

REVIEW ARTICLE



Nanomaterials based sustainable bioenergy production systems: Current trends and future prospects

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ABSTRACT

The global energy crisis affects all of us. With a growing global population and finite fossil fuel supplies, we must find new energy sources. Alternative energy sources must be prioritized. Biofuels like biodiesel, biohydrogen, biomethanol, and bioethanol have come a long way in recent decades. These alternative fuels are from low-cost, renewable sources like algal, microbial, and plant biomass. Several governments, including India, are improving their renewable energy production capabilities. The main obstacles to rapid biofuel adoption are time and cost. For biofuel to truly become a viable alternative to fossil fuels, nanotechnology has recently provided the much-needed impetus. Nanomaterials' unique structural behavior, such as small size (nanoscale size), has increased their use in biofuel production. It improves efficiency and reduces the time required to convert waste into biofuels. This review addresses the latest information on various types of nanoparticles, and challenges faced and the future prospects of emerging applications of nanoparticles in biofuel production.

ARTICLE HISTORY

Received: 17-06-2022

Revised: 8-11-2022

Accepted: 28-11-2022

KEYWORDS

Bioenergy;
Nanotechnology;
Nanomaterials;
Biofuel;
Biodiesel

1. Introduction

People are aware that fossil fuel consumption is accelerating, suggesting that petroleum-derived fuels will be depleted within the next few decades. Concerns about petroleum-derived fuels, detrimental effects on the environment, the economy, and energy conservation are significant factors in our reliance on them. Therefore, much effort has been put into finding a new energy source that can lessen our reliance on fossil fuels (Beig et al., 2021). Due to their distinct properties,

biofuels have recently gained global recognition as an alternative to fossil fuels (Manikandan et al., 2022). Many plant materials, including vegetables, sugarcane, corn, palm oil, soybeans, jatropha, and fruit wastes, are being used as feedstock for biofuel production on nearly every continent (Raschke et al., 2021; Usmani et al., 2022; Pathak et al., 2022a). Unlike most other biofuels, biodiesel has the potential to either replace or supplement fossil-based diesel. Biodiesel is made using renewable biolipids in a trans-esterification process (Beig et al., 2021). Nanotechnology is

an emerging area of science which is applied in different sectors for human welfare like bioenergy production, agriculture, medical science and environmental sustainability (Pathak et al., 2022b; Ranaa et al., 2021; Srivastava et al., 2021; Thakur et al., 2022; Tripathi et al., 2017, 2018). Using nanotechnology and nanomaterials to improve product quality while lowering costs is becoming increasingly common in biofuel research (Lafarga, 2021; Srivastava et al., 2021; Pandey, 2022). Because of their small size and unique properties, such as a high surface area to volume ratio and special attributes such as crystallinity, adsorption capacity, catalyst activity, and stability, using nanoparticles for biofuel synthesis has many advantages. Biofuel production is commonly aided by metal oxide nanoparticles, which have additional properties that increase the potential for recovery (Srivastava et al., 2021; Vasistha et al., 2021). Gasification, pyrolysis, hydrogenation, and anaerobic digestion have all been shown to be effective in producing biofuels when combined with nanotechnology (Arya et al., 2021). Nanomaterials with characteristics are promising option for optimizing and improving the efficiency of biofuel and bioenergy production. The novelty of this review is that it utilises the most recent knowledge for advancement in the biofuel production of nanoparticles (NPs) in terms of their applications, difficulties, and prospects for the future.

2. A Global View of Bioenergy and Biofuel

The global energy crisis has risen to the level of a significant issue affecting the growth of economies worldwide. The 4% decline in global energy demand in 2020 will be more than offset

by a 4.6% rise in 2021 (IEA, 2021). To meet this enormous demand, biofuels and bioenergy can be used as an alternative. The production of biofuels has proliferated in recent years all over the world (Fig. 1). Because of China's biofuel output growth, Asia accounts for half of the global production growth in the most common case (IEA, 2021). Increasing demand for road transport fuel and new policy initiatives are stimulating biofuel production in Asian countries. These countries are increasingly mandating domestically produced biofuels to improve air quality and increase demand for agricultural products while enhancing energy security. In 2018, the largest producers of biofuels were the United States and Brazil (IEA, 2018). Together, they account for 40% of the forecast biofuel output growth from 2019 to 2024 and two-thirds of the primary scenario production in 2024. Ethanol and biodiesel production in the United States is the highest globally (IEA, 2020).

