EQUILIBRIUM JOURNAL OF CHEMICAL ENGINEERING
*Homepage:*https://jurnal.uns.ac.id/equilibrium

Application and Future Prospects of Nanotechnology in Bioenergy Systems - A Review

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DOI: *ttps://dx.doi.org/10.20961/equilibrium.v8i2.85794*

Article History
Received: 31-03-2024, Accepted: 08-11-2024, Published: 18-11-2024

Keywords:
Application,
Bioenergy,
Characterization,
Nanocatalyst,
Synthesis

ABSTRACT. Nanotechnology has emerged as a promising avenue for enhancing bioenergy production systems across various industries. This review paper examines the synthesis, characterization, applications, and future prospects of nanoparticles and nanomaterials in bioenergy production. The utilization of nanoparticles, sourced from both natural and artificial resources has revolutionized the field by significantly improving production yield and efficiency. Advanced analytical techniques enable precise determination of nanoparticle size, facilitating their tailored application as heterogeneous catalysts in processes such as transesterification. Moreover, nanoparticles exhibit physicochemical properties that enhance biochemical processes, thereby augmenting yield through improved cell membrane penetration. Overall, this review highlights the vital role of nanotechnology in addressing challenges and optimizing efficiency in bioenergy production systems.

1. INTRODUCTION

In recognition of its potential to improve the quality of biofuels, nanomaterials have drawn significant interest as nano-catalyst for bioenergy production [1,2]. While conventional catalyst poses challenges like ease of deactivation, sintering, ageing, coking, nanomaterials (NMs) are incredibly well suited as nano catalysts due to their durability, good selectivity, high reactivity, recyclability, morphology, functionality, and high specific surface area to pore volume ratio [1]. Nanomaterials are particulate substances characterized by having at least one dimension less than 100 nm [3–5]. Depending on the morphology of the material, it could have a zero, one, two or three dimensions with distinctive ultra-small size (ranging from 1 to 100 nanometers). They also possess unique physicochemical properties that can significantly influence the overall performance of the resulting nanocomposite materials [6,7]. Nanoparticles (NPs) refers to a class of nanomaterials composed of nano-objects such that all its external dimensions fall within the nanoscale region and there is no significant difference between the longest and shortest axes of the nano-object [4].

Given the negative environmental implications of excessive fossil fuel use, bioenergy can be a vital alternative energy source. Biomass is the main source of bioenergy. However, there are numerous issues with the initial steps involved in converting biomass into bioenergy, including pretreatment, biomass cultivation, and enzymatic hydrolysis. When it comes to converting and storing biomass sources into bioenergy, nanomaterials can be a key component in solving several issues. It offers distinct active areas for processing and response. Additionally, nanomaterials offer a significant deal of promise to improve biomass-to-bioenergy generating efficiency [5,8].

The use of nanomaterials as nano catalysts can be crucial in resolving issues with bioenergy production and storage since it offers active reaction sites for improved conversion [9]. The demand for renewable energy sources has been growing due to the dwindling supply of fossil fuels and increasing energy consumption. Solar, wind, hydropower, and other renewable energy sources, as well as biofuels, offer a new method of meeting global energy requirements. Biofuels are distinguished for their sustainability and ability to fulfill the vision of a worldwide bioeconomy [10,11]. However, poor functional efficiency and lower yields caused by lack of a suitable catalyst has limited the optimal production of energy from these sources [12].

Pandit et al. (2023)reported that the output of biodiesel generation depends on the quantity of nano catalysts utilized. It was further revealed that net biodiesel production was zero when no catalyst was loaded in the stated reaction conditions, suggesting that the quantity and presence of nano catalysts affect the efficiency of biodiesel synthesis. Shorter reaction times, faster mixing rates with the reactants, and quick and easy purification are only a few of the unique advantages of the esterification process mediated by nano catalysts [10]. Luna-delRisco et al. (2011) studied impact of nano- and micro-sized CuO particles in the reactor for biogas production. They demonstrated that the production of biogas is more adversely affected by CuO nanoparticles than by ZnO nanoparticles. In comparison to the control sample, they found that the addition of 15 ml/l of nano sized CuO resulted in a 30% drop in biogas output. Furthermore, the addition of 15 ml/l concentration micro-sized CuO to the reactor did not result in a reduction in the amount of biogas produced. However, a decrease in biogas generation was noted upon increasing the dose to 120 mg/l. Furthermore, adding 120 mg/l of nano-sized and 240 mg/l of micro-sized ZnO reduces the formation of biogas [13]. Shahbeik et al. (2023) reported that using nanostructured catalyst reduced coke formation in upgraded bio-oil from 14.3% to 3.9% [14]. Otero-González et al. (2014) documented the short- and long-term impacts of adding nanoparticles (NPs). They found that introducing low CuO NP concentrations to a reactor containing anaerobic granular sludge has a more detrimental long-term effect on methanogenesis than adding the same concentration of CuO NPs to the reactor for a short period of time [15].

One important tactic to increase the nano-catalyst's activity for effective bioenergy generation is to change the way it is synthesized. Consequently, the cycle of nano catalyst reusability and the final biodiesel output depend critically on the various synthesis techniques used [16]. Alaei et al. (2018) used a $MgO/MgFe_2O_4$ nano-catalyst to compare two distinct synthesis techniques for the transesterification of SFO: hybrid and conventional. Impregnation, precipitation, precipitation-hydrothermal, precipitation-ultrasonic, and combustion were the techniques employed. The sheet-like form is evident in the nano-catalyst made using precipitation and precipitation-hydrothermal techniques. The one that was synthesized instead of burned produced particles with smaller diameters, low porosity, pore volume, and specific surface area. The combustion process was the best synthesis method since it produced the most biodiesel (92.9%) out of all the methods [17]. Mahdi et al. (2023)investigated a top-down technique of nano-catalyst production for the transesterification of Jatropha oil utilizing a 29.9 nm-sized $CaO–Al_2O_3$ nano-catalyst. This nano-catalyst was employed three times and produced a lower yield of 82.3% at a 5:1 methanol:oil ratio [18]. Akinfalabi et al.(2020) converted sugar cane bagasse into biochar without the use of chlorosulfonic acid. They investigated the following four sulfonation parameters: mass of SCB-biochar, duration, volume, and temperature. With 2 g of SCB-biochar, the authors were able to achieve the optimal sulfonation values at 300 °C for 5 hours and 200 ml. With particle sizes ranging from 1.95 to 3.92 nm, the nano-catalysts' surface area and pore volume were, respectively, 98–298 m2/g and 0.09–1.17 cm3/g [19]. Khalid et al. (2019) investigates the combined impact of alkaline pretreatment and magnetite nanoparticles (MNPs) on biogas yield from rice straw. The study found that treating rice straw with 2% NaOH and MNPs significantly enhances biogas and methane production. Specifically, 2% NaOH alone increased yields by 57% and 60%, respectively, while the optimal MNP dose (100 ppm) alone improved yields by 37% and 33%. The synergistic effect of both treatments at 120 ppm MNPs resulted in a 100% and 129% increase in biogas and methane, respectively[20].

