

Review

Current Trends and Future Prospects of Nanotechnology in Biofuel Production

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Abstract: Biofuel is one of the best alternatives to petroleum-derived fuels globally especially in the current scenario, where fossil fuels are continuously depleting. Fossil-based fuels cause severe threats to the environment and human health by releasing greenhouse gases on their burning. With the several limitations in currently available technologies and associated higher expenses, producing biofuels on an industrial scale is a time-consuming operation. Moreover, processes adopted for the conversion of various feedstock to the desired product are different depending upon the various techniques and materials utilized. Nanoparticles (NPs) are one of the best solutions to the current challenges on utilization of biomass in terms of their selectivity, energy efficiency, and time management, with reduced cost involvement. Many of these methods have recently been adopted, and several NPs such as metal, magnetic, and metal oxide are now being used in enhancement of biofuel production. The unique properties of NPs, such as their design, stability, greater surface area to volume ratio, catalytic activity, and reusability, make them effective biofuel additives. In addition, nanomaterials such as carbon nanotubes, carbon nanofibers, and nanosheets have been found to be cost effective as well as stable catalysts for enzyme immobilization, thus improving biofuel synthesis. The current study gives a comprehensive overview of the use of various nanomaterials in biofuel production, as well as the major challenges and future opportunities.

Keywords: nanoparticles; biofuel; transesterification; catalyst; immobilization

1. Introduction

It is very well known that the consumption of fossil fuels is increasing rapidly with an increase in population growth rate and urbanization, leading towards the exhaustion of petroleum-derived fuels in the near future. The limited availability of fossil fuels is a major problem around the globe. Moreover, high dependency on petroleum-derived fuels has raised many questions about its adverse effects on the environment, economy, and energy saving. Therefore, significant research has been focused on the search for an alternative source that can reduce the consumption of fossil-derived fuels [1].

Biofuels are considered as an alternative to fossil-based fuels and have gained worldwide attention in recent years due to their distinct properties [2]. The production of biofuel

is being carried out using many plant sources such as vegetables, corn, soybean, sugarcane, palm oil, and *Jatropha* (used in Africa) as feedstock in almost every continent [3,4]. In countries such as the USA and Brazil, bioethanol is successfully being applied as biodiesel for otto-cycle engines in combination with gasoline [1]. Biodiesel on the other hand is an important type of biofuel, having the capability to either substitute or replace fossil-based diesel. The production of biodiesel is carried out through a trans-esterification process using renewable bio lipids [5]. Some of the potential feedstocks used to produce biodiesel are oil extracts of seeds or kernels of non-edible crops. An important non-edible oil plant is *Jatropha* which is native to Central and South America and is being considered as a reliable source for the production of biodiesel due to its high oil content [6]. In addition, edible oils obtained from plants like sunflower, soybean, palm, etc. are also being used as substrates for biodiesel production [7–9].

The use of nanotechnology and nanomaterials in biofuel research has risen as a promising tool in providing cost-effective techniques to improve production quality. There are multiple advantages to using nanoparticles (NPs) over other sources for biofuel synthesis due to their size and unique properties such as the high surface area to volume ratio and special attributes such as a significant extent of crystallinity, catalytic activity, adsorption capacity, and stability [10–12]. Carbon nanotubes and metal oxide nanoparticles are generally used as nano-catalysts for biofuel production because of their additional properties which aid in high potential recovery [13]. Nanotechnology in combination with other processes such as gasification, pyrolysis, hydrogenation, and anaerobic digestion has proven to be useful for the synthesis of biofuels [14,15]. The present review addresses the advancement of NPs over biofuel production in terms of their applications and challenges, with future perspectives.

2. Biofuel Types

Biofuels are generated from renewable sources, thus protecting the environment and solving the problem of depletion of fossil fuels and are considered as an alternative to fossil fuels. Biofuels are mainly divided into three main generations, namely first generation, second generation, and third-generation [16,17]. First-generation biofuel requires edible sources such as vegetable oils, starch and sugar as raw material for conversion. Microorganisms and enzymes are mainly utilized to act as a catalyst to convert saccharides into alcohol during the fermentation process. Production of biofuel is low due to limited feedstock supplies and the biofuel produced is costlier than that of petrol-based fuel. The production of biofuels in the second generation is expensive and requires a non-edible source for its production [18]. Third-generation biofuel requires advanced instruments (Figure 1). Biofuel production in this type of generation is mainly from algal and lignocellulosic biomass [19]. Advancements in each generation have led to the utilization of non-usable biomass, making the production cost-effective and increasing the biofuel production in lesser time. Therefore, to overcome these issues nanotechnology has been employed for biofuel-based processes. Several biofuels such as biohydrogen, biodiesel, bioethanol, biogas, etc., have been produced with the application of nanotechnology. Two main reactions, trans-esterification and esterification, are adopted for the conversion of triglyceride to biofuels. Nano-catalysts such as nanotubes, nanosheets, and nanoparticles are largely available from microbial fuel cells for biofuel generation.

