Biofuel and Biorefinery Technologies 5

Neha Srivastava · Manish Srivastava
Himanshu Pandey · P. K. Mishra
Pramod W. Ramteke *Editors*

Green Nanotechnology for Biofuel Production

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Biofuel and Biorefinery Technologies

Volume 5

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Preface I

Second-generation nonfood lignocellulosic biomass has tremendous potential for the biofuel production which was first came to light in the year of 1970. Nowadays, biofuels from waste biomass are gaining much attention because of limited availability and harmful environmental influences. Agriculture industries produce a huge amount of cellulose-rich biomasses in form of waste which is generally disposed off after the commercial processing. These biomasses are the potential; source value-added product besides biofuels production. Production of the biofuels from cellulosic wastes is a sustainable approach and also helps to resolve the economic constraints. For practical viability of biofuels, various advancements are required to bring the production economically sustainable. Cellulosic substrate availability, structural complexity of biomass, pretreatment, enzyme efficiency and denaturation, low product recovery, and its overall cost of the process are some serious issues which need to be addressed sustainable production of biofuels. Among various sustainable to improve production process of biofuels, application of nanotechnology seems to be very auspicious and may help to improve production of biofuels by altering major changes at the biochemical and molecular level both.

Nanotechnology has a broad range of engineering and technological applications due to their versatile physicochemical properties. It is anticipated that the industrial market of nanomaterials will increase sharply in the coming decade, and it is likely to increase approximately 58,000 tons in 2011–2020.

The aim of this volume on Green Nanotechnology for Biofuels Production Subtitle: Nanomaterials for Biofuels Generation is to keep the reader informed on the latest opportunity and practical feasibility in biofuels production technology using nanotechnology applications. The volume is consisting of 10 different chapters contributed by the author(s) having vast experience in teaching and research in the wide area of bioprocess technology and biofuels production as well as in nanotechnology. An introduction of biofuels and nanotechnology with application opportunity of nanotechnology has been given in Chapters "Introduction to Biofuels and Potentials of Nanotechnology"–"An Introduction of the Nanotechnology in the Field of Biofuel Production". A detailed application of nanomaterials as a nanocatalyst to improve biofuels production has been provided in Chapters

"Nanocatalyst for Biofuel Production: A Review" whereas use of nanomaterials as nanoaddaditives has been described in Chapter "Nanoadditives: Propitious Alternative for Increase Biofuel Performance". Chapter "Strategies of Porous Carbon Materials for Future Energy" focused on the feasible application of porous carbon for various forms of energy in order to make it sustainable. Further, Chapters "Nanotechnology Applied for Cellulase Improvements"– "Exploring Application of Nanoparticles in Production of Biodiesel" provide detailed information about different types and different modes of action of nanomaterials role in various biofuels production technologies such as in biobutenol, bioethanol, and biodiesel production. The main focus of this book is to introduce nanotechnology as a sustainable and potential option to improve process technology for biofuels production. All chapters included in this book present different views and approaches to enhance the various bioenergy productions by altering the process. Recent developments and ideas given by the experts in the various aspects of nanomaterials for bioenergy option have been discussed, to make this book more suitable for the students of students, scholars, and eminent scientist.

We express our deep felt indebtedness to all the contributed authors, people involve direct/indirect for sustained guidance, invaluable prolonged discussion, criticism and all that went to contribute substantially in the completion of this task.

We extend our thanks to Department of Chemical Engineering and Technology, IIT (BHU) Varanasi (U.P., India). Editor Manish Srivastava acknowledges DST, Govt. of India for DST-INSPIRE Faculty [IFA13-MS-02] 2014 award.

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Preface II

Biofuels such as biohydrogen, bioethanol, biobutenol, algal biofuels, and biodiesel are the potential alternative source of renewable energy. Globally, efforts are directed toward developing innovative technologies to produce this important source of green-energy cost-effectively. In the series of recent advances, nanotechnology is gaining attention due to its wide range of applications. Nanomaterials have tremendous potential for their commercial exploitation, and the industrial market is expected to increase in the coming decades. There is a need to collate and assess the potential and feasible applications of nanotechnology in biofuels production to guide the future course of research and suggest implementable actions.

Publication of the book on “Green Nanotechnology for Biofuels Production” is indeed a commendable endeavor in this direction and I pen this message with great pleasure and satisfaction. This book consists of 10 chapters focusing on different kinds of biofuels, technologies including nanotechnology for their production, and limitations of the current technologies of biofuels production. The book suggests possible ways for the improvement in all existing biofuels production technologies. This book also includes a critical market analysis for commercial biofuels production and future impacts on how nanotechnology can play a critical role to reduce the market price of biofuels. I hope that this book will serve as a depository of information for the scientists, researchers, teachers, and students.

