Chapter 8
Nanotechnological Interventions for Sustainable Production of Microbial Biofuel and Bioenergy

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Abstract Energy plays a pivotal role in the socio-economic development of every country and serves as the backbone of any nation. However, a continuous increase in energy demand due to the ever-growing population and industrial globalization leads to a rapid depletion in sources of fossil fuels. In addition, the burning of fossil fuels has led to the emission of greenhouse gases which raised many environmental challenges such as climate change and global warming. All these concerns have pressed toward exploring sustainable and renewable energy sources in the form of bioenergies. Bioenergies mainly include the biofuels (bioethanol, biodiesel, bio-oils, bio hydrogens, methane, butanol, etc.) obtained from a variety of biological materials like biomass, algae, etc. Different conventional methods have been developed and routinely used for the production of second-generation biofuels. However, all such methods have certain limitations such as high energy demand and specialized processing equipment which ultimately escalate the associated cost. In this context, considering the widespread applications of nanotechnology in various fields including biofuel production, it is believed that the utilization of nanotechnology-based solutions would be promising alternatives. Application of different nanomaterials, particularly magnetic nanomaterials, in the development of nanocatalysts for biofuel production facilitates the easy recovery and reuse of the same nanocatalyst for multiple cycles which help to reduce the cost and make the process ecofriendly and economically viable. The present chapter mainly focuses on an overview of

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biofuels and different conventional methods available for the production of nanomaterials. Apart from these, a special focus has been given on interventions of nanotechnology in the sustainable production of biofuels. Moreover, other aspects such as challenges in the application of nanotechnology in biofuels production are also discussed briefly.

Keywords Bioenergy · Biomass · Nanotechnology · Nanomaterials · Sustainable · Renewable · Global warming

8.1 Introduction

Environmental pollution is one of the most serious global challenges that humanity faces, attempting to preserve biodiversity, ecosystems, and human health worldwide (Xu et al. 2018). This problem has intensified over the last few years, with an increase of industrial and transport activities,that uses fossil fuels (Covert et al. 2016). Burning fossil fuels (e.g., diesel, gasoline, or coal) emits air pollutants, such as nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and carbon dioxide (CO_2), which are released into the atmosphere (Mitchell et al. 2018). According to the NASA-Global Climate Change website (2020), the emission of these pollutant gases was strongly decreased, and the air quality was improved due to the recent lock-downs as a result of the spread of COVID-19. However, in a normal situation (Fig. 8.1), the accumulation of pollutant gases is worrying. One alternative to reduce the consumption of fossil fuels and, at the same time, mitigate the greenhouse effects is the use of alternative green fuels, such as hydrogen, biofuels (ethanol, biodiesel),

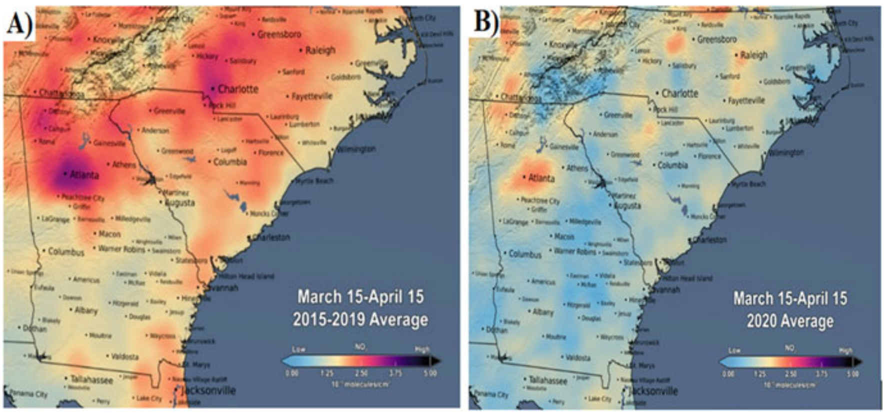

Fig. 8.1 Tropospheric NO_2 Column. (**a**) March 15–April 15, 2015–2019 Average and (**b**) March 15–April 15, 2020 Average, Southeast USA, With Cities. Pictures were obtained from the NASA-Global Climate Change website (2020)

fuel cells, etc. which have been extensively studied aiming to optimize their production in the pilot- or large-scale and their techno-economic viability.

Biofuels are classified as first- (ethanol, biodiesel, biogas, etc.), second- (bio-oil, lignocellulosic ethanol, butanol, etc.), third- (ethanol and biodiesel obtained from microorganism), and fourth-generation biofuels (biohydrogen, biomethane, and synthetic biofuels) (Itskos et al. 2016). Second-generation ethanol produced from lignocellulosic biomass has been extensively studied over the last few decades. According to the SCOPUS database, more than 500 articles on this topic have been published only in 2019 (SCOPUS 2020). Most of these studies have focused on the development of suitable and more efficient technologies for the deconstruction of recalcitrant biomass, the optimization of cellulose hydrolysis, and the optimization of the fermentation process. Recently, innovative technologies have attracted the interest of researchers. One of those is the promising use of nanoparticles in biofuel industries mainly due to their high surface area, reactivity, and functional properties, which promote the better performance of the process (Khan et al. 2019). In this context, to date various kinds of nanomaterials have successfully been used in different processes involved in biofuel production. For example, Ingle et al. (2020a, b) demonstrated the use of acid-functionalized magnetic nanoparticles (MNPs) for the pretreatment of lignocellulosic biomass. In another study, MNPs were used as support for immobilizing cellulase enzymes aiming at enzymatic hydrolysis of biomass (Gaikwad et al. 2018).

Nanotechnology has been applied in biodiesel and biohydrogen production processes, improving the recyclability of the catalyst and the performance of the process by increasing the activity and stability of immobilized enzymes such as lipases (Sarno and Iuliano 2019; Teo et al. 2019) or improving the stabilization of oil-in-methanol Pickering emulsions which can be used as interfacial catalysts in the transesterification reaction for biodiesel production (Peng et al. 2020). As already discussed in this section, the development of innovative technologies for biofuels production is a current challenge. Considering these facts, in the present chapter, we have discussed the concepts and applications of nanotechnology in biofuels production.

8.2 Biofuels: Green Alternative Fuels

A fuel produced using renewable biomass-based resources (plant biomass, microorganisms, or animal by-products) is referred to as a biofuel. Global biofuel production is mainly directed to the transportation sector and it is believed that an increase in the supply of these fuels is essential to assure both energy security and the reduction of greenhouse gas emissions (OECD/FAO 2019). According to Kamani et al. (2019), biofuels have the following benefits over fossil fuels:

- Biodegradability, renewability, and contribution towards a sustainable economy;
- Availability limited only by the amount of biomasses resources;

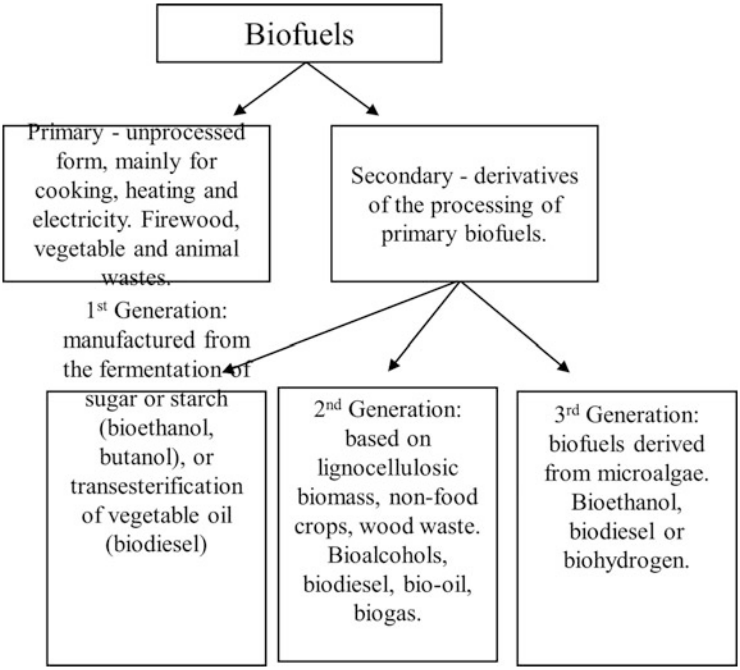

Fig. 8.2 General classification of biofuels (Source: Fatma et al. (2018), Kamani et al. (2018), Paul et al. (2019))

- Reduction of the environmental impacts related to agriculture wastes disposal;
- Lower impact on the environment as compared to fossil fuels.
- Achievement of energy security;
- Fortification of the economy by creating more opportunities related to agriculture and raising of agricultural incomes;
- Intensification of industrial investments;

Biomass is the important feedstock used for the production of the majority of biofuels (or biomass-based fuels) and is usually obtained through thermal, physical, or biological processes (Kamani et al. 2019). Despite a variety of definitions of biofuels found in literature, biofuels are generally classified by their chemical nature or are based on the feedstock source. Regarding their chemical nature, biofuels can be derived from alcoholic fermentation, from the esterification of vegetable oils or animal fat, or even from anaerobic digestion (Kamani et al. 2019; Roberts and Patterson 2014). Fig. 8.2 shows three generations of evolution of the feedstocks utilized for biofuel production.