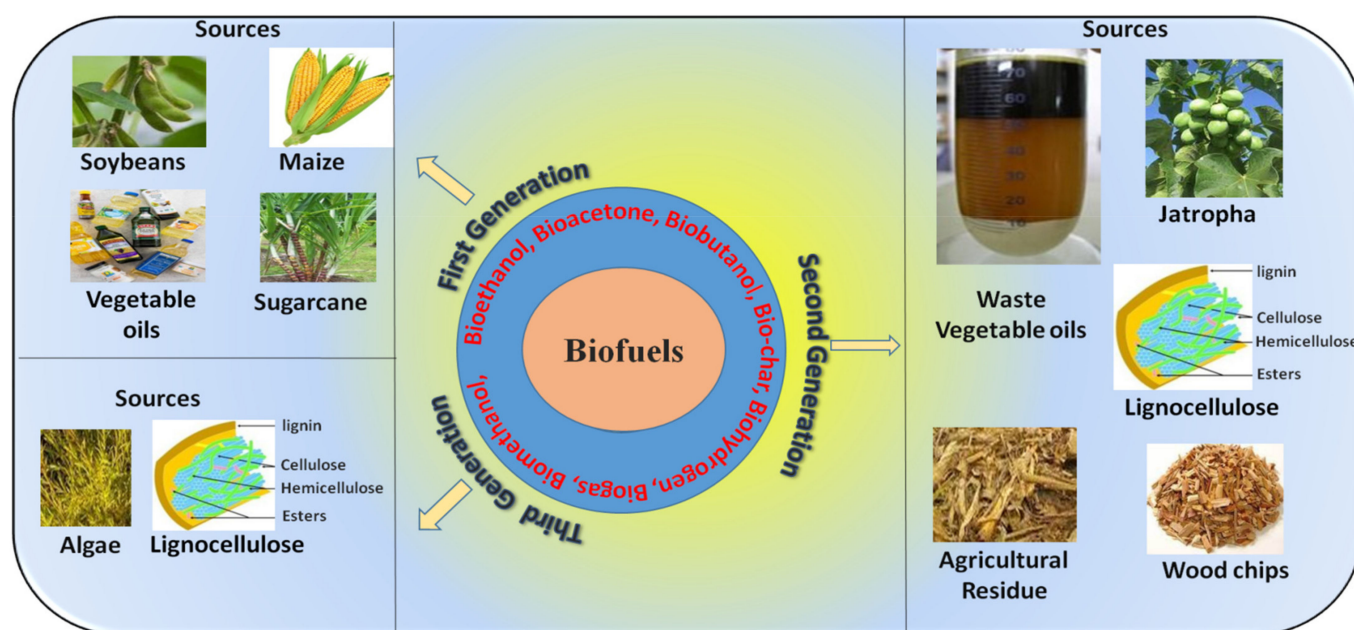


Figure 1. Representation of biofuel types and their sources.

3. Different Nanoparticles in Biofuel Production

Nanoparticles possess large surface area and super magnetic properties under the applied field which make them easier to separate from a biofuel cell and help in the recycling of enzymes. Several nanoparticles are used for biofuel production and form a support system for the catalyst to form a nano-catalyst. Some of these are magnetic nanoparticles and carbon nanotubes (CNTs), which act as a support system for enzymes. Other than these, metal, metal oxide, heterogeneous catalysts, acid-functionalized, etc. are used.

3.1. Carbon Nanotubes (CNTs)

CNTs are allotropes of carbon formed by rolling up sheets of graphene to a cylindrical shape. Due to their potential in carrying redox reactions and electron transfer kinetics, these nanotubes are primarily used in the fabrication of biosensors and microbial fuel cells [20]. The CNTs are of two types, Multi-Walled Carbon Nanotubes (MWCNTs), having multiple layers of graphene, and Single-Walled Carbon Nanotubes (SWCNTs), consisting of a single atomic layer of carbon atoms [21–23]. CNTs have characteristic features such as stability, high surface area, and less toxicity, and are used as a catalyst for biofuel production. Various studies have been performed on CNTs for biofuel synthesis. As their precursors are renewable, CNTs emerged as a promising nanomaterial because of their cost-effectiveness [24]. Liu et al. reported that the addition of 100 mg/L CNTs into anaerobic sludge blanket (UASB) reactors enhanced biohydrogen production with a production rate of 5.55 L/L/d and hydrogen yield of 2.45 mol/mol glucose [20]. The addition of CNTs during the anaerobic digestion process resulted in a reduction of start-up period and enhanced performance as compared to other activated carbon (AC) particles. In a similar kind of study, the immobilization of *Enterobacter aerogenes* over functionalized multi-walled carbon nanotube (MWCNT-COOH) enhanced the hydrogen production rate (2.72 L/L/h), hydrogen yield (2.2 mol/mol glucose), and glucose degradation efficiency (96.20%) in comparison to the free cells [25]. The immobilization process also reduced the lag phase duration of the anaerobic digestion process as compared to the free cell. There are different ways to synthesize CNTs, such as chemical vapor deposition, laser removal, arc discharge, etc. These particles are made up of graphite sheets rolled up into round and hollow shapes and are used for enzyme immobilization [26]. CNTs have a high capacity for loading enzymes due to their large surface area [27]. Enzymes can be immobilized on CNTs, thereby increasing the reusability and maintaining the catalytic activity of the immobilized

enzyme [28–30]. It has been shown that MWNTs functionalized with amino groups improve the thermal stability of CNT [31]. Furthermore, usage of CNTs in biofuel generation increases the overall enzyme concentration and some properties of CNTs, such as porosity and conductivity, make it an important candidate for enzyme immobilization [1]. It was reported that functionalization of carbon nanotubes with ferrocene (Fc) and 2, 2'-azino-bis (3ethylbenzothiazoline-6-sulfonate) diammonium salt (ABTS) as mediator improves the catalytic activity in comparison to a glass carbon electrode, and maximum power output was also found to be 100 times greater than that of a carbon electrode without the incorporation of nanotubes. Here, ferrocene was utilized as an anodic mediator and ABTS as a cathodic mediator on the developed CNTs. $100 \mu\text{Wcm}^{-2}$ power was generated when both anode and cathode were paired with nanostructures and their suitable mediators [32].

In another study conducted on Multi-Walled Carbon Nanotubes (s-MWCNTs), these were sulfonated, turned to s-MWCNT and tested for different parameters such as possess high catalytic activity [29]. In just half an hour from 1.5–2.0 h, 95.12% methanol was converted to oleic acid at temperature 210°C when increased from 180°C using s-MWCNT as a catalyst. The stability of carbon nanostructures was demonstrated after treatment with H_2SO_4 , where no effects on the structure of carbon nanotubes were found. Additionally, a coupled reaction was performed to produce oleic acid, first when only the reaction was carried out, and later when the equilibrium was shifted by removing water. The first reaction was stopped after 4.5 h, while the coupling reaction stopped after 1.5 h and methanol recycled from each process was again reacted for a further 3 h to give 95.46 wt.% yield from the first process and 98.28 wt.% from the latter. Again, the reaction continued, for 1.5 h for the first process, but the yield remained unchanged, and for the coupling reaction the yield increased to 99.10 wt.% in just 1 h [33].

In several investigations, it was observed that MWCNTs functioned better than SWCNTs due to enzyme immobilization being consistent with their structural configuration, which increased the catalytic activity of the immobilized enzymes. MWCNTs surpassed the cellulose hydrolysis from *Aspergillus niger* with an efficiency of 85–97% and maintained their recyclable potential at 52–75% following 6 cycles of hydrolysis [34,35].

3.2. Magnetic Nanoparticles

Enzymes like cellulases and lipases are frequently used in the biofuel industries [36,37]. Many studies on magnetic nanoparticles suggest that they play an important role in the immobilization of enzymes for biofuel generation. Enzymes can be reused after immobilizing them to a support matrix coated with certain nanomaterial and this process is suitable for hydrolysis of lignocellulosic biomass [38]. The immobilization of enzymes used for hydrolysis of lignocellulosic biomass can be improved by altering various properties of enzymes [39]. The super magnetic property of magnetic nanoparticles is useful in the separation of immobilized enzymes, thus increasing reusability [40]. Many such attempts have been made to immobilize cellulose on magnetic nanoparticles for hydrolysis of biomass [41].