To the best of our knowledge, despite numerous publications in this area of research, no study has been able to summarize the state of events on the application of nanomaterials as nano catalyst in bioenergy production. In this review we aim to provide an extensive analysis in this context. Firstly, we elucidate on the classification, synthesis, and characterization of nanomaterials. We then critically examine the application, challenges, and prospects of nanomaterials as nano catalysts in bioenergy production systems.

2. CLASSIFICATION AND SOURCES OF NANOMATERIALS

Nanomaterials are generally classified based on dimension, source, and materials composition[4].

2.1 Classification based on dimensions

Nanomaterials are classified based on their dimension into four main categories zero-dimensional(0-D), one-dimensional (1-D), two-dimensional (2-D) and three -dimensional (3-D) [3].

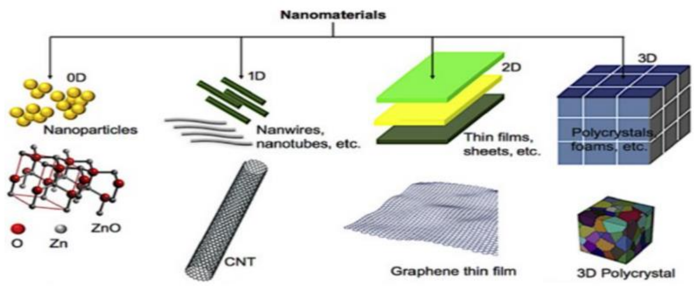

Figure 1. Classification of Nanomaterials based on Dimension [21]

Nanospheres and quantum dots are common names for nanomaterials that fall within the category of zero-dimensional nanoparticles. All three dimensions of these nanoparticles are found in the nanoscale range, which normally spans from 1 to 100 nanometers. They have a great degree of symmetry and are homogeneous in size and shape. Zero-dimensional nanoparticles comprise of semiconductor quantum dots, metal nanoparticles, and fullerenes [2].

One-dimensional nanomaterials are elongated structures with two dimensions in the nanoscale range and one dimension significantly longer. They possess a high aspect ratio, meaning their length is much greater than their width or thickness. Common examples of one-dimensional nanoparticles include nanowires, nanorods, and nanotubes. These nanoparticles exhibit unique properties due to their elongated structure and high surface-to-volume ratio [11]. The property of possessing two dimensions in the nanoscale range characterizes two-dimensional nanomaterials, also referred to as nanosheets. Nanosheets, nanofilms, and nanolayers are a few specific examples. Nanomaterials in three dimensions are not limited to the nanoscale. In general, they are not dimensionally restricted to the nanoscale. Bulk powders, nanowires, and arrays of nanotubes are a few examples.

2.2 Classification Based on Material Composition

Nanoparticles can be grouped according to the materials from which they are composed. They can be of any shape or size, including spheres, cylinders, cones, tubular shapes, irregular shapes, and more [6].

Organic Nanoparticles

Nanoparticles consisting of proteins, carbohydrates, lipids, polymers, or any other organic substances fall under this category. The most well-known examples of this class include ferritin, liposomes, micelles, and dendrimers. (Shown in Fig. 2).

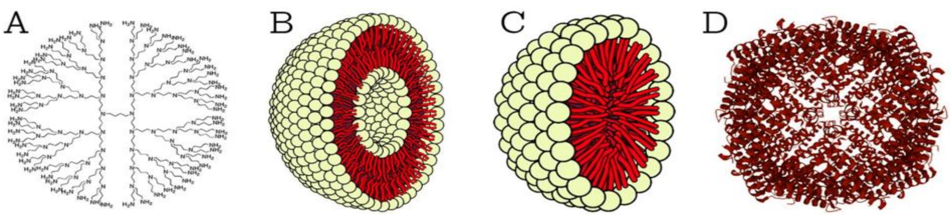

Figure 2. Organic Based Nanomaterials; A- Dendrimers; B- liposomes; C- micelles; and D- ferritin [6]

Carbon-based Nanoparticles

This category is defined by nanoparticles composed exclusively of carbon atoms, showcasing a unique array of physicochemical properties. Among these, fullerenes, carbon black nanoparticles, and carbon quantum dots stand out for their specific structures and functionalities (see Fig 3). Fullerenes, in particular, are noted for their distinctive, symmetrically structured closed-cages of carbon atoms [22]. The applications of such carbon-based nanoparticles are remarkably diverse, extending across various domains including drug delivery systems, energy storage technologies, bioimaging techniques, photovoltaic devices, and environmental sensors. These applications are profoundly influenced by the nanoparticles' exceptional qualities such as unparalleled electrical conductivity, superior mechanical strength, significant electron affinity, and their remarkable optical, thermal, and adsorptive properties [2].

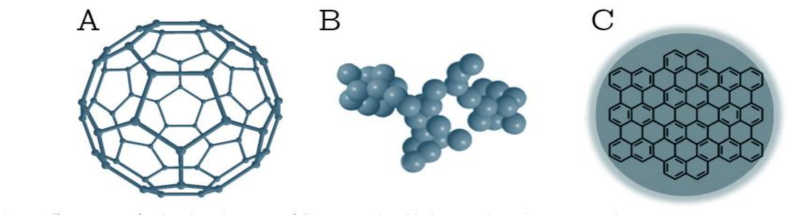

Figure 3. Carbon Based Nanomaterials: A- C60 fullerene; B- carbon black NPs; C- carbon quantum dots [6].

Inorganic Nanoparticles

This category includes nanoparticles that are neither carbon-based nor organic. Typical instances of these nanoparticles include those made from metals, ceramics, and semiconductors. Metal nanoparticles (MNPs) consist solely of metal precursors and may be categorized as monometallic, bimetallic, or polymetallic, according to the composition they possess [23,24].

