Nanotechnology in Bioethanol/Biobutanol Production

Deepika Kushwaha, S. N. Upadhyay and P. K. Mishra

Abstract Biofuels will become competitive globally only when they can be delinked from food crops. All non-food feeds for bio-alcohols (bioethanol/biobutanol) production have the inherent difficulty of conversion from cellulose to simpler sugars that can be fermented into end products. The process currently being used to convert complex cellulosic feedstocks into sugars is costly; hence, the biofuels obtained through these routes are not economical. Enormous efforts are currently being made worldwide to convert second- and third-generation feedstocks into bioethanol/biobutanol, and several prominent global energy-producing companies are investing large sums of money to realize this dream. The complexity and cost of different stages of bio-alcohols production can be minimized with the application of different nanoparticles. A three-pronged approach is required to comprehend the economic production of bioethanol which begins with technology for better crop production, improved feedstock processing, and development of new biofuels such as biobutanol and renewable hydrocarbons. Various kinds of nanoparticles such as iron oxide, nickel cobaltite, zinc oxide and different nanocomposites, etc. have been used for production of biofuels. The present chapter deals with the present status on the application of nanoparticles in different stages of bio-alcohols (bioethanol/biobutanol) production. Involvement of these nanomaterials in different bioconversion processes provides a sustainable way by reducing the raw biomass processing as well as production costs and lowering down the harmful environmental impacts.

D. Kushwaha · S. N. Upadhyay · P. K. Mishra (✉)
Department of Chemical Engineering and Technology,
Indian Institute of Technology (BHU), Varanasi 221005, India
e-mail: pkmishra.che@itbhu.ac.in

N. Srivastava et al. (eds.), *Green Nanotechnology for Biofuel Production*, Biofuel and Biorefinery Technologies 5,
https://doi.org/10.1007/978-3-319-75052-1_8

1 The Global Biofuel Scenario

Reducing availability of fossil fuels and increasing atmospheric pollution through their use are the major global concerns. Demand for energy is expected to increase up to 53% by the year 2030; consequently, the petroleum consumption will increase from 89.41 million barrels per day in 2012 to 136.80 million barrels per day by 2030 (Shahid and Jamal 2011; Noraini et al. 2014). Due to increasing global demand of petro-fuels and decreasing availability of crude petroleum, biofuels are currently receiving considerable attention as possible replacement for the fossil fuel resources (Kumar and Gayen 2011). Biofuels like ethanol, butanol, biodiesel, and biogas are being considered as the sustainable and viable options because of their renewable nature and potential to replace most petroleum-derived fuels. According to the Navigant Research, USA, global demand of biofuels transportation will increase from 32.4 billion gallons per year (BGPY) in 2013 to 51.1 BGPY by 2022 (Navigant Research 2014). In 2014, the global biofuel production increased by 9.0%, i.e., to 127.7 billion liters including all types of biofuels (ethanol, biodiesel, and hydrotreated vegetable oil) (Renewable Energy Policy Network for the 21st Century (REN21), Global Status Report 2015). Among this, ethanol alone accounted for 74% of the total global production involving top five countries—United States, Germany, Brazil, China, and Argentina. The USA alone accounted for 58% of the total ethanol production due to large availability of the raw biomass (Xue et al. 2013; Balat and Balat 2009). On the basis of the type of raw biomass, biofuels are broadly categorized as first-, second-, and third-generation biofuels. Production of biofuels from food materials has been completely ruled out by different researchers and also banned by the governments due to the food versus fuel dispute. Inspite of this, several countries are producing the major biofuel, i.e., ethanol from food crops. United States of America is producing ethanol from corn; Brazil from sugar crops; and China from sweet sorghum, cassava, and other non-grain crops (REN21, Global Status Report 2015). Considerable effort has been made globally to adapt a sustainable approach for biofuel production; in this regard, lignocellulosic and algal biomasses are attracting much attention. In the European Union (EU), straw and other agricultural wastes are the major feedstocks for bioethanol production (Raposo et al. 2009). According to the White Paper on Renewable Energy Sources, published by the European Commission in 1997, bio-renewables utilization in the production of energy is likely to increase to 20% by 2020 (Mascal and Nikitin 2008).

