Prospectus of Nanotechnology in Bioethanol Productions

Vincent Vineeth Leo and Bhim Pratap Singh

Abstract Technological advancements and global energy requirements of the twenty-first century has resulted in alarming global warming situations and depletion of nonrenewable fossil fuels. The search for alternative sources of energy to curb the dependency on fossil fuels has, in turn, affected the attention toward biofuels like bioethanol. Bioethanol is one of the highly useful fuel additives given its eco-friendly and renewable potentials. Bioethanol production uses fermentation technology to convert carbohydrate rich biomass to biofuel, though high production costs and some technical glitches deemed a drawback. Nanotechnology could help overcome such challenges and help in the sustainable production of such biofuels. Various nanoparticles and nanomaterials have already been reported to have an impact on the biofuel productions like bioethanol. In this chapter, we explore the various interesting approaches and current trends of the usage of nanotechnology retrospective to bioethanol productions.

Keywords Biofuels · Bioethanol · Nanotechnology · Nanomaterials Nanoparticles

1 Introduction

Among the sources for recovery for bioethanol plant-based materials dominate as the major feedstock, followed by the algal biomasses. But certainly, some plants are easier to convert into usable bioethanol than others and can be cultivated for this purpose. While some plants might grow like wild varieties with limited growth resources, some plants harvested residues could be a useful feedstock. Interestingly

V. V. Leo
Molecular Microbiology and Systematic Laboratory, Department of Biotechnology, Mizoram University, Aizawl 796004, Mizoram, India

B. P. Singh (✉)
Department of Biotechnology, Mizoram University, Aizawl 796004, Mizoram, India
e-mail: bhimpratap@gmail.com

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_9

almost all plants and most algal varieties do posses sugars and hence can be harvested and fermented to make bioethanol by chemical, thermal, enzymatic, or a combination of all. Bioethanol has gained immense interest in this century, given the depletion of fossil fuels and increased environmental pollutions. Bioethanol as such is considered a clean and renewable fuel replacing gasoline or an additive to petrol or diesel. The usage of this has been projected to reduce the global warming emissions of approximately 20% from corn ethanol and 85% from cellulosic ethanol while entirely eliminating the release of acid rain-causing sulfur dioxide (De-Oliveira et al. 2005). The usage of bioethanol to gasoline for transportation has been in practice in countries like Brazil, USA, etc.

In recent years almost all bioethanol produced in the world has a starch or sugar-based plant origin. These edible plants majorly have simple sugar end products readily available forms the first-generation biomass source and are very easy to extract, ferment, and produce bioethanol in large quantities. The major such edible plants considered as feedstocks are starch from corn, wheat, rice, etc., and sucrose from sugarcane and sugar beet (Naik et al. 2010). Even though these primary source of biomass are the most exploited, their over dependency and lack of complete exploitation of these edible plants for biofuel production has resulted in focus onto nonedible biomasses or plants (Leo et al. 2016).

These are deemed the second-generation biofuel source or biomasses with the lignocellulosic materials like wood wastes, perennial grasses, forest litters, some agricultural residues, and others (Patumsawad 2011; Eggert and Greaker 2014). Lignocellulosic biomasses that are majorly dominated by cellulosic components followed by hemicelluloses and less amount of lignin are nonfood-based and could be dedicated energy crops, industrial, or other wastes too. Though the usage of these feedstocks provide numerous advantages, with most of this biomass being relatively abundant, with their growth of these purposefully grown energy crops harvested from marginal lands not suitable for other crops These relatively waste products and most of them are not used for human consumption also. Given these polymeric carbohydrates are relatively difficult to hydrolyze to simpler sugar forms and subsequently, their conversion into ethanol form will be a challenge and could turn out to be slightly time consuming, technological glitches, and costly (Wongwatanapaiboon et al. 2012; Naik et al. 2010).