I congratulate Prof. (Dr.) Pramod W. Ramteke (SHUATS, Allahabad), Dr. Neha Srivastava (IIT-BHU, Varanasi), Dr. Manish Srivastava (DU, Delhi), Prof. (Dr.) P. K. Mishra (IIT-BHU, Varanasi), and Dr. Himanshu Pandey (SHUATS, Allahabad) for bringing out the publication on "Green Nanotechnology for Biofuels Production" to cater the long-felt need of scientists, teachers, researchers, and students. My sincere thanks are for the editors for their untiring efforts, devotion, and dedication in this endeavor. All the authors and editors of the Series of Biofuels and Biorefinery Technologies deserve sincere appreciations for their commendable achievements.

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Introduction to Biofuels and Potentials of Nanotechnology

Jadwiga R. Ziolkowska

Abstract In recent decades, the development trends of biofuel technology worldwide have been staggering. In the US, the transition from conventional biofuels (derived from food crops) to advanced biofuels (cellulosic and algae-based fuels) occurred in less than a decade. Advanced biofuel technologies involve breaking down cellulose in plant biomass or extracting lipids from algae biomass, both of which are expensive processes driving up production costs. As of today, advanced biofuels are still cost-prohibitive, especially as they compete with low crude oil prices or even conventional biofuel prices. Despite unfavorable economics, both cellulosic ethanol and algae-based fuels help reduce GHG emissions, while also counteract the tradeoff between food and fuel production, as given with conventional biofuels/feedstocks. Nanotechnology has been implemented in the biofuel production process as a potential solution to economic infeasibility of advanced biofuels either by altering the feedstock or by increasing the biomass content. Although nanotechnology bears potential opportunities for biofuels production, full implementation of this technology is still challenging, while some studies report potential risks as well. This chapter presents an overview of different conventional and advanced biofuels and feedstocks, their developments and production trends at the global and US level. It also points out current challenges for advanced biofuels and discusses potentials and risks related to nanotechnology application in biofuels production.

1 Introduction—Biofuel Types and Feedstocks

Establishing biofuels as a part of the energy portfolio worldwide has taken more than five decades. The beginnings of biofuels date back to 1900 when Rudolf Diesel (German inventor and mechanical engineer) presented an engine run on peanut oil at the World Exhibition in Paris. This invention was followed by a

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Table 1 Biofuels classifications, products, and feedstocks

Classification	Product	Feedstocks
First generation (food feedstocks)	Ethanol	Corn, cereals, sugar beet/sugarcane
	Biodiesel	Soybean, rapeseed, palm oil, animal fats, waste oils
Second generation (biomass)	Cellulosic ethanol	(a) Energy crops (switchgrass, miscanthus, wheat straw, poplar, willow, jatropha)
		(b) Green waste (corn stover and other field residues, e.g., stalks and stubble (stems), leaves, seed pods, as well as forest/park residues)
Third generation	Biodiesel/ ethanol	Algae
Fourth generation	Biodiesel/ ethanol	(a) "Drop in" biofuels, GM crops for biofuels
		(b) Renewable solar fuel (e.g., Joule)

Model T engine designed to run on what is today called corn ethanol, among other potential fuels, and was introduced by Henry Ford (American industrialist) in 1908. The revolution of vegetable oils as a feedstock for diesel fuels began in the 1930s and 1940s. The development of the biofuels technology (both ethanol and biodiesel) took different paths in different countries and was regulated with different policies.

In the United States (US), the 1970 Clean Air Act introduced by the Environmental Protection Agency (EPA) set the first standards for fuel additives. Since 1992, a strong governmental support for alternative fuels was enacted with the Energy Policy Act to ensure independence from foreign oil. In 2005, the Energy Policy Act implemented amendments to the MTBE (methyl tert-butyl ether) (additive in gasoline) due to its scientifically proven carcinogenic characteristics. This development opened a wide market niche for biofuels and facilitated a fast uptake of this technology. At the same time, a variety of different feedstocks have been explored to expand biofuels portfolio. The 2007 Energy Independence and Security Act substantiated those developments with Renewable Fuel Standards (RFS) that set minimum production and blending requirements for each biofuel type.