2 Nanotechnology in Bioethanol/Biobutanol Production

Over the past few years, "nanotechnology" has spread to almost every aspect of science and technology with several applications in day-to-day life also. Major applications of these nanomaterials are in cosmetics and other personal care products, fabrics, coating industry, biofuel cell, drug delivery, photocatalytic degradation of industrial dyes and contaminants, solid rocket propellants, thin film solar cell, water purification, wastewater treatment, biofuels production, etc (Shah et al. 2010). Nanotoxicology and nanodiagnostics are other emerging fields that are gaining attention of researchers and are likely to be the major nanotechnology application areas in the near future. Researchers working in the fields of biological and chemical sciences have found these as boon for effecting target specific modifications in biocatalysts to assist the bioconversion of biomass components into biofuels in a healthier way (Kim et al. 2005).

Nanoparticles are characterized as nanofibers, nanorods, nanowires, nanoclusters of metal and metal oxides, etc. These nanocatalysts are different from conventional bulk catalysts in terms of their size that provides very large area-to-volume ratio and the resultant large active surface for chemical reaction to take place (Sirajunnisa and Surendhiran 2014). Nanomaterials can accelerate the reaction by providing the active sites for reactants in solid, liquid, or gaseous phase. Full exploitation of nanotechnology requires development of different forms of nanomaterials such as nanospheres, nanowires, nanotubes, etc. that may have applications in a wide range of industries.

Use of nanoparticles in the bioenergy sector for sustainable energy supply and long-term environmental care has attracted attention throughout the world. Application of nanoparticles during the alcohol production helps in improving the overall effectiveness of the process by increasing the efficiency of pretreatment, enzymatic hydrolysis, and increasing the reaction rate during the fermentation step. The major factors responsible for the generation of end products and permitting effective control of the reaction rate are particle size and morphology, surface area, nature of nanoparticles, and type of biomass utilized (Chaturvedi et al. 2012). The main drawbacks of conventional methods of bioethanol/biobutanol production are low reaction rate, high cost of biomass processing, and low product yield. To overcome these issues, nanoparticles have been successfully used for bioethanol production and are making its way to enhance the productivity. But in the case of biobutanol scanty work has been reported till date.

2.1 Nanomaterials in the Preprocessing of Raw Biomass

Nanoparticles are of special interest for improving the efficiency of biochemical reactions. Their application in the processing of second and third generation of biomass and production of different liquids (biodiesel and bioethanol/biobutanol) and gaseous biofuels is an emerging area having the capability of lowering down the processing and production costs and improving both the quality and quantity of the end product. Use of nanocatalysts in the field of bio-alcohols production is attracting the attention of the researchers because of their reusability (Kim and Lee 2016). However, there is still much to be explored with regard to the use of nanocatalysts in the field of bio-alcohols production.

Pretreatment of biomass is an unavoidable but a costly step and a significant improvement in the preprocessing of the biomass is the foremost step for bioethanol/ biobutanol production at an economical rate. Application of nanoparticles for this purpose in conjunction with the different alternative approaches for the pretreatment of raw biomass makes the process more robust (Razack et al. 2016; Pena et al. 2012). Nanoparticles can efficiently be used during the pretreatment for improving the chemistry at molecular level and also enable the specific and targeted modification of biocatalysts in addition to elimination of the pollution caused by the chemical pretreatment (Razack et al. 2016). Metal nanoparticles are highly efficient in penetrating the cell wall of raw biomass due to their small structure and effortlessly interact with the biomolecules to release carbohydrates to be used for bioethanol/biobutanol production. Razack et al. (2016) achieved nearly 15.26% of the total carbohydrate yield from *Chlorella vulgaris* biomass (150 μg/g of silver nanoparticles (AgNP) prepared through biological route) within 40 min of incubation at 100 rpm. Higher concentration of nanoparticles lowered the incubation time to rupture large portion of cell wall area to release intracellular components (carbohydrate/lipid). Efficient destruction of cell wall may result due to the strong interaction between the nanoparticles and cell wall components (cellulose/proteins) that provide large surface area to nanoparticles to act upon the cell. Pena et al. (2012) used acid-functionalized (perfluoroalkylsulfonic (PFS) and alkylsulfonic (AS)) magnetic nanoparticles for the pretreatment of wheat straw at different temperatures (at 80 °C for 24 h and 160 °C for 2 h). Cobalt spinel ferrite was used to prepare the magnetic core of nanoparticles, and silica coating was used as shell to protect the surface from oxidation. High hemicellulose to oligosaccharides conversion (66.3%) was achieved compared to the control (50.9%) using PFS nanoparticles at 160 °C, showing the high efficacy of nanoparticles for the pretreatment of feedstock. Separation of these magnetic particles can be achieved under strong magnetic field for further utilization in the next pretreatment cycle, thus enabling reduction in the overall cost of preprocessing.

