World Applied Sciences Journal 35 (8): 1305-1311, 2017
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2017.1305.1311

An Overview of Applications of Nanotechnology in Biofuel Production

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Abstract: The rapidly depleting energy resources is the greatest challenge that the world is currently facing and mankind is forced towards exploring the various alternatives that are available to meet the rising energy demands. Biofuel is one of the alternative sources of energy and is basically the energy stored in materials that is made with the help of living things. Various ways of enhancement of biodiesel and biogas production are continuously being explored and nanotechnology is one growing field that can contribute effectively to the biofuel production industry. The various nanomaterials production techniques and the methods through which they are made functional and stable are analyzed in this study. Further to that, several literature studies have been reviewed in order to provide a panoramic view of the use of nanomaterials to improve the production processes of biodiesel and biogas. On one hand, nanocatalysts and nanomaterial bound microbial enzymes are used to improve the biodiesel production rate and on the other hand, several types and kinds of nanomaterial additives are used to increase the biogas production yield. Based on the various studies reviewed, it was found that the lipase enzyme from Pseudomonas cepacia bound to Fe_3O_4 nanoparticle and nano zero valence iron additive were relatively more effective in the production of biodiesel and biogas respectively.

Key words: Nanomaterials · Renewable energy · Biodiesel · Biogas

INTRODUCTION

Increasing price of crude oil and its refined products is a clear indication of the continuing depletion of global non-renewable fossil fuels, namely, coal, crude oil and natural gas. One study has indicated that the world's fossil fuel reserves would be diminished by 2050 at this rate of consumption, which is roughly about 10^5 times faster than that the nature can actually create [1]. Apart from the rising prices, fossil fuels are also said to contribute considerably to environmental pollution and ecological devastation, causing depletion of ozone layer, global warming and destroying both the biosphere as well as the geosphere. The environmental concentration of the main greenhouse gas, carbon dioxide, has been steadily rising to reach a level of about 390 ppm and is expected to reach 750 ppm by the end of this century [2]. This carbon dioxide is capable of trapping the sun's infra-red radiation and thereby causing a rise in the global temperature. These two factors have led the fuel industry to move towards sustainable sources of alternative energy or in other terms, renewable energy sources.

Sustainable sources of alternative energy can range from solar, wind, tidal and geothermal energies to energies generated from biomass, termed as biofuels. Currently about 90% of the world's energy demands are met by fossil fuels, which is expected to reduce to around 50% by 2040 with the advent of the above-mentioned renewable energy sources [3]. Biofuels utilize domestically available renewable resources [4] and are biodegradable and non-toxic [5]. They can be produced from various feedstocks such as vegetable oils and biomass [6]. Anaerobic digestion of agricultural residues [7], animal manures [8], organic food wastes [9], sewage sludge [10] and various other energy crops [11] yield yet another renewable source of energy known as biogas.

In 1959, Feynman introduced the term "nanotechnology", which refers to the manufacture and use of nanometer-scale materials (materials with at least one dimension less than 100 nm) [12]. Since then, many researchers and scientists around the world have explored the effects of nanomaterials in a wide variety of fields, ranging from integrated circuits, food products and energy conversion devices [13], [14]. Compared to their

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large-scaled materials, the nanomaterials are said to have unique optical, electronic, magnetic, mechanical and chemical properties [15]. Nanomaterials are said to play an important role in energy fields due to their unique structure, high energy electrical storage capacity, relatively high specific area and comparatively good efficiency of lighting and heating [16], [17]. Dimension-wise, they can be compared to biological macromolecules like enzymes or nucleic acids [18], [19].

Production and Characteristics of Nanomaterials: At the outset, it is first essential to understand the production mechanisms and basic characteristics of nanomaterials before using them to enhance biofuel production. Nanomaterials basically include a variety of substances ranging from nanoparticles, nanotubes, nanosheets, nanocomposites, nanocrystalline materials, metal based nanomaterials to carbon based nanomaterials. There are various ways of nanomaterial production. However, one of the two major ways is the top down method, where in, the bulk materials such as gold, silicate, etc. are broken down into nanoscale sized materials. This is the method that is commonly used to produce consumer sunscreen products and solar cells. The other major type of method is the bottom up approach, where, nanoparticles are assembled atom by atom or molecule by molecule [15]. The latter approach is said to be more difficult and expensive, but has also found to contribute effectively to the sectors of energy development, transportation and electronics [20].

The other methods by which nanomaterials can be produced include the dealloying and thermal annealing method, co-precipitation method, arc discharge, laser ablation, chemical vapour deposition technique, electrospinning, self-assembly and phase separation technique and thermal exfoliation method. Each of these methods produce different kinds of nanomaterials and are discussed below. Generally, the nanomaterials, be it nanoparticles or nanofibers or nanotubes, are first produced as dry powders by either physical or chemical methods and then dispersed into a suitable fluid using intense magnetic force agitation or high-shearing mixing or ultrasonic agitation or homogenizing and ball milling [21].