$\text{CaSO}_4/\text{Fe}_2\text{O}_3\text{-SiO}_2$ NPs are being used in a study to demonstrate biodiesel production from *Jatropha curcus* [42]. The pore size of nanoparticles is measured at 90 nm and a volume of $0.55 \text{ cm}^3/\text{g}$ with a high surface area of $391 \text{ m}^2/\text{g}$. In optimum conditions, biodiesel production from crude *Jatropha* is measured at 94%, but after four cycles, it decreased to 85% and then gradually decreased further due to the inactivation of the nanoparticles. Further investigation was done to find the reason behind the inactivation of NPs. The results showed that the deposition of components of the reaction medium was blocking the pores after the fourth, seventh and ninth cycles. The surface area was also reduced to $252 \text{ m}^2/\text{g}$, which was less than earlier.

In another study, $\text{Fe}_3\text{O}_4\text{-NH}_2$ and reduced graphene oxide were incorporated into aniline for the formation of a nanocomposite, a polyaniline (PANI) matrix. The nanocomposite is shown to have improved the function in bio-electro catalysis of glucose oxidase. Investigation of the performance of $\text{rGO/PANI/f-Fe}_3\text{O}_4/\text{Frt/GOx}$, a bio anode, was carried out.

Glucose oxidase immobilized on rGO/PANI/f-Fe₃O₄ showed a very high catalytic current. Furthermore, reduced graphene oxide coated with PANI has a high surface area and a high electrical conductivity. The results have demonstrated that the nanocomposite is efficient in electron transfer. When applied to an enzymatic biofuel cell (EBFC), the maximum current produced was 32.9 mA cm⁻² at a glucose concentration of 50 mM [43].

In biodiesel production, magnetic nano ferrites doped with calcium have been observed to have a significant effect, enhancing production yield by almost 85% from soybean cooking oils [44]. It was demonstrated that employing sugarcane leaves and MnO₂ nanoparticles increased bioethanol production. At various stages, it catalyzed this process. Sugarcane leaves are transformed to bioethanol in this technique and due to their large surface area, MnO₂ nanoparticles are accountable for the binding of enzymes to their active sites, improving ethanol synthesis [45]. It was discovered that the immobilization of yeast cells on the magnetic nanoparticles resulted in the higher production of ethanol [46,47]. Previous research has demonstrated the potential of implementing MNPs to hydrolyze the microalgae cell wall by immobilizing cellulase on MNPs accompanied by lipid extraction (Figure 2) [48]. Mahmood et al. studied the effect of iron nanoparticles addition over anaerobic digestion and hydrogen production using an aquatic weed, water hyacinth (*Eichhornia crassipes*) as the substrates [49]. Results of this study revealed that a specific concentration of iron nanoparticles enhanced the hydrogen yield reaching 57 mL/g of the dry weight of plant biomass. The enhancement of hydrogen production while using glucose as the substrate has also been reported in some studies [50,51]. In addition to zero-valent nanoparticles, iron oxides nanoparticles, such as Fe₂O₃ and Fe₃O₄ have been explored for the production of biohydrogen using glucose, wastewater, and sugarcane bagasse [52–54]. Nano zero-valent iron (nZVI) and Fe₂O₃ have also been explored for the enhancement of biogas production using waste-activated sludge [55]. The addition of 10 mg/g of total suspended solids (TSS)nZVI and 100 mg/g TSS Fe₂O₃NPs increased the methane production by 120% and 117% of control. These results confirmed that the addition of a low concentration of NPs promoted microbial growth as well as activities of key enzymes, leading to higher biogas production.

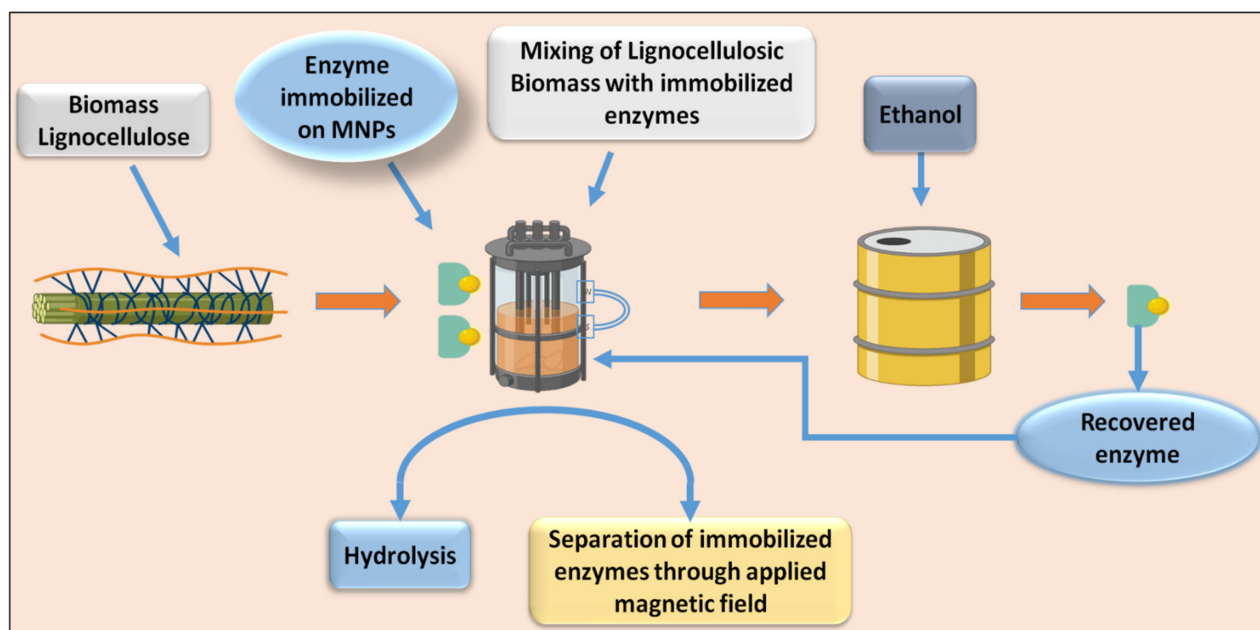


Figure 2. Biofuel production with the use of cellulase incorporated in MNPs (magnetic nanoparticles) to break down cellulose.

3.3. Acid Functionalized Nanoparticles

The potential pre-treatment strategies for lignocellulosic biomass include different methodologies based on acid and base. In this context, acid-functionalized nanoparticles are believed to play a key part in the hydrolysis of different biomasses, which are further used for bio-fuel generation. Transesterification and esterification methods are generally employed for triglycerides and fatty acids, respectively, and by making use of acid and base catalysts to improve reaction for FAME (fatty acid methyl ester) biodiesel production (Figure 3). The base-catalyzed process is somewhat easier than the acid-catalyzed process. On the other hand, acid-catalyzed reaction processes are cheaper in terms of the biomass they utilize [56].