8.3 Global Production of the Major Biofuels

Nowadays, approximately 10% of the world's total primary energy supply is represented by bioenergy, with a global production of 154 billion liters in 2018. Biofuels production is led by United States, Brazil, European Union, ASEAN, China, and India; it is mainly represented by bioethanol, biodiesel, and biogas, although other fuels exist in the state of solid (biochar), liquid (biobutanol, biomethanol, bio-oil, 2,5-dimethylfuran) or gas (biohydrogen) (Sindhu et al. 2019).

Bioethanol production relies on the alcoholic fermentation of plant biomass performed by yeasts. Globally, the most used crops for bioethanol production are corn, sugarcane, cassava, sugar beets, wheat, and other grains. Since bioethanol is mainly used for transportation, this biofuel offers an excellent opportunity to reduce the utilization of crude oil and to scale down CO_2 atmospheric accumulation, an imperative maneuver to mitigate the negative effects of the climatic crisis upon the environment and our society and economy (Kamani et al. 2019).

Biodiesel has originated from the transesterification of natural lipids present in plants such as soybean, rapeseed, canola, palm and corn, waste oils, or animal fat (Carvalheiro et al. 2008). Algae are especially suitable for biodiesel production due to their ability to consume atmospheric CO_2 to produce large amounts of oil: on a dry basis, the lipid content of microalgae biomass is between 20 and 50%, but under certain conditions, it can reach nearly 80% (Kamani et al. 2019; Nobre et al. 2013).

In the case of biodiesel, emissions of non-combusted hydrocarbons or CO are lower than conventional diesel as well as there is no sulfur or aromatic compounds in its composition. Furthermore, this biofuel outstands regarding its potential for industrial scale-up and has been broadly marketed in numerous countries such as the United States, European countries, Brazil, and Australia (Beschkov 2012; Kamani et al. 2019).

Biogas, on the other hand, is produced by the anaerobic digestion of biological wastes using microbes. Its main component is methane (50–80%) and minor constituents are CO_2 (30–50%), CO, H_2S, nitrogen, oxygen, hydrogen and ammonia (Chen et al. 2015). Agricultural waste treatment generates expressive volumes of biogas, which has a great heating power and can be used for heat or electricity generation and, in specific cases, for internal combusting engines (Beschkov 2012; Kamani et al. 2019). Besides biogas, biohydrogen is another important biofuel generated from gasification of biomass. Several studies have been done toward the sustainability of biohydrogen production. It is considered that the generation of a coproduct simultaneously with biohydrogen from biomass is a path to ensure the economic viability of the process (Sindhu et al. 2019). The production of important biofuels using conventional approaches has been discussed in the following section.

8.3.1 Bioethanol

Through the expansion of modern biorefineries concept and the exploitation of renewable bio-based fuels, the world's demand for more environmentally friendly, less hazardous, and sustainable sources of energy has become one of the major targets for a prosperous and ecological future (Boboescu et al. 2019). In accordance with this fact, bioethanol has been a long-studied biofuel worldwide and a variety of carbon sources have been utilized for its production. For instance, several countries such as India, Brazil, the USA, and many others have been applying crops for ethanol generation although from different raw materials comprising mainly sugarcane molasses, sugarcane stalk juice, and corn, respectively (Soam et al. 2018; Costa et al. 2015; Cheng and Timilsina 2011). On the other hand, using food crops as a source for biofuel production is considered first generation (1G) and competition may intensify between food and energy supply, thereby increasing the prices in the food market which can become a global issue (Lazar et al. 2018).

A solution to this problem is the substitution of the direct use of crops for agricultural wastes and food wastes such as lignocellulosic materials (e.g., sugarcane bagasse, wheat straw, corncob, rice straw, etc.) (Banerjee et al. 2010). For several years, these materials were considered as wastes but due to extensive efforts of scientists and researchers, now these materials can be utilized for the production of high-value products. Therefore, lignocellulosic biomasses represent one of the possible substrates for second-generation (2G) ethanol and biofuels in general. To summarize the key role of agro-wastes implementation, Table 8.1 briefly displays a variety of industrial bioproducts which have an overwhelmingly positive impact on realistic environmental problems.

Keeping this in mind, it is of great importance to comprehend how the substrate may influence the overall process of bioethanol synthesis. In the case of lignocellulosic materials, it is well known that its compact structure is a rigid and complex mixture of polysaccharides and a macromolecule is composed of cellulose (30–50%), hemicellulose (25–30%), and lignin (10–35%), respectively (Spyridon and Willem Euverink 2016). In brief, cellulose is a linear glucose polymer-bonded within ß-1,4-glycosidic linkages that provides a high degree of crystallinity due to the extensive hydrogen bonds among the hydroxyl groups, whereas hemicellulose is a heteropolymer of a short and highly branched chain of pentoses, hexoses sugars, with some traits of organic acids (Limayem and Ricke 2012). Furthermore, the macromolecule lignin is composed of 4-hydroxyphenylpropanoid units which are considered its precursors. These units are linked throughout the chain via ether (C-O-C) and carbon (C-C) bonds. Furthermore, its arrangement acts as a protection structure and ensures entrapment of the restrained molecules in accordance with the degree of entanglement among the polysaccharides and lignin (de Gonzalo et al. 2016).

These components are linked tightly together to form a recalcitrant structure to hydrolytic attack and non-readily bio-digestible biomass (Bugg et al. 2011). To

Table 8.1 Bioproducts synthesized using different lignocellulosic carbon sources

Biomass	Microorganism	Process technique	Product	Reference
Corncob hydrolysate	*S. bombicola* NBRC 10243	Submerged fermentation	Biosurfactant	Konishi et al. (2015)
Opuntia ficus-indica cladode	*Kluyveromyces marxianus*	Submerged fermentation	Ethanol	López-Domínguez et al. (2019)
Digestate (bio-waste)	*Bacillus thuringiensis*	Solid-stated fermentation	Biopesticide	Cerda et al. (2019)
Agave bagasse hydrolysate	*Yarrowia Lipolytica*	Submerged fermentation	Lipids	Niehus et al. (2018)
Sugarcane bagasse hydrolysate	*C. guilliermondii* FTI 20037	Submerged fermentation	Xylitol	Sarrouh and da Silva (2010)
Elephant grass	*S. cerevisiae* CAT-1	Submerged fermentation	Ethanol	Scholl et al. (2015)
Apple pomace	*A. niger* NRRL-567	Solid-state fermentation	Cellulase	Dhillon et al. (2012)
Pulp and paper solid waste	*Rhizopus oryzae* 1526	Solid-state fermentation	Fumaric acid	Das et al. (2016)
Olive pomace	*Xantophylomyces dendrorhous*/*Sporidiobolus salmonicolor*	Solid-state fermentation	Pigment (astaxanthin)	Eryılmaz et al. (2016)
Wheat straw	*Bacillus* sp. BBXS-2	Solid-state fermentation	Amylase	Qureshi et al. (2016)

enhance microbial digestibility, a wise step pretreatment is required to depolymerize, reduce the degree of crystallinity of cellulose and hemicellulose as well as remove the lignin fraction. Moreover, the disruption of the fibers also reduces its compactness which, in turn, facilitates microbial accessibility to the fermentable sugars (Rastogi and Shrivastava 2017; Hendriks and Zeeman 2009). The bottleneck of 2G bioethanol relies significantly on the pretreatment features and progress. Thus, to analyze whether the overall process is having a negative impact and to quantify energy requirements and greenhouse gases emission, currently, there are practical tools such as life cycle assessment (LCA) that evaluates environmental issues in any step of biofuel production, including measurement of downstream processing and waste materials generation (Cherubini et al. 2009; Dadak et al. 2016).

In alignment with the strategy of minimizing the deleterious effects of rendering the pretreatments of lignocellulosic biomass, several methods have been developed from the necessity to mitigate the excessive use of chemicals and energy. In this respect, pretreatment assays may be carried out by a variety of approaches, including chemical, physical, physicochemical, and biological. Each technique aims to exert distinct effects on the biomass having inherent advantages and disadvantages. The most common ones are mechanical comminution, irradiation, acid (sulphuric or hydrochloric acid), alkali (such as calcium hydroxide), steam explosion, or combined processes that demand large energy input and high-cost equipment utilization (Kumari and Singh 2018; Ruane et al. 2010). Likewise, biological pretreatment is based on the natural ability of microorganisms to degrade lignin via enzymatic performance in a step termed delignification. The cultivation and growth of the targeted cells may be performed under submerged or solid-state fermentation (Zabed et al. 2017; Yahmed et al. 2017; Mishra et al. 2017).