$Ag_{78}Au_{22}$ alloy foils are chemically dealloyed in concentrated nitric acid at room temperature to produce nanoporous gold particles [22]. This method is known as the dealloying and thermal annealing method. Co-precipitation method is yet another method to prepare nanoparticles. In this method, the nanoparticles are collected with a magnet as precipitate and are washed repeatedly with water to remove non-magnetic by-products [23].

Good quality carbon nanotubes can be produced by arc discharge which requires a carbon source and electricity [24] or by laser ablation which requires a carbon source and high intensity light or by chemical vapour deposition technique that requires a carbon source and heat [25]. The electrospinning technique uses electrostatic forces to produce nanofibers from polymer solutions using a high voltage power supply, a spinneret and a grounded collecting plate [26]. Sill &Recum explain that the high voltage injects a charge of certain required polarity into the polymer solution which is then moved towards the collector that is of opposite polarity [27].

Thermal exfoliation method is used to produce nanosheets. A classic example is the production of nanographene sheet where graphite powder is allowed to react with concentrated sulfuric acid, nitric acid and potassium chlorate at room temperature and nanographene sheet is exfoliated by the process of rapid heating at 1050ºC in the presence of argon gas [28]. Soon after preparation of the nanomaterials, they undergo a crucial step known as surface functionalization which is essential to increase their efficiency [29]. This process is basically to provide stability and biocompatibility to the nanomaterials and is also said to affect the dispersability and interaction capacity of nanomaterials with enzymes [30].

The process of surface functionalization is to add required functional groups to the nanomaterial's surface [31] and the materials that are commonly used include natural polymers such as starch, chitosan, gelatin, or synthetic polymers such as polyacrylic acid, biopolymers, dendrimers [12]. The functional groups that are added may serve different purposes such as to change the surface charge of the support material or to chemically link with other functional groups in the target, or even to decrease the pore entrance size in order to trap the enzymes [32].

Compared to their larger size counterparts, the nanomaterials tend to have different properties in terms of their electrical or heat conducting capacity, reflecting light, rates of reactivity, strength, etc. [33]. For example, aluminum, in its usual state is stable; however, becomes combustible in the nanoscale. Likewise, inert materials such as gold, silver and platinum serve as catalysts in their nanoscale and nano silver is also said to possess anti-microbial properties [34].

Biodiesel: Enhanced Production Using Nanotechnology: Vegetable oils are said to possess properties such as density, air/fuel ratio and heat of vaporization similar to mineral diesel and are also know to reduce carbon monoxide, sulphur oxide and smoke emissions. In the usual method of biofuel preparation from vegetable oils, the oils are transesterified with methanol in the presence of a suitable alkaline catalyst, mostly NaOH. The major problems associated with this process include saponification, deactivation of the catalyst and low reaction rate. In order to overcome the above mentioned hiccups, Ti-incorporated SBA-15 (Santa Barbara Amorphous) mesoporous silica was found to be a highly efficient and recyclable solid acid catalyst to produce biofuels from vegetable oils [35].

High pressure liquefaction of air dried wood results in a complex mixture of volatile and non-volatile organic components, known as bio-oil [36]. One study illustrates that used cooking oil can be effectively converted to biodiesel by four different ways, namely, directly blending with mineral diesel, microemulsion method, thermal cracking and transesterification [37]. As highlighted earlier, even though transesterification is the most commonly used process for the production of biodiesel, it had its own set of problems that include presence of free fatty acids, water content of oils or fats, reaction temperature and time and molar ratio of glycerides to alcohol. Nanotechnology was effectively used in several studies to overcome these shortcomings in the production of biodiesel.

As it is, biodiesel fuel is said to substantially reduce the emissions of unburned hydrocarbons and carbon monoxide. To take this a step further, addition of nano-cerium oxide particles to the biodiesel fuel was found to promote complete combustion and enhance hydrocarbon oxidation, thereby reducing hydrocarbon and oxides of nitrogen emissions [38].

The enhancement of transesterification process was mainly explored by using several different types of nanocatalysts at different preparation conditions. A good yield of about 95% or more of biodiesel was obtained with nano-magnetic solid base catalyst of $KF/CaO\text{-}Fe_3O_4$ [39], with KF/CaO nanocatalyst from Chinese tallow seed oil [40], with heterogeneous solid base nanocatalyst from soybean oil [41], with lithium impregnated calcium oxide solid catalyst from karanja and jatropha oils [42], with tandem lipases [43] and magnetic nanobiocatalyst aggregates [44] from waste grease and with sulfated zirconia nanoparticle catalysts [45]. Several studies have also demonstrated that biodiesel production is enhanced using carbon-based catalysts [46], carbon-based nanostructured catalysts [47] and sodium titanate nanotube catalysts [48].