3. SYNTHESIS OF NANOPARTICLES

Nanoparticles have been synthesized by several researchers for several applications especially for bioenergy production systems. The production of nanoparticles has significantly impacted the creation of biodiesel, particularly through the application of NiO nano-catalysts. Nickel oxide (NiO) nanoparticles are profoundly important because of their distinctive electronic, magnetic, and catalytic characteristics, which find applications in fields such as energy, biomedicine, magnetism, and electronics. Furthermore, nickel oxide nanoparticles exhibit enhanced chemical stability and electron transfer capabilities, making them suitable for use in various applications, including anti-inflammatory, photocatalytic, and antibacterial activities [25]. Takami et al. (2007) developed a technique for creating surface-altered iron oxide nanoparticles through a hydrothermal process in an aqueous environment. Their methodology involved heating an aqueous iron sulfate solution alongside a surface-modifying agent, either $CH_3(CH_2)_9COOH$ or $CH_3(CH2)_9NH_2$. Although these surface modifiers do not blend with water at ambient temperatures, they were able to integrate into the aqueous solution when the water's dielectric constant decreased, allowing them to react with the nanoparticles' surface [26]. conversely, Patil et al. (2012) innovated a synthesis method for palladium nanoparticles, utilizing concentrated solar energy (refer to Fig. 4). In this method, citric acid is employed as an eco-friendly reducing agent, and polyvinyl pyrrolidone (PVP) serves as a stabilizing agent, together facilitating the formation of multi-twinned particles in aqueous solutions alongside a palladium precursor [27].

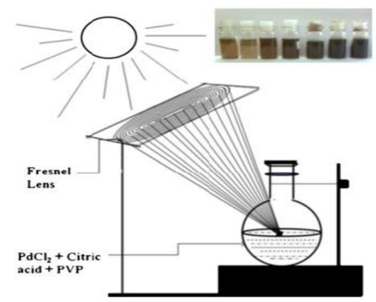

Figure 4. Graphic illustration of the setup for the reaction, with changes in color indicating the progress of the reaction. [27]

Nanoparticles have been utilized to enhance thermal energy storage systems. The abundant renewable solar energy can be efficiently captured and stored as thermal energy, which is subsequently transformed into electrical power through a power cycle. Integrating nanoparticles into thermal storage systems can significantly enhance this process. Li et al. (2022) conducted research where they developed and encased nickel (Ni) within zeolite for the hydro-deoxygenation of biodiesel, specifically targeting the dehydro-oxygenation of phenolic compounds. They undertook this approach due to the diminished activity of zeolite alone, which was attributed to the clustering of metal particles. Their investigations revealed that the Ni particles exhibited significantly improved dispersion within the Ni@ZSMe5s catalysts post-encapsulation, in comparison to the Ni/ZSMe5 catalysts prepared through wet impregnation. The enhanced distribution of Ni resulted in the Ni@ZSMe5s catalysts demonstrating superior hydro-deoxygenation (HDO) performance for phenolic substances, attributed to the increased adsorption and transfer of active hydrogen facilitated by the finely dispersed Ni entities. Specifically, the Ni@ZSMe5e50 catalyst, with a silicon to aluminum ratio of 50, achieved a cyclohexane yield of 91.6% at a temperature of 250°C [28] Nithiyanantham et al. (2022) conducted a study focusing on how the size of SiO2 NMs influences the stability and thermophysical characteristics of molten binary nitrate salt mixtures. Their research involved examining SiO2-enhanced nanofluids through real-time high-temperature assessments and zeta potential measurements. The findings revealed that nanofluids containing nanoparticles with a size exceeding 450 nm displayed enhanced stability in comparison to those with 27 nm-sized nanoparticles [29]. Rozina et al. (2021) produced biodiesel from the inedible oil of Cordia dichotoma seeds utilizing a green NiO nano-catalyst synthesized with the aqueous leaf extract from Anagallis arvensis L. In their method, about 20 g of the leaf powder was mixed with 500 mL of distilled water and subjected to heating at 100^{o}C. They observed that the transesterification process, facilitated by NiO nanoparticles as the catalyst, resulted in the highest fatty acid methyl ester (FAME) yield of 94%. Additionally, the biodiesel obtained was characterized by an exceptionally low sulfur content [25].

Other researchers such as Vinayan et al. (2013) developed an innovative approach for creating palladium nanoparticles (Pd NPs) with a triangular shape, which are then applied to nitrogen-doped graphene. The process begins with the generation of nitrogen-doped graphene (N-G) through the even application of a nitrogen-rich polymer on graphene that has been modified with a polyelectrolyte, followed by pyrolysis. Subsequently, the Pd NPs are attached to the N-G substrate (forming Pd/N-G) through a carefully managed polyol reduction technique. Comparative hydrogen storage evaluations reveal that N-G and Pd/N-G can store hydrogen at a capacity of 1.1 wt% and 1.9 wt%, respectively, when subjected to a hydrogen equilibrium pressure of 2 MPa at a temperature of 25^{o}C [30].

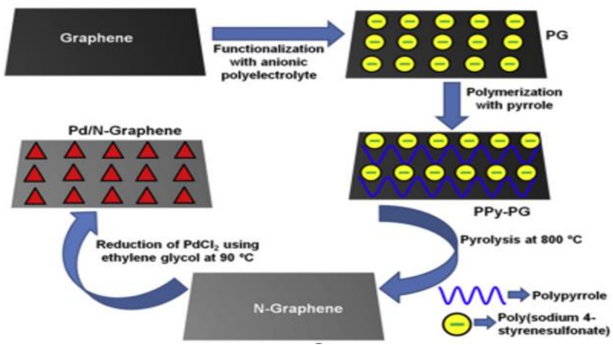

Figure 5. Illustrative representation of the synthesis method used for fabricating triangular palladium nanoparticles embellished nitrogen-doped graphene nanocomposite [30].