The aforementioned techniques are prerequisites to increase the availability of cellulose and hemicellulose for enzymatic hydrolysis necessary to the conversion of those into their respective fermentable sugars (Lamb et al. 2018). Specific enzymes can hydrolyze cellulose and hemicellulose to selectively release their monomeric sugars in relatively low temperatures ranging from 45 to 50 °C by the active sites of cellulases and hemicellulases (xylanases), respectively (Duff and Murray 1996). In summary, cellulase is a cocktail of enzymes that exert desirable effects onto cellulose molecules and typically involves the synergistic action of endoglucanase, exoglucanase, and ß-glucosidase (Sun and Cheng 2002). Endoglucanase is responsible to hydrolyze internal (ß-1,4) glycosidic bonds throughout the D-glucan polymer chain, producing cellodextrins out of the amorphous regions of cellulose, thereby releasing free chain ends, whereas exoglucanase cleaves cellobiose and cellotriose units from the non-reducing terminal. The response to this system generates dimers termed cellobiose as an output which is a disaccharide of glucose that is consecutively converted into glucose by the selective action of ß-glucosidase (Dotaniya et al. 2019; Zabed et al. 2017). To give a more illustrative representation of the cellulase mechanism, Fig. 8.3 displays the summarized dynamics of cellulose degradation according to the selectivity of each enzyme required.

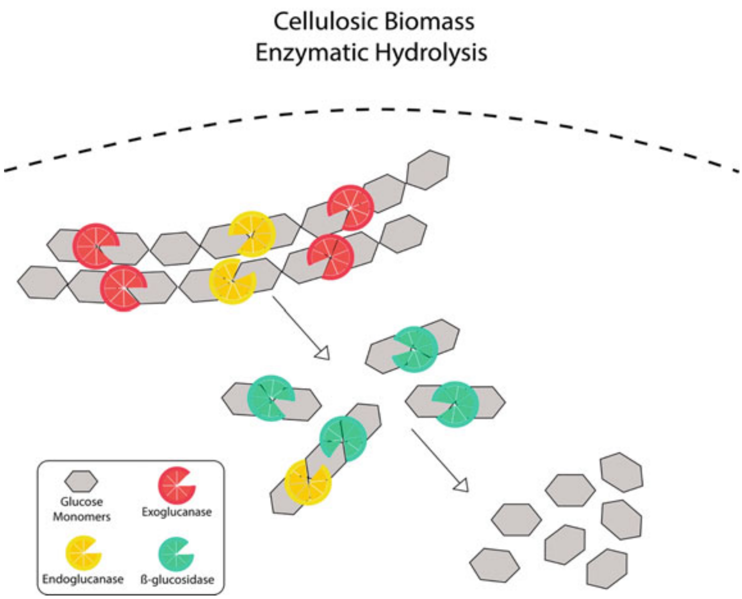

Fig. 8.3 Schematic representation of cellulose hydrolysis by cellulase catalysts

The enzymatic machinery to break down the heteropolymer hemicellulose is quite more complex due to its branched-chain and the specificity of the internal bonds. Therefore, the xylanase (hemicellulase) system contains usually endoxylanase, exoxylanase, ß-xylosidase, α-arabinofuranosidase, α-glucoronisidase, etc. Similarly, endo- and exo-xylanases catalyze selectively the breakdown of the main chain of xylans resulting in reduced size chains. Furtherly, ß-xylosidase cleaves xylo-oligosaccharides into xylose. The other enzymes rather act on the backbone of the xylan polymer and are responsible for the release of arabinose and 4-o-methyl glucuronic acid (Saha 2003).

The resulting concentration of pentoses and hexoses may vary according to the preceding pretreatment and the type of enzymes implied along with the hydrolysis. Therefore, the fermenting microorganism must be suitably selected in order to obtain maximum yield and productivity as well as avoid unwanted catabolic repression by the substrates and inhibitory compounds (Banerjee et al. 2010). The ability to co-assimilate C5 and C6 sugars is crucial for any bioethanol facility plant. For instance, the utilization of *Saccharomyces cerevisiae* and *Zymomonas mobilis* is frequently common to produce ethanol from hexoses; however, their inability to concomitantly consume pentoses delays the development of more robust processes. On the other hand, organisms that can ferment pentoses (e.g., *Pichiastipitis*, *Pachysolenthannopilus*, *Candida shehatae*) offer very low efficiency in the conversion factor (Hahn-Hägerdal et al. 2007). Yet, within the advances in metabolic engineering tools, pertinent efforts toward genetically modified microorganisms attempt to address this issue and to enhance co-assimilation of C5 and C6 sugars (Wackett 2011).

Contemporarily, fermentation processes may be carried out by several approaches including Separate Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF), Simultaneous Saccharification and Co-Fermentation (SSCF), and finally, a Consolidated Bioprocess (CBP) (Rastogi and Shrivastava 2017). SHF consists of rendering a two-stage process, wherein enzymatic hydrolysis is operated separately from fermentation. Albeit sugar accumulation throughout hydrolysis inhibits enzyme activity, positive aspects are encountered in this strategy, involving the implementation of optimal operation conditions of each stage (Vohra et al. 2014). SSF offers advantageous features such as reduction of inhibitors, less energy demand, and is economically attractive. It is performed simultaneously with the hydrolysis step at the same unit which in turn prevents undesired effects of sugar accumulation, thereby obtaining a higher ethanol yield conversion if compared to SHF (Foust et al. 2009; Brethauer and Wyman 2010).

Moreover, SSCF integrates C5 and C6 sugar assimilation into only one stage. By that, different methods may be reliable to concretize this operation which involves the use of a consortium of organisms having distinct metabolic pathways consuming synergistically both carbon sources. However, hexoses consumers grow faster, and it may lead to growth inhibition of pentose-utilizing microorganisms. Furthermore, one single bacteria or yeast may be genetically modified to efficiently incorporate C5 and C6 substrates rather than the use of capable natural-born wild strains that frequently lead to lower ethanol productivity (Sanchez and Cardona 2008).

Nevertheless, CBP is a robust attempt to integrate cellulolytic enzymes excretion, saccharification, and fermentation at the same operation step mediated uniquely by a microorganism community. The advantages rely strongly upon the fact that expenditures associated exclusively with enzyme production are avoided by combining those steps mentioned above. Aside from that, saccharification and fermentation are entirely compatible regarding operational parameters (Vohra et al. 2014). To gain insight, López-Domínguez and collaborators (2019), investigated the capability of *Acinetobacter pittii* and *Kluyveromyces marxianus* isolated from *Opuntia ficus-indica* toward decay of cladode to produce cellulase and simultaneously saccharify the targeted biomass and synthesize ethanol. The novelty of this study was the utilization of wild strains which possess naturally metabolic machinery that can achieve significant and promising yields of bioethanol in the near future.

To summarize, there is a broad scientific avenue favorable to the development and implementation of diverse techniques in the enzymatic and bioprocessing fields. The substitution of regular fossil fuels for biofuels still to some extent lacks optimization and cost-effectiveness. Therefore, further discussion in this chapter attempts to introduce the role of nanotechnology in enzymatic hydrolysis enhancement and bioconversion of ethanol.

8.3.2 Biodiesel and Biohydrogen

Nowadays, alternative energy resources such as wind, solar, and biofuel have grabbed the attention of scientists, researchers, and governments due to the rapid consumption of fossil resources, global climatic change, and the interest in more secure fuel supplies (Semwal et al. 2011; Chozhavendhan et al. 2020). Among renewable sources of energy, biodiesel has been considered a notable candidate to reduce environmental pollution and achieve sustainable development (Mahlia et al. 2020).

Biodiesel is typically produced through the transesterification process, in which triglycerides react with an alcohol in the presence of a catalyst to obtain mono-alkyl esters. These triglycerides may be obtained from micro-and macro-algae, fungi, animal fat, and vegetable oil, lignocellulose material, etc. (Sharma et al. 2008; Mahmudul et al. 2017). Since methanol is the most frequently used alcohol due to its low cost, other common names for biodiesel are fatty acid methyl esters (FAME) or B100, which means 100% FAME (Singh et al. 2020).

Biodiesel has many advantages such as it is eco-friendly, non-toxic, biodegradable; has a low emission profile, and is a renewable energy resource (Avhad and Marchetti 2015). In this sense, biodiesel is usually classified as first-, second-, and third-generation based on the raw materials used in its production. First-generation biodiesel is derived from edible feedstocks such as soybean oil, coconut oil, rapeseed oil, palm oil, sunflower oil, etc. (Mahdavi et al. 2015), while second-generation biodiesel is obtained from agricultural wastes and non-edible feedstocks such as neem oil, jatropha oil, nagchampa oil, karanja oil, etc. (Atabani et al. 2013). However, these categories generate conflict between land use and food supply (Mahlia et al. 2020). The case of third-generation biodiesel involves the use of high oil-content microalgae further alternate sources for biodiesel production (Leong et al. 2018). Moreover, a fourth classification has emerged from the metabolic engineering of photosynthetic organisms, which has been transformed through synthetic biology tools as another sustainable alternative (Chua et al. 2020).