The COVID-19 pandemic brought the entire world to a halt. There was an 8% drop in the total demand for biofuels for transportation from 2019 to 2020, exceeding the Renewables 2020 forecast of 248 billion litres (2,590 kb/d). Ethanol production in Brazil and the United States and biodiesel production in Europe saw the most significant year-on-year decreases in output. 90% of the decline in biofuel production from 2019 to 2020 was due to lower output in these markets (Khan et al., 2021). It is clear from the accelerated case study that with better market conditions and policies, biofuel production could rise in future. Ethanol production could increase by 25 billion litres compared to the baseline scenario, with most of the additional production taking place in China, India, and the USA (IEA, 2019).

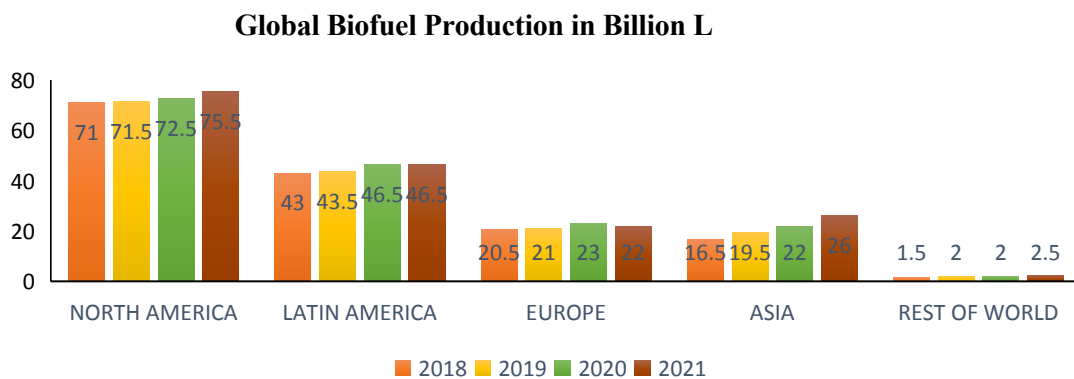


Figure 1. Global Biofuel Production in Billion L (Source: IEA, 2018, 2019, 2020, 2021).

3. Nanotechnology in Bioenergy

Nanotechnology and nanomaterials are increasingly being used in biofuel research to improve production quality at a low cost. The high surface-to-volume ratio of nanoparticles (NPs) and unique properties like crystallinity, adsorption and catalytic activity, make nanoparticles (NPs) ideal candidates for biofuel production (Arya et al. 2021). They offer several advantages over other sources for biofuel synthesis. Biofuel production is facilitated by using carbon and metal oxide nanoparticulate as catalysts because of their additional properties that aid in the recovery of biofuels (Arya et al., 2021; Vasistha et al., 2021). Pandey (2022) discussed the potential of nanomaterials for environmentally friendly bioenergy production and explained how nanomaterials could be used to increase the effectiveness of bioenergy storage and conversion in biofuels like bioethanol and biodiesel. Advancements have facilitated increased biofuel production in each generation's use of biomass that would otherwise go to waste. As a result, the use of nanotechnology in biofuel production has been found to be an effective solution. Nanotechnology has been used to make a variety of biofuels, including biohydrogen, biodiesel, bioethanol, and biogas.

Nanomaterials can be applied in current battery technologies. Lu et al. (2016) researched the application of nanotechnology to the creation of battery components for electric vehicles. Battery life and recharge times are the biggest problems with electric vehicles. Nanomaterial powered by batteries is used to solve this issue. The nanoparticles enhance the batteries' functionality and storage capacity (Khan et al. 2022). Triglycerides can be converted to biofuels using transesterification. Anaerobic digestion and gasification, as well as hydrogenation and nanotechnology, have all been shown to be effective for biofuel synthesis (Arya et al., 2021; Srivastava et al., 2021). For biofuel generation, the microbial fuel cell provides a wide range of nano-catalysts, including nanotubes, nanosheets, and nanoparticles, which are readily available.

4. Different Nanoparticles in Biofuel Production

Nanoparticles have a large surface area and show magnetic behavior under a magnetic field, making

it easy to separate from a biofuel cell and aiding enzyme recycling. To create a nano-catalyst, a support system composed of several nanoparticles is employed to produce biofuels. This includes nanoparticles with magnetic properties and carbon nanotubes (CNTs). Different heterogeneous catalysts are also used in addition to metal oxide, acid-functionalized metals, etc.

