Chapter 1
Bioenergy and Biofuels: Nanotechnological Solutions for Sustainable Production

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Abstract Rather than using fossil fuels, the world is focusing on finding or developing alternative modes of energy production. This is due to the fact that fossil fuels are exhausting and the emission products of these fuels have been causing several damages to the environment. In this context, nanotechnology can play an important role for sustainable bioenergy and biofuel production. Different nanomaterials, such as metal nanoparticles, nanofiber, nanotubes, nanosheets, and others, have been reported to have a number of direct or indirect applications (as nanocatalyst) in the production of biofuels such as bioethanol and biodiesel. Actually, these biofuels are eco-friendly and renewable energy resources and hence have been receiving attention as an alternative energy source. Also, nanotechnology offers interesting approaches such as the use of magnetic nanoparticles. These particles can be used as carrier to immobilize enzymes that can be applied in bioethanol or biodiesel production. Moreover, magnetic nanoparticles can also be used for biogas production due to strong paramagnetic property and high coercivity during the process of methanogenesis. In this chapter, after introducing a global view about bioenergy and biofuel, different and interesting approaches regarding the application and solutions that nanotechnology can offer to bioenergy and biofuel production will be discussed followed by a section about safety issue concerning this technology.

Keywords Nanotechnology • Bioenergy • Biofuels • Ethanol • Biodiesel • Nanocatalysts

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1.1 Introduction

Worldwide, the concerns about environmental problems have driven a number of researchers to seek for innovative solutions. Particularly, the requirement for replacing resources as petroleum and coal by renewable energy and biofuel sources has motivated a large number of professionals to search for novel technological approaches. In fact, this requirement has gained pivotal importance regarding current problems as depletion of more readily available oil reserves, forcing to seek it in places more difficult to access, resulting in higher production costs. As a consequence, there is intense demand for energy in developing countries. The environmental problems such as greenhouse gas emission, especially due to the CO_2 generated during the burning of fossil fuels, has resulted into climate change that has become more clear for the scientific community (Huber et al. 2006; Cherubini 2010; Boudet 2011). For example, the importance of replacing fossil fuels in motors for energy derived from renewable sources can be easily verified considering that the transport sector can be responsible by 60 % of the estimated oil demand for 2030, in around 116 million barrels per day (IEA 2007).

Renewable energy includes a number of options such as solar, wind, geothermal, and biomass. The interest in the latter has been increased considering the abundant quantity of vegetable waste that can be used to generate electricity or liquid and gaseous fuels. This use can be in direct from burning biomass to generate vapor and electricity or after some transformation that allows a more efficient use of this energy source. However, the technologies for biomass processing remain limited by technological and economical constraints. Thus, new and creative approaches are necessary to achieve feasible processes as well as larger and faster change of global energy matrix.

Among the new developments, nanotechnology has been a fertile field of research, which includes promising possibilities in different application areas of social and industrial interest. This technology can be used in different fields such as electronics, material development, pharmaceutical, and life sciences, among others, and has along other converging technologies (biotechnology, information technology, and cognitive sciences) great potential to enhance human life (Wolf and Medikonda 2012; Demetzos 2016).

In biofuels and bioenergy field, nanotechnology has different applications such as modification in feedstocks, development of more efficient catalysts, and others. For example, enzymes have been largely used to hydrolyze biomass to produce biofuels such as ethanol and biogas or to catalyze biodiesel production from oils and fats (Michalska et al. 2015; Verma and Barrow 2015; Terán-Hilares et al. 2016). In this context, nanostructures can be used to replace the enzymes or to immobilize them, resulting into more efficient catalysis or favoring the recovery of biocatalysts from medium. Moreover, this technology includes alternatives in which magnetic properties are added to immobilized systems (Verma and Barrow 2015; Rai et al. 2016).

This chapter presents an overview of the possibilities of the use of nanotechnology as an interesting tool to solve some technological problems in bioenergy and biofuels production. It also includes a global view of the world energetic matrix, mainly considering renewable resources. Moreover, it is complemented with a section regarding safety issues.