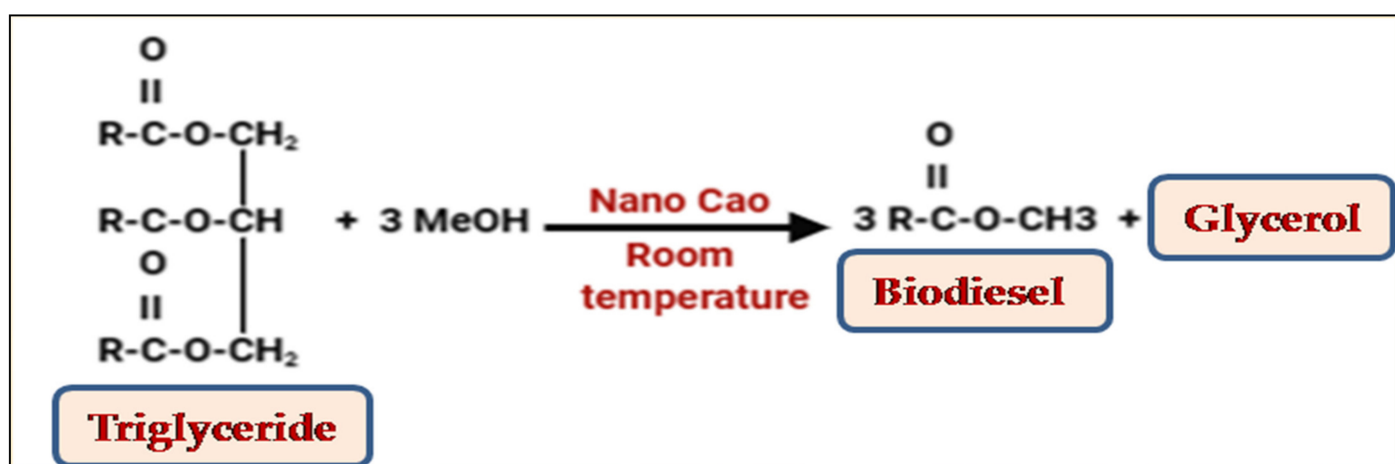


Figure 3. Preparation of FAME (fatty acid methyl ester) Biodiesel from Triglyceride.

According to Wang et al., silica-coated Fe/Fe₃O₄ MNPs assisted by sulfamic acid and sulfonic acids have been used for biodiesel production [57]. Transesterification of glyceryl trioleate and esterification of oleic acid have been carried out using sulfonic acid-functionalized/sulfamic acid-functionalized magnetic nanoparticles. It has been shown that 88% conversion of glyceryl trioleate in sulfonic acid-functionalized and 100% in sulfamic acid-functionalized in trans-esterification process was achieved at 100 °C in 20 h and it was 100% for oleic acid in just 4 h through an esterification process. Moreover, only 62% conversion was recorded when the sulfonic acid-functionalized catalyst was used, and 95% conversion was achieved for the sulfamic acid-functionalized process in the fifth cycle consecutively.

A recent study demonstrated the capability of nanotechnology by using acid-functionalized magnetic nanoparticles (MNPs) as catalysts in the hydrolysis of cellobiose from lignocellulose biomass. It was observed in the study that acid-functionalized MNPs with a 6% sulfur concentration resulted in 96% conversion of cellobiose, higher than the traditional conversion of 32.8%, in the absence of the catalyst [58]. Due to their nano-catalyst characteristics for the immobilization of various enzymes, these acid functionalized MNPs could accelerate the hydrolysis reaction. Apart from this, the high surface-to-volume ratio of such MNPs promotes the hydrolysis rate in comparison to the chemical pre-treatment. It was revealed that sulfonate-supported silica MNPs may be used to hydrolyze lignocellulose biomass, making them viable hydrolysis catalysts. Furthermore, these nanoparticles are thermally stable and can be easily separated from reaction mixture [59]. Enzymes associated with the production of biodiesel or bioethanol can be immobilized using MNPs as a medium. MNPs' strong coercivity and paramagnetic properties during the methanogenesis process also make them suitable for biogas production [60,61].

3.4. Metallic Nanoparticles

Although metallic nanoparticles have not been explored widely, various studies have been performed to check their efficiency in biofuel production. Metallic NPs are known for

their higher surface area and nano-size that enable many enzymes such as oxidoreductase to bind with magnetic nanoparticles, consequently improving electron transfer [62]. Many catalytic nanoparticles have been constructed for a higher rate of ion transfer and oxygen reduction rate activity. It has been hypothesized that metallic NPs may be incorporated in a structured way to enhance electrocatalytic activity and creating a biofuel cell with high loading capacity and good electron transfer rate when employed in a layer-by-layer assembly with suitable polymers and enzymes [63].

Hybrid nano-catalysts have been designed using metallic NPs of gold, platinum, and Pt_{0.75}-Sn_{0.25} by installation in acid-functionalized Multi-Walled NCTs, whereas gold NPs were encapsulated in poly (amidoamine) PAMAM dendrimer structure in another method. HR-TEM analyses have shown that dendrimer encapsulated NPs are highly arranged and very efficient. Biofuel cells have been configured with gold, platinum, and Pt_{0.75}-Sn_{0.25} supported by MWCNTs, whereas gold NPs demonstrated great electrical conductivity and biocompatibility, and better catalytic activity than platinum NPs. The combination of platinum and tin NPs showed high oxidation activity for ethanol [64].

In another study, gold NPs were synthesized via laser ablation in an aqueous solution, which demonstrated good catalytic activity even on the 10th cycle, with great electrocatalytic efficiency. The LA-Au NPs outperformed, even with a lower surface area. This makes LA-Au a suitable candidate for biofuel cell development [65].

Various forms of nanomaterial have been used for the synthesis of biohydrogen. Gold nanoparticles (5 nm) improve substrate utilization capacity by 56% and boost biohydrogen generation rate by 46% [66]. Because of their smaller size and larger surface area, Au nanoparticles facilitate biohydrogen generation by adhering microbial cells to active sites. These nanoparticles also increase the enzymatic activity in the biohydrogen synthesis machinery, which is essential for biohydrogen production. Silver nanoparticles have also been observed to optimize substrate utilization which in turn promotes biohydrogen production. These nanoparticles shorten the lag period of bacterial and algal development while also activating the acetic reaction, which is the primary biohydrogen generation pathway. In photosynthetic microbes, nanoparticles promote the synthesis of biohydrogen. Nanoparticles added to the growth medium improve microbial growth, physiological processes and photosynthetic efficiency, protein synthesis, and nitrogen metabolism and, as observed in *Chlorella Vulgaris*, the optimal concentrations of Ag and Au nanoparticles increased its photosynthetic activity [67]. It has been demonstrated that the addition of zerovalent iron nanoparticles enhances biogas generation from waste matter [68,69]. Nickel nanoparticles have also been widely utilized in the hydrogenation process for converting glucose into sorbitol [70].

