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Review

Nanomaterials Utilization in Biomass for Biofuel and Bioenergy Production

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Abstract: The world energy production trumped by the exhaustive utilization of fossil fuels has highlighted the importance of searching for an alternative energy source that exhibits great potential. Ongoing efforts are being implemented to resolve the challenges regarding the preliminary processes before conversion to bioenergy such as pretreatment, enzymatic hydrolysis and cultivation of biomass. Nanotechnology has the ability to overcome the challenges associated with these biomass sources through their distinctive active sites for various reactions and processes. In this review, the potential of nanotechnology incorporated into these biomasses as an aid or addictive to enhance the efficiency of bioenergy generation has been reviewed. The fundamentals of nanomaterials along with their various bioenergy applications were discussed in-depth. Moreover, the optimization and enhancement of bioenergy production from lignocellulose, microalgae and wastewater using nanomaterials are comprehensively evaluated. The distinctive features of these nanomaterials contributing to better performance of biofuels, biodiesel, enzymes and microbial fuel cells are also critically reviewed. Subsequently, future trends and research needs are highlighted based on the current literature.

Keywords: bioenergy; biofuel; nanotechnology; nano-catalysts; nano-additives

1. Introduction

The current primary energy consumption is dominated by conventional fossil fuels including coal, oil and gas [1], leading to sustainability problems such as a declining amount of fossil fuels, environmental impacts and huge price fluctuations [2]. Greenhouse gas emissions, global climate change as well as intense energy demand have driven a number of professionals to develop novel solutions to replace fossil fuels. Among the alternative energy sources, biomass accounts for around 80% of the energy produced by global renewable energy carriers [3]. It can be stored and employed to generate heating, fuels and electricity when required. These are called bioenergy which is defined as solid, liquid or gaseous fuels produced from biological origin.

Bioalcohol derived from corn, wheat, sugar beet and sugarcane as well as biodiesel produced by transesterification of oils extracted from rapeseed, palm, soybean and sunflower are examples of bioenergy generated from first-generation feedstock. Non-food feedstocks like lignocellulosic and microalgae biomass are second- and third-generation feedstocks used to produce bioenergy, respectively. The biomass can be processed using thermal conversion technologies such as combustion, gasification and pyrolysis which converts biomass to bio-oil (a liquid fuel) and biochar (a solid residue), while syngas, which can be further processed to biofuels and electricity, is produced by the gasification of biomass [4]. Furthermore, anaerobic digestion has been employed commercially to produce biogas, which is also a type of bioenergy. The biogas produced has been utilized to generate heat and electricity. It plays an important role to provide the necessary energy to rural areas for cooking and lighting [4]. In addition, bioenergy can be produced by microbial fuel cells (MFCs) which uses naturally occurring microorganisms with biological electricity-generation ability.

Despite having numerous scientific breakthroughs, there are still various technical barriers to tackle for bioenergy production so that it can compete with fossil fuels. For instance, for microalgal biofuels production, cultivation of algae on a large scale effectively and efficiently, maintenance of the desired culture with alien species, harvesting cost of algae and energy efficiency and the best conversion method to biofuels remain uncertain [5]. Moreover, pretreatment methods are required to extract fermentable sugars from lignocellulosic biomass before proceeding to biofuel generation processes [6]. Other than technological barriers in production, challenges like insufficient existing infrastructure for the production process and high production cost compared to first-generation biofuels are apparent [7]. These drawbacks necessitate the development of production and optimization strategies to achieve high quality and high yield of bioenergy. For example, processes regarding pre-treatment, enzymes and fermentation can be looked into so that bioenergy production can be made to more energy-efficient and cost-effective [8].

Nanomaterials are the fundamental principle of nanoscience and nanotechnology application. The application of nanostructure science and technology covers a wide interdisciplinary area of research and development activity which has grown explosively worldwide in the past research discipline. Nanoscale materials are defined as a set of substances, where at least one dimension is less than approximately 100 nm. This extremely tiny size gives a large ratio of surface area to volume and increases the number of active sites for various reactions and processes. These nanoparticles (NP) also have the ability to exhibit different morphologies that have broadened their applications in different fields [9]. In addition, nanostructured materials, in comparison with large particles, have a faster reaction rate with other molecules [10]. The existence of nanomaterials has already influenced significant commercial impact, and the awareness of nanomaterials will raise due to its unique optical scale properties which are impactful for various fields such as bioenergy, electronics, mechatronics, medicine, pharmaceutical, ionic liquids, polymer and many more.

A number of direct and indirect applications of nanomaterials in bioenergy production have been reported. Nanomaterials are exceptional candidates in numerous biofuel systems due to their large surface areas and special characteristics including high catalytic activity, crystallinity, durability, efficient storage, stability as well as adsorption capacity [11]. The effects on metabolic reactions of bioprocesses producing biofuel are enhanced with nanoparticles such as nanofibers, metallic nanoparticles and nanotubes [9]. Nanoparticles, which are usually used as catalytic agents, take part in enhancing the activity of anaerobic consortia, reducing inhibitory compounds and transferring electrons in order to improve the process yields. Nanomaterials such as nano-crystals, nano-droplets and nano-magnets are also used as nano-additives in order to enhance the blending efficiency of biofuel with petrol and diesel [12].

This paper comprehensively reviews the recent approaches and applications related to nanotechnology incorporated processes for bioenergy production. The fundamentals of nanotechnology are introduced with the uses and benefits of various nanoparticles. Then the next section covers applications of nanotechnology on biomass including microalgal biomass and lignocellulosic biomass. Then, recent advances in the nanotechnology-based biofuel industry including nano-catalysts for higher biofuel yields and nano-additives for better fuel blends performance are presented. The conversion of chemical energy to electrical energy via MFCs with the aid of nanoparticles is also discussed. Moreover, future works and challenges are highlighted to provide insights for the future development of bioenergy production using nanomaterials. This study with in-depth comparison analysis will contribute to the bioenergy field where it provides a clear outline to the concerned researchers in how nanotechnology can improve bioenergy production.