It is essential to have an enzymatic hydrolysis step for completing the preprocessing of the biomass. Requirement of these enzymes depends upon the type of biomass being utilized, for example, this step is mandatory for the lignocellulosic biomass while optional for the third generation of feedstocks (algal biomass). This involves the conversion of cellulose and hemicellulose into monomeric sugars by the action of different enzymes such as cellulases, hemicellulases, β-glucosidases, etc. and has to be highly efficient (Maitan-Alfenas et al. 2015). Procurement of these enzymes for every cycle of hydrolysis is highly costly and is not feasible at industrial scale. Cellulase is the major enzyme required for the enzymatic hydrolysis of the biomass during fermentative production of alcohols. Activity and stability of enzymes are the major concerns during the processing, and the possibility of the use of nanomaterials for this purpose has aroused much interest (Dutta et al. 2014). Srivastava et al. (2014) reported the effect of $NiCo_2O_4$ nanoparticles on cellulase enzyme production from *Aspergillus fumigatus* NS and observed improvement in its thermal stability. The nanoparticles used by these workers were synthesized via the hydrothermal method, and it was observed that addition of 1 mM nanoparticles in the media increased the filter paper activity of the produced enzyme by 40%. Further, it was also observed that the presence of $NiCo_2O_4$ nanoparticles affected the activity of other enzymes such as endoglucanase, β-glucosidase, and xylanase by 49, 53, and 19.8%, respectively. Additionally, in the presence of these nanoparticles, the enzymes were thermally stable up to 7 h at 80 °C while control sample (without nanoparticles) was thermally stable only for 4 h at the same temperature. These results clearly prove the effectiveness of the nanoparticles in bioconversion processes as well as in improving the activity and stability of enzymes.

Several researchers have reported the use of metal nanoparticles as co-factor for increasing the enzymatic stability and immobilization of enzymes onto a support material for enhanced enzymatic activity (Srivastava et al. 2016). Enzyme immobilization over the nanomaterials decreases the process cost due to their easy recovery and reusability. Efforts are being made to make it a viable process at industrial scale. It has been shown that conventional methods of immobilization resulted in loss of the specific activity of enzymes during use (Mohamad et al. 2015). Process efficiency is enhanced using different nanoparticles as these particles provide large immobilization surface to enzymes, prolong self-life and stability (Kim et al. 2006). Srivastava et al. (2015) showed that iron nanoparticles (Fe_3O_4) and nanocomposites (Fe_3O_4/Alginate), both efficiently increased the enzymatic activity and stability up to a significant level by providing suitable support for enzyme immobilization. Fe_3O_4 nanoparticles and uniquely structured nanocomposites were prepared by co-precipitation method for use in bioalcohol production. Jordan et al. (2011) successfully immobilized the cellulase enzyme complex onto magnetic nanoparticles of less than 1 μm size via carbodiimide activation that can be further utilized for the processing of cellulosic materials during bioethanol/biobutanol production. Hermanova et al. (2015) covalently immobilized lipase enzyme from *Rhizopus oryzae* onto a graphene oxide nanobed and showed that it possessed high solvent tolerance and thermal stability and an increased activity (65% at 70 °C). The covalent binding of the enzymes onto the support matrix increases the self-life of the enzyme, and its reusability reduces the overall cost. Graphene-based nanomaterials are highly durable and biocompatible and also provide large surface area for immobilization of enzymes and catalytic site for ethanol oxidation (Gokhale et al. 2013; Kakaei et al. 2016). Enzyme immobilization over the graphene oxide surface could take place without using any cross-linking reagent and surface modification, and does not affect the thermal and solvent tolerance properties of enzyme (Zhang et al. 2010; Hermanova et al. 2015).