Raguram et al. (2022) synthesized copper-doped TiO2 NPs using the sol-gel method, adjusting the molar concentrations of the copper precursor to varying levels (0.025 MCT1, 0.05 MCT2, 0.1 MCT3, and 0.2 MCT4). Their findings indicated that the most effective dopant concentration was 0.1 M of copper, which when combined with TiO2, showed optimal performance for applications in dye-sensitized solar cells (DSSC) and photocatalysis [31]. Shi et al. (2017) constructed a solar thermal evaporation system utilizing carbon nanotubes (CNTs) enhanced with Fe3O4 magnetic nanoparticles (Fe_3O_4@CNT). This system allows for the magnetic separation of the materials from water. They reported that the retrieval efficiency of the Fe_3O_4 nanoparticles and the Fe_3O_4@CNT composite was between 97.9% and 98.7%. The inclusion of Fe_3O_4 NPs within the CNT structure significantly boosts the solar energy absorption capacity, surpassing that of standalone CNTs. Furthermore, the recovery efficiency and effectiveness can be modulated by varying the magnetic field intensity and the proportion of Fe_3O_4 to CNTs [32]. Cote et al. (2003) explored the continuous hydrothermal production and crystallization of spinel $CoFe_2O_4$, employing ferric nitrate and cobalt nitrate reacting with sodium hydroxide. The process occurred at temperatures between 475 and 675 K under a pressure of 25 MPa. They achieved uniform $CoFe_2O_4$ nanoparticles using a cold mixing approach. They suggested a particle formation mechanism that starts with the precipitation of metal hydroxides under normal conditions, followed by their dissolution as the temperature rises, leading to the swift formation of metal oxides at high temperatures. However, the hot mixing method resulted directly in metal oxide precipitation due to the introduction of hot hydroxide solution. In both methodologies, the result was the production of finely particulated $CoFe_2O_4$ within the studied processing parameters (see Fig. 6) [33].

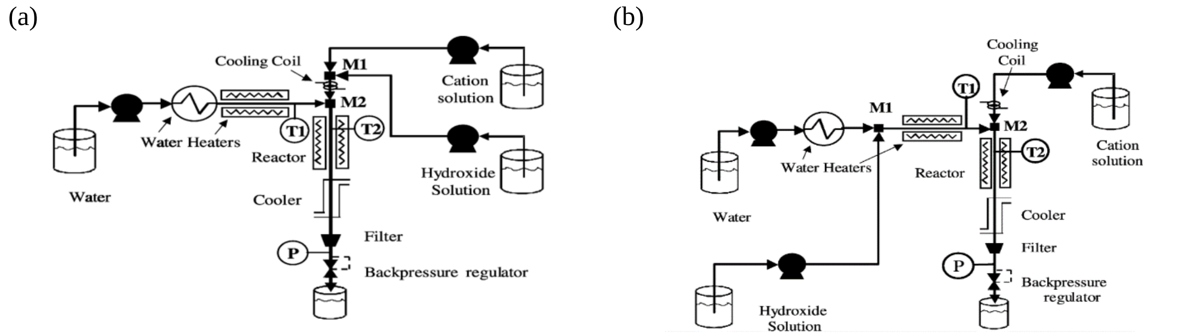

Figure 6. (a) Diagram illustrating the setup for conducting flow experiments using a configuration for cold mixing; (b) diagram depicting the setup for conducting flow experiments with a configuration designed for hot mixing [33].

Baruwati et al. (2006) produced ZnO nanoparticles using a hydrothermal method at 120°C. The research explored the nanoparticles' ability to detect gases by reacting with four different substances, namely Liquefied Petroleum Gas (LPG), ethanol (EtOH), hydrogen, and ammonia. The findings indicated that these nanoparticles exhibit significant sensitivity towards LPG and ethanol, particularly at low temperatures. Furthermore, the addition of Pd to the nanoparticles was found to enhance their sensing capabilities, notably in terms of response and recovery durations. Future studies are suggested to focus on the augmentation of Pd onto the nanoparticle surfaces to improve both the speed and efficiency of the sensors in bioenergy production systems [34].

4. CHARACTERIZATION OF NANOPARTICLES

The definition provided by the European Commission is all-encompassing, covering engineered, incidental, and naturally occurring nanoparticles in an environmental framework. Within the broad spectrum of nanomaterials (NMs), significant attention has been devoted to exploring two primary categories: carbon-based and metal-based NMs, for a multitude of applications [15]. Nanoparticles are colloidal particles that fall within the size range of 1 to 100 nm [16]. The prefix "nano" originates from the Greek term "nanos," signifying extreme smallness. Various kinds of nanoparticles are categorized based on their shape and physicochemical characteristics, including polymeric, carbon-based, ceramic, semiconductor, metallic, and lipid-based nanoparticles, among others [18].

Significant advancements have been made in the biomedical potential of functionalized NMs, which include varieties such as polymeric nanoparticles, gold inorganic nanoparticles, iron oxide NPs, CNTs, and mesoporous silica nanoparticles (MSNs), following their development, characterization, and fabrication. Nanoparticles are deemed functionalized when alterations are applied to their structure or surface [35]. The process of surface functionalization is utilized to improve the efficacy of nanoparticles. For example, functionalized polymeric NPs are categorized into four distinct generations. Initially, the first generation includes extended stealth NPs, succeeded by the second generation of lectin-receptive polymerized NPs. Subsequently, the third generation encompasses polysaccharide-infused nanoparticle systems, culminating in the fourth generation with ligand-targeted nanoparticles [35,36]. Functionalized polymeric NPs are utilized in a wide array of drug delivery applications, targeting areas like the vagina, brain, cancerous tissues, gene therapy, among others. Recent years have seen considerable progress in the development of these nanoparticles, with innovations such as externally stimulated drug release, precision-targeted drug delivery, magnetic nanocarriers, ligand-focused polymeric nanoparticles, nanogels, and beyond. Such progress has facilitated efficient drug encapsulation and precise targeting, thereby minimizing adverse side effects [36]. Furthermore, functionalized mesoporous silicon nanoparticles (MSNs) have shown responsiveness to a range of environmental stimuli, including pH, temperature, redox conditions, light, ultrasound, electric, magnetic fields, enzymes, reactive oxygen species (ROS), glucose, ATP, or combinations thereof. This ongoing advancement in MSNs has significantly broadened their prospective uses in the field of biomedical engineering [37,38].