2. Fundamental of Nanomaterials

Redesigning a material at the molecular level state is also known as engineered nanomaterials in which modification is made toward their small size and novel properties which are generally not visualized in their conventional and bulk counterparts. The distinct properties of these materials at the nanoscale are their relatively large surface area which triggers the novel theory of quantum effects. Nanomaterials provide a much greater surface area to volume ratio compared to their conventional forms, which is beneficial as this can provide greater chemical reactivity created by their specialty [13]. Considering the reaction on a nanoscale level, the properties and characteristics of materials including novel optical, electrical and magnetic behaviors can be more vital due to the quantum effects [14].

The most common terms for nanostructured materials are classified as zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D) nanostructures [15]. These dimensionalities of nanomaterials are characterized using an ultrafine grain size less than 50 nm or limited to 50 nm. Various modulation dimensionalities can be formed such as 0-D (e.g., atomic clusters, filaments and cluster assemblies), 1-D (e.g., multilayers), 2-D (e.g., ultrafine-grained overlayers or buried layers) and 3-D (e.g., nanophase materials composed of equiaxed nanometer-sized grains). Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nanotechnology where they display different physical and chemical characteristics from normal-sized chemicals.

The most fundamental component in a nanostructure fabrication is nanoparticles. NPs with diverse size and morphology can be fabricated via several synthetic routes which offer superior quality of NPs, but the fabrication procedures such as biosynthesis are still under development for further improvement [16]. Organic nanoparticles have been widely investigated up-to-date, with liposomes, polymersomes, polymer constructs and micelles, all being employed for imaging or drug and gene delivery techniques [17]. Meanwhile, inorganic nanoparticles have also attracted attention in recent years attributed to their unique material- and size-dependent physicochemical properties, which are incomparable with traditional lipid- or polymer-based nanoparticles. A common reason to what makes inorganic nanoparticles attractive is their physical properties (e.g., optical and magnetic), in addition to their chemical properties such as inertness, stability and ease of functionalization [18]. Thus, inorganic nanoparticles such as magnetic, gold, quantum dots and carbon nanotubes have vast potential in various modern applications. For example, carbon nanotubes, metal-oxide and magnetic nanoparticles (MNPs) are employed for bioenergy production. Table 1 summarizes the advantages and disadvantages of magnetic nanoparticles.

Table 1. Advantages and disadvantages of magnetic nanoparticles [19].

Advantages	Disadvantages
• Excellent biodegradability • Readily to be customized • Ease of separation • Low cytotoxicity to biomass cell • Ease of synthesis • Ability to bind multiple targeted compounds • Large surface-to-volume ratio • Maintain stability after mechanical, physical and chemical modification	• Poor dispersion abilities • High cost of synthesis material • Limitation in scale up production processes • Mobility dependent on environment compatibilities

MNPs which comprise of a magnetic core (e.g., magnetite (Fe_3O_4) or maghemite (g-Fe_2O_3)) are some of the most profound inorganic nanomaterials [20]. The MNPs are most frequently used over all the nanoparticles examined for bioenergy production since their magnetic properties give them easy recoverability. Enzymes used in biodiesel or bioethanol generation can be immobilized with MNPs as a carrier. High coercivity and great paramagnetic property of MNPs during the methanogenesis process also make them useful for biogas production [21]. However, metals such as cobalt and nickel which are incorporated in the synthesis exhibit toxic and susceptible compounds when subjected to the oxidation process, thereby more research studies are required to overcome these problems [22].

3. Biomass

The world energy production of CO_2 has been tremendously rising due to the exhaustion of fossil fuels. On top of that, the concern relating to energy safety and environmental pollution has been an appointment in searching for alternative sources for bioenergy production. Lignocellulosic biomass involves plants and agricultural residues composed of cellulose, hemicellulose, lignin as well as other components (i.e., proteins, pectins and extractives). It was estimated that only 3% out of 13 billion t/y of plant residues were fabricated into manufacturing goods and the remaining were left for decomposition [23]. Thereby, these lignocellulosic residues should be properly managed by converting them into bioenergy where researchers have proven that the composition of lignocellulose has the capability to transform their monomers or building block into biofuels (e.g., bioethanol and biodiesel). On the other hand, ongoing studies have also shown the ability of microscopic filamentous photosynthetic microorganism, or well-known as "microalgae", regarding the conversion of algal lipids into biofuels. These microalgae-based biofuels have similar chemical properties compared to those from fossil fuels which are deemed to be a promising natural source for bioenergy production. Thus, incorporating nanotechnology into these alternative biomasses could greatly contribute to bioenergy production by acting as an aid to improve efficiency in various applications such as manufacturing, energy resources, transportation, mechatronics, health care and pharmaceutical technologies.

3.1. Lignocellulose for Conversion of Cellulose to Biofuel

The conversion of cellulose to biofuels faces some difficulties such as the recalcitrant structure of cellulose and the rigidity of the cell wall from lignocellulose biomass. The preliminary step involves depolymerization of cellulose polymer into its monomers, delignification of cellulose into cellulolytic enzymes, hydrolysis of cellulolytic enzymes into carbohydrates and fermentation of hydrolyzed sugars into biofuel production [24]. In some cases, enzymatic hydrolysis and fermentation (e.g., simultaneous saccharification (SS), simultaneous saccharification and co-fermentation (SSCF) and consolidated bioprocessing (CB)) were combined to reduce the major steps involved in biofuel production from lignocellulose biomass.