On the other side, the biological production of hydrogen (biohydrogen) is another alternative that fits well with the renewable energy concept. Among known fuels, hydrogen has the highest gravimetric energy density and is compatible with electrochemical processes (Mudhoo et al. 2011). The conventional method of hydrogen generation is based on steam reforming or oxidation of natural gas and coal gasification. However, these primary sources for the production of hydrogen are nonrenewable and release carbon dioxide as a byproduct, which creates an environment negative effect (Hibino et al. 2018).

Thus, the sustainable production of hydrogen through biological routes such as photobiological and fermentative processes has been reported as a different approach (Rupprecht et al. 2006; Srivastava et al. 2020). Moreover, the generation of biohydrogen has also been reported through the combination of different methods. The advantages of these alternative processes include the production of hydrogen from renewable sources and the generation of emissions free of pollution (Singh et al. 2015; Sampath et al. 2020). The microorganisms involved in biohydrogen production are classified into two groups: photosynthetic and non-photosynthetic or fermentative hydrogen producers (Das and Veziroğlu 2001). Also, metabolic engineering has been an exceptional tool for improving the hydrogen productivity of available microbial sources rather than discover new strains (Chandrasekhar et al. 2015).

In the case of photobiological hydrogen production which includes bio photolysis, indirect bio photolysis, and photo fermentation, solar radiation is the driving force for the process. Among the microorganisms that are best suited for this light-dependent hydrogen production are some species of bacteria (purple-sulfur, and purple non-sulfur), algae, and cyanobacteria (Barbosa et al. 2001; Kovács et al. 2006). On the other hand, in dark fermentation or fermentative hydrogen production, the obligate anaerobes and the facultative anaerobes have been explored as producers for this purpose. The absence of energy light is the striking feature of this process. Since agricultural waste and organic waste generated from domestic and industrial activity can be decomposed through dark fermentation to produce hydrogen, this process is a particularly advantageous alternative (Guo et al. 2010; Łukajtis et al. 2018).

Thus, microbial electrolysis cells (MEC) represent a versatile technology for waste treatment processes. They were adapted from microbial fuel cells (MFCs) and the conversion of a wide range of organic substrates into hydrogen occurs under applied external potential (Cheng and Logan 2007; Chandrasekhar et al. 2015).

However, the microbial physiology, electrode materials, physicochemical transport processes, type of membrane used, and composition and concentration of the substrate are important factors that affect the performance of MEC and limit its commercial distribution (Hallenbeck 2011).

8.4 Limitations of Existing Conventional Methods

Though biofuels comprise a wide variety of energy sources derived from biomasses, such as bioethanol, biodiesel, biogas, biomethanol, bioethers, biohydrogen, and vegetable oils, the market seemed to be mainly focused on the first 3 i.e. bioethanol, biodiesel, biogas (Callegari et al. 2020). Currently, marketable biofuels are mostly produced from first-generation crops, which have similar drawbacks, related to limited availability and food competition, and, therefore, make room for second and third-generation feedstocks (Callegari et al. 2020). Among the second generation, biofuels derived from lignocellulosic byproducts and residues, driven by economic, environmental, and even social-political purposes have been widely explored in the last decades. Feedstocks have been selected based on their sustainability, energy content, local availability and distribution, and environmental and economic values (Karagiannidis and Perkoulidis 2009). Challenges related specifically to the feedstock have been addressed since their cost is an important issue in biofuels production technologies, such as new varieties with desirable characteristics, growing requirements, cultivation yields planting and harvesting techniques, and logistics, among others (Callegari et al. 2020; Shanmugam et al. 2020).

Extensive research has enabled important advancements in the processes for biofuels production from biomasses; however, there are still important technological barriers to overcome and to make them mature for commercial scale and competitive with fossil fuels (Khoo et al. 2020a, b). In this sense, the cost-effective release of fermentable carbohydrates from biomasses is one of the biggest challenges on biofuels production, with a high impact on the total process cost (Ingle et al. 2019a, b; Khoo et al. 2020a, b). The upstream steps include mainly biomass pretreatment and further hydrolysis of polymeric carbohydrates to release fermentable sugars, for which several methods, involving chemical, physical, biological methods and mixtures of them have been extensively studied. Despite the promising results obtained at laboratory and pilot scales with the conventional methods, the high cost jeopardizes their potential utilization at larger scales (Ingle et al. 2019a, b; Shanmugam et al. 2020). Most of the conventional methods are performed in intensive operation conditions, with high consumption of materials that are not recycled or are difficult to be reused, and generation of contaminating by-products and wastes, resulting in processes that are not economic and environmentally sustainable (Ingle et al. 2019a, b).

Particularly, in the polysaccharide (cellulose) hydrolysis after pretreatment, enzymatic technologies have been extensively studied, in order to increase hydrolysis efficiency and reduce enzyme-associated costs. In the technologies that have been mostly studied, enzymes cannot be reused or recycled, which increases the cost of this step and consequently of the process. Therefore, several studies have been focused on enzyme immobilization, in order to facilitate the separation of the enzymes and/or their reutilization in various sequential reactions, which, in turn, can reduce the overall process cost (Shanmugam et al. 2020).

In the particular case of biodiesel production, enzymatic transesterification is a remarkable alternative, since it is a less energy-intensive strategy, with higher selectivity, easier separation, less residual contamination when compared to chemically catalyzed processes. However, it has a main drawback also about the high cost associated with enzymes, which reduces its attractiveness to industrial applications (Callegari et al. 2020). Regarding biohydrogen production, which has been considered as the most efficient and cleanest form of energy, it still has important drawbacks to be addressed to achieve higher levels of readiness, such as low yield and high production cost (Shanmugam et al. 2020). According to these authors, several strategies for process intensification have been studied, including parameter optimization to improve the production rate, utilization of synthetic biology, and metabolic engineering.

Nanotechnology has the potential to increase the overall efficiency, feasibility, and sustainability of the biofuels production technologies, not only limited to the upstream steps but also the conversion processes and downstream (Ingle et al., 2019; Xu et al. 2019; Khoo et al. 2020a, b). Research and development on nanotechnology have grown expressively in the last years in different areas and with the participation of interdisciplinary and integrated science (Khoo et al. 2020a, b). For biofuels technology and regarding first the upstream steps, nanomaterials can be used for enzyme immobilization, named nano supports, which have advantages like large surface area, biocompatibility, non-toxic effects, a variety of physical and chemical properties that can enhance the activity of the enzyme, and the possibility of improving the recuperation and reuse of the enzymes (Rai et al. 2019; Khoo et al. 2020a, b; Shanmugam et al. 2020).

Nanomaterials can contribute not only as immobilization or encapsulation matrix for enzymes, promoting their reuse (Ingle et al. 2019a, b; Shanmugam et al. 2020) but also as nanocatalysts, which have been highlighted not only based on environmental and ecological issues compared to synthetic catalysts but also because, small particle size (related to their cell wall penetrating advantages), biodegradability, reusability and easy recuperation based on magnetic properties, functionalization possibilities, low price, and high availability (Ingle et al. 2019a, b; Xu et al. 2019; Shanmugam et al. 2020). However, some issues should be addressed regarding the safety and toxicity of various nanomaterials, nanoparticles aggregation problems, and synthesis costs (Ingle et al. 2019a, b; Khoo et al. 2020a, b).

Furthermore, in the case of biohydrogen production, nanotechnology strategies have also been studied as potentially cost-effective alternatives to improve the bioconversion step, since they can have a positive impact on the growth of the microorganism, the intracellular electron transfer, and the efficiency and protection of enzymes (oxygen-sensitive) involved in biohydrogen production (Yang and Wang 2018; Shanmugam et al. 2020). Moreover, nanotechnology strategies can improve the control of the operation conditions, such as illumination, temperature, and heat transfer, and even influence the bioreactor design (Shanmugam et al. 2020).

8.4.1 Socioeconomic and Environmental Considerations

It is an undeniable fact that an economy based on fossil fuels is no longer viable and a substantial amount of data, research studies, and public policies and future projected scenarios indicate that the shift to bioeconomy is a promising way to ensure welfare, economic, and food security to the human population. Regarding this conjecture, Johnson (2017) states that “A thriving bioeconomy that includes increasing reliance on biological processes and biobased products is a key element of the overall global sustainability transition.”