1.2 Global View of Bioenergy and Biofuel

Currently, world energy supply is provided predominantly by coal, oil, natural gas, nuclear, hydro, and renewable sources (Brazilian Energy Balance 2015). From the last decades, total global energy primary production has been increased, and the mainly current producers are (Mtoe) China (2555), United States (1989), Russia (1334), Saudi Arabia (630), India (571), Indonesia (457), Canada (452), Australia (357), Iran (308), and Brazil (26) (Yearbook Enerdata 2015a). Considering different sources, the world energy supply has been provided mainly from oil, followed by natural gas and coal. Figure 1.1 presents world energy supply profile in 1971 and in 2013.

As can be clearly observed, the world remains strongly dependent on fossil fuels. Renewable energy, on the other hand, accounts for only about 10 % of total in world scenario from around 40 years (Brazilian Energy Balance 2015). In spite of this, several countries have been using the green energy. For example, from renewable energy, electricity production is the first source of power generation (%) in Norway (98.0), New Zealand (79.0), Brazil (73.4), Colombia (70.0), Venezuela (62.8), Portugal (62.6), Canada (62.5), Sweden (58.5), Chile (42.8), and Italy (42.1) (Yearbook Enerdata 2015b). In addition to this, share of wind and solar in electricity production is strongly diffused in Portugal (24.5), Spain (23.9), New Zealand (21.7), Italy (16.7), Germany (15.2), United Kingdom (10.3), Belgium (10.0), Romania (9.6), Sweden (7.6), and the Netherlands (6.6) (Yearbook Enerdata 2015c).

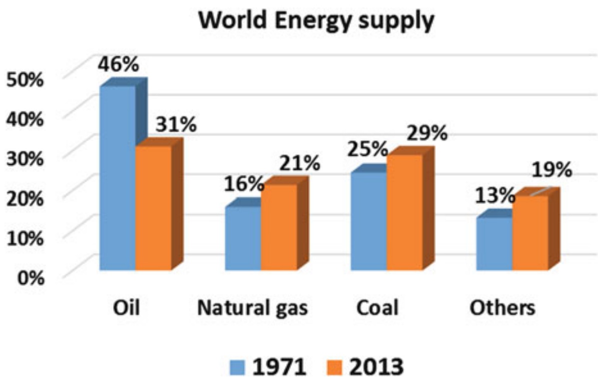

Fig. 1.1 World energy supply profile in 1971 and in 2013 (*Source*: Based on IEA data from the Key World Energy Statistics © OECD/IEA 2015, www.iea.org/statistics. Licence:www.iea.org/t&c; as modified by present authors)

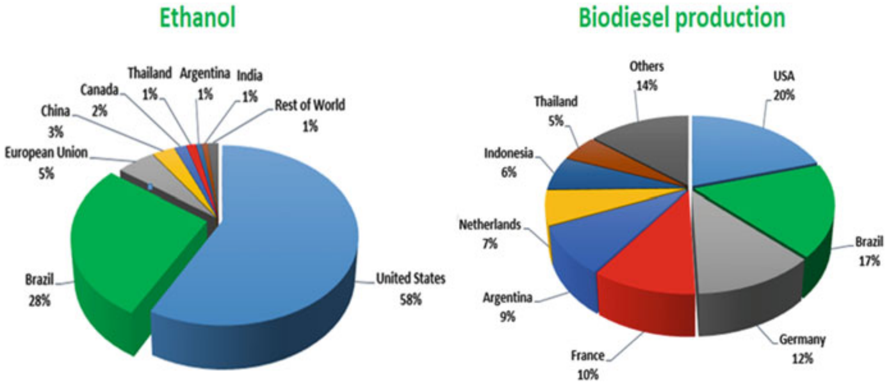

Fig. 1.2 Main world renewable fuel producers in 2015 (*Source*: Statista 2016b; Renewable Fuels Association 2015)