A study has shown the capabilities of nanotechnology where acid-functionalized magnetic nanoparticles (MNPs) are used as catalysts to hydrolyze the cellobiose (β-glucose) from lignocellulose biomass [25]. However, the disadvantage of the dispersion from some nanoparticles is the difficulty to disperse in the aqueous solution where the hydronium ions were ineffective in the solution due to the wettability of the sample. The results showed that the acid-functionalized MNPs with 6% of sulfur content achieved cellobiose conversion up to 96.0% more than the conventional conversion (32.8%) without catalyst [25]. The presence of these acid-functionalized MNPs could enhance the hydrolysis reaction by their nanobiocatalyst properties for the immobilization of different enzymes. Aside from that, the high surface-to-volume ratio of these MNPs facilitates the rate of hydrolysis compared to the chemical pretreatment approach. Likewise, the separation of these magnetic nanoparticles can be recycled for the subsequent hydrolysis process which is more preferable in minimizing the process cost as they can be separated from the reaction medium magnetically. This was supported by Lai et al. [26] and Erdem et al. [27] who demonstrated the sulfonate-supported silica MNPs for the hydrolysis of lignocellulose biomass which was deemed as a promising hydrolysis catalyst.

The presence of the silica-coated on the MNPs accelerates the mass transport in the acidic reaction due to its relatively porous structure and higher stability of the magnetic core. On the other hand, propyl-sulfonic acid-functionalized MNPs were subject to pretreatment and hydrolysis of wheat straw lignocellulose biomass, however the efficiency was not as promising compared to the above studies [25]. Recent technologies using microwaves-, ultrasonication- and electricity-assisted approaches are also recommended to be explored in the field of nanotechnology. A study by Su et al. [28] has demonstrated the potential of incorporating microwave-assisted technology with carbonaceous acid MNPs for the pretreatment and hydrolysis of sugarcane bagasse, *Jatropha* hulls and *Plukenetia* hulls. The hydrolysis performance obtained for sugarcane bagasse, *Jatropha* hulls and *Plukenetia* hulls was 58.3%, 35.6% and 35.8%, respectively. Table 2 summarizes the efficiencies of the MNPs for the hydrolysis of lignocellulose biomass.

Table 2. Comparison studies on the efficiencies of magnetic nanoparticles.

Magnetic Nanoparticles (MNPs)	Biomass Strain	Operating Condition	Yield (%)	References
Sulfonate-supported silica MNPs, FE_3O_4-SBA-SO_3H	Amorphous cellulose	1.0 g, 15 mL H_2O at 150 °C for 3 h	50	[26]
Sulfonate-supported silica MNPs, FE_3O_4-SBA-SO_3H	Cellulose	1.0 g, 15 mL H_2O at 150 °C for 3 h	26	[26]
Sulfonate-supported silica MNPs, FE_3O_4-SBA-SO_3H	Starch	1.0 g, 15 mL H_2O at 150 °C for 3 h	95	[26]
Sulfonate-supported silica MNPs, FE_3O_4-SBA-SO_3H	Corn cob	1.5 g, 15 mL H_2O at 150 °C for 3 h	45	[26]
Perfluoroalkylsulfonic MNPs, PFS-MNPs	Wheat straw	2.5% (*w/w*) biomass, 160 °C for 24 h	66.3 ± 0.9	[25]
Alklysulfonic MNPs, AS-MNPs	Wheat straw	2.5% (*w/w*) biomass, 160 °C for 24 h	61.0 ± 1.2	[25]
Carbonaceous acid MNPs, C-SO_3H-Fe_3O_4-MNPs	Sugarcane bagasse	0.027 g, 15 mL H_2O, 160–200 °C (0.5–2.2 MPa) for 3 min	58.3	[28]
Carbonaceous acid MNPs, C-SO_3H-Fe_3O_4-MNPs	*Jatropha* hulls	0.027 g, 15 mL H_2O, 160–200 °C (0.5–2.2 MPa) for 3 min	35.6	[28]
Carbonaceous acid MNPs, C-SO_3H-Fe_3O_4-MNPs	*Plukenetia* hulls	0.027 g, 15 mL H_2O, 160–200 °C (0.5–2.2 MPa) for 3 min	35.8	[28]

Yet, the limitation of MNPs has evolved nanobiocatalysts through using silica-based NPs (Si-NPs), nickel-based NPs and carbon nanotubes. Si-NPs are usually coated on the surface of the nanoparticles which functions to immobilize a lignocellulolytic enzyme such as cellulase. It has been reported that Si-NPs improved the catalytic activity in the simultaneous saccharification reaction for bioethanol production from *Trichoderma viride* cellulase [29]. Factors such as particle size, pore size and surface area are also crucial points as stated by Chang et al. [30], who evaluated two mesoporous silica NPs (MS-NPs) on commercial cellulose. These MS-NPs have the chemical binding ability to immobilized cellulase on their porous size surface for cellulose-to-glucose conversion up to 80%. Alternatively, nickel-based NPs (Ni-NPs) are also commonly used for the hydrogenation process for the conversion of glucose to a sorbitol molecule [31]. Gasification of biomass for the production of synthesis gas, also known as syngas ($CO + H_2$), can be useful as their intermediates can be further converted into biofuels. Subjecting these unstable enzymes into a high operating temperature and pressure catalytic processes would result in a lower productivity yield of biofuels. Another study has shown the use of nickel-cobaltite NPs on the stability of *Aspergillus fumigatus* cellulases at different concentrations of synthesized NPs. The results showed that the addition of 1 mM of nickel-cobaltite NPs increased enzyme activity of endoglucanase, β-glucosidase and xylanase by 49%, 53% and 19.8%, respectively [32]. Contrast to these, carbon nanotubes (CNTs) are widely known for their attractive features in electricity, thermal properties and mechanical strength [33]. Most studies have reported that multi-walled carbon nanotubes (MWCNTs) performed more effectively than single-walled carbon nanotubes (SWCNTs) as the immobilization of enzymes is compatible with their structural arrangement which enhanced catalytic activities of immobilized enzymes [33,34]. These MWCNTs outperformed the hydrolysis of cellulose from *Aspergillus niger* within 85%–97% efficiency and retained its recyclable activity at 52%–75% after six cycles of hydrolysis process [33,34].