“Implement green chemistry and sustainability principles” is not only enough to assure the success of a bioeconomy, but it is also necessary to establish coordinates and steps to make the transition from our present models to a sustainable economy. It is not only essential to develop a circular economy system, where waste generation is reduced to its minimum and all the possible uses of biomass are considered, but also to articulate social and economic sustainability in accordance with environmental health. Moreover, an integration between national and global policies is vital, along with the cooperation and comprehensive view between sectors that deal with different biomass uses (e.g., energy, transportation, agriculture, forestry) (Johnson 2017).

The production of first-generation biofuels is based on crops that are likewise used for human and animal feeding. Therefore, a concern has arisen that an increase in the production of these fuels can compromise food security (food versus fuel debate). According to Sindhu et al. (2019) life-cycle assessment (LCA) of first-generation biofuels indicates that, in most circumstances, there is a negative energy gain; however, second-generation fuel models suggest an increase in energy gain, while third-generation biofuels excel the previous categories in many aspects, such as CO_2 sequestration, expressive accumulation of neutral lipids, high biomass, and soil productivity (Sindhu et al. 2019).

Land use by biofuel crops is still a field of uncertainties, forasmuch as it is connected to a huge number of variables, for instance, demand for other applications, agriculture productivity, future demand for animal products, and the pressure upon natural environments that can be seen as idle lands (such as grasslands), which can result in biodiversity loss (OECD/FAO 2019; Sindhu et al. 2019). In this sense, it is crucial to develop public policies to regulate land use and assure the sustainability of biofuels; moreover, studies that aim at the production of biofuels with nonfood crops or lignocellulosic biomass must be supported and promoted.

8.5 Nanotechnology in Biofuels Production

Nanotechnology has emerged as a promising technology as far as biofuel industries are concerned. It is reported to have applications in the production of different biofuels like bioethanol, biodiesel, biohydrogen, etc.

8.5.1 Nanotechnology in Bioethanol Production

The use of nanotechnology in bioethanol production can improve the plant biomass pretreatment and its conversion into fermentable sugars as well as the fermentative process (Kushwaha et al. 2018). The recalcitrance properties in most agro-industrial wastes, especially in the lignocellulosic biomass, is still a bottleneck for its conversion into second-generation biofuels (Zuccaro et al. 2020) and the pretreatment plays an important role in the manufacturing process and product value. Nanomaterials can improve pretreatment efficiency and assists in bioethanol fermentation and recovery. The major applications of nanoparticles in bioethanol production are given in Fig. 8.4. Moreover, the reusability of nano compounds is an important advantage for the biofuels' economic viability (Beniwal et al. 2018).

Several types of nanoparticles have been studied for bioethanol production and are applied in biomass pretreatment for the recovery of the sugars in different lignocellulosic materials as feedstock. Pena et al. (2012 & 2014) studied the effects of different acid-functionalized nanoparticles for the pretreatment of wheat straw and corncob. Ingle et al. (2019a, b, 2020a, b) evaluated the pretreatment of sugarcane bagasse and sugarcane straw using two different acid-functionalized magnetic nanoparticles (alkyl sulfonic acid—Fe_3O_4_MNPs@Si@AS, and butylcarboxylic acid—Fe_3O_4_MNPs@Si@BCOOH), that presented maximum xylose recovery for

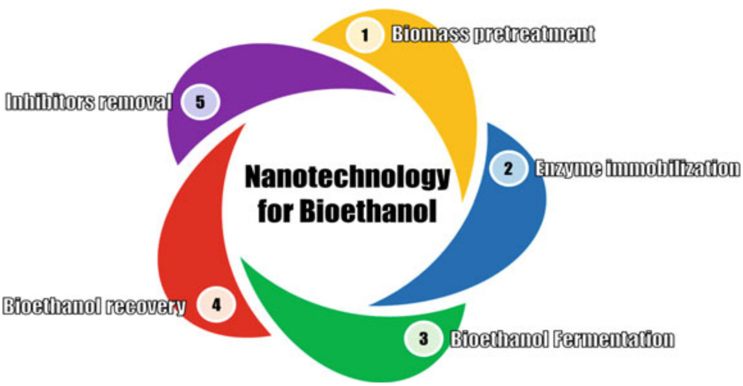

Fig. 8.4 Major applications of nanoparticles in bioethanol production

sugarcane bagasse (18.83 g/L and 18.67 g/L), and sugarcane straw (17.06 and 15.40) using the 500 mg/g of biomass.

Another utilization for nanoparticles in bioethanol production is for the immobilization of the enzymes. Enzymes are biological catalysts produced by bacteria and fungi and are a key factor for environment-friendly production biofuels because enzyme such as cellulases and hemicellulases play importanat role in the breakdown of cellulose and hemicellulose present in the lignocellulosic biomass (Mood et al. 2013). However, the utilization in the industrial scenario presents some obstacles to become economically viable, such as costly production and reuse of enzymes as they can contribute up to 30% of total processing cost in 2G sugars production (Sánchez-Ramírez et al. 2016; Chandel et al. 2018).

The immobilization of enzymes is an alternative for reducing costs with enzymes in an industrial scenario. Several supports can be used, such as inorganic materials, hybrid materials, polymers, and metal-organic frameworks (Suo et al. 2020). Immobilization methods vary in categories where the enzymes can be (1) bonded to support, which acts as a carrier or matrix, (2) entrapped in an encapsulation structure, or (3) cross-linked (Vaghari et al. 2015). The utilization of nanoparticles as an immobilizing agent presents several benefits to the enzymatic process. The immobilization of enzymes not only promotes increased yields and multiple cycles but is also presented as an environment-friendly alternative for enzyme application, also protecting them from inhibitory effects of alcohol and organic acids formed during fermentation (Sekoai et al. 2019). Cherian et al. (2015) studied the immobilization of cellulases using manganese dioxide (MnO_2) nanoparticles for the hydrolysis of sugarcane leaves to bioethanol (21.96 g/L), presenting 75% binding efficiency and 60% of catalytic activity, after five cycles. The biocompatibility, high specific surface area, stability and low toxicity, and resistance to mass transfer are highlighted, although the most prominent advantage is that immobilized enzymes can be recovered for repetitive applications in catalytic reactions, which can contribute to the overall reduction of costs in a biorefinery (Chandel et al. 2018; Suo et al. 2020).

The utilization of magnetic nanoparticles (MNPs) can be advantageous after the pretreatment of biomass as the catalysts can be recovered by the application of an external magnetic field and reused in subsequent pretreatment cycles (Ingle et al. 2020a). The utilization of magnetic fields in iron oxide (Fe_3O_4) nanoparticles for β-glucosidase immobilization in bioethanol production, studied by Verma et al. (2013), resulted in 93% binding efficiency and 50% catalytic activity after 16 cycles. Fe_3O_4 NPs and Fe_3O_4/Alginate nanocomposites were used for the immobilization of cellulases produced by *Aspergillus fumigatus* and evidenced an increased enzyme activity, resulting in a high sugar release during the rice straw pretreatment (Srivastava et al. 2015). The improvement in the activity and the thermal stability was also observed by Poorakbar et al. (2008), where cellulases from *Penicillium funiculosum* were employed with magnetic gold silica and showed a binding efficiency of 76% to the support matrix, and recycled for five cycles. Still, nickel oxide (NiO) nanoparticles were also used as bio-nanocatalysts in simultaneous saccharification and fermentation of potato peel waste was studied by Sanusi et al. (2020), and showed an increased bioethanol yield (19%). Even though nanoparticle utilization may be advantageous to bioethanol production, its use must be limited to its optimum values as it can inhibit the growth of microorganisms in higher concentrations (Sekoai et al. 2019).

Cells are microbial factories capable to synthesize enzymes for several industrial purposes. Though the nanomaterials use in enzyme immobilization, these compounds also act as supports to immobilize microorganisms (Rai et al. 2016a, b). Calcium alginate is commonly used as a matrix for cell immobilization, but the combination method with nano-structure materials has been demonstrated as promising alternatives for enhancing bioethanol production. Beniwal et al. (2018) achieved up to 0.42 g/g ethanol yield in 36 h with *Saccharomyces cerevisiae* and *Kluyveromyces marxianus* yeasts co-immobilized in calcium alginate using cheese whey as substrate. The authors immobilized β-galactosidase in a silicon dioxide nanoparticles matrix in a bioreactor for the same vessel hydrolysis and fermentation, demonstrating the nanoparticle reusability of 5 cycles. Besides increasing bioethanol yield in fermentation, nanoparticles could enhance the production of bioethanol in the syngas platform, as demonstrated by Kim et al. (2014) by using methyl-functionalized silica nanoparticles (0.3 wt %) during *Clostridium ljungdahlii* fermentation.