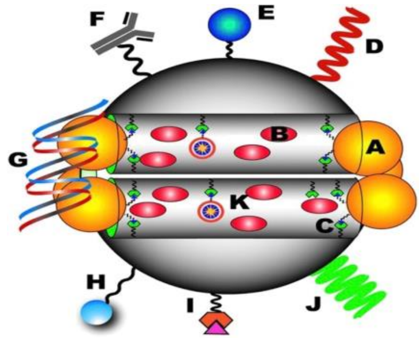

Figure 7. Illustrates the range of techniques available for functionalizing MSNs, which encompass: A) the use of functionalized gatekeepers; B) enhancing the interaction between the encapsulated molecules and the MSNs in the pores to improve retention duration; C) applying stimuli-responsive linkers to chemically attach gatekeepers to MSNs; D) using functionalized polymers like PEG to stabilize the nanoparticles; E) incorporating functionalized bioimaging agents such as magnetic nanoparticles, quantum dots, or fluorophores; F) attaching specific targeting ligands for cell receptor specificity; G) creating complexes with plasmid DNA; H) adding extra functionalized ligands to boost cell penetration efficiency; I) integrating functionalized diagnostic markers; J) utilizing stimuli-responsive functionalized polymers; and K) employing functionalized groups capable of altering cellular metabolism [38].

Characterization is essential for identifying different attributes of NPs, such as their form, dimensions, specific surface area, and configuration. The process of nanoparticle characterization can be divided into two main areas. The initial area concentrates on evaluating physical attributes, including the form, dimension, crystalline structure, and uniformity of distribution. The second area is concerned with the examination of chemical properties, like the identification of attached molecules, linked ligands, and the zeta potential [39–42]. Techniques used for the physical characterization of nanoparticles encompass scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet (UV) spectroscopy, X-ray diffraction (XRD), differential centrifugal sedimentation, and dynamic light scattering, among others. These methods offer crucial information on the physical properties and structural details of nanoparticles [42–44]. However, chemical characterization methods are employed to investigate the chemical attributes of nanoparticles. Such methods encompass nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, gel electrophoresis, and inductively coupled plasma mass spectrometry (ICP-MS), among others. These chemical characterization techniques are pivotal in detecting and analyzing specific molecules, functional groups, and elemental compositions in nanoparticles. Through the integrated use of both physical and chemical characterization techniques, researchers gain a thorough insight into the nanoparticles' characteristics and behaviors, facilitating advancements in their creation, modification, and practical applications [45,46].

The precise measurement of particle size is vital in the characterization of nanoparticles, influenced by variables like excipients, polymers, and the methods used in their preparation. The size of the particles significantly affects several secondary properties, such as surface area, degradation, toxicity, targeting, and the mechanism of uptake, making the knowledge of particle size distribution imperative. Photon correlation spectroscopy and electron microscopy stand out as the principal methods for determining particle size. Electron microscopy such as transmission scanning electron microscopy (SEM), electron microscopy (TEM), and freeze-fracture methods, enabling the assessment of individual particle sizes and their distribution. Electron microscopy, known for its relatively quick results, provides crucial data on particle size attributes.

Specifically, Transmission Electron Microscopy (TEM) operates by directing a beam of electrons through a sample. The differences in the beam's amplitude and phase, as it passes through, generate a contrast in the resulting image that depends on the sample's size, thickness, and composition. The image produced is then magnified and projected onto an imaging screen with an objective lens, offering a higher resolution than light-based imaging methods. Utilizing methodologies like TEM and electron microscopy allows researchers to gain precise and comprehensive data regarding particle size, enhancing the understanding of the nanoparticles' behavior and characteristics [41–43,45,46].

To encapsulate, the field of nanotechnology has witnessed substantial progress in the creation and application of diverse nanomaterials (NMs) across various industries. Predominantly, carbon-based and metal-based NMs have been thoroughly investigated within this domain. These NPs, which vary in size from 1 to 100 nm, are now employed in numerous disciplines. Significant progress has been made in the development, characterization, and biomedical uses of functionalized nanomaterials, including polymeric nanoparticles, inorganic gold NPs, CNTs, and MSNs. Functionalization pertains to altering the nanoparticles' structure or surface to boost their functionality. Various generations of functionalized polymeric nanoparticles have emerged, paving the way for their use in drug delivery, gene therapy, and precise therapeutic interventions. These advancements in functionalized nanoparticles have led to efficient drug encapsulation, precise targeting, and minimized adverse effects.

5. APPLICATION OF NANOTECHNOLOGY IN BIOENERGY SYSTEMS

While there have been several initial milestones in the transfer from fossil fuel energy resources to biobased fuel, current developments in nanotechnology and their application in the bioenergy sector have enabled a paradigm shift toward the efficient production and use of biobased fuel. Biofuel was the second-most popular renewable energy source in 2019 after wind and hydropower, making up almost 1% of the world's total energy consumption, according to BP's statistical evaluation of global energy. According to Bidir et al. (2006), biofuels are typically created by chemical, thermochemical, or biochemical processes, as seen in Fig. 8 below. Since the introduction of nanoparticles, these processes have seen some notable improvements [47].

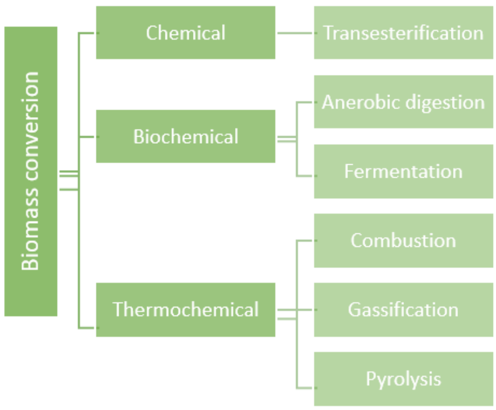

Figure 8. Biomass conversion processes [48]

5.1 Nanoparticles as Catalyst for Transesterification

According to Saadia Nasreen et al. (2018), non-catalyzed transesterification in the synthesis of biodiesel is typically accomplished at higher temperatures and pressures, requiring a greater amount of energy. Additionally, the usage of homogenous catalyst typically presents separation issues for downstream processes [49]. Therefore, in the transesterification process (see Fig. 9), heterogeneous catalysis is generally favored because of its low energy cost, high yield quality, and simplicity of downstream separation [50].