Biofuel types are determined and characterized by feedstocks used for their production (Table 1). The most common classification categorizes biofuels as "*conventional*" and "*advanced*" biofuels.[1] Conventional (i.e., first generation) biofuels encompass ethanol and biodiesel produced from eatable crops, which has raised questions about their competition for resources (e.g., water, energy, land) with food production (Rathmann et al. 2010; Harvey and Pilgrim 2011, Ajanovic 2011). Advanced biofuels (second- to fourth-generation biofuels) were defined by the 2007 Energy Independence and Security Act as liquid fuels from non-food/non-feed

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[1] In addition to this classification, other terms are known in the biofuels methodology, e.g., "bioalcohol" that describes a broader group of biofuels, including ethanol, methanol, propanol, and butanol. As this contribution is focused on cellulosic ethanol and algae-based fuels, other alcohols will not be discussed in this chapter.

sustainably grown feedstocks and agricultural (municipal) wastes. Accordingly, advanced biofuels need to meet sustainability requirements, i.e., reduce greenhouse gas (GHG) emissions by a higher percentage than conventional biofuels and not create any competition with food crop production.

In the discussion of the most economically feasible feedstocks, scientists are still divided with their research findings of energy efficiency of corn ethanol compared to gasoline (Shapouri et al. 2002; Pieragostini et al. 2014; Sheehan et al. 2003). On the other hand, research studies have been more unanimous about positive energy balance of advanced biofuels (i.e., cellulosic ethanol) and their lower environmental footprint compared to gasoline (Bansal et al. 2016; Schmer et al. 2008). They have also been commended as a viable option to counteract the competition for resources with food production. This chapter will address two biofuel types: cellulosic ethanol and algae-based fuels and ways how nanotechnology can impact their production and processing.

Cellulosic ethanol can be produced from crop residues or from energy crops planted specifically for biofuels production. Even though cellulosic ethanol unveiled prospective opportunities for the biofuels market, many challenges need to be overcome to make it a feasible solution in the long term. The key challenge is economic feasibility related to the complex process of breaking down cellulose, hemicellulose, and lignocellulose in plant materials, which requires high energy inputs and expensive enzymatic reactions. Nanotechnology has been found to provide a possible solution to this problem, and it will be discussed in more detail in Sect. 3.

In addition, algae-based (third generation) biofuels have expanded the biofuels market and have been embraced by private investors as the most energy-efficient biofuel with relatively low environmental impacts (Jones and Mayfield 2012; Singh et al. 2011). However, although algae biomass can produce between 10 and 100 times more oil per acre compared to traditional oil crops (e.g., oil palm) and can grow 20–30 times faster than food crops (Ziolkowska and Simon 2014), economic feasibility of algae-based fuels has also been a challenge (Doshi et al. 2016; Vassilev and Vassileva 2016). Nanotechnology has been applied in algae fuel production to increase efficiency of algae biomass and decrease production costs, thus making it a cost-competitive addition to the biofuel market.

In the context of biofuels discussion, the question of sustainability has played an important role in evaluating both economic, and environmental and social feasibility of each conventional and advanced feedstock. Accordingly, life cycle assessment, sustainability and environmental indicators, the energy concept, and uncertainty analyses have been among the most applied methods to determine short- and long-term sustainability of different biofuels and feedstocks (Chang et al. 2017; Saladini et al. 2016; Lazarevic and Martin 2016; Ziolkowska 2013, 2014a).

2 Biofuels Production Trends, Economic Feasibility, and Environmental Impacts

Global ethanol production has surged reaching more than 75 billion liters in 2009, doubling production volumes from 2004. The largest contributors to the ethanol market are the US (with its corn ethanol production of ~40 billion liters in 2009) and Brazil (with its sugarcane ethanol production of almost 30 billion liters in the same year) (Timilsina and Shrestha 2011). Other countries and country associations (like the European Union–EU), China, India, and Canada contribute to the global ethanol production to a smaller extent (Fig. 1).

A similar trend was recorded for biodiesel production at the global scale, with 2.3 billion liters in 2004 and 17 billion liters in 2009 (an increase by 672%) (Timilsina and Shrestha 2011). Production of biodiesel in the US has increased as a total, with temporary production variations over time. Brazil, France, and the rest of the EU have expanded their biodiesel production over time, while Germany's production was rather stable between 2004 and 2009. Also, Argentina and Italy contributed to the global biodiesel production at lower rates (Fig. 2).