2.2 Nanomaterials in the Bioethanol/Biobutanol Fermentation

During production of liquid fuels through fermentation, nanoparticles influence the biochemical conversion process by affecting either the enzymatic activity or the gas–liquid mass transfer rate. Various metal nanoparticles such as oxides of iron, cobalt, copper, manganese, etc. have been found to act as effective catalytic material in the area of renewable energy production. Kim et al. (2014) reported enhanced bioethanol production (166.1%) with methyl-functionalized silica nanoparticles in syngas fermentation, and the only drawback was inefficient reuse of nanoparticles. In this study, they used six different types of nanoparticles: palladium on carbon, palladium on alumina, silica, hydroxyl-functionalized single-walled carbon nanotubes, alumina, and iron (III) oxide. Among these silica nanoparticles proved their efficiency for enhanced gas–liquid mass transfer which was further modified with hydrophobic functional groups (methyl and isopropyl) to improve the activity. On the other hand, Kim and Lee (2016) used methyl-functionalized magnetic nanoparticles for enhanced bioethanol production during syngas fermentation, and nearly 213.5% higher production was obtained with the application of methyl-functionalized cobalt-ferrite-silica ($CoFe_2O_4@SiO_2\text{-}CH_3$) nanoparticles. Further, the efficient recovery and reusability of these magnetic nanoparticles make the whole production process highly cost-effective (Kim and Lee 2016). Surface-modified $CoFe_2O_4@SiO_2$ nanoparticles with methyl functional group provide large hydrophobic surface area for gas–liquid mass transfer with resultant increase in ethanol production. Surface modification of catalysts helps in improving the properties of active sites that increase the interaction between the nanoparticles and the molecules significantly (Zhao et al. 2000). A number of composite metallic nanoparticles such as activated Mg–Al hydrotalcite (by co-precipitation and hydrothermal activation with aqueous $Ca(OH)_2$) (Wang et al. 2015), $Fe_3O_4@SiO_2$ (by coating Fe_3O_4 core with silica shell (Mehrasbi et al. 2017) functionalized with 3-glycidoxypropyl trimethoxysilane), CaO-based catalysts having supported gold nanoparticles (by impregnation method Bet-Moushoul et al. 2016), and SrO nanopowder and SrO/SiO_2 composite (by microwave irradiation under inert atmosphere Naor et al. 2017) have been developed. Surface modification of all these catalysts has been performed for improved process efficiency and better yields of biofuels mainly biodiesels. Application of such type of modified nanoparticles has not been reported much in the production of bioethanol/biobutanol till date.

Ivanova et al. (2011) reported improvement in bioethanol fermentation in the presence of alginate/magnetic nanoparticles (with entrapped yeast cells) covalently immobilized on chitosan-magnetite microparticles and cellulose-coated magnetic nanoparticles. They concluded that the efficiency of entrapped yeast cells magnetic nanoparticles was better over the other when both were used in a column reactor. Ethanol yield was reported to be nearly 91% of the theoretical yield with the yeast cells entrapped in matrix of alginate/magnetic nanoparticles and immobilized on magnetite-containing chitosan. The self-life of these magnetic nanoparticles was also examined and found to be more than 1 month at 4 °C in saline.

Carbon nanotubes (CNTs) are different form of nanostructured materials. They not only have a high specific surface area for the immobilization of biological molecules but also possess high tensile strength, remarkable mechanical and thermal stability, and are lighter in weight (Chaturvedi et al. 2012). Immobilization of molecules on the inner and outer sides of the CNTs requires the attachment of chemically active side groups to increase the activity of the surface. Integration of metallic nanoparticles and nanocomposites can lead to increased biomolecules activity by increasing the interaction between these two and consequently increasing the oxidation of reactants (Pan et al. 2007). CNTs loaded with rhodium (Rh) particles have been used as a reactor by Pan et al. (2007), where carbon monoxide reacts with hydrogen resulting in ethanol production. This is the first example, where a gas-phase catalyzed reaction has been shown to experience a significant increase in activity and selectivity through a process carried out in a nanosize reaction vessel.