3.5. Metal-Oxide Nanoparticles

The synthesis of metal oxide NPs is fundamental for successful application and solution phase methods that give a great deal of control over the synthesis product. Metal oxide NPs are frequently arranged using the sol-gel technique, where the reaction is stopped before gelation occurs, like precipitation strategies. The properties of NPs are ascertained by the development, nucleation, and aging mechanisms.

Metal oxide NPs are known for their uses in sensors, catalysis, natural remediation, and electronic materials. Metal oxides have been used for the conversion of vegetable oil to biofuel. The metal oxides used as a catalyst are KOH, MoO₃, ZnO, V₂O₅, Co₃O₄, and NiO, and have the capacity to catalyze the transformation of oil into organic liquid products [71].

Metal oxides have been used as a support system with high catalytic activity but lower selectivity. Production of biodiesel has been carried out with the use of nano-catalysts CaO and Al₂O₃. Jatropha oil has been a good source of feedstock and biodiesels are synthesized by the process of transesterification with 82.3% yield using methanol and oil [72].

The metal oxide catalyst of ZrO₂ has been shown to employ both esterification and transesterification contemporaneously using a mixed feedstock of free fatty acids and soybean oil. ZrO₂ has been reported as highly stable, hard, and having both acidic and

basic properties. The yield of fatty acid methyl ester (FAME) of 89–86% has been shown in both contemporaneous processes. The higher temperature condition for the metal oxide catalyst of ZrO_2 has been reported to achieve higher FAME yields [73]. Moreover, other NP catalysts such as MeO-SBA-15, ZnO-SBA-15, La_2O_3 -SBA-15, etc., have been used to increase the biofuel production from waste cooking oils [74].

In biohydrogen production via the dark fermentation process, silica (SiO_2) nanoparticles have been employed. The nanocomposite produced by the combination of SiO_2 nanoparticles with iron oxide (Fe_3O_4) has higher catalytic activity and stability, hence making them increasingly significant in biohydrogen production. Moreover, these nanocomposites provide additional advantages such as stability at high temperatures and low toxicity [75–77]. It has been reported that, with the addition of $\text{Fe}_3\text{O}_4/\text{ZnMg}(\text{Al})\text{O}$ nanoparticles, biodiesel productivity increased [78]. Nanoparticle functionalization is another process for increased biodiesel production. For example, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoconjugates can be used in biodiesel synthesis. Using nano-conjugates, biodiesel production can be increased by up to 97.1%. Various types of cooking and algal oils have been utilized in this technique and, with the availability of these iron-silica nanocomposites, algal oils have a high productivity rate [79]. Si-NPs are often deposited on the surface of nanoparticles for the immobilization of lignocellulolytic enzymes such as cellulase. Si-NPs have been shown to increase catalytic activity in the synchronous saccharification step for bioethanol synthesis using *Trichoderma viride* cellulose [80].

4. Nanoparticles in Heterogeneous Catalysis

Heterogeneous catalysts have emerged as an advancement on homogenous catalysts as they do not need too much water and are easy to separate from the reaction mixture [81]. The heterogeneous catalyst has been used for biofuel production [82,83]. Their separation is easy, and one can obtain contaminant-free products, which are normally non-corrosive, eco-friendly, and with high selectivity and long lifetimes. In some studies, the conversion of lignocellulosic biomass to biofuel has been demonstrated using NPs as heterogeneous catalysts [84]. The catalytic activity and selectivity of dispersed metal nanoparticle catalysts in heterogeneous catalysis were improved by using hybrid support made up of metal-organic framework (MOF) crystals and partially reduced graphene oxide (PRGO) nanosheets. Palladium nano-catalysts incorporated into a 3D hierarchical nanocomposite, Pd/PRGO/Ce-MOF, consisting of a Ce-based MOF wrapped in thin PRGO nanosheets, providing a heterogeneous tandem catalyst for the hydrodeoxygenation of vanillin, a common component in lignin-derived bio-oil, under mild reaction conditions. The developed heterogeneous catalyst Pd/PRGO/Ce-MOF has been shown to maintain its optimal catalytic activity and selectivity over four runs [85].

5. Applications

Biofuel as an alternative fuel source has many applications in various sectors globally. It may alleviate the problem of the constant degradation of petroleum-derived fuel. Nano-catalysts can increase the catalytic activity of biofuel-based reactions. These nano-catalyst/particles are of various types and have been developed continuously for their incorporation into biofuel cells as discussed in the above sections.

5.1. Biohydrogen Production

Generally, two different fermentation methods, i.e., (i) photo fermentation and (ii) dark fermentation are utilized for biological hydrogen production. Photo fermentation is carried out by microorganisms such as cyanobacteria and green algae in the presence of sunlight and water during the oxygen photosynthesis process. In the case of dark fermentation, anaerobic bacteria play a major role in the degradation of substrate or biomass for the production of biohydrogen [86,87]. Although this method is the most commonly adopted for the production of biohydrogen, the formation of by-products during the fermentation process inhibits the hydrogen production. Low hydrogen yield, the major limitations of this

process can be solved by the application of nanoparticles. The unique physical and chemical properties of the nanoparticles have diversified their application in dark fermentation process leading to enhancement in hydrogen production. Several metal (Ag, Au, Cu, Fe, Ni) and metal oxide (Fe_2O_3 , Fe_3O_4 , TiO_2) nanoparticles have been successfully explored over the last few years. A summary of the application of various NPs in biohydrogen production is given in Table 1.

Table 1. Summary of application of nanoparticles in biohydrogen production process.