Recently the third-generation biomass—“algal biomass”-based macro-algal and micro-algal research for bioethanol productions have gained momentum (Ahmad and Sardar 2012). The usage of these as feedstocks does indeed have a distinct advantage over the terrestrial biomass with respect to economic and environmental constraints. Algae are renowned to have massive turnovers in ideal conditions and can be grown at sustainable rates as a source of feedstock for bioethanol production. Being a nonessential food, rising prices even of edible algae should not pose a threat of famine to developing countries. Though harvesting of algal biomass and conversion process during fermentation to bioethanol could face its challenges, this is one field that is blooming (Reznik and Israel 2012).

Thus, given these facts, there is an ever existing demand to develop proficient technologies capable of resolving the issues that have risen up in the field of bioethanol production. It is in this context nanotechnology can step in and resolve the major bottlenecks facing this field. In recent years, nanotechnology has advanced quickly worldwide, providing important breakthroughs and benefits to a growing number of products from diverse areas, including biotechnology energy, environment, health, agriculture, and food (Pérez-López and Merkoci 2012). The use of nanotechnology to develop "nanomaterials" is that they can be molded into applicable and technological forms. These nanomaterials exhibit different physical and chemical properties in comparison to these materials in normal state, especially its increased chemical reactivity due to a greater surface area and its reusability. In biofuels and bioenergy field, nanotechnology has different applications such as modification in feedstocks, development of more efficient catalysts, and others (Rai et al. 2016). In this context, this chapter aims at exploring the recent developments on nanomaterials used in the field of bioethanol productions.

2 Nanomaterials

Nanomaterials are a crucial part of the ever evolving branch of nanotechnology and these different nanomodels do find immense application in the field of bioenergy. They could be ranging from simpler nanoparticles to different nanomodels like nanofibers, nanotubes, nanopores, nanocomposites, nanosheets etc. These particles have been reported to have a direct or indirect effect on the biofuel production processes (Verma et al. 2013). Applications of these nanoparticles are mostly used in the enzymatic hydrolysis of lignocellulosic biomasses and for their efficient usage of these enzymes by immobilization technology. The initial lignocelluloses degrader enzymes like cellulases, hemicellulases, laccases, etc., are immobilized into matrices made of either by magnetic or metal oxide nanoparticles (Rai et al. 2016). Such nanomaterial-enabled enzymes called nanocatalyst are renowned to be more efficient and are currently gaining interest. Nanomaterials also do find numerous such applications in the process of converting biomass to bioethanol and can be separated into the four major categories pretreatment, catalytic hydrolysis, saccharification and purification. Some of these nanomaterials that are gaining keen interest recently are discussed below.

3 Nano-Shear Hybrid Alkaline Technique (NSHA)

This is one technique that finds its application in pretreatment process of lignocellulosic biomass initial conversions to simpler sugars. This process uses high-speed shear within specific reactors called nanomixer, combined with chemical reagents in presence of mild temperatures. It is mostly applied for the removal of lignin entities on short-term treatment of lignocellulose biomasses (Wang et al. 2013). The usage of nano-shear hybrid method pretreatment of lignocelluloses and combining it into a one-step process by the addition of chemical reagents as pretreatment agent was made into a process under patent no 20120036765 A1 (Lee et al. 2012). Wang et al. (2013) used corn straw while Ji and Lee (2013) studied wheat straw pretreatment through NSHA for separation of lignin entities from the cellulosic and hemicellulosic components. Both the studies used NaOH as the chemical agent with the former using 1: 1 proportions of NaOH to biomass, while the later study using 0.4–4% w/v of NaOH and sheared for limited time interval within nanomixer. The addition of cationic polyelectrolyte deemed to be a useful addition to the wheat straw, which helped in effective hydrolytic enzyme action on addition to the lignin removed from cellulosic microfibrils (Ji and Lee 2013). NSHA pretreatment did prove from these studies that this procedure is effective in removing lignin significantly and up to an extend hemicelluloses thereby promoting cellulose nanostructure disruption.