Currently, biofuels have also gained special highlight and have been manufactured in different countries, with an increasing production. Among them, for example, bioethanol has world production of around 25 millions of gallons per year. The larger producers of bioethanol include the United States, with around 14,000 millions of gallons per year by using corn as a raw material, followed by Brazil, with around 7000 millions of gallons per year, by using sugarcane juice as carbon source (Renewable Fuels Association 2015). According to Goldemberg (2006), if just ethanol produced from sugarcane juice could replace 10 % of total consumed gasoline in the world, carbon emissions could be reduced up to 66 million tons per year. Biodiesel, another important biofuel, is usually produced by a chemically catalyzed transesterification reaction between low chain length alcohols (mainly methanol) and oils and fats from animals or plants. The manufacturing of this compound has also been increased. For example, European Union currently produces around 3.35 billions litre of biodiesel, which can be increased up to around 4.14 billion gallons in 2025 (Stastista 2016a). In 2014, the world's biggest biodiesel producers were (billion liters) the United States (4.7) followed by Brazil (3.4), Germany (3.4), Indonesia (3.1), and Argentina (2.9) (Stastista 2016b). Figure 1.2 shows an overview of the main world renewable fuel producers in 2015.

One of the most important potential materials for biofuel production is the vegetal biomass, mainly taking into account lignocellulosic compounds that are the most abundant renewable carbon source in the world. These materials have an estimated generation from 10 to 50 billion tons per year, with about billion tons of primary biomass potentially available for reuse (Zhao et al. 2012). In many industrial processes, biomass is burning in boilers for self-sustainable energy production. Also, vegetal biomass is composed of two thirds polymeric carbohydrates such as cellulose and hemicellulose (Antunes et al. 2014) and hence can be used in bioprocesses for producing biofuels or other value-added compounds.

In this scenario, green technology along with nanotechnology has great potential to supply different industrial sectors with high demand of production within the required conception of sustainable development process.

1.3 Nanotechnological Solutions

Nanotechnology is the developing branch of science, which is applied for assessment of new technological replacements. It is the most significant study in modern science, which allows chemists, engineers, biotechnologists, and physicians to work at molecular and cellular levels.

Current researches have indicated that nanotechnology applied in nanomaterials can exhibit advanced properties that are exceptional in science (Engelmann et al. 2013). Nanotechnology can deal promising solutions for bioenergy production by changing the features of feed materials. Different nanomaterials, such as carbon nanotubes, magnetic and metal oxide nanoparticles, and others, are advantageous to become an essential part of sustainable bioenergy production (Rai et al. 2016).

1.3.1 Nanotechnology in Bioenergy Production

Nanotechnology has the potential to enhance the bioenergy production by using different forms of the nanoparticles. Nanoparticles have potential physical, chemical, and electrical properties, which differ from the bulk material. They have ability to increase the energy production and can serve as solution, which can tackle the problem of energy production. Water, solar, and biogas energies are different kinds of renewable sources and its production can be enhanced by applying nanotechnology (Hussein 2015).

1.3.1.1 Nanotechnology in Biogas Production

Biogas is produced from anaerobic digestion of organic wastes such as plant, agriculture, and animal and human wastes. Organic waste is rich in carbon and nitrogen sources, and the release of energy from anaerobic process depends on the C:N ratio (Feng et al. 2014). There are evidences that addition of certain metal ions in trace amounts increase the activity of methanogenic bacteria, and thus, acts as a catalyst which increases the production of energy. Since methanogenic bacteria require small amount of iron, cobalt, and nickel for the anaerobic digestion, researchers demonstrated that instead of using atomic or bulky materials, nanomaterials are beneficial (Feng et al. 2010). Magnetic nanoparticles have a strong paramagnetic property and high coercivity, and hence, can be used in the process of methanogenesis (Yang et al. 2015). Abdelsalam et al. (2015) found that cobalt and nickel nanoparticles enhanced the methane gas production. They have also compared the activity of iron nanoparticles with iron oxide nanoparticles and reported that the latter presented more activity as compared to iron nanoparticles. In a more recent study, Abdelsalam et al. (2016) reported that the effect of different nanoparticles such as Fe, Fe_3O_4, nickel (Ni), and cobalt (Co) yields the highest biogas and methane production from anaerobic digestion of cattle dung. Also, Casals et al. (2014) reported that when Fe_3O_4 nanoparticles were applied to the organic waste in the anaerobic digester, enhancement of the activity of disintegration as well as increasing yield of methane and biogas production was observed.

