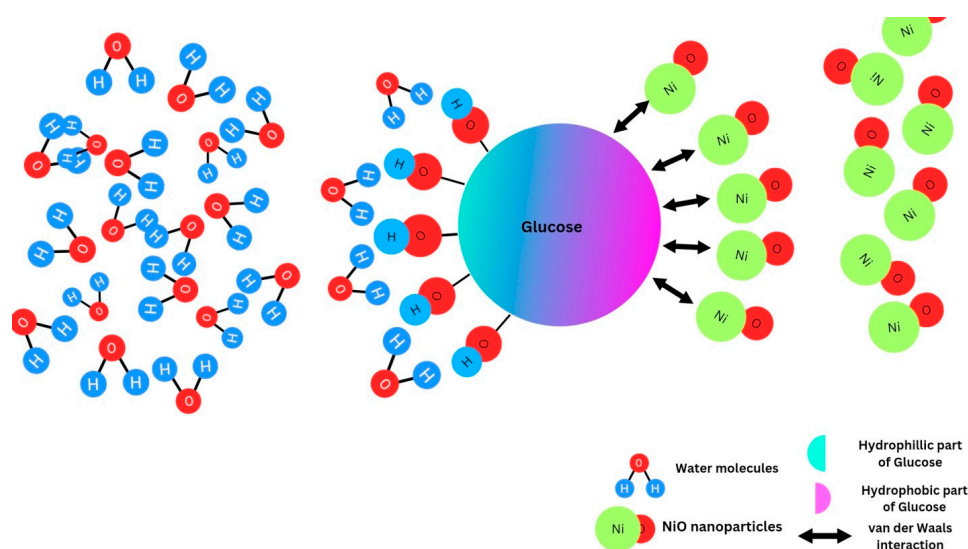


Figure 6. Possible mode of interaction of glucose molecules with the nanoparticles during the fermentation process of lignocellulosic biomass, facilitating glucose availability.

6. Factors Affecting NPs Synthesis and Its Performance in Bioethanol Production

The role of NPs in the biofuel production process is significant, as their performance directly impacts the outcome. Various factors influence the synthesis of NPs, as well as their performance, including temperature, pressure, and medium pH, which are key variables detailed in Tables 4 and 5. To ensure the NPs' effectiveness, it is crucial to enhance their desired characteristics and identify the optimal operating conditions.

6.1. Factors Affecting NP Synthesis

6.1.1. Effect of Temperature on NP Synthesis

In the synthesis of NPs, temperature is an influential parameter. Metal NPs undergo calcination in a temperature range of 100 to 900 °C, depending on the specific synthesis methods employed [158–161]. Chemical and physical methodologies involve the utilization of temperatures surpassing 300 °C, whereas biological methodologies typically operate at more moderate temperatures, such as 100 °C or even ambient conditions. The temperature plays a major role in determining the size, shape, and stability of NPs [162]. The mean diameter of spherical Ag NPs exhibited a reduction from 7.88 nm to 3.29 nm as the calcination temperature increased from 400 °C to 800 °C, respectively [161].

To establish the effect of high temperature on the stability of NPs, hydrolysis of alkali pretreated wheat straw was carried out using both a nanobiocatalyst and free pectinase. After 60 h of agitation at 50 °C, the maximum concentration of reducing sugar was found to be 1.39 g/L with free pectinase and 1.59 g/L with the nanobiocatalyst. These results suggest that the nanobiocatalyst exhibited improved efficiency in producing reducing sugar compared to free pectinase, possibly due to its enhanced stability at high temperatures. To confirm this, enzymes were then incubated at a temperature of 70 °C for a duration of 90 min. It was observed that the free enzyme completely lost its activity under these conditions. However, the immobilized enzymes exhibited retention of 70% activity for pectinase, 56% activity for xylanase, and 69% activity for cellulase. This also indicates that the stability of the enzymes increased after being conjugated to NPs and could be effectively utilized for the continuous hydrolysis of pectin and xylan at this temperature. Furthermore, it was found that the nanobiocatalyst generated a greater amount of reducing sugars (1.5 times higher) under the mentioned conditions compared to the free enzymes. Moreover, when the hydrolysate was fermented with Baker's yeast at 30 °C for 24 h, the maximum concentration of ethanol obtained was 0.37 g/L for the free enzyme and 0.5 g/L for the nanobiocatalyst [163].