3.2. Nanotechnology for Bioenergy Production from Microalgal Biomass

Microalgae are widely researched as the third-generation biofuels feedstock with a diversity of photosynthetic species [35,36]. The ability of microalgae to grow in harsh environments, high carbon dioxide uptake and rapid productivity have made them an alternative biofuel feedstock. In addition, the composition of microalgae which is rich in proteins, carbohydrates, lipids and carotenoids makes them an excellent choice compared to lignocellulosic biomass [37]. However, these microalgae-based biofuels face some challenges such as being difficult to manage in industrial-scale production, in addition to the high cost for biomass production and harvesting, which requires efficient technologies for biofuel conversion.

Previous studies have shown the feasibility of using MNPs for the hydrolysis of the microalgae cell wall by immobilizing cellulase on MNPs followed by lipid extraction [38]. Subjecting the immobilized cellulase to MNPs allows the microalgae cell wall composed of polysaccharide cellulose to be hydrolyzed for the release of lipid composition. Under optimal conditions, the maximum yield (93.56%) of biodiesel was achieved. A similar study also utilized MNPs replaced with metal-oxide MgO as an aid linked with the cellulase enzyme to improve the hydrolysis of cellulose from *Chlorella* sp. CYB2. The results showed that the glucose yield obtained was 91% performed by the mechanism of metal-oxides. Meanwhile, Nematian et al. [39] reported the use of superparamagnetic nano-biocatalysts for the conversion of bio-oil extraction from *Chlorella vulgaris* microalgae to biodiesel production. The results showed that the transesterification reaction using 3-aminopropyl triethylenesilane-glutaraldehyde (MNPs-AP-GA) was 69.8 wt %. The study also claimed that the covalent bonding of lipase showed a reliable method for improving enzyme loading and productivity. Apart from that, microwave-assisted with MNPs for the enhancement of biogas and biohydrogen production from microalgae were also studied. The biogas and hydrogen productions were 328 mL and 51.5%, respectively [40]. However, there is still a lack of study regarding the feasibility and economic analysis of these MNPs in large-scale production which is a gap to-be-filled for researchers dealing with nanomaterials.

4. Impacts of Nanomaterial for Enhancement of Biofuels Production

The development of nanomaterial has expanded by modification with different functionalized groups (e.g., amino-based, nickel-based, hydrophobic-based, gold-based) for the enhancement of biofuel production. Nanomaterials are also capable of improving these enzymes' activities by introducing it into the cultivation medium [41]. The properties of these nanomaterials have proven to generate stress during cultivation conditions such as high metal concentration (Fe), which affects lipid accumulation in *Chlorella vulgaris* microalgae [42]. Introducing these nanoparticles with silica and iron oxide composition in the cultivation medium would result in a strong sheer between the nanoparticles and the cell as these nanoparticles act as a competitor for nutrients uptake. In terms of extraction and recovery of lipids, these nanoparticles have also demonstrated excellent extraction ability to replace these conventional solvents (e.g., chloroform, methanol and hexane) in the extraction. The benefits of these nanoparticles are to prevent algae from dying and bring up the re-cultivation process from these extracted microalgae [43].

4.1. Nanomaterial Incorporation as Nanocatalyst in Microalgae Processing

These unique nanomaterials stimulate the photosynthesis growth of microalgae by inducing a mild stress condition for the accumulation of lipid without harming the cells. Several studies have implemented nanoparticles as a nutrient in the culture medium (e.g., iron and magnesium) [42]. The iron nanoparticles also generate various reactive oxygen species (ROS) via Fenton-type reaction which causes oxidative stress to the microalgae [44]. However, a study by Kang et al. [45] reported that a high concentration of TiO_2 nanoparticles in the presence of light would induce the viability of the cell. On the other hand, Mg-aminoclay nanoparticles have also been tested positively for the growth of *Chlorella* sp. KR-1 and *Chlorella vulgaris* as the amino clay nanoparticles are composed of metal cations such as Ca^{2+}, Mg^{2+} and Fe^{3+} covalent bonded on the center of the nanoparticles [46]. The supplement of $MgSO_4$-NPs has shown its enhancement activity in both photosynthesis and reduced glycerol consumption in the mixotrophic cultivation of *C. vulgaris* [47]. The implementation of $MgSO_4$-NPs induces the flocculation of microalgae by reducing the penetration of light, resulting in an increase of chlorophyll content.

The impact of these nanoparticles has also been applied as an enzyme immobilizer via covalent bonding for biodiesel production. The previous study has reported that *Porcine pancreas* lipase, *Candidarugosa* lipase and *Pseudomonas cepacia* lipase were subjected to amino-functionalized MNPs for enzymatic transesterification reaction and achieved a high conversion of biodiesel up to 67% [48,49]. A similar study also modified the amino-functionalized MNPs with a glutaraldehyde crosslinker which aided a higher immobilized lipase on the surface of the MNPs [50]. Results showed that the presence of this crosslinker coated on the MNPs was efficient to achieve a biodiesel conversion of 90% where the superior properties of glutaraldehyde activated the surface availability for enzyme immobilization. Aside from that, hydrophobic MNPs were also investigated for the transesterification of immobilized lipase to biodiesel. These hydrophobic MNPs have the ability to adsorb lipases or immobilize lipase on their hydrophobic interfaces by their lids and protein chains [51]. The conversion of extracted oil to fatty acid methyl esters was 70% along with a biodiesel production rate of 43.5 g/L/h under optimized conditions [52]. The enhancement and separation of C-phycocyanin from *Spirulina platensis* microalgae using a fabricated chitosan-modified nanofiber membrane has also shown a purification factor of 3.3-fold and 66% recovery, respectively [53]. The function of this fabricated chitosan-modified nanofiber membrane enables the coordination binding of contaminated proteins via electrostatic interaction by separating and purifying the targeted C-phycocyanin molecules during the separation process. A recent study by Cheah et al. [54] also utilized a fabricated chitosan-modified nanofiber on the antibacterial activity with *Escherichia coli* which exerted antibacterial activity up to 99.5% effectively. The presence of a polycationic charge from the fabricated chitosan-modified nanofiber membrane forms an electrostatic bond with the negatively charged site on a bacterium cell wall. This deformed the permeability of the cell wall due to the stress condition, hence leading to cell lysis and death. Other fabricated nanomaterials such as carbon nanotubes, mesoporous, nanofibers, electrospun nanofiber, ferric-silica and gold-based support were also incorporated as engineered nanoparticles to enhance the immobilization of enzymes for higher biofuel production [51,55,56]. Yet, there is still a lack of insight and studies regarding its optimized condition for an ideal immobilized enzyme for biodiesel conversion.