1.3.2 Nanotechnology in Biofuel Production

The first-generation biofuel is produced from different food feedstocks such as starch from corn, sucrose from sugarcane, animal fats, and plant oils (Naik et al. 2010). The regular use of these feedstocks present some concerns, and hence, new notion of second-generation biofuel has been gaining ground in the world scenario for production of biofuel by using non-food feedstock, e.g., lignocellulosic materials such as, wood wastes, agricultural residues, and others. (Patumsawad 2011; Eggert and Greaker 2014). Although, second-generation biofuels have certain benefits as waste materials used in this case, they have some drawbacks such as high cost of production and infrastructure as well as technological problems. Therefore, keeping these truths in mind, researchers need to develop proficient technologies to solve these concerns in mass processing and increase productivity in biofuels. Aiming to these perspectives, application of nanotechnology can overcome the aforementioned difficulties by proposing the chance to modify the characteristics of feedstock materials for biofuel production.

Nanoparticles have strategic uses in biofuel production because of its exceptional physiochemical properties. Many nanomaterials such as TiO_2, Fe_3O_4, SnO_2, ZnO, carbon, graphene, and fullerene, presenting unique properties, have been applied for biofuel production. Moreover, magnetic nanoparticles have wide applications in biofuel production because of its high surface to the volume ratio, quantum properties, and immobilizing property due to their small size. Besides, the most significant property of these nanoparticles is that they can be easily recovered from reaction mixture by applying suitable magnetic field (Ahmed and Douek 2013).

1.3.2.1 Nanocatalysts in Biodiesel Production

Biodiesel is a mix of esters, which are commonly produced by transesterification of vegetable oils or animal fats with short-chain alcohols (methanol or ethanol) that meets specific standards to be used as fuel in diesel engines. Compared to

Table 1.1 Different nanocatalyst and feedstock used for biodiesel production

Sr. No.	Nanocatalyst	Feedstock	Yield (%)	Reference
1	MgO	Sunflower oil and rapeseed oil	98.0	Verziu et al. (2008)
2	$K_2O/\gamma\text{-}Al_2O_3$	Rapeseed oil	94.0	Heyou and Yanping (2009)
3	KF/CaO	Chinese tallow seed oil	96.8	Wen et al. (2010)
4	Lithium-impregnated calcium oxide (Li-Cao)	Karanja oil and *Jatropha* oil	99.0	Kaur and Ali (2011)
5	ZrO_2 loaded with $C_4H_4O_6HK$	Soybean oil	98.03	Qiu et al. (2011)
6	Hydrotalcite-derived particles with Mg/Al oxides	*Jatropha* oil	95.2	Deng et al. (2011)
7	ZnO nanorods	Olive oil	94.8	Molina (2013)
8	MgO nanoparticles on TiO_2 support	Soybean oil	95.0	Mguni et al. (2012)
9	$Cs/Al/Fe_3O_4$	Sunflower oil	94.8	Feyzi et al. (2013)
10	TiO_2-ZnO	Palm oil	92.2	Madhuvilakku and Piraman (2013)
11	Iron/cadmium and iron/tin oxide nanoparticles	Soybean oil	84.0	Alves et al. (2014)
12	$KF/\gamma\text{-}Al_2O_3$/honeycomb ceramic (HC) monolithic catalyst	Palm oil	96.0	Gao et al. (2015)
13	Sulfamic and sulfonic acid-functionalized silica-coated crystalline Fe/Fe_3O_4 core/shell magnetic nanoparticles	Glyceryl trioleate	95.0	Wang et al. (2015)
14	$Ca/Fe_3O_4@SiO_2$	Sunflower oil	97.0	Feyzi and Norouzi (2016)
15	CaO	*Jatropha* oil	98.54	Reddy et al. (2016)