Another important use of nanomaterials is for bioethanol recovery from the broth. The presence of the bioethanol produced during the fermentation presents a negative effect on cell growth and viability, consequently decreasing the product yield (Xue et al. 2016). Pervaporation is considered a promising method for bioethanol recovery since it allows the integration of fermentation and biofuel recovery in situ (Fan et al. 2019). However, yeast cells can contaminate these membranes, fouling during the pervaporation, but the use of carbon nanotubes coupled in membrane filters assists the bioethanol recovery and enhances the antifouling performance (Xue et al. 2016). Besides, a nanofiltration membrane combined with a forward osmosis system was demonstrated to be effective for the removal of fermentation inhibitors and the concentration of fermentable sugars in rice straw hydrolysate (Shibuya et al. 2017). Nanotechnology enhances bioethanol production, especially assisting in enzyme immobilization (Rai et al. 2016a, b), helping to overcome bottlenecks and reducing costs in the manufacturing process.

Several factors such as the synthesis approach (co-precipitation method, thermal decomposition, microemulsion, hydrothermal synthesis, synthesis using biological organisms (fungi and algae), synthesis using plant materials, temperature range (100–700 °C), pressure, pH, and size may influence the performance of nanoparticles in fuels. These factors affect the morphology, size, and stability of nanoparticles as they have their advantages and disadvantages (Sekoai et al. 2019).

8.5.2 Nanotechnology in Biodiesel Production

The use of biofuels has been increasing over the last century; the ever-growing energetic demand, alongside environmental issues, has stimulated the search for alternative renewable fuel sources (Gardy et al. 2019). Biodiesel is a biodegradable, non-toxic, and environment-friendly alternative to petrol diesel. It consists of a mixture of monoalkyl esters derived from the esterification or transesterification of vegetable oils and animal fats with an excess of acyl acceptors, mostly short-chain alcohols, such as methanol or ethanol, with alkaline or acid catalysts. The fatty acid methyl or ethyl esters have properties similar to those of petrol diesel.

The biodiesel quality depends on several physicochemical properties, such as viscosity, specific mass, cetane number, cold flow plugging point, flash point, etc. The physicochemical properties and specifications limits are regulated by the National Agency of Petroleum, Natural Gas and Biofuels (ANP) in Brazil, European Standards (ES) in Europe, and the American Society for Testing and Materials (ASTM) in the USA. Biodiesel can be used directly in diesel engines or a mixture with petrol diesel. Several countries across the world have legally included biodiesel in the energetic matrix. In Brazil, biodiesel is obligatory mixed with diesel oil since 2008 and its use has increased currently to 12% v/v (B12), with a prediction of 20% (B20) in 2022 (Flumignan et al. 2012; ANP 2020).

The most common, though not exclusive, path for biodiesel synthesis is the reaction of feedstocks (in special, vegetable oils) with methanol and homogenous alkaline catalysts. Recent research shows emerging alternative methods to obtain biodiesel from sources like animal fats, residual oils, and other non-food feedstocks. The use of other synthesis routes, such as interesterification (with methyl acetate and dimethyl carbonate) and hydro-esterification (chemistry, enzymatic or supercritical) is also reported (Flumignan et al. 2012).

8.5.2.1 Biodiesel Feedstocks

Oils and fats are composed of triacylglycerides, which consist of three fatty acid chains esterified to a glycerol backbone. Generally, oils consist mostly of the unsaturated fatty acid chains and are in the liquid state, while fats have a majority of saturated fatty acid components and are solid at room temperature.

The use of crude vegetable oils in diesel engines is possible, but their high viscosity and cold flow behavior cause overall damage to the engines. Thus, it is more interesting to apply vegetable oils as a source to obtain biodiesel. Nowadays, biodiesel derives majorly from refined vegetable oils (soy, corn, rapeseed, sunflower, etc.), but the use of other feedstocks, such as residual oils and fats (waste cooking oil, fish oil, beef tallow, chicken fat, etc.) and non-food crude oils (jatropha, macaw, crambe, etc.) has been growing. Residual and non-food feedstocks are an appealing alternative for environmental and economic reasons. Nevertheless, there are limitations to the use of such feedstocks in the transesterification process employing the usual conditions. In the presence of homogeneous alkaline catalysts, high free fatty acid and water contents can shift the reactants towards the saponification side reaction (Gardy et al. 2019).

Moreover, heterotrophic microalgae can be considered a neutral source of bioenergy; hence, the fact that they consume CO_2 from the environment around them. In comparison to vegetable sources, microalgae growth is faster and cheaper, and its use as a source of bioenergy does not compete well with other industrial sectors (Zhang et al. 2013). Microalgae can accumulate up to 60% (w/w) of lipids, which can be extracted and converted into biodiesel. Also, recent studies show that microalgae biomass can be used in direct transesterification without the need for lipid extraction (Pandit and Fulekar 2017, 2019). In this context, microalgae are presented as an economic and environmentally interesting source for biodiesel production.

8.5.2.2 Catalysts for Biodiesel Production

Catalysts are applied in chemical reactions to conduct the synthesis of the products through a path that requires lower activation energy when compared to catalyst-free reaction, without being consumed. The occurrence of esterification and transesterification of oils and fats to obtain biodiesel requires the use of catalysts. More commonly, alkaline catalysts provide highly efficient ester conversion in relatively short reaction times, when compared to acid catalysts (Gardy et al. 2019).

Homogenous catalysts are in the same phase as reactants in the reaction medium, whereas heterogeneous catalysts are in different phases. The use of homogeneous catalysts is widely known, but can also cause corrosion of systems, soap formation and require tedious purification steps to achieve recovery of products, which increases both process cost and waste production. In this context, heterogeneous catalysts can also provide efficient conversions and are easily removed from the reaction medium with simple purification steps such as decantation, filtration, and centrifugation. Furthermore, recyclable heterogeneous catalysts may be presented as a more efficient, alternative industrial application (Gardy et al. 2019; Jain et al. 2014; De and Boxi 2020; Zhong et al. 2020).

8.5.2.3 Nanocatalysts for Biodiesel Production

The use of nanosized particles as catalysts instead of other heterogeneous catalysts is advantageous considering the high surface/volume ratio of nano-compounds as well as high selectivity, easier recovery, and overall stability of catalytic activity when applied in successive reactions. The nanocatalyst quality depends on the physical properties of the materials used, such as size, shape, active sites distribution, thermal stability, chemical stability, and spatial and electronic properties (Gardy et al. 2019; Jain et al. 2014).

Table 8.2 Metal oxide nanocatalysts for biodiesel production via transesterification process

Reference	Feedstock	Catalyst	Transesterification conditions	Biodiesel Production
Pandit and Fulekar (2017)	*A. obliquus* biomass	CaO eggshell waste (1.7% w/w)	Algae:MeOH 1:10 (w/v)/70 °C/3.6 h	91.86% conversion; 86.41% yield
Pandit and Fulekar (2019)	*S. armatus* biomass	CaO eggshell waste (1.61% w/w)	Algae:MeOH 1:10 (w/v)/70 °C/3.6 h	90.44% yield
De and Boxi (2020)	Palm oil	Cu impregnated TiO_2 (3% w/w)	Oil:MeOH 1:20/ 45 °C/45 min	90.93% yield
Tan et al. (2017)	WCO	CaO ostrich shell waste (1.50% w/v)	Oil:MeOH 1:10/ 65 °C/2 h	98.97% yield
Abdelhady et al. (2020)	Sunflower oil	CaO eggshell waste (1.50% w/v)	Oil:MeOH 1:4.5/ 75 °C/1 h	94.70% yield
		CaO beet sugar waste (1%)		93% conversion
Borah et al. (2018)	*M. ferrea* oil	Co doped ZnO (2.5% w/w)	Oil:MeOH 1:9/ 60 °C/3 h	98.03% conversion
Borah et al. (2019)	WCO	Zn doped CaO from waste eggshell (5% w/w)	Oil:MeOH 1:20/ 65 °C/4 h	96.74% conversion
Baskar et al. (2018)	Castor oil	Ni doped ZnO (11% w/w)	Oil:MeOH 1:8/ 55 °C/1 h	95.20% yield
Feyzi and Shahbazi (2015)	Refined vegetable oil blend	Cs-Ca/TiO_2-SiO_2	Oil:MeOH 1:12/ 60 °C/2 h	98% yield
Raj et al. (2019)	*N. oculata* lipid extract	PEG capped Mn-ZnO (3.5% w/w)	Oil:MeOH 1:15/ 60 °C/4 h	87.5% yield
Justine et al. (2020)	WCO	ZnO	Oil:MeOH 1:6/2 h	81.6%
		ZnO-SiO_2		54.6%
Botti et al. (2020)	Soybean oil	Na-geopolymer (3% w/w)	150% MeOH/70–75 °C	85.1–89.9% yield

The reaction will occur in the active sites distributed throughout the surface of the material. Thus, the smaller the size of the particle, the greater the surface area and the greater the catalytic activity achievable. Also, nanosized particles can be dissolved, precipitated, and crystallized successively, depending on the conditions of the medium, which makes recyclability easier. Nanocatalysts can be obtained through chemical, physical, and biological processes (Jain et al. 2014). Different types of nanotechnology-based heterogeneous catalysts for biodiesel synthesis through transesterification are explored hereafter. Table 8.2 summarizes results from transesterification of vegetable and waste cooking oil (WCO) as well as algal biomass and crude oil by applying different nanosized metal oxide particles and geopolymers.