Carbon nanotube-enzyme bioreactors was produced by incorporating iron oxide nanoparticles into single-walled carbon nanotubes which resulted in magnetic single-walled carbon nanotubes. This bioreactor enabled to recycle the immobilized enzyme thereby improving the efficiency of the bioreactor and reducing capital costs [49]. Compared to their bulky conventional materials, nanomaterials have been found to be good enzyme immobilization supports due to their large surface area to volume ratios, thereby leading to higher enzyme loading and good biocatalytic potential [19].

Microbial enzymes have been bound to nanomaterials to enhance the process of biodiesel production. Transesterification of soybean oil is effected using the enzyme lipase from *Pseudomonas cepacia* and several studies have explored the effectiveness of this enzyme when bound to different types of nanomaterials such as nanoporous gold [50], Fe_3O_4 nanoparticle [51], [52] and PAN nanofiber [53]. Transesterification of rapeseed oil is also effected using the same enzyme bound to polyacryonitrile nanofiber [54]. Lipase from *Thermomyces lanuginosa* has been covalently bound to Fe_3O_4nanoparticle for the production of biodiesel from soybean oil [55] and waste grease [44]. Lipase from *Rhizopus miehei* was encapsulated in silica nanoparticle for the production of biodiesel from triolein [56]. Lipase from *Burkholderia sp*. was adsorbed onto magnetic nanoparticles [57] and ferric-silica nanocomposite [58] for the effective transesterification of olive oil.

Biogas: Enhanced Production Using Nanotechnology: Biogas is a flammable gas composed of a mixture of gases, mainly carbon dioxide and methane. It is usually produced by anaerobic digestion of biomass and sewage sludge. The major sources of biogas production include sewage treatment plants, landfills, cleaning of organic industrial waste streams and mesophilic and thermophilic digestion of organic wastes [59]. The process of anaerobic digestion includes four main steps, namely, hydrolysis, acidogenesis, acetogenesis and methanogenesis [60], [61]. In this process, several nanomaterials are added as additives to improve the biogas yield.

Nano TiO_2 in the size range of 7.5nm and at a concentration of 1120 mg/l was found to increase the biogas production from waste water treatment sludge by 10% [62]. Nano CeO_2 in the size range of 192nm and at a concentration of 10 mg/l was found to increase the biogas production from UASB sludge by 11% [63]. A very good increase in the biogas yield was seen with 7nm sized Fe_3O_4 nanoparticles at a concentration of 100 ppm from waste water sludge. The increase in biogas production was 180% and there was also about 234% increase in methane production [64].

Nano zero valence iron (NZVI) is said to be a low release electron donor for the methanogenesis step during the anaerobic digestion process and this aids in the improvement of biogas production rate [65]. One study found that 20nm sized NZVI particles increased the biogas production and methane production by 30.4% and 40.4% respectively [66] and another study found that 50nm sized NZVI particles increased the methane production from 58 mmol to 275 mmol [67]. 10% increase in methane production was also recorded in another study with NZVI additives [68].

The effect of metal nano substances encapsulated in porous SiO_2 on anaerobic digestion was also studied by Al-Ahmad et al. The metals studied included nickel (Ni), cobalt (Co), iron (Fe) and platinum (Pt). Significant increase in methane production was observed in the range of 70% with Ni nanoparticle, 48% with Co nanoparticle, 7% with Fe nanoparticle and 6% with Pt nanoparticle [69].

Micro/nano fly ash (MNFA) and micro/nano bottom ash (MNBA) were also found to have an effect on the anaerobic digestion as they tend to provide more habitats for anaerobic organisms. MNFA was found to increase the biogas production by 2.9 times and MNBA was found to increase the biogas production by 3.5 times [70].

Further research can be directed in terms of using bioactive nano-metal oxides and nano-zero valence metals in various proportions. Another area to explore would be the photoactive nano-metal oxides to increase the amount of hydrogen produced which eventually increases the methane production [71].

CONCLUSION

This study provides an extensive overview of the various nanomaterials that have been potentially explored for their capabilities to improve the production of biofuels, be it, biodiesel or biogas. Nanomaterials are widely used as catalysts in biodiesel production and as additives in biogas production to improve efficiency in both cases. From all the studies that are reviewed here, it is quite evident that the lipase enzyme from *Pseudomonas cepacia* when bound covalently to Fe_3O_4 nanoparticle and NZVI additives are relatively more effective in the production of biodiesel and biogas respectively. At the same time, nanomaterials have also shown to reduce hydrocarbon and oxides of nitrogen emissions to a considerable extent, thereby safeguarding our environment. Thus, it is evident that nanotechnology can be effectively used to reduce both the environmental impact and usage of fossil fuels.

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