RCOOR'
/
HC - OOCR" + 3 ROH ----> RCOOR + RCOOR" + RCOOR"' + HC
\
RCOOR"'
(triglyceride) (alcohol) (mixture of alkyl esters) (glycerol)

Figure 9. Transesterification reaction

These benefits are further enhanced by the application of nanoparticles in heterogeneous catalysis due to their physicochemical properties. An improvement in the yield and efficiency of biodiesel production was reported when nanoparticles of lanthanum titanium dioxide ($LaTiO_3$) was used in the transesterification of wild mustard seed oil in the presence of methanol, due to the reusability of the catalyst material after eight production circles [51]. Using a similar method, adding CaO nanoparticles to the transesterification procedure at 80°C increased the fatty acid profile of biodiesel made from algal oil [52]. Perhaps a distinctive benefit facilitated by nanoparticles in chemical catalysis is the ease of catalyst regeneration after each process circle, leading to a reduced cost of production and low environmental footprint associated with catalyst wastes. This benefit has been investigated in a literature where nanoparticles of magnetic alumina-ferric oxide supported by KOH were used in the recovery of biodiesel from microalgae cultivated in wastewater [53]. The nanoparticle enhanced catalytic activity and stability after several circles while allowing separation of catalyst material from tissues and carcasses of microalgae due to enhanced magnetic properties. Several other works have been conducted on the benefits offered by nanotechnology in biodiesel production for accelerating the transition from linear economy to circular bioeconomy [1,25,54].

5.2 Nanoparticles as Catalyst for Biochemical Processes

Biochemical process involves the use of microorganisms and/or chemicals to facilitate recovery of fuels through processes such as fermentation or digestion (anaerobic) of biomaterials. Nanoparticles may not always directly catalyze biochemical processes, but they are instrumental toward improving yield in biochemical processes due to their ability to infiltrate the cell membrane and decrease the lag phase of microorganisms [55]. Fig 10 shows a simple process flow application of nanoparticles in fermentation of lignocellulos material for bioethanol recovery.

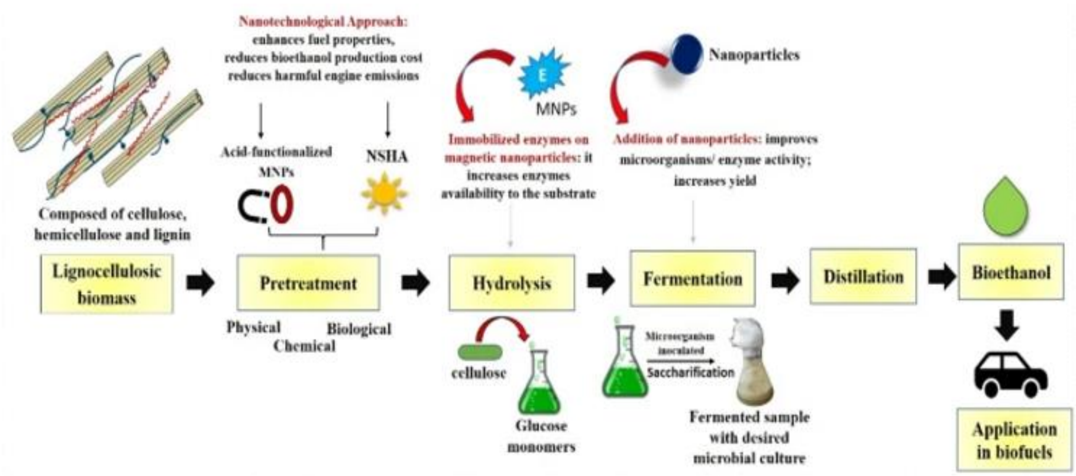

Figure 10. Nanoparticles application in bioethanol production [56]

Nanoparticles have also been shown to enhance bioethanol recovery from syngas fermentation where they facilitate syngas-water mass transfer. For instance, an increase in ethanol and acetic acid by 213.5% and 59.6% respectively were recorded in a syngas fermentation by Clostridium when aided with nanoparticles of methyl-functionalized cobalt ferrite-silicate [57]. Similarly, silicon dioxide nanoparticles were used to immobilize beta-galactosidase in ethanol production from batch hydrolysis and fermentation of cheese whey using K. marxianus and S. cerevisiae [58].

The use of nanoscale Zero Valent Iron (nZVI) in anaerobic digestion has also gain attention in recent years for maximizing biogas recovery from biowaste and sludge [59]. Although nZVI is shown to inhibit methanogenesis in anaerobic digestion resulting from reductive decomposition of the cell membrane, higher yields of biogas (mostly hydrogen) can be obtained [60]. In a study to enhance methane potential from domestic sludge digestion, zeolite was coated with nZVI which resulted in higher methane generation than the control, although caused a lag period before biogas generation was observed [61]. Several other works have been conducted on the application of nZVI with the goal of improving environmental sustainability and economic viability of anaerobic digestion process for sewage sludge [62,63].

5.3 Nanoparticles as Catalyst for Thermochemical Processes

Biomass is first transformed into gases in thermochemical conversion, which can then be used directly as syngas or used to further synthesise the needed products [64]. Combustion, pyrolysis, and gasification are typical thermochemical reactions, although these procedures mostly produce products that are incompatible with the majority of vehicle engines and have low yield or performance characteristics. However, it has recently been demonstrated that using nanomaterials in the thermochemical conversion of biomass improves both process yields and product quality. For example, the generation of biofuels with greater heating values and stability under air pressure has been made possible by the use of nano-catalyst in pyrolysis [65].

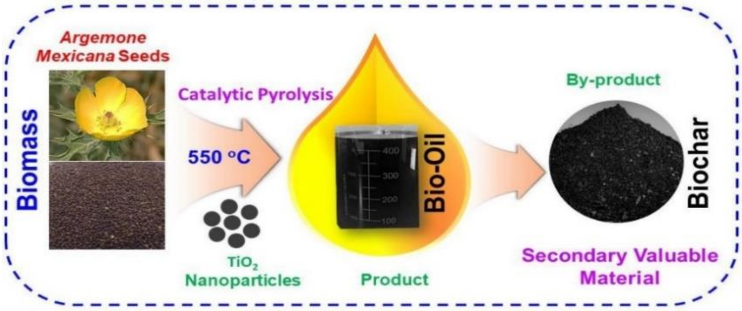

Figure 11. Catalytic pyrolysis of biomass [64]

Nano-catalyst of TiO2 was used in fast pyrolysis of leucaena leucocephala in a fluidized bed reactor to improve the catalytic efficiency. A comparison between the product yields from Leucaena leucocephala wood in the absence of nano-catalyst and in the presence of TiO2 at the same catalytic temperature range of 400-600ºC, showed an increase from 54.21% to 67.1% depending on catalyst to feedstock ratio, along with a decrease in oxygen content from 27.1% to 24.5% [65]. In a similar manner, ketonization of bio-oil from fast pyrolysis can be enhanced by employing nano-catalyst. This was reported in a study aimed at upgrading bio-oil, where nanomaterials of FeOx and MnOx were utilized for ketonization by increasing acetic acid and propionic acid adsorption from the aqueous phase of the thermal bio-oil [66].