Nanoparticles	Substrate/ Feedstock	Reaction Conditions	Summary	Reference
Ag	Glucose	Mixed culture; pH-8.5; temperature-35 °C; rotation-120 rpm;	Higher hydrogen yield (2.48 mol/mol glucose) observed compared to blank. Reduction in lag phase observed with addition of Ag NPs. Reduction in ethanol production observed in presence of Ag NPs.	[86]
Au	Acetate	Anaerobic sludge; pH-7.2; temperature-35 °C	The hydrogen production rate reached 105 2 mL/L per day with the addition of Ag NPs.	[87]
Au	Artificial wastewater	Anaerobic culture; pH-7.2; temperature-35 °C	Maximum cumulative hydrogen production 4.48 mol per mol sucrose achieved with 5 nm Au NPs.	[66]
Cu	Glucose	<i>Enterobacter cloacae</i> 811101 and <i>Clostridium acetobutylicum</i> NCIM 2337; pH-7.0 (<i>E. cloacae</i>), 6.0 (<i>C. acetobutylicum</i>); temperature-37 °C; duration-24 h	The conversion efficiency of sucrose to hydrogen reached 56%. The Cu-NPs were found to have a more inhibitory effect on biohydrogen production. Addition of Cu NPs in fermentative process showed higher inhibitory effect than the CuSO_4 supplementation.	[88]
Fe	Glucose	Anaerobic sludge, pH-5.5; temperature-37 °C	Cu NPs with concentration less than 2.5 mg/L enhanced hydrogen production. The hydrogen and biogas yield of the control test were 247 and 391 mL/g VS, respectively. Addition Ni^{2+} ions improved hydrogen production by 55%.	[89]
Fe	Water hyacinth	Mixed culture and <i>Clostridium butyricum</i> TISTR, temperature-35 °C; duration-4 days	A maximum hydrogen yield 57mL/g of the plant biomass equal to 85.50% of the theoretical maximum is obtained.	[35]
Fe	Glucose	<i>Enterobacter cloacae</i> DH-89, pH-7.0; temperature-37 °C	Supplementation of Fe NPs significantly improved the hydrogen yield. A maximum H_2 yield 1.9 mol mol^{-1} glucose utilized was observed with addition of 100 mg/L FeNPs, which increases the glucose conversion by two-fold.	[51]
Ni	Industrial wastewater	Anaerobic sludge; pH-7.0; temperature-55 °C; rotation-180 rpm	Ni-Gr NC dose of 60 mg/L exhibited the highest improvement (105%) in H_2 production. H_2 production was improved by 67% compared with supplementation of Ni nanoparticles.	[90]
Iron oxide	Glucose	<i>E. cloacae</i> 811101; pH-7.0; temperature-37 °C; duration-24 h;	Maximum hydrogen yields $2.07 \text{ mol H}_2/\text{mol}$ glucose and $5.44 \text{ mol H}_2/\text{mol}$ sucrose were achieved with addition of 125 mg/L and 200 mg/L iron oxide NPs. Enhancement of hydrogen production was higher with addition of iron oxide NPs compared to ferrous iron supplementation.	[91]

Table 1. Cont.

Nanoparticles	Substrate/Feedstock	Reaction Conditions	Summary	Reference
Fe ₂ O ₃	Glucose	Anaerobic sludge; pH–5.5; temperature–60 °C; rotation–150 rpm	Maximum hydrogen yield reached 1.92 mol H ₂ /mol glucose with a hydrogen content of 51%. Metal NPs are not consumed by the microbes and only act as hydrogen production enhancer.	[52]
Fe ₃ O ₄	Wastewater	Mixed culture; pH–6.0; temperature–37 °C; rotation–200 rpm	The maximum hydrogen production rate and specific hydrogen yield reached 80.7 mL/h and 44.28 mL H ₂ /g COD with supplementation of NPs.	[53]
Fe ₃ O ₄	Sugarcane bagasse	Anaerobic sludge; pH–5.0; temperature–30 °C	Highest cumulative volume of hydrogen (380 mL), hydrogen content (62.14%) and % COD reduction (72.5) was obtained under the optimal conditions.	[54]
TiO ₂	Malate	<i>R. sphaeroides</i> NMBL–02; pH–8.0; temperature–32 °C	Addition of 200 mg/L Fe ²⁺ and magnetite NPs enhanced the HY by 62.1% and 69.6%, respectively. Highest hydrogenase gene activity was confirmed by immobilized cultures on magnetite nanoparticles. Hydrogen production rate enhanced by 1.54 fold and duration by 1.88 fold in the presence of 60 mg/mL of TiO ₂ NPs in comparison to the control.	[92]
			Maximum hydrogen production 1900 mL/L with 63.27% malate conversion achieved.	

5.2. Effectiveness of Nanoparticles in Biogas Generation for Industrial Benefits

Biogas generation has four main phases: (a) Hydrolysis, that converts organic waste into simple monomeric or dimeric units, (b) Acidogenesis, where the hydrolysis product is utilized for the fermentation, (c) Acetogenesis, which leads to the formation of acetate with H₂ and CO₂, and (d) Methanogenesis, which is the final stage where methane is produced from the early generated acetate, H₂ and CO₂ [93]. Nanotechnology plays an important role in biogas and methane production as it has a bio-stimulating effect on the methanogenic phase. Some studies have suggested that trace element-based NPs (Co, Fe, Fe₃O₄ and Ni) at various levels of concentration with significant particle size decrease the duration of lag phase as well as the time taken to attain the peak conversion rate [94]. Nano zero valence iron (NZVI) has been shown to affect the anaerobic digestion by increasing the production of biogas and methane. Moreover, NZVI stimulates the methanogenesis in the process of AD while inhibiting dichlorination [95]. Different types of NP have demonstrated their use for the synthesis of biogas (Table 2).

Table 2. Summary of application of nanoparticles in biogas production process.

Nanoparticles	Substrate/Feedstock	Reaction Conditions	Summary	Reference
Ni	Manure slurry	Temperature–37 °C; rotation–20 rpm (in 1 min interval)	Addition of 2 mg/L Ni NPs enhanced the biogas production by 1.74 times in comparison to control. The methane volume increased by 2.01 times. Highest specific biogas (614.5 mL per g VS) and methane (361.6 mL per g VS) production were attained with 2 mg/L Ni NPs.	[94]

Table 2. Cont.