Another potential application of nanoparticles in bioethanol/biobutanol production processes is the detection of compounds using immobilized metal nanoparticles onto the nanosheet structure. Santos et al. (2016) used glassy carbon electrode modified with graphene oxide containing copper nanoparticles for the determination of total reducing sugars and achieved better accuracy and reusability of the prepared system. Lin et al. (2016) synthesized ultrathin two-dimensional polycrystalline ZnO nanosheets with uniformly dispersed Ag nanoparticles by a two-step hydrothermal method to increase the surface reaction for ethanol detection. The noble metal silver was selected purposely due to its excellent gas sensitivity. The activity of ZnO–Ag composite was detected by change in resistance by introducing or releasing the ethanol vapor using gas sensors that can function even at an ultralow ethanol vapor concentration. Gas sensitivity was defined by the formula:

$$S = (R_0 - R)/R_0,$$

where R_0 is the initial resistance and R is the real-time resistance.

This heterojunction is also appropriate for other transition metal oxides–metal systems which can be used for other purposes such as photoluminescence, catalytic fields, and transparent functional coating (Lin et al. 2016).

3 Discussion and Future Perspective

A concise summary of the available reported work on the use of nanomaterials in preprocessing of biomass, fermentation of pretreated feedstock, and detection of degradation and fermentation products is presented in Table 1. From the foregoing literature review and table content, it is clear that a wide variety of nanomaterials have been used for pretreatment of biomass and converting it to liquid fuels and their efficacy has been successfully demonstrated on the laboratory scale. It has been conclusively shown that the suitability and reusability of nanomaterial-based methods are superior over conventional catalysts.

Though the application of nanomaterials in the field of production of biofuels from renewable and sustainable feedstocks has attracted attention only recently, laboratory-scale results have conclusively shown that nanotechnology has the potential to give new directions to the energy sector by conquering the problem of preprocessing of feedstock and better biofuel productivity. Nanomaterials have the capability to play an important role in achieving the target of bioethanol/biobutanol production on industrial scale at economical rate and their application is likely to increase with the advancement in the field of bio-alcohols production through fermentation. Large-scale utilization of these particles as support for immobilizing enzymes is likely to give the production technology a new direction by increasing the availability and stability of immobilized enzymes, by lowering the production cost through the reusability of the nanomaterials, by providing large specific surface area for reaction, etc. Immobilization over the bi-functionalized nanosupport materials provides best exposure to the enzyme active sites and also increases the activity and stability many folds (Cipolatti et al. 2014). Method of synthesis of nanocomposites is the other aspect of nanotechnology that affects the efficiency of the process. From the review of available literature, it is seen that a large number of nanoparticles and nanocomposites have been synthesized and used for the purpose of efficient bioethanol production through fermentation. Application of these nanomaterials in biobutanol fermentation is still an untouched area and requires a lot of work to be done. Further, the use of nanomaterials in the detection of different process intermediates and end products still needs to be explored to find economical ways of preparation for better monitoring and control of the fermentation process and cost optimization.

From the foregoing discussion, it is seen that noteworthy progress has been made in the field of nanotechnology in the last few years and nanomaterials have shown immense prospects for the production of biofuels through greener processing of biomass for achieving higher product selectivity and yield in an economical way. Still, a number of challenges are associated with it that needs to be overcome. In particular, following issues deserve the attention of researchers working in this area:

- Synthesis of more versatile nanocatalysts that can be used for a range of biomass processing,
- Development of more selective nanocatalysts to convert bio-derived sugars to biofuels,
- Greener route of nanoparticles synthesis for use as biocatalysts carriers so that these can easily be utilized for fermentation of bio-alcohols,
- Development of sensors for detection of intermediate metabolites and end products, and
- Commercialization of these nanoparticles.

There is enormous intrinsic potential of this technology and a lot more is needed to be done to overcome the technical hurdles in the field of bio-alcohols production using nanomaterials.