Eliminating tar from thermochemical products is also thought to be a critical component of process development in green energy enterprises in order to achieve sustainability goals. By preserving stability in the carrier microporous structure and preventing the generation of CO, the application of biochar-based nano-catalyst was found to be advantageous in this regard, transforming 87% of the tar produced from pyrolysis into hydrogen-rich syngas [67]. Due to its rapid reaction and short residence time, supercritical water gasification of biomass is another method of recovering biofuels from waste. A study by Marcelino et al. (2023) showed that impregnation of coconut shell with nickel nano catalyst for supercritical water gasification of biomass lead to an increase in hydrogen yields from 8.8 mol% to 17.2 mol%, alongside the gasification efficiency from 47.6% to 58.6% [70] However, the development of systems required for such processes is not without its difficulties, such as the process's high energy intensity and low product yield as highlighted by [69].

5.4 Nanoparticles as Additives for Biofuels Blends

It has been observed that the use of solid additives in combustion engines improves octane number, cold flow behavior, antioxidant, and anti-knocking properties of automotive systems; however, the subject also tends to generate controversy due to environmental concerns of particulate emission from exhaust gas stream and limitation of accurate understanding into its future implications [70]. An approach to fast-tracking the energy transition within the transport sector would involve varying of biodiesel content in petro-diesel thereby reducing complete dependency on fossil fuels. In research examining how a blend of biodiesel influences the functionality and emission traits of a compression ignition engine, alumina nanoparticles were incorporated at concentrations up to 90ppm within biodiesel-diesel mixtures. The study noted enhancements in parameters including power, brake thermal efficiency (BTE), and exhaust gas temperature (EGT), which showed increases of 3.67%, 8.12%, and 5.57%, respectively [71]. The CO and unburn hydrocarbon were also observed to decrease, although an increase in NOx was recorded which was attributed to the high exhaust gas temperature. Similar performance improvements were also recorded in another experimental work where nanoparticles of Cerium oxide (CeO_2) and Alumina (Al_2O_3) were used to enhance biodiesel-diesel blend in a single cylinder direct injection engine [72]. By using nanoparticles as blend additives in automotive engines, a shorter ignition delay is experience within the cylinders leading to increase in peak pressure rate and heat release rate [73].

6. RELEVANT STUDIES ON NANOMATERIALS AND THEIR APPLICATIONS IN BIOENERGY

Several other works have been carried out in recent years to further understand the advantages of nanoparticles towards advancing bioenergy and biotechnology systems. The table 1 below gives a list of research conducted in recent times on nanoparticles applications in biotechnology.

Table 1. Nanomaterials applications in biotechnology.

Author	Nanomaterial	Application	Biofuel	Improvement/Function
Abdelwahab et al.(2023)	Nickel nanoparticles	Anaerobic digestion	Biogas	Improve hydrolysis rate
Wang et at. (2021)	Nano-zero-valent iron	Anaerobic digestion	Biogas	Improve acidogenesis
Yacob & Sulaiman (2023)	Calcium oxide nanoparticles	Transesterification of Rice Bran Oil	Biodiesel	Improve reaction kinetics
Lu et al. (2017)	Nickel nanoparticles	Gasification	Hydrogen enriched producer gas	Tar regulation
Kim et al. (2018)	Nickel nanoparticles	Pyrolysis and gasification	biohydrogen	Improve product selectivity
El-Sheekh et al. (2023)	Magnesium zinc ferrite nanoparticles	Pretreatment for fermentation	Biohydrogen	Enhance fermentable sugar
Bitire et al.(2023)	Copper nanoparticles	Additive	Biodiesel-Diesel blend	Improve engine efficiency.

6.1 Applications of Nanotechnology as Nano catalysts in Bioenergy Production

Biohydrogen Production

Numerous nanomaterials have been integrated into the biofuel production processes, with researchers harnessing nanoscale materials as catalysts to enhance the efficiency and yield of biohydrogen production, as elucidated in this specific subsection.

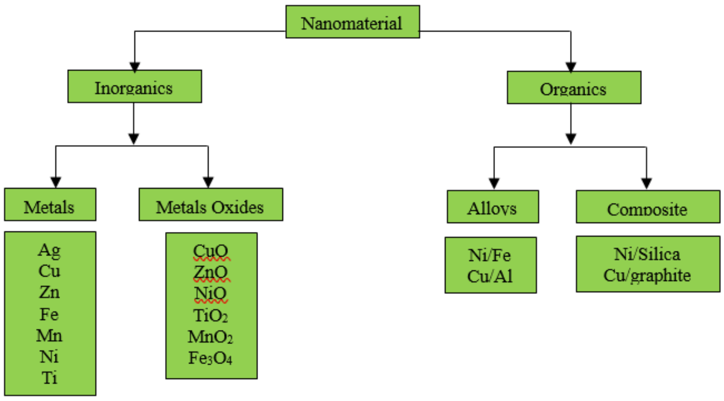

Figure 12. Typology of Nanoparticles Utilized in the Production of Biohydrogen [81].

Fig. 12 serves to depict the comprehensive categorization of nanoparticles that have been extensively employed across diverse pathways of biohydrogen synthesis [81]. Employing nickel and cobalt oxide as inorganic nanoparticle sources, Mishra et al. (2018) embarked on a study centered on hydrogen production from palm oil mill effluent [70]. Using a hydrothermal technique, nanoparticles were synthesized to evaluate their effectiveness in enhancing hydrogen production. Specifically, a hydrogen production rate of 0.563 L H_2/g Chemical Oxygen Demand (COD) was recorded when utilizing a concentration of 1.5 mg/L of nickel oxide (NiO) NPs. This concentration yielded a hydrogen production rate of 21 mL H_2 per liter of palm oil per hour. Furthermore, the introduction of cobalt oxide (CoO) NPs resulted in an optimized hydrogen yield of 0.4887 L/g COD removed. This optimal yield was achieved with a CoO NP concentration of 1.0 mg/L and a loading rate of 18 mL/L of palm oil per hour. The combination of NiO and CoO NPs with palm oil effluent significantly increased hydrogen yields, showing enhancements of 1.51 and 1.67-fold, respectively. Additionally, the inclusion of these NPs improved COD removal efficiency by 15% and 10%, respectively, compared to experiments without NPs in the palm oil effluent. The concentration of nanoparticles utilized was 3.0 mg/L and introduction into Luria-Bertani (LB) medium resulted in a diminution of bacterial proliferation by 63% and 83% for Nickel Oxide (NiO) and Cobalt Oxide (CoO) NPs, respectively. When accurately administered into wastewater treatment processes, both NiO and CoO nanoparticles demonstrated significant capability in augmenting hydrogen production efficiency.