Calcium oxide (CaO) based catalysts are derived from waste produced in agricultural and industrial activities, such as animal bones, egg and animal shells, paper

Table 8.3 Magnetic nanocatalysts for biodiesel production via transesterification process

Reference	Feedstock	Catalyst	Transesterification conditions	Biodiesel production
Liu et al. (2016)	Soybean oil	$MgFe_2O_4@CaO$ (1% w/w)	Oil:MeOH 1:12/ 70 °C/3 h	98.3% yield
Mapossa et al. (2020)	Soybean oil	$Ni_{0.3}Zn_{0.7}Fe_3O_4$ (2% w/w)	Oil:MeOH 1:12/ 180 °C/1 h	94% yield
Feyzi and Norouzi (2016)	Sunflower oil	$Ca/Fe_3O_4@SiO_2$	Oil:MeOH 1:15/ 65 °C/5 h	97% yield
Baskar and Soumiya (2016)	Castor oil	Fe (II) doped ZnO (14% w/w)	Oil:MeOH 1:12/ 50 °C/55 min	91% yield
Alaei et al. (2018)	Sunflower oil	$MgO/MgFe_2O_4$ (4% w/w)	Oil:MeOH 1:12/ 110 °C/4 h	91.2% conversion
Amani et al. (2019)	Sunflower oil	$MgO/MgFe_2O_4$ (3% w/w)	Oil:MeOH 1:12/ 110 °C/3 h	92.5% conversion
Banerjee et al. (2019)	*N. oleoabundans* lipid extract	Fe_2O_3 (1% w/w)	Biomass:MeOH 1:5 (w/v)/65 °C/6 h	86% yield

industry, etc. Such catalysts are highly alkaline, relatively economical, and require mild reaction conditions to obtain efficient ester conversions. They are obtained through the calcination of materials, which convert $CaCO_3$ into CaO (Pandit and Fulekar 2017, 2019; Tan et al. 2017; Abdelhady et al. 2020).

Zinc oxide (ZnO) can be obtained through precipitation in an aqueous solution and annealing in a heated oven. Also, doping of CaO and ZnO with metals such as cobalt and nickel shows interesting results in biodiesel conversion from vegetable oils (Borah et al. 2018, 2019; Baskar et al. 2018). Titanium dioxide (TiO_2) nanoparticles are also widely used for catalysis in different industrial sectors, including biodiesel production (De and Boxi 2020; Feyzi and Shahbazi 2015). Nanocomposites and geopolymers (alkaline aluminosilicate powders) can also be applied to oil and fat conversion into methyl esters (Raj et al. 2019; Justine et al. 2020; Botti et al. 2020; Bai and Colombo 2018). MNPs are composed of elements with magnetic properties, most commonly of iron, nickel, and cobalt. They can be obtained through combustion, co-precipitation, and thermal decomposition, amongst others methods (Liu et al. 2016; Mapossa et al. 2020; Feyzi and Norouzi 2016; Baskar and Soumiya 2016; Alaei et al. 2018; Amani et al. 2019; Banerjee et al. 2019). The magnetic properties are interesting to reduce the cost and labor of purification processes; MNPs can be easily removed from the reaction medium by using a magnet to apply an external magnetic field. Table 8.3 summarizes the results of the transesterification catalyzed by MNPs.

The use of MNPs as catalysts for biodiesel production and also the use of biocatalysts is interesting considering chemical catalysis. The use of enzymes (lipases) as catalysts for transesterification of oils and fats, when compared to chemical alkaline or acid catalysts, provides higher product selectivity and is advantageous for avoiding soap formation and other contaminations. However, enzyme cost still limits the application in industrial scales. In this context, enzyme

Table 8.4 Enzymatic magnetic nanocatalysts for biodiesel production via transesterification process

Reference	Feedstock	Catalyst	Transesterification conditions	Biodiesel production
Nematian et al. (2020)	*C. vulgaris* lipid extract	*R. oryzae* lipase immobilized in Fe_3O_4 nanoparticles	Three-step addition MeOH/45 °C/24 h	69.8% conversion
Xie and Huang (2018)	Soybean oil	*C. rugosa* lipase immobilized in grapheme oxide/Fe_3O_4 nanocomposite	Three-step addition of MeOH/40 °C	92.8% yield
Xie and Huang (2020)	Soybean oil	*C. rugosa* lipase immobilized in poly(glycidyl methacrylate-*co*—methacrylic acid)/Fe_3O_4 nanocomposite	Three-step addition of MeOH/40 °C	92.8% yield
Badoei-dalfard et al. (2019)	WCO	Cross-linked lipase aggregates with Fe_3O_4 (0.3% w/w)	Oil:MeOH 1:3/35 °C/36 h	71% conversion
Ashjari et al. (2020)	WCO	*R. miehei*lipase immobilized in $Fe_3O_4@SiO_2$ nanoparticles (15.2% w/w)	Three-step addition of MeOH/40 °C/48 h	55.3% yield
		*T. languginosus*lipase immobilized in $Fe_3O_4@SiO_2$ nanoparticles (18.6% w/w)		81% yield

immobilization is an alternative to reduce overall cost, for it makes it possible to recycle and reuse the biocatalysts. Immobilization consists of attaching the enzymes to the pores and/or surface of a chosen support material and can also enhance enzyme stability and improve kinetics (Zhong et al. 2020; Nematian et al. 2020).

Table 8.4 summarizes the results of the transesterification catalyzed by enzymatic MNPs. It is worth mentioning that there are specific (i.e. *C. rugosa* and *T. languginosus*) and 1,3-specific (*R. miehei* and *R. oryzae*) lipases; specific lipases can achieve a full ester conversion, whereas 1,3-specific lipases can only convert 2/3 of the fatty acids from the triacylglyceride. Also, lipases are inactivated by high concentrations of methanol. Thus, the three-step addition of the solvent to the medium is important to achieve high yields. Also, the immobilization of lipases in MNPs makes it possible to recycle the biocatalysts for an average of 3–5 cycles without significant activity loss (Xie and Huang 2018, 2020; Nematian et al. 2020; Badoei-dalfard et al. 2019; Ashjari et al. 2020).

The immobilization of lipases for biodiesel production is a promising field. Other recent researchers are focusing on the development of nanoparticles as support for lipase immobilization, though still without application in the transesterification reaction for biodiesel production (Atiroglu 2020; Asmat and Husain 2019).

8.5.2.4 Nanotechnology in Biohydrogen Production

Fossil fuels lead to serious environmental problems, which are responsible to worsen the greenhouse effect; however, the continuous growth of the world population and industrialized economy made them indispensables (Gaurav et al. 2017; Moreira et al. 2017). Thus, fossil fuels such as oil, coal, and natural gas have been known as the main source of energy over the last century so that they have contributed to 80% of the total energy produced, and dependence on them is expected to decrease to 78% by 2040 (Höök and Tang 2013). Therefore, the establishment of alternative energies (biofuels) is a top priority in developments sectors and is a target of big research efforts directed through process intensification to enhance the efficiency of biomass conversion in biorefineries (Gaurav et al. 2017).

Biohydrogen is the most efficient and cleanest carbon-free energy, and it is considered a valuable and alternative fuels carrier to fossil ones (Kumar et al. 2019b; Sindhu et al. 2019). It also has the potential to reduce greenhouse gases emissions, especially from the energy and transportation sectors. Biohydrogen production has been attracting global attention due to its social, economic, and environmental merits, and due to its high content of energy with an approximate value of 122–141 kJ/g, which is higher than that of other fuels, such as methane (55.65 kJ/g) and ethanol (29.7 kJ/g).

Hydrogen has been produced from fossil fuels, biomass, water, and the reform of natural gas; besides, hydrocarbon oxidation, coal gasification, electrolysis of water, and finally dark fermentation of organic substrates (Kumar and Himabindu 2019; Sindhu et al. 2019). Biohydrogen production by dark fermentation to generate hydrogen energy is a friendly environmental alternative to fossil fuels to help meet the needs of carbon emission reduction (Ren et al. 2011). Nevertheless, the quantity of biohydrogen produced via dark fermentation is low (Kumar et al. 2019b).

Nowadays, several advances and tools have been developed to increase the chance of enhancing dark fermentation for biohydrogen production. Recently, an application of nanoparticles (NPs) to enhance bioactivity and metabolite recovery during dark fermentation has gained enormous attention due to the unique surface and quantum size effect. Some examples of inorganic NPs that were used for enhancing biohydrogen production are silver, cobalt, titanium, nickel, and iron; the last one is one of the most promisors because of its versatility and compatibility with other additives (Kumar et al. 2019a). The effect of those nanomaterials could show a positive impact on metabolic key processes.