6.1.2. Effect of pH on NP Synthesis

The manipulation of pH values plays a significant role in regulating the shape, size, synthesis rate, and uniformity of particle distribution in nanomaterials. This is due to the influence of variations in pH on the generation of nucleation centers, which are crucial for the development of these materials. While synthesizing NPs, the manipulation of pH levels can be employed as a means to regulate both the size and geometry of the particles, as observed in case of silver NPs generated from algal species [164]. It has been observed in multiple investigations that the size of NPs is anticipated to be greater in acidic fluids compared to basic media for selected nanomaterials. As the pH increased from 7.0 to 11.0, there was a decrease in the average size of the NPs [165]. Another study revealed that the size of Au NPs exhibited its maximum magnitude under neutral conditions (pH 7.0), while it reached its minimum size under alkaline conditions (pH 11.0) [166]. In contrast to the mentioned anticipations, several studies show the opposite results. In a separate investigation, it was observed that the dimensions of zinc oxide NPs experienced an increase from 13.8 to 33 nm as the pH level of the solution was elevated from 6 to 13 [167].

The pH of a solution also influences the shape and morphology of the particles and the evenness of particle dispersion. Specifically, at low pH levels, the particles exhibit a rod-like shape, whereas at higher pH levels they assume a spherical shape. The dimensions and robustness of silver NPs (AgNPs) are dependent upon the pH level of the surrounding solution. In a study, AgNPs that were synthesized in solutions with higher pH levels (specifically, pH 8 and 10) exhibited polyhedral shapes, possessed a fine structure, displayed a narrow size distribution, and demonstrated stability, whereas the stability of NPs synthesized in solutions with low pH levels (2, 4, and 6) began to deteriorate after 10 days of experimentation. Additionally, the particle size distribution exhibited a wide range [168]. According to another study, it was observed that at a pH of 9.8, the majority of the particles exhibited a spherical morphology compared to the particles formed in solutions with lower pH values [169].

Multiple studies have demonstrated that the synthesis pH of metallic NPs, such as Zn, Au, Cu, Ag, Pd, and others, exerts an influence on their performance and effectiveness [166,170]. NPs exhibit increased stability and tend to aggregate when exposed to pH levels lower than 7, thereby contributing to the enhancement of their overall durability.

The properties of NPs can vary depending on the pH of the medium, resulting in their ability to exhibit characteristics of either ligands or metals. NPs display a positive charge and exhibit a preference for interaction with antagonistic ligands under conditions of lower pH [171]. Conversely, under higher pH conditions, NPs display a negative charge and exhibit a response to antagonistic ligands. The augmentation of NP concentration amplifies their aggregation, especially when pH values are in proximity to the point of zero charge [172].

6.1.3. Effect of Pressure on NP Synthesis

In a reaction medium, it is standard procedure to apply suitable pressure in order to attain the desired morphology, size, and aggregation of NPs [163,173]. This level of control contributes to improved efficacy across a range of applications and facilitates the customization of properties and functionalities within the nanocomposite. Previous research has indicated that higher pressure conditions can result in an enhancement of NP size [171]. High-pressure synthesis techniques, such as hydrothermal and solvothermal methods, have been extensively utilized for the purpose of manipulating the growth of NPs. In their study, Yazdani and Edrissi [174] demonstrated that the increase in pressure from 300 to 6000 mbar can lead to a substantial increase in the size of NPs, from 8.3 to 16.8 nm at a temperature of 25 °C, inducing notable alterations in the properties of these NPs. This phenomenon may be attributed to various physical characteristics of magnetite, such as its high surface-to-volume ratio, surface tension, and supersaturation. Another study demonstrated that the increase in the size of NPs is roughly proportional to the square of the applied pressure [175].