4 Nanocatalysts

Hydrolytic enzymes that act on lignocellulosic materials like cellulase, xylanase, laccase, etc., on immobilizing on nanoscaffold support materials has been reported to have enhanced long-term enzyme stability even under certain extreme conditions (Verma et al. 2013). Immobilization of these enzymes onto nanoparticles could be by physical adsorption, covalent bonds, cross-linkages or specific ligands. These nanoparticle-based immobilized enzymes are collectively termed nanocatalyst or nanobiocatalyst (Misson et al. 2015; Budarin et al. 2013; Mohamad et al. 2015). Immobilized enzymes are retained in nanocarriers like nanofibers (NF), nanocages, mesoporous nanocontainers, zeolite based carriers etc.

The major hydrolytic enzyme involved after any initial pretreatment is cellulase as this is capable of converting the major lignocellulosic biomass to simpler sugar. Hence this enzymes usage constitutes an important part of its total cost in the bioethanol production process. Hence the usage of immobilized nanocellulases could certainly enhance the recovery percentage and the recycling potential of these enzymes (Alftren 2013; Rai et al. 2016). Mostly cellulases recovered from fungal strains like *Aspergillus niger* and *Trichoderma viridae* and a few known commercial cellulases has been immobilized into nanocarriers and applied for sugar recovery and subsequent bioethanol productions (Ahmad et al. 2014; Khoshnevisan et al. 2011; Zang et al. 2014).

The nanomaterials applied for nanobiocatalyst thus ranged from certain acidic nanoparticles, transition metal oxides, zeolitic materials to functionalized silica nanomaterials. Qi et al. (2011) worked on another nano acidic resin like Dowex 50wx8–100 in presence of liquid ionic (EMIM) chloride ion that had a glucose recovery of 83%. Another acidic nanoparticle made of aluminotungstic acid yielded about 68% glucose while carbonaceous acid nanoparticle of GC-SO_3H in presence of (BMIM) chloride ion helped recover almost 72% glucose recovery (Ogasawara et al. 2011; Guo et al. 2012). The usage of transitional metals oxides as nanomaterials has also yielded 42–69% of glucose when cellulase was applied with nanoscale metal oxide catalyst [Zn–Ca–Fe] in a study carried out by Zhang et al. (2011). Given the durability and versatility of zeolite materials, nanozeolites based catalyst were developed by Malyala et al. (2017), that successfully used biovapors comprising of C5 and C6 compounds derived form decomposed biomass to be converted into biofuels, by allowing the vapors to come in contact with a catalyst composition comprising a nanozeolite. The usage of mesoporous nanocellulase that was made in carbon-supported ruthenium, yielded only 40% glucose though as reported by Kobayashi et al. (2010). Functionalized inert element silica-based nanoparticles-based enzymes made of either silica–carbon nanocomposite (Van de Vyver et al. 2010) or water-tolerant silica-supported perfluorobutylsulfonylimide (Feng et al. 2014) yielded reducing sugar percentages of 50% and 60% respectively. An interesting study on utilizing a 3rd gen biomass algae *Chlorella* sp. was carried by Fu et al. (2014), in which cellulase that was immobilized onto an electrospun polyacrylonitrile (PAN) nanofibrous membrane, which reported 62% hydrolyzing capability and 40% recovery of the hydrolyzed product even after five reuses.

5 Nanomagnetic Nanocatalyst

It has been stipulated over the years that magnetic nanomaterials do have immense industrial applications especially given its magnetic properties to hold onto substrates, its nano size, reduced toxicity concerns and potency for enhanced chemical reactions (Sirajunnisa and Surendhiran 2016). The magnetic particles capability to conjugate with biological systems and even enzymes makes them an interesting class of nanomaterials deemed as bio-nanoparticles (bio-NP), especially its high catalytic specificity and recycle capability of costly biocatalysts (Alcalde et al. 2006). Magnetic nanoparticles-based immobilized cellulase, hence could be an ideal candidate for the bioethanol production cost reduction and enhanced productivity. The fact that with the use of external magnetic source the magnetic nanoparticles could be easily separated, which allows this usage of cellulase immobilized enzymes repeatedly (Chen et al. 2012; Sirajunnisa and Surendhiran 2016).