5. Application of nanoparticles in biofuel production

Carbon nanotubes (CNTs), acid-functionalized nanoparticles, metal-oxide nanoparticles, magnetic nanoparticles and metallic nanoparticles were reported to be the most commonly encountered types of nanoparticles used in biofuel solutions (Thakur et al., 2022). Each type of nanoparticle has a wide range of applications and potential benefits. In addition, it has been discovered that nanomaterials, such as carbon nanotubes, nanosheets and carbon nanofibers, are stable catalysts for enzyme immobilisation that are both cost-effective and efficient, which improves biofuel production (Table 1). Nanomaterials help in the production process of biofuels (Fig. 2).

5.1. Biodiesel

Biodiesel has the potential to be a significant fuel source in the future. It is environmentally friendly because it is primarily made from biodegradable renewable energy sources or biomass that helps reduce combustion emissions (Saleem, 2022;

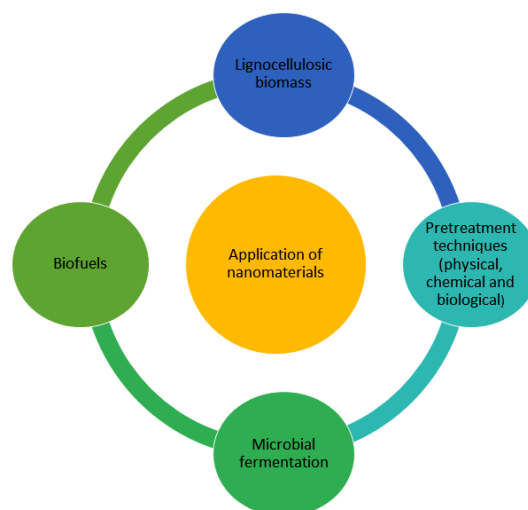


Figure 2. Application of nanomaterials in biofuel production.

Table 1. Different nanocatalysts used for the production of various biofuels.

S. No.	Nanoparticle classification	Examples	Uses	References
1.	Metal/ non-metal oxide	TiO ₂ Fe ₃ O ₄ ZnO CaO SiO ₂ Al ₂ O ₃	<ul style="list-style-type: none"> TiO₂ NPs can be filtered and reused without losing much activity and results in a pure biodiesel yield reaction. Dramatic increase in the catalytical activity and stability of the nanocomposites of Fe₃O₄ is high. Stabilizing agents to further improve biocompatibility before being replaced by green synthesized ZnO NPs. CaO is a highly active, readily available, and inexpensive solid catalyst for transesterifying various oils and fats into biodiesel. SiO₂ NPs' application in biodiesel decreases costs because they are reusable. 	Taib et al., 2021; Chingakham et al., 2019; Shakeel et al., 2020; Degirmenbasi et al., 2015; Karthikeyan et al., 2020; Sateesh et al., 2021
2.	Carbon-based	Carbon nanotubes (CNT) Multi-walled carbon nanotubes (MWCNT) Fullerene Graphene	<ul style="list-style-type: none"> CNTs NPs with low toxicity, high stability, and surface area are excellent biofuel catalysts. MWCNTs are more stable, inert, and have a higher thermal conductivity than other carbon nanotubes. Fullerenes are great candidates for enzyme immobilization because of their high porosity and conductivity. This makes them ideal for H₂ production and storage. Graphite sheets are rolled into hollow shapes to immobilize enzymes. In addition, graphene's large surface area allows them to load enzymes quickly. 	Sateesh et al., 2021; Suzuki and Mori, 2018; Gundoshmian et al., 2021; Mishra et al., 2021; Tang et al., 2020
3.	Metallic	Ni Ag Au Pt	<ul style="list-style-type: none"> Improve electrocatalytic activity and make a biofuel cell with a high loading capacity and a good rate of electron transfer. Producing biodiesel with more environmentally friendly process that is also more cost effective and less time consuming. 	Bharath et al., 2020; Zhou et al., 2020; Gong et al., 2022
4.	Core-shell	Ag/SiO ₂ Au/SiO ₂ Ni/SiO ₂ Fe ₃ O ₄ /SiO ₂ Au/TiO ₂ Fe/C FeNi/SiO ₂ ZnO/SiO ₂	<p>Helps in higher production of biofuels.</p> <p>Helps in conversion of Low-quality oils into higher grade biofuel.</p>	Asikin-Mijan et al., 2021; Zhang et al., 2021; Lee et al., 2020 Verma, 2020; Bravo-Suárez et al., 2013; Cong et al., 2021; Myint, 2018
5.	Hybrid	Pd/PRGO/ Ce-MOF CuMo	<p>Catalytic activity and selectivity were shown to be maintained over four runs for the newly developed heterogeneous catalyst Pd/PRGO/Ce-MOF</p> <p>CuMo NPs separation is simple, non-corrosive, and results in clean, environmentally friendly products with high selectivity.</p>	Arya et al., 2021; Justine et al., 2021; Mirzayanti et al., 2019