Nanoparticles	Substrate/Feedstock	Reaction Conditions	Summary	Reference
Nano zero-valent iron (nZVI)	Waste activated sludge	Temperature–35 °C; rotation–120 rpm; duration–30 days	Addition of 10 mg/g total suspended solids (TSS)nZVI increased methane production to 120% of the control. Low concentrations of nZVI promoted a number of microbes (Bacteria and Archaea) and activities of key enzymes. Methane yield enhanced by 25.2% in the presence of nZVI.	[55]
nZVI	Sewage sludge	pH–7.0; temperature–37 °C; duration–30 days	COD removal efficiency was 54.4% in presence of nZVI, higher compared to control (44.6%). The addition of nZVI showed positive impact on the removal of chlorinated pharmaceutical and personal care products.	[96]
nZVI	Domestic sludge	Temperature–37 °C; duration–14 days	Methane content was stimulated up to 88% with addition of nZVI.	[97]
Co	Manure slurry	Temperature–37 °C; rotation–20 rpm (in 1 min interval)	Addition of 1 mg/L Ni NPs enhanced the biogas production by 1.64 times in comparison to control. The methane volume increased by 1.86 times.	[94]
Cu	Granular sludge	pH–7.2; temperature–30 °C; rotation–120 rpm	Cu NPs caused severe methanogenic inhibition. The 50% inhibiting concentrations determined towards aceto-clastic and hydrogenotrophic methanogens were 62 and 68 mg/L.	[98]
ZnO	Waste activated Sludge	Temperature–37 °C; duration–14 days	100 mg/L Zn ²⁺ exhibited 53.7% reduction in methane production compared to control. Less VFA consumed during methanogenesis when more ZnO ENMs were present.	[99]
ZnO	Granular sludge	pH–7.2; temperature–30 °C; rotation–120 rpm	The 50% inhibiting concentrations determined towards aceto-clastic and hydrogenotrophic methanogens were 87 and 250 mg/L.	[98]
CuO	Municipal waste activated sludge	Temperature–35 °C	Methanogenic inhibition is due to the release of toxic divalent Zn ions caused by corrosion and dissolution of the NPs. Increase in CuO NP concentration from 5 to 1000 mg per gTS, and an increase in the inhibition of AD from 5.8 to 84.0% was observed. EC ₅₀ values of short- and long-term inhibitions were calculated as 224.2 mg CuO per g TS and 215.1 mg CuO per g TS, respectively.	[100]

5.3. Bioethanol

In contrast to petroleum derivatives, NPs have been utilized to improve gas-liquid mass transfer, which in turn improves cell mass concentration for the generation of bioethanol by syngas fermentation [101]. Bioethanol is considered a reasonable and eco-accommodating biofuel. It has been reported that bioethanol is has favorable chemical properties such as high dissipation enthalpy and a high-octane number. Currently, bioethanol is delivered from edible and non-edible vegetable oils, squander materials, algal, and bacterial biomass. Initially, microalgae have been a good source of bioethanol in terms of their quantity [102–104]. Genetically engineered microorganisms have been shown to produce a higher quantity of bioethanol than normal microorganisms [105]. Different types of NP have growing applications in the generation of bioethanol. Practically, it has been

shown that MnO₂ nanoparticles increase the production of bioethanol utilizing agricultural waste and sugarcane leaves [46]. Various NPs utilized in ethanol production are shown in Table 3.

Table 3. Summary of application of nanoparticles in bioethanol production process.

Nanoparticles	Substrate/ Feedstock	Reaction Conditions	Summary	Reference
NiO	Potato peel waste	<i>S. cerevisiae</i> BY4743; Instantaneous saccharificationfermentation (NIISF); temperature–37 °C, rotation–120 rpm, duration–24 h	<ul style="list-style-type: none"> • 59.96% enhancement in bioethanol production. • Addition of nanoparticle improved bioethanol productivity by 145% and acetic acid concentration by 110%. 	[106]
NiOand Fe ₃ O ₄	Potato peel waste	<i>Saccharomyces cerevisiae</i> BY4743; temperature–30 °C; rotation–120 rpm; duration–72 h	<ul style="list-style-type: none"> • Maximum ethanol yield of 0.26 g/g, 0.22 g/L/h ethanol productivity and 51% fermentation efficiency at 0.01 wt%. • 1.60-fold and 1.13-fold using NiO and Fe₃O₄ NPs, respectively 	[107]
ZnO	Rice straw	<i>Fusariumoxysporum</i> ;temperature– 20 to 25 °C; pH–6.0 to 8.0; rotation –100 to 200 rpm; duration –72 h	<ul style="list-style-type: none"> • Maximum ethanol yield of 0.0359 g/g of dry weight-based plant biomass was obtained at 200 mg/L concentration of ZnO nanoparticles. • Characterization of nanoparticles was carried out using UV–Vis spectroscopy, FTIR, XRD, SEM, TGA and DTA analysis. 	[108]
Magnetic nanoparticles	Corn starch	Immobilized <i>Saccharomyces cerevisiae</i> ; pH–4.0; temperature –60 °C	<ul style="list-style-type: none"> • Ethanol productivity reached 264 g/L.h. • The prepared immobilized cells were stable at 4 °C in saline for more than 1 month. 	[47]

5.4. Biodiesel

Biodiesel has many promising future applications due to the emission of fewer pollutants, is eco-friendly, and is produced from edible as well as non-edible oils. Oils are converted to biodiesel through the process of transesterification. The process utilizes homogeneous and heterogeneous catalysts [109]. Nanomaterials have promising results in biodiesel production. NPs can enhance the catalytic reaction during transesterification, thereby improving the production of biodiesel [110]. It is reported that the biodiesel production yield was enhanced in the presence of CaO based nano-catalysts as heterogeneous catalysts [111]. Microalgae biomass was also reported as a potential source to produce biodiesel [112]. Vegetable oils containing triglycerides have been utilized to produce biodiesel, which acts as a substitute for diesel. The process of transesterification is carried out to lower the viscosity of the vegetable oil [113].

Nanostructure provides emerging immobilization support due to the nanoscale size and large surface area. Microbial enzymes such as lipase from *Pseudomonas cepacia* are immobilized on the surface of nanoparticles and enhance the production of biofuel due to an enhanced transesterification reaction. Fictionalization of the nanoparticle process also increases the production of biodiesel. Nanoconjugates have also been shown to increase the production of biodiesel. Iron-silica nanoconjugates such as Fe₃O₄/SiO₂ have emerging

applications in biodiesel production [114]. In this process, various types of cooking and algal oils have been used. Algal oils have a high yield production in the presence of these iron-silica nanocomposites [79]. The use of different NPs in biodiesel production is explained in Table 4.

Table 4. Summary of application of nanoparticles in biodiesel production process.