The manipulation of pressure has been further demonstrated as a viable means of controlling the rates of rapid reaction and reduction [176]. In a study, the researchers observed that increasing the pressure of hydrogen resulted in a more efficient reduction of γ -Fe₂O₃ to α -Fe at considerably reduced temperatures [177]. Furthermore, a separate investigation demonstrated that an increase in carbon dioxide (CO₂) pressure exerted during a chemical reaction significantly increased the synthesis rate of Dy₂Ce₂O₇ NPs [178]. In addition, the utilization of high-pressure synthesis methods presents significant benefits, such as increased crystallinity, diminished defects, and enhanced stability of NPs.

Overall, the utilization of high-pressure fabrication strategies presents a prospective pathway for the development of advanced nanocomposites characterized by improved mechanical strength and thermal stability. This, in turn, creates novel opportunities for diverse applications across multiple industries.

6.1.4. Other Characteristics

The dimensions of NPs have a direct impact on their morphology, resulting in an increase in surface area per unit volume and subsequently an increase in surface energy [179]. An additional observation has demonstrated that the incorporation of functional groups onto nanomaterials enhances their properties [180]. This phenomenon establishes a correlation between the functional groups present on two or more nanomaterials, diverse surface charges, and a reduction in the size of pore entrances. Consequently, this development holds potential for the immobilization of enzymes.

Table 4. Summary of factors affecting the synthesis of NPs.

Factors	Size	Stability	Shape	Rate of Reaction	References
Temperature	Size of NPs decreases as the calcination temperature increases	Nanobiocatalyst stability increases at high temperature	-	-	[161–163]
pH	Size of NPs is greater in acidic fluids compared to basic media for selected nanomaterials	Stability of NPs synthesized in solutions with low pH levels (2, 4, and 6) began to deteriorate after 10 days of experimentation	At low pH levels, the particles exhibit a rod-like shape, whereas at higher pH levels, they assume a spherical shape	-	[165–168]
Pressure	Higher pressure conditions can result in an enhancement of NP size	Higher pressure conditions can result in an enhanced stability of NPs	-	Control the rates of rapid reaction and reduction	[171,178]

6.2. Factors Affecting NP Performance in Bioethanol Production

6.2.1. Effect of Temperature and pH on the Bioethanol Production Process

Temperature influences not only the synthesis of NPs that are used during bioethanol production, but also the hydrolysis process of lignocellulosic biomass in which these NPs are used. This was seen in a study where the optimal temperature for the hydrolysis of *Sesbania aculeate* biomass was determined to be 30 °C on utilization of cellulase bound magnetic NPs, which achieved the maximum bioethanol yield of 5.31 g/L [181]. In a related study by Zang et al. [182], magnetic chitosan NPs (Fe₃O₄-chitosan) were synthesized and employed as a support for immobilizing cellulase through covalent bonding facilitated by glutaraldehyde as a coupling agent. The highest hydrolysis efficiency of lignocellulosic biomass was observed at a pH of 5 and a temperature of 50 °C.

The effect of pH on the bioethanol production process was observed in a study [183], where lignocellulosic bioethanol production using *Saccharomyces cerevisiae* was more efficient when the pH is below 7, whereas the optimal pH for this process was 3.7.

6.2.2. Effect of Size and Concentration of NPs on the Bioethanol Production Process

In the context of biofuel production, the size and concentration of NPs incorporated throughout the process are crucial factors that are taken into account [184]. Therefore, each process necessitates the identification of an optimal combination of operational variables. Several studies have extensively examined the utilization of NPs across different sizes and concentrations, resulting in the identification of a suitable combination of characteristics. NPs ranging in size from 5 to 100 nm have been utilized to enhance the yield and reduce the reaction time of biofuel. This is attributed to their favorable surface characteristics and significant number of apertures [172]. In general, the efficiency of a catalyst becomes more pronounced as the particle size decreases. Thus, the conversion efficiency of sunflower oil into biofuel utilizing a NP catalyst was determined to be 99.05% [185].