The controversy in utilizing nanomaterials especially carbon nanotubes (e.g., Al_2O_3, CuO, ZnO and TiO_2) faces challenges due to its toxicity to microalgae which covers oxidative stress, agglomeration and the inconsistent supply of nutrients and synthesis cost of these nanomaterials. In addition, on a molecular chemistry level, the internalization mechanisms of these functionalized NPs are still not clearly understood. This calls for researchers to further evaluate these problems where to date, the economic analysis, environmental safety and life cycle analysis (LCA) are subjects of interest as standardized processes are much more preferable for an appropriate assessment of these lacking issues.

4.2. Nano-Additives Blended Biodiesel in Diesel Engines

Nanomaterials have also been tested as nano-additives on fuel properties due to their distinctive properties of nanofluid which enhance various properties such as viscosity, flash point density, cetane number and many more. An experiment has evaluated the effect of physicochemical properties of biodiesel using metal-oxide NPs as a fuel additive [57]. The presence of these metal-oxide NPs acts as an oxygen buffer resulting in a simultaneous oxidation process of hydrocarbons by reducing the emission of oxides from nitrogen. Metal-oxide NPs exhibit a high surface-to-volume ratio that improves the fuel efficiencies of this biodiesel compared to those of a conventional powder form. The results showed that a higher dosage of these cerium oxide NPs increases the fluid layer resistance and viscosity where lower fuel viscosity is incapable of lubricating the fuel injection pump which will cause leakage and easily wear off, reducing the fuel delivery performances. Clearly, this showed that metal-oxides NPs are thermally stable to promote the oxidation of hydrocarbon and the reduction of nitrogen oxide.

The addition of nano-additives blended with fuel improves the cetane number and calorific value resulting in better performance of combustion. Studies have shown that aluminum- and silicon-based NPs improve the combustion quality of biodiesel engines [58]. This was also supported by another study using zinc oxide-based NPs diesel–pomoplion stearin wax biodiesel blends where the improvement of calorific value and cetane index were observed significantly [59]. Carbon nanotubes were also used by Singh and Bharj [60] who reported that the cetane index improves when the concentration of carbon nanotubes increases. Other nanoparticles such as iron oxide-based NPs were evaluated showing the benefits from these NPs in enhancing both cetane number and calorific value for an ideal combustion quality as well as reducing the emission release from diesel engines [61,62]. Nanofluids as additives are also promising for the improvement of brake thermal efficiency of diesel engines, as these additives promote complete combustion due to the higher evaporation rates, reduced ignition delay, high flame temperatures and lengthy flame sustenance [58,63]. Other effects such as carbon monoxide emission, hydrocarbon emission, NO_x emission, combustion and evaporation can be resolved by adding nano-additive blends into biodiesel fuel.

Despite its benefits, the major issues of NPs remain at the production cost that hindered the commercialization of nanofluids. Studies regarding NPs as fuel additives are still limited to be implemented at this point in time. Problems regarding nanoparticle aggregation, settling and erosion are yet to be resolved and this requires better characterization of nanofluids to boost its effective usage. On top of that, insufficient experimental results and poor understanding of the theoretical mechanism of heat transfer are the main points to be tackled before commercializing these nano-additives in diesel engines.

5. Bioelectrochemical System (BES)

Bioelectrochemical system (BES) is defined as the combination of biological and electrochemical processes, involving the use of electrochemically-active bacteria to degrade organic matters in various sources, such as industrial wastewater and biomass wastes [64,65]. The end products obtained are electricity, hydrogen or other valuable compounds such as ethanol, hydrogen peroxide (H_2O_2) and formic acid (CH_2O_2). BES is widely applied for wastewater treatment, and at the same time, the production of bioenergy. Therefore, BES is a promising technology for managing water pollution and global energy crisis [65]. Basic microbial fuel cells (MFC), photosynthetic MFC, plant MFC and biophotovoltaics [66] are examples of several forms of BES. Due to the simple operation and mild conditions, MFC nowadays attracts great interest from researchers worldwide as a new source of renewable bioenergy of the future.

5.1. What Is MFC

In 1911, Potter first came up with the idea of utilizing the microbes to produce electricity [67] followed by the development of first microbial half fuel cells by Cohen in 1931. MFC involves the electrochemical interactions between the microorganisms or electrogenic microbes and organic matters in which the electrons are transferred from the substrate to the anode electrode. This process is known as extracellular electron transport (EET) [68]. The electrogenic microbes are the microorganisms that serve as the main biocatalysts by transferring the electron produced from the metabolism of organic compounds to the electrode through a series of chemical reactions, for instance, c-type cytochrome or nanowires of the bacteria [69]. The examples of electrogenic microbes are bacteria (e.g., *Geobacter sulfurreducens*, *Shewanella putrefaciens*, *Clostridium cellulolyticum*, *Enterobacter cloacae*, *Rhodoferax ferrireducens*, *Clostridium butyricum*) and fungi (e.g., *Aspergillus awamori*, *Phanerochaete chrysosporium*) [70–73]. The microbes on the anode are responsible for generating electrons and protons by utilizing the organic substrates. The protons (H^+) produced will pass through the membrane and the electrons then flow through the electric circuit to the cathode at which oxygen reduction reaction (ORR) occurs [74,75]. As a result, bioelectricity is produced.