Siddiki et al., 2022). The quantities currently available are insufficient to meet the current demands for biofuel. As a result, microalgae, a non-edible raw material, is gaining importance in today's economy for biofuel production. Microalgae can be helpful in biofuel production because of their high energy yield, rapid growth and high biomass production (Sekoai et al., 2019; Siddiki et al., 2022). Vegetable oils are the most essential raw material in biodiesel production (Bezerra et al., 2017; Xie et al., 2014). However, their use in cooking and food production is becoming increasingly expensive due to the fierce competition they face. Low-cost biodiesel feedstocks include inedible oils, animal fats, frying oils, soaps, and greases are used. Immobilized enzymes were used to convert methanol and soybean oil to biodiesel (Tahvildari et al., 2015; Xie et al., 2014), and no loss in activity was observed after four cycles of the biocatalyst use. Biodiesel from soybean oil was produced using an enzyme to a magnetic microsphere on Fe_3O_4 /poly styrene-metacrylic acid (Xie et al., 2014). In a study by Tahvildari et al. (2015), calcium oxide (CaO) and magnesium oxide (MgO) nanoparticles produced by sol-gel self-combustion methods were used. In terms of biodiesel yield, CaO nanoparticles outperformed MgO nanoparticles. Wen et al. (2010) made a KF/CaO nanocatalyst by impregnation with a size of 30–100 nm and used it to produce biodiesel from Chinese tallow seed oil. Studies found that nanocatalysts had a biodiesel yield, demonstrating the potential of nanocatalysts in the biodiesel industry (Tahvildari et al., 2015; Wen et al., 2010, Marcelino et al., 2020). In another study, nanoparticles were examined by Bidir et al. (2021) concerning the generation of biofuel, and they reported that adding nanoparticles to biodiesel can improve a diesel engine's performance. Interdisciplinary biotechnology and nanotechnology collaboration is a promising avenue for increasing biodiesel production, as outlined above. Nanobiocatalytic systems that are stable and efficient could make biodiesel more profitable if they could be reused.

5.2. Bioethanol

Nanosystems are being used to increase ethanol production by optimizing second-generation ethanol (E2G) production from agricultural waste using enzymes (magnetic nanoparticles).

Lignocellulose biomass-based nanosystems are still in the early stages of development. As a non-food alternative, ethanol offers several advantages, including lower conversion costs and a minimal environmental impact (Lupoi and Smith, 2021; Rodríguez-Couto, 2019; Sudheer et al., 2021). In order to meet the rising demand for ethanol, the biofuel industry has been searching for new biocatalysts. E2G production from lignocellulose trapped in magnetic nanoparticles could be achieved using a cellulase enzyme complex with the following characteristics: higher storage stability, higher pH, higher substrate affinity, temperature tolerance and reusability in reactions (Lupoi and Smith, 2021; Rodríguez-Couto, 2019; Sudheer et al., 2021). To produce cellulosic ethanol, Lupoi and Smith (2021) used an entrapment method to immobilize the glucosidase enzyme on polymer magnetic nanofibers. Cellobiose is converted to glucose by the enzyme glucosidase, which microorganisms can use to produce bioethanol. According to Rana et al. (2023), nanocellulose extracted from pine needles showed good thermal and mechanical strength. They reported gasification as one of the appealing methods for converting pine needles into bioenergy. Whereas, physical, chemical and biological factors must be optimized and considered when developing new technologies such as nanosystems.

5.3. Biohydrogen

It is possible to produce biohydrogen, which is a second-generation biofuel, using biological pathways that require less energy and emit less CO_2 . Dark fermentation, water biophotolysis, photo-fermentation, and indirect biophotolysis are just a few of the processes that can be used to produce biohydrogen and each has its own pros and cons (Seelert et al., 2015). Photo and dark fermentation are the most widely studied and documented techniques in the literature because of the cheap organic substrates that can be used, such as food and industrial waste (Cai et al., 2019). Several researchers studied Biohydrogen bioproduction using nanomaterials (Haque et al., 2022; Srivastava et al., 2019, 2020, 2021, 2022). A study found that both the bulk and nanoparticle forms of iron sulphate had the highest cumulative hydrogen production at the same concentration of mg/L of iron sulphate (Dolly et al., 2015). This enzyme, hydrogenase, relies on the presence of Fe