The concentration of NP also plays a crucial role in determining both the efficacy and magnitude of a process. A study was conducted to find out the effect of pH, glucose concentration and nickel nanoparticle concentration on dark fermentation process. A maximum biohydrogen production of 3000 mL was achieved with 20 mg/L nanomaterials (nickel) at a glucose concentration of 10 mg/L and pH of 5.5 [186]. In another investigation, a concentration of 0.01 wt% of Fe₃O₄ NPs had the greatest effect on ethanol production, with an 11.80% improvement in the ethanol concentration observed from the control experiment (4.66 g/L). All other NPs showed a sharp decline in ethanol concentration at NPs concentrations greater than 0.02 wt%. For every metallic oxide nanoparticle tested, the concentration of NPs increased from 0.04 to 0.08 wt%, and the ethanol content decreased accordingly [119]. Hence, even with the application of small quantities of NPs, the NPs can provide extensive and dynamic surface areas, thereby reducing the need for a large dosage of catalyst.

Although some studies have been conducted on bioethanol production concerning the size of NPs, the constructive relation between them was not achieved. Hence, further research is needed to determine the optimal conditions for incorporating NPs into the bioethanol production process to maximize its benefits.

Table 5. Factors affecting the performance of NPs in biofuel production.

Factors	Preferable Conditions	Examples	References
Temperature	Moderate	Optimal temperature for the hydrolysis of <i>Sesbania aculeate</i> biomass was determined to be 30 °C on utilization of cellulase bound magnetic NPs The highest hydrolysis efficiency of lignocellulosic biomass was observed at a pH of 5 and a temperature of 50 °C.	[181,182]
pH	Acidic	Optimal pH for lignocellulosic bioethanol production using <i>Saccharomyces cerevisiae</i> was 3.7. The highest hydrolysis efficiency of lignocellulosic biomass was observed at a pH of 5 and a temperature of 50 °C.	[183]
Size of NPs	5 to 100 nm enhance yield and reduce reaction time of biofuel	-	[171]
	Efficiency of a catalyst increases as the particle size decreases (~50 nm)	Conversion efficiency of sunflower oil into biofuel utilizing NP catalyst was determined to be 99.05%	[185]
Concentrations of NPs	Efficiency of a process increases with smaller amounts of NPs	Concentration of 0.01 wt% of Fe ₃ O ₄ NPs had the greatest effect on ethanol production	[119]

7. Conclusions and Future Prospects

Recently, there has been increased interest in the use of nanotechnology to produce bioethanol from LB, which aids in establishing efficient, economical, and environmentally friendly processes. This review has outlined several nanotechnological methods with multiple advantages in the pretreatment of various LB with recent examples. The use of magnetic NPs offers the benefits of easy recovery and reusability of the immobilized enzymes, reducing the overall process cost. The usage of acid-functionalized magnetic NPs is advantageous and economical, however further research is needed to improve the effectiveness of the NPs for better use. The distinctive physico-chemical characteristics of nanoparticles, such as their huge surface-area-to-volume ratio, strong reactivity, excellent dispersibility, high specificity, etc., are mostly responsible for this enhanced performance.

Although, this area is relatively in its infancy, there are tremendous opportunities for future research and development. A few of the many ways that nanotechnology is improving pretreatment, hydrolysis, and fermentation technologies have already been addressed in this review. Developments in various other areas, including the application of nanocatalysts to alter the microbe's metabolic pathway and to stimulate ethanol generation, have shown promise. In addition, functionalized NPs can also be used to encapsulate and deliver nutrients, vitamins, or cofactors in a controlled manner for yeast growth and ethanol production, improving fermentation performance and optimizing yeast metabolism. Nanotechnology-based membranes, such as nanofiltration or reverse osmosis membranes, can enhance ethanol separation and purification, improving purity and yield. Nevertheless, the successful implementation of this technology on a commercial scale requires overcoming certain technical barriers and conducting more investigation in uncharted domains.

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