fossil fuels, biodiesel presents many advantages, such as biodegradable and superior lubricant properties, without generation of harmful emissions, as well as the possibility to be produced by renewable resources (Feyzi and Norouzi 2016).

About application of nanotechnology, Table 1.1 summarizes different nanocatalysts and feedstock used for the production of biodiesel, as well as the yield related to each process.

As shown, there are a number of different possibilities of application of nanocatalysts in this field. Several functionalized nanomaterials have been successfully used in the production of biodiesel. For example, Wang et al. (2015) synthesized acid-functionalized magnetic nanoparticles and demonstrated their use as heterogeneous nanocatalysts for biodiesel production. In this study, acid-functionalized, i.e., sulfamic and sulfonic silica-coated crystalline Fe/Fe_3O_4 core/shell, magnetic nanoparticles were synthesized and used for the production of biodiesel from transesterification of glyceryl trioleate. Authors reported that both acid-functionalized nanocatalysts showed the significant catalytic activities. However, the sulfamic acid-functionalized nanocatalysts showed comparatively more activity than the sulfonic acid-functionalized nanocatalysts. In another investigation, Tahvildari et al. (2015) investigated the production of biodiesel from cooking oils, using CaO and MgO nanoparticles synthesized by sol-gel and sol-gel self-combustion methods, respectively. CaO nanoparticles showed significant increase in the biodiesel yield compared to MgO nanoparticles.

Other interesting approach is the use of magnetic nanocatalysts that can be easily recovered and reused, favoring the economic viability of the process. In this context, Alves et al. (2014) proposed a rapid and easy nanotechnological approach for the production of biodiesel from soybean oil. In this study, authors used a mixture of iron/cadmium and iron/tin oxide nanoparticles with magnetic properties, prepared by coprecipitation method as nanocatalysts for the biodiesel production. Between the two used nanocatalysts, iron/tin oxide nanoparticles showed maximum efficacy by producing about 84 % biodiesel. These nanocatalysts presented significant potential toward hydrolysis, transesterification, and esterification of soybean oil and their fatty acids. Similarly, Qiu et al. (2011) demonstrated the synthesis by ZrO_2 nanocatalyst loaded with $C_4H_4O_6HK$ (potassium bitartrate), in size range of 10–40 nm. Further, authors investigated the production of biodiesel by using the synthesized nanocatalysts for the transesterification of soybean oil and methanol in different molar ratios and other parameters like reaction temperature, nanocatalyst concentration, and reaction time. The obtained results showed that reaction mixture containing methanol and oil in the ratio 16:1 having 6.0 % nanocatalyst at 60 °C for 2.0 h resulted in maximum biodiesel yield of about 98.03 %.

Several other studies have been reported using nanocatalysts for biodiesel production. For example, Wen et al. (2010) synthesized KF/CaO nanocatalyst by impregnation method having size in the range of 30–100 nm and further used it for the production of biodiesel from Chinese tallow seed oil. This study reported about 96.8 % of biodiesel yield showing potential of such nanocatalyst for biodiesel industry. In another study, Deng et al. (2011) obtained about 95.2 % yield of biodiesel from pretreated *Jatropha* oil using nanocatalysts, hydrotalcite-derived particles with Mg/Al oxides synthesized by a coprecipitation method using urea as precipitating agent. In a novel proposal, Feyzi et al. (2013) reported a new nanocatalyst, Cs/Al/Fe_3O_4, that was synthesized and evaluated regarding its catalytic efficacy for biodiesel production. This investigation demonstrated the effect of different Cs/Al and Cs/Fe molar ratio and calcination conditions on the catalytic performance. These nanocatalysts, in the molar ratio of 2.5:1 and 4:1, respectively, showed potential for production of biodiesel, resulting in 94.8 % of process yield at 58 °C with constant stirring for 120 min.