Nanoparticles	Substrate/Feedstock	Reaction Conditions	Summary	Reference
$\text{Fe}_3\text{O}_4/\text{ZnMg}(\text{Al})\text{O}$	Microalgal oil	Temperature–65 °C; duration–3 h; methanol to oil ratio: 12:1	Biodiesel yield reached 94% under the optimal conditions. 82% biodiesel yield was observed after 7 times regeneration. Increase of the molar ratio of methanol to oil increased biodiesel yield. Dry cell weight increased by 177% and 210% by adding SiO_2 and $\text{SiO}_2\text{--CH}_3$ NPs.	[78]
SiO_2 and $\text{SiO}_2\text{--CH}_3$	<i>Chlorella vulgaris</i>	Methanol/sulfuric acid–85:15 v/v; temperature–70 °C; duration–40 min	Addition of NPs increased CO_2 mass transfer rate. Nano MgO alone is not capable of catalysing the transesterification reaction due to weaker affinity. Nano MgO in combination with CaO increased the transesterification yield. The biodiesel yield reached 98.95% of weight.	[115]
CaO and MgO	Waste cooking oil	For CaO: weight–1.5%; methanol to oil ratio–1:7; duration–6 h. For MgO: weight–3% (0.7 g of Nano CaO and 0.5 g of Nano MgO); alcohol to oil ratio–1:7; duration–6 h.	95.20% higher biodiesel yield was observed under optimum conditions. The reusability study of nano-catalysts showed efficient for 3 cycles. Presence of Cu ions facilitated an increase of 5.5–85% in the conversion values in methyl esters.	[116]
Ni doped ZnO nanocatalyst	Castor oil	Methanol to oil ratio–1:8; catalyst loading –11% (w/w); temperature–55 °C, duration–60 min	Cu^{2+} ions doping influenced in the structure, morphology and magnetic properties of nano-ferrites.	[117]
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ doped with Cu	Soybean oil	Methanol to oil ratio–1:20; catalyst loading–4% (wt); temperature–180 °C, duration–1 h,	96.2% yield of methyl ester was achieved under optimum conditions. CaO-NPs reused for five consecutive cycles with minimum loss of activity. The oil conversion was in the range of 90–97% under optimum conditions. The nano-catalysts were stable up to 10 cycles without loss of activity.	[44]
CaO	Bombaxceiba oil	Methanol to oil ratio–30.37:1; catalyst loading–1.5% (wt); temperature–65 °C; duration–70.52 min	95.7% conversion of sunflower oil achieved. The prepared catalyst was stable for 6 cycles. Size, shape and crystallinity of catalysts are important parameters affecting biodiesel production.	[118]
Calcite/Au	Sunflower oil	Methanol to oil ratio–9:1; catalyst loading: 0.3% (wt); temperature–65 °C; duration–6 h	95.2% biodiesel yield was achieved under optimal conditions. The catalyst showed reliable performance for 8 consecutive cycles.	[119]
$\text{MgO}/\text{MgAl}_2\text{O}_4$	Sunflower oil	Methanol to oil ratio–12:1; catalyst loading–3% (wt); temperature–110 °C; time–3 h	92.2% FAME conversion and 92% yield was attained within 5 h at 60 °C. The synthesized catalysts were characterized by XRD, FT-IR, and FE-SEM.	[120]
Hydrotalcite particles with Mg/Al	Jatropha oil	Methanol to oil ratio–0.4:1 (v/v); catalyst loading–1% (wt); temperature–44.85 °C; duration–1.5 h; anhydrous methanol–40 mL; sulfuric acid–4 mL	93% FAME yield observed after 120 min under optimum conditions. The reusability of catalyst revealed that the FAME yield decreased significantly after fifth cycle.	[121]
$\text{TiO}_2\text{--ZnO}$	Palm oil	Methanol to oil ratio –6:1; temperature–50–80 °C; duration–5 h		[122]
CaO	Rice bran oil	Methanol to oil ratio–30:1; temperature–65 °C; duration–120 min; catalyst loading = 0.4%(wt)		[123]

Table 4. Cont.

Nanoparticles	Substrate/Feedstock	Reaction Conditions	Summary	Reference
CaO	Microalgae oil	Methanol to oil ratio–10:1; temperature–70 °C, duration– 3.6 h, methanol/oil; catalyst loading–1.7% (wt)	The nanoparticles are of spherical shape with average particle size of 75 nm. 86.41% microalgal biodiesel yield reported under optimal conditions. Reusability study of catalyst revealed 86.41% to 67.87% loss in biodiesel production after the sixth cycle. FAME conversions yield up to 96% achieved under ultrasonic irradiation.	[124]
ZnO	Waste cooking oil	Methanol to oil ratio–6:1; temperature–60 °C; duration– 15 min; catalyst loading–1.5% (wt)	Synthesized biodiesel properties such as density and viscosity were at par with standard biodiesel.	[125]

6. Current Challenges and Future Perspectives for Biofuel Production with the Implementation of Nanotechnology

Biofuel is the future of petroleum-based industries, as it is more environmentally friendly, cleaner, renewable and safe to use. Furthermore, the limited availability and increasing demand have led to price hikes for petroleum-derived fuels, prompting researchers to think about biofuels as a suitable alternative [113]. Even though it is safer and cleaner to use, the production of biofuels is still a complex process.

The main factor in the production of biofuel is the availability of biomass which can be easily obtained from woods, plants, organic waste, agricultural waste, municipal solid waste, etc. Still, there are many challenges and opportunities available for improvement in order to replace commercially available petroleum-based oils. Pre-treatment strategies for lignocellulosic biomass require high operation costs [126]. Algal biomass is also being used for biodiesel production as it is oil-rich, carbon-neutral, and can grow rapidly. It is considered that this may replace fossil fuels for biodiesel production. On the other hand, the cultivation of algal biomass is costly, and the lipid extraction is energy intensive [127]. Implementing nanotechnology to produce biofuels at an industrial scale is challenging as nano-catalyst based biofuel production has not fully emerged. In addition, studies are still improving biofuel production using available resources. Up to now, usually edible crops such as maize, sugarcane, etc., have been utilized for the large-scale production of biofuels. Biofuel production from non-edible sources is lower in comparison to edible sources. Nanotechnology is accelerating biofuel production and increasing the amount of biofuel produced from non-edible sources. It will still be problematic to replace petroleum-derived fuel with commercially available biofuel because it must be mixed with other fuels for usage and it is not cost-effective. The possibility of using biofuel as an alternative and green energy source will be significantly higher in the near future.

7. Conclusions

It is clear from the current review that the incorporation of nanoparticles during biofuel production enhanced this significantly. This enhancement is mainly due to the unique physico–chemical properties of nanoparticles such as large surface-area-to-volume ratio, high reactivity, good dispersibility, high specificity, etc. Several nanoparticles such as metal, metal oxide, magnetic, and carbonous materials are successfully used for enhancement of biofuel production from various substrates. Apart from the production process, nanoparticles are also used in the pretreatment process to enhance the digestibility of substrate leading to enhanced biofuel production. However, successful commercialization of this process requires the addressing of several technical barriers. These barriers include synthesis and application nanoparticles that are non-toxic to microorganisms, use of less expensive and environment friendly nanoparticles, and adaptation of biological

nanoparticle synthesis methods in place of chemical methods, which requires stringent operational conditions.

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