Biogas Production

In recent times, the utilization of advanced methodologies for nanoparticle synthesis and characterization has resulted in the development of high-quality, fine-tuned nano-catalyst systems, including metal oxide nanoparticles, magnetic nanoparticles, and carbon nanotubes. These advancements have played a pivotal role in enhancing biofuel production efficiency. The nanoparticles have showcased remarkable potential in the context of biogas production processes, particularly within anaerobic pathways. These pathways involve biochemical conversions of diverse organic materials into biogas and its constituent elements. Nanoparticles, functioning as electron donors, acceptors, and cofactors for crucial enzymes like [Fe]- and [Ni-Fe]-hydrogenase, have demonstrated promising outcomes in this regard [82]. For instance, nanoparticles exert a positive impact on the hydrolysis of organic matter due to their expansive surface-to-volume ratio. This unique feature facilitates microorganisms in binding to the active sites of molecules, thereby enhancing the hydrolytic processes [83].

Bioethanol Production

Gupta et al. (2020) strategically employed zinc oxide NPs to bolster bioethanol production from rice straw. This application resulted in the attainment of a peak ethanol yield of 0.0359 g/g, calculated based on the dry weight of the plant biomass. This impressive accomplishment was realized at a specific ZnO nanoparticle concentration of 200 mg/L [86]. Additionally, the advantageous prospect of recycling and recovering these nanoparticles significantly contributes to the overarching economic feasibility of the entire process. Similarly, in an independent investigation conducted by Ivanova et al., an innovative strategy was explored to enhance the process of bioethanol fermentation [85]. This method involved harnessing alginate magnetic nanoparticles as carriers to encapsulate yeast cells. The outcome of this pioneering approach was striking, with the productivity rate surging to an impressive 264 g/Lh. This noteworthy achievement was observed when utilizing a particle loading of 70%.

Biomass Conversion

Nanotechnology-based strategies leverage nanomaterials with the unique ability to penetrate the cell walls of lignocellulosic biomass, establishing interactions with its constituents such as cellulose and hemicellulose. This interaction facilitates the release of monomeric and oligomeric sugars [86]. Nanoparticles, along with their microemulsions, have exhibited hydrolytic effects akin to chemical pretreatment, a significant aspect of processing lignocellulosic biomass [87]. The remarkable advantage of nanoparticle application lies in their efficient biomass pretreatment with minimal quantities, coupled with their potential for reusability in subsequent cycles. A specific study delved into the synergistic impact of alkaline pretreatment alongside magnetite (Fe_3O4) nanoparticles on rice straw, yielding substantial enhancements in both biogas and methane production [88]. Furthermore, the utilization of nanoparticles has demonstrated a positive influence on sugar production during pretreatment, exemplified by the elevated hemicellulose yield from yellow poplar sawdust [89]. However, despite the promising potential, reports focusing on the application of nanoparticles in biomass pretreatment remain limited, attributed to the nascent stage of nanotechnology's integration in biomass refining [87].

While the prospect of nanotechnology and nanomaterials contributing to bioenergy production from lignocellulosic biomass is captivating, various concerns necessitate addressing. For instance, to counteract enzyme leaching during reactions, immobilization via covalent binding assumes paramount significance, particularly when solid materials function as carriers [90]. However, the interaction dynamics between lipase and these carriers remain insufficiently understood, urging further investigation to fully harness the potential of nanomaterials in bioenergy generation. Another facet deserving attention is the intricate toxicity mechanism of nanoparticles that remains incompletely elucidated. The minute size of metal nano-catalysts raises the possibility of perturbing normal human cell function or instigating toxicity in living organisms [91]. Moreover, the presence of nanoparticles in biofuels can precipitate within lung tissues, through emissions from vehicles or industries, subsequently triggering respiratory ailments such as asthma or bronchitis. Consequently, meticulous safety assessment stands as a pivotal requirement to navigate energy, safety, and environmental apprehensions connected to the utilization of nanomaterials in biofuel generation [87,92].

7. CONCLUSION

The utilization of nanomaterials as nano catalysts in bioenergy production systems presents a promising avenue to overcome challenges and enhance efficiency. This critical review emphasizes the unique physicochemical properties of nanomaterials, including high reactivity and recyclability, positioning them as ideal catalysts for bioenergy conversion processes. We highlight the absence of a comprehensive summary on nanomaterials application in bioenergy production underscoring the need for further exploration and understanding in this field.

Nanomaterials are classified based on dimensions (0-D, 1-D, 2-D, and 3-D) and material composition (organic, carbon-based, and inorganic), providing a structured understanding. We reveal the symmetry of zero-dimensional nanoparticles and the high aspect ratio of one-dimensional counterparts. Synthesis methods, driven by innovation and sustainability, contribute to diverse applications in bioenergy and other domains. The evolving field of nanotechnology witnesses significant progress, particularly in the development and application of functionalized nanomaterials, such as polymeric nanoparticles and mesoporous silica nanoparticles. This progress translates into breakthroughs in biomedical applications, including drug delivery, gene therapy, and targeted treatments, with a notable reduction in side effects.

Characterization techniques, both physical and chemical, play a pivotal role in comprehending and advancing nanomaterial properties. TEM, among other methods, stands out for accurate particle size determination, providing crucial insights for further research and application. Exploring nanotechnology in bioenergy processes reveals significant strides in catalysis for transesterification, biochemical reactions, thermochemical processes, and the use of nanoparticles as additives for biofuel blends. These advancements contribute to improved catalytic activity, increased yields, and optimized processes, enhancing overall efficiency and sustainability of bioenergy production. Nevertheless, this review acknowledges persistent challenges, such as nanoparticle toxicity and public health concerns necessitating further investigation and careful consideration. The responsible integration of nanotechnology in bioenergy systems requires continued research to address potential risks and ensure sustainable and safe applications. Navigating the future of nanomaterials as nano catalysts in bioenergy, we should let the principles of simplicity, clarity, and precision guide our discourse and actions to propel this transformative field forward.

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