Table 1 Nanomaterials in bioethanol/biobutanol production and other related processes

S. No.	Nanomaterials	Preparation method	Typical application	Reference
1.	Iron and copper nanoparticles	Sun Innovators, USA (Laboratory reagent)	Production of lignocelluloses degrading enzymes in the fungus *Trametes versicolor*	Shah et al. (2010)
2.	Methyl-functionalized cobalt-ferrite-silica ($CoFe_2O_4@SiO_2$-CH_3) nanoparticles	Co-precipitation	Ethanol production	Kim and Lee (2016)
3.	Silver nanoparticles (AgNPs)	Biosynthesis using *Bacillus subtilis*	Cell wall destruction to release carbohydrate/lipid from *Chlorella vulgaris*	Razack et al. (2016)
4.	Perfluoroalkylsulfonic acid-functionalized magnetic nanoparticles	Microemulsion method	Pretreatment of wheat straw	Pena et al. (2012)
5.	Calcium hydroxyapatite nanoparticles	Sigma-Aldrich	Improved production of reducing sugars from rice husk and rice straw	Chakrabarti (2014)
6.	$NiCo_2O_4$ nanoparticles	Hydrothermal-assisted post-calcination process	Improved thermal stability of cellulase enzyme obtained from *Aspergillus fumigatus* NS	Srivastava et al. (2014)
7.	ZnO nanoparticles	Sol–gel method	Improved thermal and pH stability of cellulase enzyme obtained from *Aspergillus fumigatus* AA001	Srivastava et al. (2016)
8.	Fe_3O_4/Alginate nanocomposite	Co-precipitation	Enzymatic hydrolysis of rice straw	Srivastava et al. (2015)
9.	Methyl-functionalized silica nanoparticles	Co-precipitation	Ethanol production	Kim et al. (2014)
10.	Entrapped yeast cells magnetic nanoparticles	Co-precipitation	Ethanol production	Ivanova et al. (2011)
11.	Rh particles inside CNTs	–	Enhanced ethanol production	Pan et al. (2007)
12.	Graphene oxide containing copper nanoparticles	–	Determination of total reducing sugars	Santos et al. (2016)
13.	Silver nanoparticles decorated polycrystalline zinc oxide nanosheets	Hydrothermal method	Improved ethanol detection	Lin et al. (2016)
14.	MnO_2 nanoparticles	Co-precipitation	Improved hydrolysis of agricultural wastes for ethanol production	Cherian et al. (2015)

(continued)

Table 1 (continued)

S. No.	Nanomaterials	Preparation method	Typical application	Reference
15.	ZnO nanoparticles	Precipitation	Ethanol production	Zada et al. (2014)
16.	Gold and silver nanoparticles	Citrate reduction	Alcohol-dehydrogenase enzyme immobilization and stability analysis	Petkova et al. (2012)
17.	Fe_3O_4 nanoparticles	Co-precipitation	Saccharification of wheat straw and *Eucalyptus globulus*	Valenzuela et al. (2014)
18.	Reduced graphene oxide functionalized Fe_3O_4 nanoparticles	Co-precipitation	Hydrolysis of cellulose	Yang et al. (2015)
19.	TiO_2 nanoparticles	Co-precipitation	Enzymatic hydrolysis of cellulose	Abushammala and Hashaikeh (2011)
20.	Fe_3O_4 nanoparticles	Hydrothermal technique	Improved thermal stability of β-glucosidase and use in cellobiose hydrolysis	Verma et al. (2013)

References

Abushammala H, Hashaikeh R (2011) Enzymatic hydrolysis of cellulose and the use of TiO_2 nanoparticles to open up the cellulose structure. Biomass Bioenerg 35:3970–3975

Balat M, Balat H (2009) Recent trends in global production and utilization of bio-ethanol fuel. Appl Energ 86(11):2273–2282

Bet-Moushoul E, Farhadi K, Mansourpanah Y, Nikbakht AM, Molaei R, Forough M (2016) Application of CaO-based/Au nanoparticles as heterogeneous nanocatalysts in biodiesel production. Fuel 164:119–127

Chaturvedi S, Dave PN, Shah NK (2012) Application of nano-catalyst in new era. J Saudi Chem Soc 16:307–325

Cherian E, Dharmendirakumar M, Baskar G (2015) Immobilization of cellulase onto MnO_2 nanoparticles for bioethanol production by enhanced hydrolysis of agricultural waste. Chin J Catal 36:1223–1229

Cipolatti EP, Silva MJA, Klein M, Feddern V, Feltes MMC, Oliveira JV, Ninow JL, Oliveira DD (2014) Current status and trends in enzymatic nanoimmobilization. J Mol Catal B Enzym 99:56–67