Jordan et al. (2011) used magnetic Fe_3O_4 nanoparticles that were used to immobilize enzymes capable of hydrolyzing crystalline cellulose with additional usage of carbodiimide to link the enzymes to the nanomaterial. The study revealed that given the magnetic nature of the nanomaterial used, the enzyme was capable of reuse and recovery of six times. The following year Goh et al. (2012) reported similarly on an enzyme involved in lignocellulose hydrolysis and subsequent bioethanol production. The enzyme was immobilized in single-walled nanotubes having lined on the sides with magnetic iron oxide nanomaterials. This study helped reveal the regulation capability of the magnetic nanoparticles over the catalytic effect by controlling the concentration of iron oxide. Another study conducted by Abraham et al. (2014) showed a maximum hydrolysis of 93% on hemp hurd biomass (HHB) with *T. reesei* cellulase on magnetic nanoparticle with the addition of zinc was doped into magnetite. The result revealed a hydrolysis yield of 89% by 48 h maintaining, 50% activity even after five repeated usages at 80 °C. Recently Ladole et al. (2017) worked on ultrasonic hyperactivation of cellulase immobilized on magnetic nanoparticles, and the study revealed that at 24 kHz, 6 W power, and 6 min of incubation time a 3.6 fold increase in the catalytic activity of cellulase was observed and was applied in biomass conversion. Salehi and Mirjalili (2017), worked on a bio-based magnetic nanocatalyst made by immobilization of –OPO_3H groups on a Fe_3O_4@nanocellulose surface. This work reported this enzyme to be high yielding and catalytic reusability.

Among bioethanol production process is by syngas, with this gasification–fermentation as an alternative to complicated and time-consuming saccharification step (Kootstra et al. 2009). However, the effect of this process on increasing gas to liquid mass transfer rate technique that is crucial for this syngas conversion has its limitation, which has led to the usage of nanoparticles that in turn could enhance this gas–liquid transfer rates (Zhu et al. 2010). Kim and Lee 2016, studied in detail the usage of two nanoparticles on the enhancement of bioethanol production after syngas based fermentation by *Clostridium ljungdahlii*. The two magnetic nanoparticles methyl-functionalized silica and methyl-functionalized cobalt ferrite–silica ($CoFe_2O_4$@SiO_2–CH_3) nanoparticles were applied to progress syngas mass transfer. Among them, $CoFe_2O_4$@SiO_2–CH_3 was more efficient in comparison to the control and the bioethanol recovery of 213.5% and its reusage of the magnetic nanomaterial after initial fermentation.

6 Nanofibers

Lee et al. (2010) did a study regarding the usage of nanofibers or electrospun nanofibers coated or crosslinked with β-Glucosidase (βG) enzymes in immobilized form. Given the capability of βG enzymes on converting the excess cellobiose production that might occur during hydrolytic enzyme activities of exo- or endo-cellulases on biomass fermentation, this enzyme will be of huge usage especially on overcoming inhibition due to excess cellobiose. The study revealed that on applying such technique the enzyme retained almost 90% of its activity even after 20 days of fermentation; with an enhanced enzyme retention possibility due to the usage of magnetic nanofibers for recycled usage.

7 Nanofiltration

Among the major factors that affect bioethanol yield and purification are the presence of microbial and chemical contaminants. Membrane separation technology like nanofiltration has found interest in the field of bioethanol purification because of their minimal energy requirements, operational flexibility, lesser labor costs and workspace. Nanofiltration could be applied during fermentation also, which could help in concentrating the sugar within the solution and remove any potential inhibitors for yeast-based fermentation. Similarly, it could find application during enzyme recovery, removal of other by-products of fermentation, pervaporation of low concentrated bioethanol, etc. Nanofiltration is one such membrane filtration technique usually used with high pressure and finds applications in bioethanol separation (Kang et al. 2014). One of the early studies regarding the usage of nanofiltration for ethanol and sugars separations was carried out by Verhoef et al. (2008) who used hydrophobic nanofiltration membrane for the separation of ethanol from multicomponent mixtures. Bras et al. (2013) used three nanofiltration membranes NF270, NF90, and SW30 of which NF270 was found to be the most efficient in the separation of bioethanol from the fermented liquors of olive stones. This nanofiltration membrane showed 98% sugar rejection and 28% of lower ethanol rejection, which indicated that this separation membrane ideal for recovery of bioethanol from such sugars. Recently Shibuya et al. 2017 used a hybrid of nanofiltraion (NF) and forward osmosis (FO) technique successfully for enhancing bioethanol concentration from xylose-assimilating *S. cerevisiae* whose liquid fraction after diluted 1.5 fold. This hybrid system was found to be useful in the removal of renowned fermentation inhibitors like acetic acid too. Such hybrid nanofiltrations systems are of significant potency for efficient separation of bioethanol from pretreated lignocellulosic biomass.