Yang and Wang (2018) described two mechanisms that enhance hydrogen production during fermentation and were related to a decline in the oxidation-reduction potential in the system, providing a better environment for fermentative bacteria, assisting in the removal of undesired oxygen, thereby contributing to a higher activity of the oxygen-sensitive hydrogenase. Both these mechanisms were studied in zero-valent iron nanoparticles (FeO NPs) supplementation. In this study, it was also proposed that Fe0 NPs could accelerate electron transfer between ferredoxin and hydrogenase and promote the activity of key enzymes by the released Fe^{2+}. The hydrogen yield obtained with Fe0 supplementation (400 mg/L) in this research was 73.1% higher than that of the control group. In 2016, Taherdanak and collaborators, also reported the use of Fe and Ni nanoparticles on dark hydrogen fermentation, specifically Fe0 and Ni0, and they compared them with their equivalents in ion form. Results showed that the order of the hydrogen yield effects was as follows: Ni^{2+} ion (55%) > FeO NPs (37%) > Fe^{2+} ion (15%) > NiO NPs (0.9%) compared with the control without supplementation.

In 2014, Mohanraj and collaborators also reported that an enhancement of ferredoxin oxidoreductase activity in response to NPs addition has been considered to be important to increase the hydrogen production yield during dark fermentation. Thereafter, in 2015, Gadhe and collaborators, showed that an improvement of biohydrogen production with a co-addiction of hematite (Fe_2O_3) plus nickel oxide (NiO) NPs at optimum concentration can be attributed to a higher activity of the ferredoxin oxidoreductase, ferredoxin, and hydrogenase enzymes by surface and quantum size effects of NPs. The hydrogen yield obtained by the co-addiction of Fe_2O_3 and NiO (50 mg/L and 10 mg/L respectively) was 1.2-fold higher than that of the addition of individual nanoparticles. Also, Zhang and collaborators (2018) studied other configurations of iron nanoparticles (ferric oxide/carbon nanoparticles—FOCNPs) for hydrogen production enhancement. Fe_2O_3/C NPs also showed good performance when added to a dark fermentative process based on glucose, reaching 33.7% improvement when FOCNPs were added in a concentration of 200 mg/L.

In 2015, Seelert and collaborators, used magnetite (Fe_3O_4) nanoparticles functionalized with chitosan and alginic acid polyelectrolytes, to promote bacterial attachment (immobilization). They used *Clostridium beijerinckii* with these nanoparticles, and its kinetics resulted in a shorter lag growth phase effect. The greatest hydrogen yield was 2.1 ± 0.7 mol H_2/mol glucose, corresponding to substrate conversion and energy conversion efficiencies of 52 ± 18 and 10 ± 3%, respectively. According to Zhong and collaborators (2020), the addition of magnetite nanoparticles resulted in the formation of electronic conductor chains that enhance the electron transport efficiency and enhance key coenzymes activity in a complex consortium (anaerobic sludge), promoting a relative abundance of ethanol-hydrogen-producing bacteria. Results showed that an addition of 50 mg/L magnetite NPs improved H_2 production by 53.7%.

All these research advances show biohydrogen as one of the most promisor biofuels in the near future. However, there are many bottlenecks in this interesting bioprocess, such as sustainable pretreatments for substrates availability, enhancement stability of key enzymes and coenzymes, better performance in fermentation modes, etc. Thus, the inorganic nanoparticles could be a promising additive in practical application to achieve high hydrogen production, enhancing some of the main challenges that could currently appear in the main steps in bioprocesses.

8.6 Challenges in the Application of Nanotechnology in Biofuels Production

Apart from the advantages of the utilization of nanomaterials in the production of biofuel, several concerns and risks have arisen from the application of nanotechnology. In this regard, the challenges of the use of nanoparticles in biofuel production can be categorized into the following issues.

8.6.1 General Challenges

The nanoparticles could be applied successfully for the development of biofuel production. However, the characterization of many nano-additives studied for biofuel production has not been recognized well. In this regard, physical properties such as particle size, shape, and clustering have been paid less attention (Hossain et al. 2019). More studies should be carried out to solve the problems related to the use of nanomaterials which are accompanied by agglomeration, settling, and erosion. Moreover, little is known about the mechanisms of heat transfer where nanomaterials are applied (Khoo et al. 2020a, b).

On the other hand, enough availability of nanomaterials should be provided for industrial applications since a low quantity of nano-additives is used for laboratory scale. Furthermore, the choice of a proper nanomaterial, scientific approach used for the preparation of nanoparticles for biofuel production should be taken into account to attain the highest production of biofuels (Hossain et al. 2019).

8.6.2 Deleterious Effect of Nanoparticles on the Biofuel Producing Microorganisms

Biofuels are mainly produced by microorganisms. In this context, different yeast, bacteria, and microalgae are exploited for the production of liquid biofuels such as bioethanol, biobutanol, and biodiesel. Furthermore, gaseous biofuels such as biohydrogen as transportation biofuel are produced by microorganisms particularly bacteria (Abdeshahian et al. 2014; Shukor et al. 2014). There is a controversy about the deleterious effect of nanomaterials on microorganisms. It has been reported that carbon nanotubes such as Al_2O_3, CuO, ZnO, and TiO_2 cause toxic effects on the microalgae with oxidative stress, agglomeration, and inappropriate supply of nutrients to algal cells (Khoo et al. 2020a, b). The utilization of nanoparticles in electrodes made for microbial fuel cells (MFC) may cause toxic effects on electrogenic microorganisms including bacteria and fungi, which in turn decreases electricity generation.

8.6.3 The Cost-Effectiveness of Nanomaterials for Biofuel Production

One of the main limitations of the use of nanomaterials is the production costs of biofuel using nanoparticles. In this regard, many nano-materials are relatively expensive which affects their industrial utilization for the economical production of biofuel (Khoo et al. 2020a, b). The exploitation of nanomaterials in the chain of biofuel production consisting of the raw materials to end-product utilization could be analyzed in the aspect of the economic viability of the process. Hence, techno-economical assessment is necessary to evaluate whether the use of nanomaterials for biofuel production is economically variable as the commercialization of biofuel production using nanoparticles is drastically targeted in transportation sectors (Hossain et al. 2019).

8.6.4 Environmental Effect of Nanomaterials

The environmental toxicity of the nanoparticles has been poorly studied. It has been found that nanoparticles have toxic effects on the environment (Khoo et al. 2020a, b). Several nanoparticles are not degradable and can enter the environment and remain for a long time. The nanoparticles settled in the soil can penetrate the deeper layer of the ground and enter the groundwater sources (Engelmann and Hohendorff 2019).

The major concerns are related to the adsorption of the nanoparticles to living organisms which could be accumulated in the cells. In this line, it has been found that due to the low size of nanoparticles, biomolecules such as protein, lipid, and DNA could react with nanoparticles, thereby causing toxic effects on the organism cells. The toxicity of nanomaterials should be studied further in animal models to determine the possible damages to the human cells in the environment (Rai et al. 2016a, b).

8.6.5 Deleterious Effect of Nanomaterials on the Human Body

The nanoparticles could enter the human body through the respiratory system, alimentary canal, and skin injuries. Owing to the small size of the nanoparticles, there is a danger of entering the bloodstream (Engelmann and Hohendorff 2019). Nanoparticles can go to different organs via bloodstreams and enter human cells. They make oxidative reactions in the cells which, in turn, lead to cytotoxic reactions in many tissues. The organs with high metabolism such as the kidney, lung, heart, and liver are at a higher risk of the toxic effects obtained from nanomaterials. Hence, it is necessary to conduct more scientific research to find out the toxicity of the nanomaterials on the human body (Rai et al. 2016a, b).

8.7 Conclusions

It is a well-known fact that the continuous increase in global population and industrialization considerably increases the demand for fossil fuels and looking at limited resources of these fuels, these fuels may be depleted soon. However, environmental concerns like climate change and global warming are the other issues raised due to the burning of fossil fuels. In this context, biofuels are the only alternatives that are reported to mitigate these problems at a significant level. Considering the limitations of conventional approaches commonly used for biofuel production, nanotechnology has come up with the most promising solutions which can make biofuels production easy and economically viable. The direct or indirect use of nanotechnology in general and nanomaterials in particular in the production of various biofuels has been found to be the most effective move which can boost the conventional biorefining industries. Although primary studies conducted so far presented the positive side of nanotechnology in this aspect, there is a constant debate on the use of nanomaterials due to their toxicological concerns. There has been always a difference of opinions from the scientific community about the toxicity of nanomaterials, but we strongly think that further extensive studies are essentially required so that concrete evidence can come out about the toxicity of nanomaterials to the environment and associated living beings.

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