Dutta N, Mukhopadhyay A, Dasgupta AK, Chakrabarti, K (2014) Improved production of reducing sugars from rice husk and rice straw using bacterial cellulase and xylanase activated with hydroxyapatite nanoparticles. Bioresour Technol 153:269–277

Gokhale AA, Lu J, Lee I (2013) Immobilization of cellulose on magneto responsive graphene nano-supports. J Mol Catal B Enzym 90:76–86

Hermanova S, Zarevucka M, Bousa D, Pumera M, Sofer Z (2015) Graphene oxide immobilized enzymes show high thermal and solvent stability. Nanoscale 7:5852–5858

Ivanova V, Petrova P, Hristov J (2011) Application in the ethanol fermentation of immobilized yeast cells in matrix of alginate/magnetic nanoparticles, on chitosan-magnetite microparticles and cellulose-coated magnetic nanoparticles. Int Rev Chem Eng 3(2):289–299

Jordan J, Kumar CSSR, Theegala C (2011) Preparation and characterization of cellulase-bound magnetite nanoparticles. J Mol Catal B Enzym 68:139–146

Kakaei K, Rahimi A, Husseindoost S, Hamidi M, Javan H, Balavandi A (2016) Fabrication of Pt-CeO_2 nanoparticles supported sulfonated reduced graphene oxide as an efficient electrocatalyst for ethanol oxidation. Int J Hydrogen Energy 41:3861–3869

Kim YK, Lee H (2016) Use of magnetic nanoparticles to enhance bioethanol production in syngas fermentation. Bioresour Technol 204:139–144

Kim BC, Nair S, Kim J, Kwak JH, Grate JW, Kim SH, Gu MB (2005) Preparation of biocatalytic nanofibers with high activity and stability via enzyme aggregate coating on polymer nanofibres. Nanotechnology 16(7):S382–S388

Kim J, Grate JW, Wang P (2006) Nanostructures for enzyme stabilization. Chem Eng Sci 61:1017–1026

Kim YK, Park SE, Lee H, Yun JY (2014) Enhancement of bioethanol production in syngas fermentation with *Clostridium ljungdahlii* using nanoparticles. Bioresour Technol 159: 446–450

Kumar M, Gayen K (2011) Developments in biobutanol production: new insights. Appl Energ 88(6):1999–2012

Lin L, Liu T, Zhang Y, Liang X, Sun R, Zeng W, Wang Z (2016) Enhancing ethanol detection by heterostructural silver nanoparticles decorated polycrystalline zinc oxide nanosheets. Ceram Int 42:3138–3144

Maitan-Alfenas GC, Visser EM, Guimaraes VM (2015) Enzymatic hydrolysis of lignocellulosic biomass: converting food waste in valuable products. Curr Opin Food Sci 1:44–49

Mascal M, Nikitin EB (2008) High-yield conversion of cellulose into biofuel. Angew Chem Int Ed 47:7924–7926

Mehrasbi MR, Mohammadi J, Peyda M, Mohammadi M (2017) Covalent immobilization of *Candida antarctica* lipase on core-shell magnetic nanoparticles for production of biodiesel from waste cooking oil. Renew Energ 101:593–602

Mohamad NR, Marzuki NHC, Buang NA, Huyop F, Wahab RA (2015) An overview of technologies for immobilization of enzymes and surface analysis techniques for immobilized enzymes. Biotechnol Biotechnol Equip 29(2):205–220

Naor EO, Koberg M, Gedanken A (2017) Nonaqueous synthesis of SrO nanopowder and SrO/SiO2 composite and their application for biodiesel production via microwave irradiation. Renew Energ 101:493–499

Navigant Research (2014). https://www.navigantresearch.com/newsroom/biofuels-demand-for-road-transportaion-will-surpass-51-billion-gallons-annually-by-2022

Noraini MY, Ong HC, Badrul MJ, Chong WT (2014) A review on potential enzymatic reaction for biofuel production from algae. Renew Sustain Energ Rev 39:24–34

Pan X, Fan Z, Chen W, Ding Y, Luo H, Bao X (2007) Enhanced ethanol production inside carbon-nanotube reactor containing catalytic particles. Nat Mater 6:507–511

Pena L, Ikenberry M, Hohn KL, Wang D (2012) Acid-functionalized nanoparticles for pretreatment of wheat straw. J Biomater Nanobiotechnol 3:342–352