8 Nanotubes

Winarto et al. (2016), studied on carbon nanotubes (CNT) usage in the separation of liquid substance like water with respect to ethanol and the effect of an electrostatic interaction on this separation process. This study showed that the usage of electrostatic force nullified the effect of CNT diameter increase and ensured a uniform separation of the solvents. It revealed that this was possible because under the mild electric current given to the nanotubes, the electrostatic interactions within water molecules force them to flow through nanotubes faster than ethanol thereby helping in their preferential separation. This technology will have huge ramification in the final stages of bioethanol purification process after fermentation.

Even though carbon nanotubes were primarily used for such purification and separation processes in bioethanol productions, Pan et al. (2007) did report these carbon nanotubes being filled with certain nanocomposities for enhanced catalytic activities. They noted an improved catalytic activity of Rh particles when they were confined with nanotubes for the conversion of CO and H_2 to ethanol. Hence given the variety of plausible applications of these nanotubes, their significance in bioethanol production could be substantial in the coming future.

9 Nanosensors

Detection of ethanol after fermentation process is a crucial part bioethanol production. Nanotechnology does find its application in this field too. Recently Wang et al. (2016) reported an ethanol gas sensor based on $TiO_2/Ag_{0.35}V_2O_5$-branched nanoheterostructures that has a significantly distinct with fast response, good selectivity and high sensitivity of more than 9 times the usually trusted pure TiO_2 nanofibers used for biosensors.

10 Conclusion

The hunt for alternative energy sources to replace the ever depleting nonrenewable fossil fuels has opened up avenues for the exploration of plant and algal biomasses for bioethanol productions. Though the technology of production of bioethanol from valuable first-generation to third-generation feedstocks has gained considerable attention and applications, the major bottleneck remains higher production costs and technological advancements. In order to overcome these hurdles nanotechnology and the nanomaterials developed from this technology could be of huge assistance for sustainable production of bioethanol. The usage of various nanomaterials like nanobiocatalysts, magnetic nanoparticles, nanofibers, nanotubes, and other techniques like Nano-Shear Hybrid Alkaline Technique has played a crucial role to enhance the economic viability of production process. These materials have found its role from pretreatment requirements for the biomass conversions of simple sugars, fermentation technology to the purification of bioethanol and even its detection (Fig. 1). Nanotechnology has brought in the possibility of reuse of many of its nanomaterials and enhanced stability to this process of bioethanol production. In the future, the usage of such nanotechnological advancements may open up new avenues for the sustainable production of bioethanol.