A typical MFC (Figure 1) is made up of two electrodes (anode and cathode) and a semi-permeable membrane known as the proton exchange membrane. Different types of materials such as metals have been used in the fabrication of electrodes. The most common materials for electrodes are carbon and graphite [64]. For the production of non-carbon based electrodes, the metals used are stainless steel, cobalt, copper, silver, nickel, titanium and gold [76]. There are some factors that affect the generation of bioelectricity by MFC including the surface area, stability, porosity, durability of the anode, cathode and membrane. The ideal electrodes should have the following characteristics [77]:

- Good electrical conductivity;
- Good thermal stability;
- Low resistance;
- Good biocompatibility with the system;
- Strong stability and anti-corrosion toward the chemical used in MFC;
- Large surface area;
- Good mechanical strength;
- Low cost.

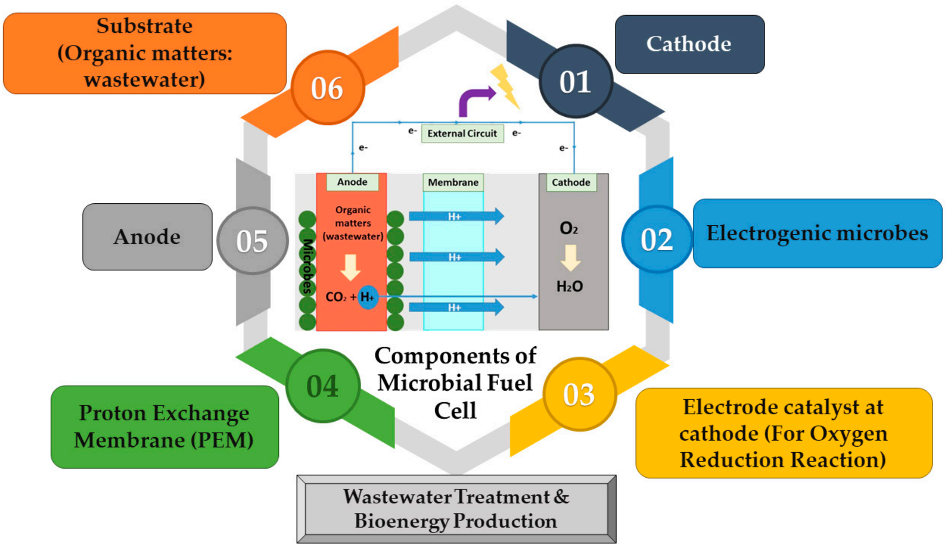

Figure 1. The component of microbial fuel cells (MFC).

The anodic chamber of MFC is made up of an anode, microbes (bacteria) and a substrate (wastewater) [66]. Being the most significant component of MFC, anode with the microbes attached to it allows the electrons flow via the electrochemical reactions of the microbes through the degradation of substrates. An essential aspect of the anode is the ability of the microbes to facilitate the formation of biofilms and increase the probability of EET to occur [66]. The most common materials used in the fabrication of anode are graphite or carbon that comes in various sizes or geometrics, for instance, carbon nanotubes, rods, felt, cloth, paper and plates [66,77–81]. On the other hand, the cathode is the electrode where the oxygen reduction reaction (ORR) will happen [75]. Overall, the ORR occurred at the cathode is the limiting factor of MFC and will affect the maximum power density, efficiency and performance of the entire MFC [66]. The catalysts have been integrated to improve the cathodic ORR [82]. The preferred cathode catalyst is platinum (Pt) due to high surface areas but the production cost is high [66]. Hence, graphite, which is cheaper than platinum, and possesses a large surface area is utilized as the cathode material to increase the efficiency of MFC [83,84]. Another component of MFC is the proton exchange membrane (PEM), a physical membrane that separates anode and cathode. There are various types of membranes that exist; for instance, cation or anion exchange membrane, nylon fibers, ultrafiltration membrane, microfiltration membrane, glass fibers and porous fabrics, but most of the membranes are not cost-effective [66]. This urges researchers to explore the low-cost material for use in the production of membrane and simultaneously increase its efficiency as the barrier between anode and cathode and proton transfer rate.

5.2. Modification of MFC Components with Nanomaterials

There are a few challenges that need to be addressed to produce bioenergy in pilot-scale by MFC. First, low power density that is insufficient to support a large population is the main bottleneck faced by MCF [85–88]. The maximum power density achieved by the conventional electrodes is about 26 mWm^{-2} for 3D graphite rods [89] or 611.5 ± 6 mWm^{-2} for 2D carbon cloth [90]. The performance of MFC is also affected by temperature as microbes cannot grow and carry out their activities at extremely low or high temperatures [91,92]. Thus, MFC needs to be conducted at an optimal temperature that is suitable for microbes. Besides, the complex, toxicity and high-cost process of manufacturing of components of MFC could hinder the practical applications and economical usage of MFC [93]. Therefore, researchers have been searching for a replacement or new materials in the production of the main components of MFC, such as anode, cathode and separator in order to improve performance and enhance the conductivity of electrons. Figure 2 demonstrates the advantages and disadvantages of MFC.