Petkova GA, Zaruba K, Zvatora P, Kral V (2012) Gold and silver nanoparticles for biomolecule immobilization and enzymatic catalysis. Nanoscale Res Lett 7:287

Raposo S, Pardao JM, Diaz I, Costa MEL (2009) Kinetic modeling of bioethanol production using agro-industrial by-products. Int J Energy Environ 3(1):1–8

Razack SA, Duraiarasan S, Mani V (2016) Biosynthesis of silver nanoparticle and its application in cell wall disruption to release carbohydrate and lipid from *C. vulgaris* for biofuel production. Biotechnol Rep 11:70–76

Renewables (2015). http://www.ren21.net/wp-content/uploads/2015/07/REN12-GSR2015_Onlinebook_low1.pdf

Santos FCU, Paim LL, Silva JLD, Stradiotto NR (2016) Electrochemical determination of total reducing sugars from bioethanol production using glassy carbon electrode modified with graphene oxide containing copper nanoparticles. Fuel 163:112–121

Shah V, Dobiasova P, Baldrian P, Nerud F, Kumar A, Seal S (2010) Influence of iron and copper nanoparticle powder on the production of lignocelluloses degrading enzymes in the fungus *Trametes versicolor*. J Hazard Mater 178:1141–1145

Shahid EM, Jamal Y (2011) Production of biodiesel: a technical review. Renew Sustain Energ Rev 15(9):4732–4745

Sirajunnisa AR, Surendhiran D (2014) Nanosilver fabrication mediated by exopolysaccharides from *Pseudomonas fluorescens*. Am J Pharm Tech Res 4:727–742

Srivastava N, Rawat R, Sharma R, Oberoi HS, Srivastava M, Singh J (2014) Effect of Nickel-Cobaltite nanoparticles on production and thermostability of cellulases from newly isolated thermotolerant *Aspergillus fumigatus* NS. Appl Biochem Biotechnol 174(3):1092–1103

Srivastava N, Singh J, Ramteke PW, Mishra PK, Srivastava M (2015) Improved production of reducing sugars from rice straw using crude cellulase activated with Fe_3O_4/Alginate nanocomposite. Bioresour Technol 183:262–266

Srivastava N, Srivastava M, Mishra PK, Ramteke PW (2016) Application of ZnO nanoparticles for improving the thermal and pH stability of crude cellulase obtained from *Aspergillus fumigatus* AA001. Front Microbiol 7:9. https://doi.org/10.3389/fmicb.2016.00514

Valenzuela R, Castro JF, Parra C, Baeza J, Duran N, Freer J (2014) β-glucosidase immobilization on synthetic superparamagnetic magnetite nanoparticles and their application in saccharification of wheat straw and Eucalyptus globulus pulps. J Exp Nanosci 9(2):177–185

Verma ML, Chaudhary R, Tsuzuki T, Barrow CJ, Munish Puri (2013) Immobilization of β-glucosidase on a magnetic nanoparticle improves thermostability: application in cellobiose hydrolysis. Bioresour Technol 135:2–6

Wang YT, Fang Z, Zhang F, Xue BJ (2015) One-step production of biodiesel from oils with high acid value by activated Mg-Al hydrotalcite nanoparticles. Bioresour Technol 193:84–89

Xue C, Zhao XQ, Liu CG, Chen LJ, Bai FW (2013) Prospective and development of butanol as an advanced biofuel. Biotechnol Adv 31:1575–1584
Yang Z, Huang R, Qi W, Tong L, Su R, He Z (2015) Hydrolysis of cellulose by sulfonated magnetic reduced graphene oxide. Chem Eng J 280:90–98
Zada B, Mahmood T, Malik SA, Zaheer-ud-din (2014) Effect of zinc oxide nanoparticles on hyacinth's fermentation. Int J Enhanc Res Sci Technol Eng 3(11):78–92
Zhang J, Zhang F, Yang H, Huang X, Liu H, Zhang J, Guo S (2010) Graphene oxide as a matrix for enzyme immobilization. Langmuir 26(9):6083–6085
Zhao XS, Lu GQ, Hu X (2000) Characterization of the structural and surface properties of chemically modified MCM-41 material. Microporous Mesoporous Mater 41(1–3):37–47