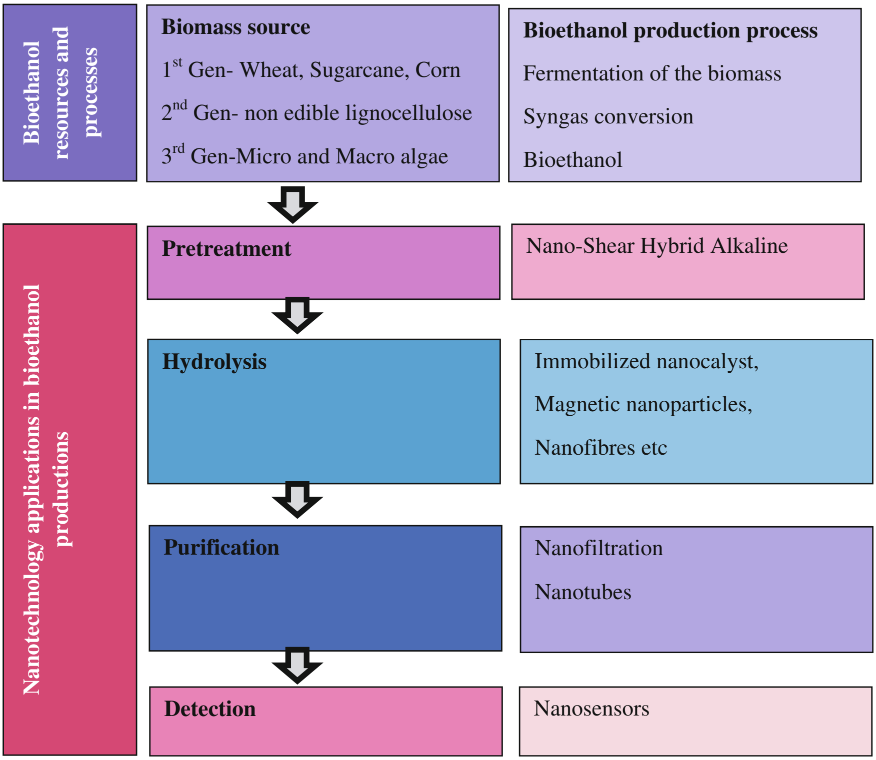

Fig. 1 An overview of various nanomaterials used in various process of bioethanol production

References

Abraham RE, Verma ML, Barrow CJ, Puri M (2014) Suitability of magnetic nanoparticle immobilised cellulases in enhancing enzymatic saccharification of pretreated hemp biomass. Biotechnol Biofuels 7:90

Ahmad R, Sardar M (2014) Immobilization of cellulase on TiO_2 nanoparticles by physical and covalent methods: a comparative study. Indian J Biochem Biophys 51:314–320

Ahmed F, Li Y, Schenk PM (2012) Algal biorefinery: sustainable production of biofuels and aquaculture feed? In: Gordon R, Seckbach J (eds) the science of algal fuels: phycology, geology, biophotonics, genomics and nanotechnology. Cellular origin, life in extreme habitats and astrobiology, vol 25. Springer, Dordrecht, The Netherlands, pp 21–41

Alcalde M, Ferrer M, Plou FJ, Ballesteros A (2006) Environmental biocatalysis: from remediation with enzymes to novel green processes. Trends Biotechnol 24:281–287

Alftren J (2013) Immobilization of cellulases on magnetic particles to enable enzyme recycling during hydrolysis of lignocellulose. PhD thesis submitted to Institute for Food, Technical University of Denmark, Lyngby, Denmark

Brás TS, Fernandes MC, Luis JC, Neves LA (2013) Recovering bioethanol from olive bagasse fermentation by nanofiltration. Desalin Water Treat 51:4333–4342

Budarin V, Shuttleworth PS, Lanigan B, Clark JH (2013) Nanocatalysts for biofuels. In: Polshettiwar V, Asefa T (eds) Nanocatalysis synthesis and applications. Wiley, Hoboken, NJ, USA, pp 595–614. https://doi.org/10.1002/9781118609811.ch16

Cai HL, Li CZ, Wang AQ, Xu GL, Zhang T (2014) Zeolite-promoted hydrolysis of cellulose in ionic liquid, insight into the mutual behavior of zeolite, cellulose and ionic liquid. Appl Catal B 123:333–338

Chen WX, Yan Z, Yu WC, Xia WH (2012) Preparation and characterization of magnetic Fe_3O_4/CRGO nanocomposites for enzyme immobilization. Trans Nonferrous Metals Soc China 22:162–168

De-Oliveira MED, Vaughan BE, Rykiel EJ (2005) Ethanol as fuel: energy, carbon dioxide balances, and ecological footprint. Bioscience 55(7):593–602