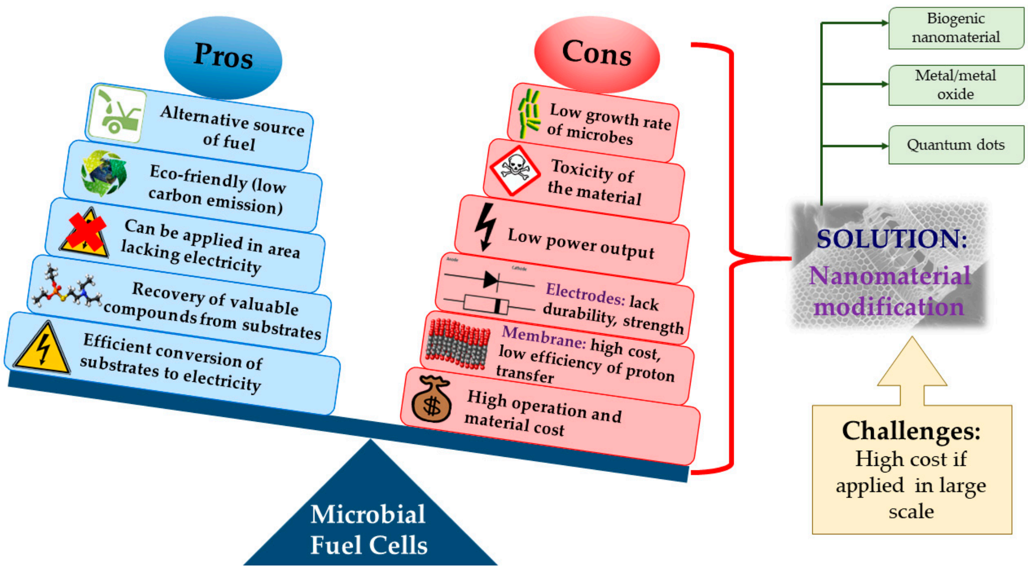

Figure 2. Advantages and disadvantages of microbial fuel cells (MFC).

Recently, nanotechnology or use of nanomaterial has revolutionized the fabrication of components of MFC to improve the performance and efficacy of traditional MFC in terms of electron conductivity, power density, cost, thermal stability, ORR rate and anti-corrosion [94,95], particularly the modification of electrodes (anode and cathode) by nanomaterials. This is because the materials used in the production of electrodes that are the major constituent of MFC are essential to determine the overall performance of MFC [96]. Thus, the production of bioenergy through MFC will be enhanced. The examples of nanomaterials for electrodes that will improve the function of MFC are metal nanoparticles (i.e., copper, gold, platinum, palladium and silver), quantum dots (i.e., Cds, CdSe, ZnS), metal-oxides (i.e., CeO_2, TiO_2, ZnO, SiO_2, Al_2O_3 and MnO_2) [93,97], graphene (2D-nanomaterials) [76], carbon nanotubes and nanocomposites (multiphase materials). However, the use of nanomaterials in the modification of components of MFC in the pilot-scale is still in progress of development due to the high production cost. Table 3 illustrates the examples of nanomaterials used in the modification of components of MFC.

Table 3. The use of nanomaterials in the modification of components of MFC.

Nanomaterial	Modified Part of MFC	Advantages	Description	Reference
Fabrication of bio-palladium nanoparticles using pure strain *Shewanella oneidensis* on carbon cloth	Anode	• Less chemicals required • Good biocompatibility • High catalytic activity • Simple and easy to be produced • Gentle reaction condition	The maximum power output and coulombic efficiency were improved by 14% and 31% as compared to unmodified anode.	[69]
Spinel type Ni-ferrite ($NiFe_2O_4$) modified composite anode	Anode	• High conductivity • Good reaction activity	As compared to control, the maximum power density achieved was increased by 26% and the internal resistance was lowered by 39%.	[98]
TiO_2 nanotubes (TN) on the surface of titanium anode	Anode	• Good biocompatibility • Stable and low cost • Resistance to corrosion • Can be synthesized in situ	The maximum current density achieved was 12.7 Am^{-2}, which was up to 190-fold as compared with bare titanium anode electrode.	[99]
Bimetallic core-shell gold-palladium nanoparticles as cathode catalyst	Cathode	• High durability • Low bulk resistance	High stability (can stable over 150 days), high durability and the power output produced was 15.98 Wm^{-3}, twice the power obtained with hollow structures-based platinum (Pt) cathodes (7.1 Wm^{-3}).	[100]
Fe_3O_4 nanoparticles/polyethersulfone (PES) nanocomposite membrane	Proton exchange membrane	• Eco-friendly • Low cost	High thermal stability and mechanical properties as well as the maximum power output produced was 9.59 mWm^{-2}, higher than commercial membrane.	[101]
Graphene oxide (rGO)/manganese oxide (MnO_2) composite on carbon felt surface	Anode	• Large surface area • High electric conductivity • Good electrocatalytic activity	The internal resistance was lowered, and maximum power density achieved was 2065 mWm^{-2}, 154% higher as compared with carbon felt anode.	[102]
Nickel oxide (NiO)/graphene nanocomposite with the addition of pectin into NiO	Anode	• Good conductivity • Appropriate pore size for movement of bacteria • Good ions accessible surface	The maximum power density achieved was 3.632 mWm^{-2}, higher than NiO anode and Pt/C anode.	[103]
Fabrication of two graphite based composite electrodes using graphene paste modified with TiO_2 (GP-TiO_2) or hybrid graphene (GP-HG)	Cathode	• Good electrocatalytic activity	The power density was increased above 80 mWm^{-2} for GP-TiO_2 and above 220 mWm^{-2} for GP-HG as compared to the control, graphite paste bare electrode (30 mWm^{-2}).	[104]