and Ni in its active site. Many studies have shown that adding these metals to the fermented solution improves the results of hydrogen production by dark fermentation bioprocess (Elreedy et al., 2017). When Ni and graphene nanoparticles were added to the anaerobic digestion process of industrial waste containing mono-ethylene glycol (used in petrochemical production), the biohydrogen production level was increased (Elreedy et al., 2017). According to Wimonsong et al. (2014), dark fermentation with sucrose as a substrate for biohydrogen production was carried out with hydrotalcite-supported metallic nanocatalysts and was described. As a result, it can be seen that nanosystems of various kinds have had an impact on biohydrogen generation methods by increasing various production parameters.

5.4. Biogas

The growing need for environmentally friendly energy is spurring an increase in scientists looking into the effects of nanomaterials (1–100 nm) on biogas production (Baniamerian et al., 2019; Kadam and Panwar, 2017). Kadam and Panwar (2017) discussed the four intricate steps involved in the anaerobic digestion of organic matter by microorganisms and enzymes, resulting in biogas production. As stated by researchers, the complete biochemical process depends on various experimental factors, including pH, organic substrates, inoculum concentration, and temperature changes (Kadam and Panwar, 2017). According to Liu et al. (2015), microorganisms can better attach to active sites in molecules when nanoparticles are present, increasing the substrate conversion rate through hydrolysis. Aside from their high reactivity and specificity, nanomaterials positively affect anaerobic digestion. According to Su et al. (2013), zero-valent iron nanoparticles are promising for improving waste-activated sludge-derived biogas yields significantly. In another study, it was reported that nano-ZnO inhibits waste-activated sludge anaerobic digestion at a level far lower than that of nano-TiO₂, nano-Al₂O₃, and nano-SiO₂ (Mu et al., 2011). Biogas production is negatively impacted by the toxicity of some other nanomaterial additives, such as Mn₂O₃ or Al₂O₃ (Alvarez et al., 2012). All of these studies suggested that nanoparticles may impact biogas production, depending on the source of the biogas or the step in which the nanoparticles are used (Srivastava et al., 2022).

6. Current bioenergy production challenges and future prospects with nanotechnology

Biofuels are less expensive and an alternative to fossil fuels is increasing in price. Because of this, biofuels are being considered a viable and cost-effective alternative (Sharma et al., 2020; Srivastava et al., 2021). Organic biomass from agricultural waste, municipal waste, and other sources is required for the biofuel production. However, there is still a need for research for improvement in biofuel production. Cost-effective pre-treatment strategies are necessary for valorization of lignocellulosic biomass (Bhutto et al., 2017; Usmani et al., 2022). Algal biomass is used in biodiesel production because it proliferates, is carbon-neutral and contains a high oil concentration. In future, it's possible that it could eventually take the place of fossil fuels in biodiesel production. It is also expensive to grow algal biomass because lipid extraction requires a lot of energy (Du et al., 2015). Biofuels require large amounts, which the available technologies cannot handle. Nanoparticles as catalysts can provide more excellent selectivity, yield, and quality and are helpful in biofuel production. The availability of biofuel feedstocks is large, and with improved processing, we could significantly lower our reliance on fossil fuels in the future. Researchers are working to improve biofuel production with the resources that are already available. Biofuels have traditionally been produced large-scale using food crops like corn, sugarcane, and other lignocellulosic biomass. Biofuel production is being boosted by nanotechnology, speeding up the production process.

7. Conclusion

As discussed in the current review, including nanoparticles during biofuel production significantly improved this. Nanoparticles' unique physical and chemical properties, such as high specificity, high reactivity, good dispersion, large surface area-to-volume ratio, etc., are mainly responsible for this improvement. Carbonous, metal oxide and magnetic nanoparticles have been successfully used to boost biofuel production from various substrates. Additionally, nanoparticles are utilized in the pretreatment process to improve substrate digestibility, which results in an increased biofuel production rate. To be commercially viable, this procedure will have to

overcome several technical obstacles. Researchers need to develop nanoparticles that aren't harmful to microorganisms, use cheaper nanoparticles that are also good for the environment, and use green synthesis methods that work better for biological nanoparticles.

Conflict of interest

The authors declare that there is no conflict of interest.

Contribution statement

Saroj Bala: Conceptualization, writing original draft

Kavya Dashora, Saba Siddiqui: Reviewing and editing

Manikant Tripathi, Deepti Diwan, Minaxi Sharma: Supervision, reviewing, editing and final checking

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