Eggert H, Greaker M (2014) Promoting second generation biofuels: does the first generation pave the road? Energies 7:4430–4445

Feng JH, Xiong L, Ren XF, Ma ZH (2014) Silica supported perfluorobutylsulfonyl imide catalyzed hydrolysis of cellulose. J Wuhan Univ Technol Mater Sci Ed 5:9–14

Fu CC, Hung TC, Chen JY, Su CH, Wu WT (2010) Hydrolysis of microalgae cell walls for production of reducing sugar and lipid extraction. Biores Technol 101(22):8750–8754

Goh WJ, Makam VS, Hu J, Kang L, Zheng M, Yoong SL, Udalagama CN, Pastorin G (2012) Iron oxide filled magnetic carbon nanotube-enzyme conjugates for recycling of amyloglucosidase: toward useful applications in biofuel production process. Langmuir 28(49):16864–16873

Guo F, Fang Z, Xu CC, Richard L, Smith Jr (2012) Solid acid mediated hydrolysis of biomass for producing biofuels. Prog Energy Combust Sci 38:672–690

Ji S, Lee I (2013) Impact of cationic polyelectrolyte on the nanoshear hybrid alkaline pretreatment of corn stover: morphology and saccharification study. Biores Technol 133:45–50

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

Kang Q, Appels L, Tan T, Dewil R (2014) Bioethanol from lignocellulosic biomass: current findings determine research priorities. Sci World J 2014:298153. https://doi.org/10.1155/2014/298153

Khoshnevisan K, Bordbar AK, Zare D, Davoodi D, Noruzi M, Barkhi M, Tabatabaei M (2011) Immobilization of cellulase enzyme on superparamagnetic nanoparticles and determination of its activity and stability. Chem Eng J 171(2):669–673

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

Kobayashi H, Komanoya T, Hara K, Fukuoka A (2010) Water-tolerant mesoporous-carbon supported ruthenium catalysts for the hydrolysis of cellulose to glucose. ChemSuschem 3 (4):440–443

Kootstra AMJ, Mosier NS, Scott EL, Beeftink HH, Sanders JPM (2009) Differential effects of mineral and organic acids on the kinetics of arabinose degradation under lignocellulose pretreatment conditions. Biochem Eng J 43:92–97

Ladole MR, Mevada JS, Pandit AB (2017) Ultrasonic hyperactivation of cellulase immobilized on magnetic nanoparticles. Biores Technol 239:117–126

Lee I, Wang W, Ji S (2012) Device and method for pretreatment of biomass. Board of Trustees of Michigan State University, assignee. United States patent US 20120036765

Lee SM, Jin LH, Kim JH, Han SO, Na HB, Hyeon TH, Koo YM, Lee JH (2010) β-Glucosidase coating on polymer nanofibers for improved cellulosic ethanol production. Bioprocess Biosyst Eng 33:141

Leo VV, Passari AK, Joshi JB, Mishra VK, Uthandi S, Ramesh N, Singh BP (2016) A novel triculture system (CC3) for simultaneous enzyme production and hydrolysis of common grasses through submerged fermentation. Front Microbiol 7

Malyala R, Jarand ML, Thompson TA, Wan H, Saha A, Chilachka I (2017) Biofuel production using nanozeolite catalyst. Cool Planet Energy Systems, Inc. US 20170009142 A1

Misson M, Zhang H, Jin B (2015) Nanobiocatalyst advancements and bioprocessing applications. J R Soc Interface 12:20140891

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

Naik SN, Goud VV, Rout PK, Dalai AK (2010) Production of first and second generation biofuels: a comprehensive review. Renew Sustain Energy Rev 14(2):578–597

Ogasawara Y, Itagaki S, Kand Y, Mizuno (2011) Saccharification of natural lignocellulose biomass and polysaccharides by highly negatively charged heteropolyacids in concentrated aqueous solution. ChemSusChem 4(4):519–525

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

Patumsawad S (2011) 2nd Generation biofuels: technical challenge and R and D opportunity in Thailand. J Sustain Energy Environ (Special Issue) 47–50