In other approach, Verziu et al. (2008) demonstrated the synthesis of MgO nanocatalyst in nanosheet form by aerogel method and proposed its use for the production of biodiesel from rapeseed and sunflower oil, verifying process yield up to 98 %. Recently, Feyzi and Norouzi (2016) synthesized a nanocatalyst $Ca/Fe_3O_4@SiO_2$ with strong magnetic properties using combination of two different approaches, i.e., sol-gel and incipient wetness impregnation method for the production of biodiesel. Synthesized nanocatalysts were shown to be very effective at optimum conditions and resulted in maximum yield of about 97 %. The magnetic nature of nanocatalyst supported its reuse for several times without significant loss in its catalytic activity. In another current report, Reddy et al. (2016) demonstrated the synthesis of novel calcium oxide (CaO) nanocatalyst, using seashell, *Polymesoda erosa*, through different steps such as calcination, hydration, and dehydration techniques. Authors also investigated the efficacy of the synthesized nanocatalyst toward biodiesel production from the non-edible crude oils like *Jatropha* oil. Maximum of 98.54 % biodiesel yield was reported at conditions of methanol to oil ratio in 5.15:1 molar ratio, 133.1 min reaction time at 0.02:1 (w/w) nanocatalyst ratio.

1.3.2.2 Nanocatalysts in Bioethanol Production

Bioethanol (ethyl alcohol) is generally produced by carbon sources of sugarcane juice, grains, and others. However, production of this alcohol by using fermentable sugars, released from vegetal biomass, such as lignocellulosic materials, is also possible. These materials are mainly composed by cellulose and hemicellulose, polymeric structures of carbohydrates, and lignin, a complex organic polymer composed mainly by phenolic compounds (Antunes et al. 2014). For the use of sugars present in cellulose and hemicellulose fractions, some pretreatments are required to break down the recalcitrance of biomass, disrupting polymeric fraction in fermentable monomers. Usually, after an initial pretreatment, cellulosic fraction of these materials is enzymatically hydrolyzed (Rai et al. 2016). By this method, monomeric glucose can be produced in milder conditions of process (lower temperature, without requirement of pressure), compared to chemical process, as well as the non-formation of undesirable fermentation inhibitor compounds.

For example, the use of cellulases for the hydrolysis of lignocellulosic biomass is responsible for about 18 % of total costs involved in the process of the bioethanol production. Therefore, the development of advanced strategies, which could provide the recovery and recycling of enzymes, can reduce production cost. Considering this fact, nanotechnology offers immobilization of various enzymes such as cellulases and hemicellulases, involved in the bioethanol production on different nanomaterials. For example, immobilization of enzyme on magnetic nanomaterials is a promising method that provides easy recovery of enzyme by applying magnetic field that allows enzyme recovery and reuse for several cycles (Alftren 2013; Rai et al. 2016).

Studies that were carried out by using magnetic nanoparticles were reported for immobilization of enzymes involved in the bioethanol production. Generally, enzyme immobilization on nanoparticles is achieved by covalent binding or physical adsorption. However, covalent binding method is more suitable because it reduces protein desorption due to formation of covalent bonds between enzyme and nanoparticles (Abraham et al. 2014). For stable immobilization of enzyme on nanomaterials, these compounds need to be modified or coated with chemically active polymer to provide the functional group for linkage of enzyme.