Table 3. *Cont.*

Nanomaterial	Modified Part of MFC	Advantages	Description	Reference
Polyaniline/graphene modified carbon cloth	Anode	• High electrical conductivity • Eco-friendly • Simple and easy	The maximum power density achieved was 884 ± 96 mWm^{-2}, 1.9 times higher than the unmodified carbon cloth anode (454 ± 47 mWm^{-2}). The voltage achieved was 573 ± 37 mV, higher than CC anode, 454 ± 34 mV.	[105]
Fabrication of polyaniline hybridized disorderly large mesoporous carbon nanocomposite with aid of nanoparticles, $CaCO_3$	Anode	• Low cost • High electric conductivity • Good electrochemical activity	The maximum power density obtained was 1280 mWm^{-2}, 1.5-fold and 10-fold higher than LMC anode (878 mWm^{-2}) plain carbon cloth anode (127 mWm^{-2}).	[94]
Nitrogen-doped carbon nanotube/reduced graphene oxide (rGO) composite with polyaniline as nitrogen source	Anode	• Good electric conductivity • Biocompatible • Stable	The power density achieved was 1137 mWm^{-2}, 8.9 times higher than carbon cloth anode.	[106]
3D graphene macroporous scaffold anode	Anode	• Large surface area • Good electrical conductivity	The MFC system was able to accommodate a high population of microbes and the power density achieved was 5.61 Wm^{-2}/11220 Wm^{-3}, 3-fold higher than planar 2D control counterparts. The highest power achieved was 3320 Wm^{-3}.	[107]
Graphene material ($RGO_{HI\text{-}AcOH}$) and graphene nanoparticles composite (RGO/Ni) as cathode catalyst	Cathode	• Large surface area • Eco-friendly	The power generated was 1683 mWm^{-2} and had good stability (can operate for 30 days and around 27 cycles) as compared to non-metal cathode MFCs.	[93]
Integration of carbon nanotube-gold-platinum nanomaterial with osmium redox polymer and *Gluconabacter oxydans* DSM 2343 in carbon felt electrode	Anode	• Stable • Can be reused for long time	The maximum power density and current density achieved were 32.1 mWm^{-2} and 1032 mAm^{-2}, respectively, showed the improvement of the system.	[108]

6. Future Works

To develop a cost-effective system of bioenergy production, a techno-economic assessment must be carried out with consideration on the cost of nanoparticle synthesis which can influence the overall production process. This also emphasizes the development of economically viable nanoparticles to make the whole process economically feasible for commercialization. Pilot-scale research is necessary to examine the viability of incorporating nanoparticles on a large-scale bioenergy production basis. Furthermore, future researches are not limited to sources and production of bioenergy where nanotechnology could address the technical limitations in science and engineering by contributing to areas of transformation, transportation, energy efficiency and storage, as well as the use of bioenergy end-product [11]. Apart from that, there are still limited studies on using NPs as fuel additives up-to-date where approaches to solving nanoparticle aggregation, erosion and settling are still required. There is a lack of practical results and an understanding of heat transfer mechanisms to commercialize these nano-additives in diesel engines. In addition, safety assessment must be carried out because nanoparticles have demonstrated obvious exposure effect in terms of human and environment with the increasing use in biofuel applications. The toxicity of nanoparticles has been examined using several approaches wherein in vitro investigation of nanotoxicity is mostly involved [109]. However, in vivo interaction should be studied extensively focusing on the nanoparticles particularly used to produce bioenergy as well as biofuel [21]. This also applies to microorganisms as nanoparticles that are safe, non-toxic and compatible with enzymes and microbes should be synthesized. For instance, NPs are toxic to microalgae as they result in agglomeration, oxidative stress and inconsistent nutrient supply. Therefore, screening studies of nanoparticles are required to investigate their broad range of concentrations with an influence on microbial and enzymatic activity. Research at the molecular level should be conducted to study the mechanism involving nanoparticles and proteins in the production process. Subsequently, the optimum process conditions of bioenergy production can be established.

7. Conclusions

The depletion of fossil fuels and intensive energy demand has motivated researchers to develop alternative energy sources. Among the renewable energy technologies, bioenergy from biomass has its unique advantages. To meet future energy requirements while overcoming the technological barriers of bioenergy production, incorporation of nanomaterials in bioenergy production has been investigated since it can improve both quality and quantity of bioenergy produced by biomass, biofuel and microbial fuel cells. The bioenergy production process can be enhanced by NPs in different approaches. Firstly, acid-functionalized MNPs could be used to improve the hydrolysis reaction of biomass using different immobilized enzymes. Furthermore, metal-oxide NPs have been tested as nano-additives to enhance the performance of combustion as well as the blending performance of biofuel and conventional diesel. BES, or more specifically MFC, which is widely employed for wastewater treatment and bioenergy production, has also been modified by fabricating its components with nanomaterials in order to promote better performance and efficacy. However, there are still technical gaps in the world of nanotechnology-based bioenergy, whereby there are limited studies on the application of NPs as fuel-additives, in vivo toxicity of NPs and molecular-scale mechanism of NPs-protein. Last but not least, economic analysis, safety assessment and life cycle analysis (LCA) on the incorporation of nanomaterials in bioenergy production are essential for providing insights and outlines for future research.

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Abbreviations

SS	Simultaneous saccharification
BES	Bioelectrochemical system
SSCF	Simultaneous saccharification and co-fermentation
CB	Consolidated bioprocessing
Si-NPs	Silica-based NPs
MS-NPs	Mesoporous silica NPs
EET	Extracellular electron transport
H+	Proton
Ni-NPs	Nickel-based NPs
MFC	Microbial fuel cells
NPs	Nanoparticles
MNPs	Magnetic nanoparticles
ORR	Oxygen reduction reaction
CNTs	Carbon nanotubes
MWCNTs	Multi-walled carbon nanotubes
SWCNTs	Single-walled carbon nanotubes
ROS	Reactive oxygen species
LCA	Life cycle analysis

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