Pérez-López B, Merkoçi A (2012) Carbon nanotubes and graphene in analytical sciences. Microchim Acta 179(1–2):1–16

Qi X, Watanabe M, Aida TM, Smith RL Jr (2011) Catalytic conversion of cellulose into 5-hydroxymethylfurfural in high yields via a two-step process. Cellulose 18(5):1327–1333

Rai M, dos Santos JC, Soler MF, Marcelino PRF, Brumano LP, Ingle AP, Gaikwad S, Gade A, da Silva SS (2016) Strategic role of nanotechnology for production of bioethanol and biodiesel. Nanotechnol Rev 5(2):231–250

Reznik A, Israel A (2012) Fuel from seaweeds: rationale and feasibility. In: Gordon R, Seckbach J (eds) the science of algal fuels: phycology, geology, biophotonics, genomics and nanotechnology. Cellular origin, life in extreme habitats and astrobiology, vol 25. Springer, Dordrecht, The Netherlands, 343–354

Salehi N, Mirjalili BBF (2017) Synthesis of highly substituted dihydro-2-oxopyrroles using Fe_3O_4@nano-cellulose–OPO_3H as a novel bio-based magnetic nanocatalyst. RSC Adv 7:30303–30309

Shibuya M, Sasaki K, Tanaka Y, Yasukawa M, Takahashi T, Kondo A, Matsuyama H (2017) Development of combined nanofiltration and forward osmosis process for production of ethanol from pretreated rice straw. Bioresour Technol 235:405–410

Sirajunnisa AR, Surendhiran D (2016) Algae—A quintessential and positive resource of bioethanol production: a comprehensive review. Renew Sustain Energy Rev 66:248–267

Van de Vyver S, Peng L, Geboers J, Schepers H, de Clippel F, Gommes CJ, Goderis B, Jacobs PA, Sels BF (2010) Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose. Green Chem 12:1560–1563

Verhoef A, Figoli A, Leen B, Bettens B, Drioli E, Van der Bruggen B (2008) Performance of a nanofiltration membrane for removal of ethanol from aqueous solutions by pervaporation. Sep Purif Technol 60:54–63

Verma ML, Barrow CJ, Puri M (2013) Nanobiotechnology as a novel paradigm for enzyme immobilization and stabilization with potential applications in biodiesel production. Appl Microbiol Biotechnol 97:23–39

Wang W, Ji S, Lee I (2013) Fast and efficient nanoshear hybrid alkaline pretreatment of corn stover for biofuel and materials production. Biomass Bioenerg 51:35–42

Wang Y, Liu L, Meng C, Zhou, Y, Gao Z, Li, X, Cao X, Xu L, Zhu W (2016) A novel ethanol gas sensor based on $TiO_2/Ag_{0.35}V_2O_5$ branched nanoheterostructures. Sci Rep 6:33092

Winarto TD, Yamamoto E, Yasuoka K (2016) Separation of water–ethanol solutions with carbon nanotubes and electric fields. Phys Chem Chem Phys 18:33310–33319

Wongwatanapaiboon J, Kangvansaichol K, Burapatana V, Inochanon R, Winayanuwattikun P, Yongvanich T, Chulalaksananuku W (2012) The potential of cellulosic ethanol production from grasses in thailand. J Biomed Biotechnol 2012(303748):1–10

Zang L, Qiu J, Wu X, Zhang W, Sakai E, Wei Y (2014) Preparation of magnetic chitosan nanoparticles as support for cellulase immobilization. Ind Eng Chem Res 53(9):3448–3454

Zhang F, Deng X, Fang Z, Zeng HY, Tian XF, Kozinski JA (2011) Hydrolysis of crystalline cellulose over Zn-Ca-Fe oxide catalyst. Petrochem Technol 40:43–48

Zhu H, Shanks BH, Choi DW, Heindel TJ (2010) Effect of functionalized MCM41 nanoparticles on syngas fermentation. Biomass Bioenerg 34:1624–1627