Lee et al. (2010) demonstrated the immobilization of β-glucosidase enzyme on polymer magnetic nanofibers by entrapment method for cellulosic ethanol production. β-Glucosidase is the enzyme responsible for the conversion of cellobiose into glucose, which can be metabolized by microorganisms to produce bioethanol. In fact, the entrapment of β-glucosidase on magnetic nanofibers provide stability to the enzyme and also the possibility of repeated use, separating them by applying magnetic field. Similarly, Verma et al. (2013b) evaluated β-glucosidase (isolated from fungus) immobilization on magnetic nanoparticles, used as nanobiocatalyst for bioethanol production. Authors verified that 93 % of enzyme-binding efficiency was recorded, showing about 50 % of its initial activity at 16th cycle. Jordan et al. (2011) also tested recycling of enzyme in the hydrolysis of microcrystalline cellulose by using carbodiimide as linking polymer for enzyme immobilization on Fe_3O_4 nanoparticles. Due to magnetic nature of nanoparticles, the enzyme could be recovered easily and recycled for six times.

In another study, Goh et al. (2012) demonstrated that enzyme involved in the bioethanol production was immobilized in single-walled carbon nanotubes, which was already incorporated by magnetic iron oxide nanoparticles to give magnetic properties. In this study, the performance of immobilized enzyme could be controlled by altering the concentration of iron oxide nanoparticles in nanotubes. Thus, immobilized enzyme can be stored in acetate buffer at 4 °C for its longer storage.

Different nanomaterials have been studied for immobilization of enzymes. For example, Xie and Wang (2012) demonstrated the immobilization of lipase on magnetic chitosan microspheres synthesized by chemical coprecipitation method. In this work, glutaraldehyde was used as linking molecules for the covalent binding between lipase enzyme and magnetic chitosan microspheres. Moreover, enzyme immobilized on TiO_2 nanoparticles by adsorption methods was also successfully used for the hydrolysis of lignocellulosic materials, aiming for the use of bioethanol production (Ahmad and Sardar 2014). In another study, Cherian et al. (2015) reported the immobilization of cellulase recovered from *Aspergillus fumigatus* on manganese dioxide nanoparticles by covalent binding. Authors verified that immobilized enzyme showed potential to enhance in its thermostability property compared to free enzymes, presenting stability up to 70 °C. Immobilized cellulase-mediated hydrolysis followed by the use of yeast leads to the production of bioethanol (21.96 g/L) from agricultural waste. After repeated use for about five cycles, immobilized enzyme showed 60 % of its activity.

Apart from magnetic nanoparticles, other nanomaterials can be used in nanotechnology process, such as silica and TiO_2, polymeric nanoparticles, and carbon materials such as fullerene, graphene, carbon nanotubes, and others. These materials have been successfully reported for immobilization of different enzymes regarding the processes of bioethanol production (Huang et al. 2011; Cho et al. 2012; Pavlidis et al. 2012; Verma et al. 2013a). For instance, Pan et al. (2007) demonstrated the use of carbon nanotubes entrapped with Rh particles to enhanced catalytic activity for production of ethanol. Actually, free cores available on the carbon nanotubes are reported as a way to facilitate the incorporation of materials of different interests. In another investigation, Lupoi and Smith (2011) studied the immobilization of cellulase on silica nanoparticles, demonstrating the efficacy of immobilized and free enzymes in hydrolysis of cellulose into glucose. Authors observed that immobilized cellulase enzyme showed increased yield of glucose when compared to free enzyme, verifying that immobilized enzymes can be used in simultaneous saccharification and fermentation.

Microbial cells can also be immobilized on the nanoparticles and applied to fermentation step of ethanol production. For example, Ivanova et al. (2011) developed an approach for immobilization of *Saccharomyces cerevisiae* cells on magnetic nanoparticles. Further, authors demonstrated continuous fermentation process for the production of bioethanol; immobilized *S. cerevisiae* cells showed high ethanol production capability. Hence, the studies performed either on the immobilization of enzyme or whole microbial cells on the different nanomaterials provide evidence that such approaches will be convenient for the safe and economical production of bioethanol from cheapest lignocellulosic materials.

1.4 Safety Issues

Unfortunately, a few studies have been made on the safety assessment of nanoparticles used for biofuel and bioenergy production. During the course of their synthesis and application, nanoparticles can be released in the environment posing threat to human and environment (Gupta et al. 2015). However, as far as human exposure is concerned, nanoparticles have ability to enter inside the human body and may affect its most sensitive areas (Pourmand and Abdollahi 2012). The easy entry is possible via the process of ingestion, inhalation, and the penetration through intact and/or fractured dermis layers (Tang et al. 2009; Gupta et al. 2012). This is because nanoparticles have smaller size, and therefore, they can easily penetrate into the human and animal cells. They can cause trouble to the normal functioning of the cell (Vishwakarma et al. 2010). For instance, metal nanocatalyst (Asharani et al. 2011), catalyst support such as carbon nanotube and carbon fiber (Simon-Deckers et al. 2008; Erdely et al. 2013), and zirconia-based nanoparticles have been reported to induce the toxicity.

As far as the use of nanoparticles in biofuel is concerned, their emission from the vehicles and industry can cause harmful effects. They can be deposited into the lung tissues through respiration. Such deposition may lead to the development of abnormality in the lung tissues, which can lead to various respiratory ailments including asthma, bronchitis, etc. (Upadhyay et al. 2015). Moreover, the worker manufacturing, along the processing of nanoparticles, has the chances of getting exposed through their dermal contact or through breathing. Platinum nanoparticles have also been investigated for their exposure effects on early stage of development. Literature reported that, depending on their concentration, they lower the heart rate, delay the hatching process, and also affect the touch response, axis curvature (Asharani et al. 2011).

Even though in-depth mechanism of toxicity is hitherto not understood, the toxicity is dependent on size (Mostafalou et al. 2013), shape, dose (Foldbjerg et al. 2011), composition, surface capping, and structure (Gupta et al. 2012). At cellular level, nanoparticles interact with the lipid bilayer envelope of the cell. This interaction disturbs the normal functioning of the cell membrane, thereby causing the pits in it, subsequently forming the cell content leakage. The nanoparticles, if exposed to the biological systems, can interact, followed by entering inside the cell, through mitochondrial membrane thereby disturbing its potential (Chen et al. 2008).The damage to mitochondria affects the energy balance of the cell consequently disturbing normal cell metabolism. Nanoparticles also induce the reactive oxygen species such as oxygen ions. The accumulated reactive radicals interact with proteins, especially with the enzymatic machinery. DNA damage by nanoparticles has also been reported to be induced by nanoparticle interaction (Kim et al. 2009; Guan et al. 2012).

On the basis of increased use of nanoparticles for biofuel applications, their exposure effect on human and environment is obvious. Therefore, for safe use of nanoparticles in such studies, safety assessment is of utmost importance. In the present scenario, various approaches are being made for assessing the toxicity of nanoparticles. Most of the studies involve in vitro evaluation of nanotoxicity. However, extensive studies are needed to focus on in vivo interaction of nanoparticles particularly used for biofuel and bioenergy production.

1.5 Conclusions

The global environmental problems, such as greenhouse effect generated by different chemicals including the use of petroleum and coal, have necessitated to search for alternative renewable energy and biofuel sources. The demand of alternative sources is also due to the rapid depletion of exiting oil reserves. Among the new alternatives, nanotechnology is gaining importance to tackle the problem of bioenergy and biofuels by different applications including use of operative catalysts and amendments in feedstocks.

Encouragingly, various nanomaterials, such as carbon nanotubes and magnetic and metal oxide nanoparticles, having unique properties, are used for biofuel production. Among all the nanoparticles tested for biofuel production, magnetic nanoparticles are frequently used because they can be easily recovered due to their magnetic property. The nanoparticles also can enhance the activity of enzymes after their immobilization. Although the use of nanotechnology for the production of biofuel and bioenergy has been beneficial and can be recommended for large-scale processing, there are safety issues concerning the environment and human being that need to be addressed meticulously after extensive long-term studies.

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