Future projections anticipate continuous increase in biofuels production worldwide (OECD 2010). Accordingly, ethanol production is expected to go up to 160 billion liters by 2019, while biodiesel production is projected to increase to 41 billion liters in 2019, and increase by ~113% and ~173%, respectively (Fig. 3). Moreover, the mix of different feedstocks in the global biofuels production has changed considerably over time. According to OECD (2010), the year 2016 will set the production peak for ethanol from coarse grains (including corn), while the

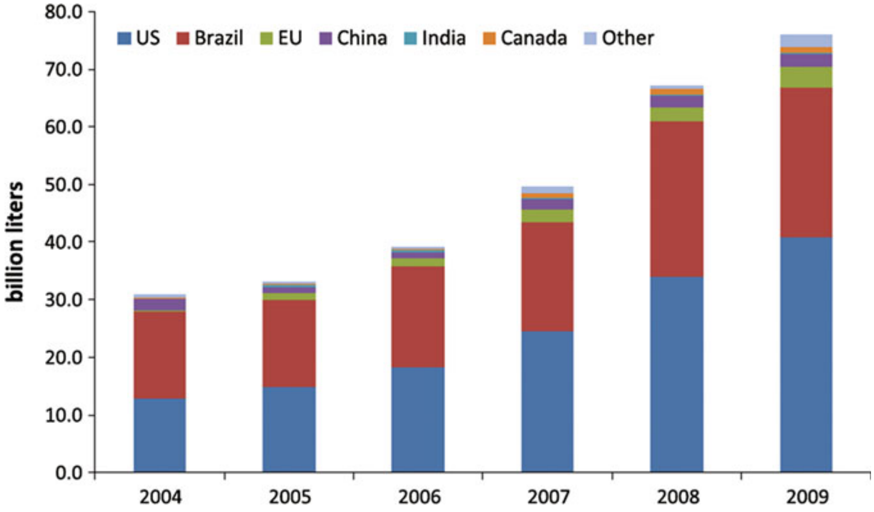

Fig. 1 Global ethanol production by country (2004–2009). *Source* Timilsina and Shrestha (2011)

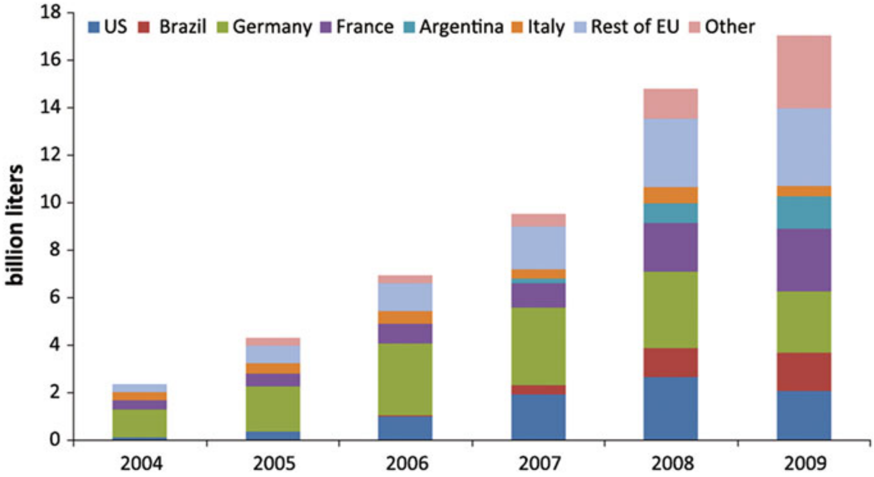

Fig. 2 Global biodiesel production by country (2004–2009). *Source* Timilsina and Shrestha (2011)

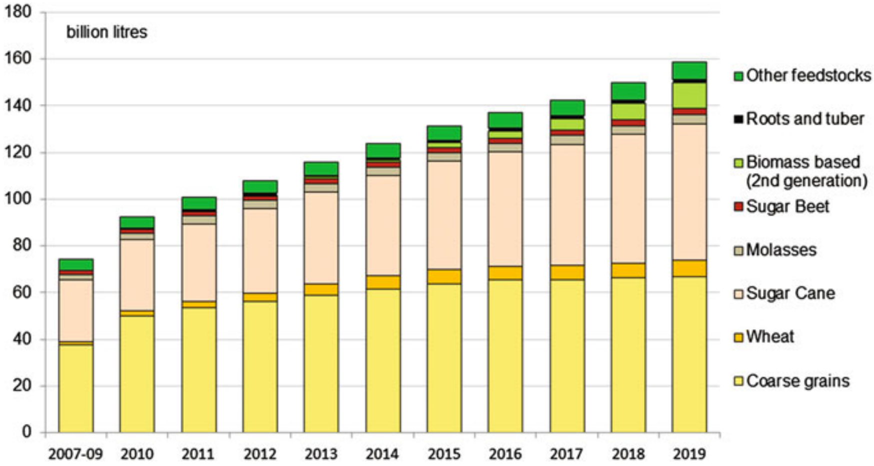

Fig. 3 Global ethanol production by feedstock—projections (2007–2019). *Source* OECD (2010)

production of sugarcane ethanol will increase throughout 2019. Furthermore, production of biomass ethanol (e.g., cellulosic ethanol) is anticipated to increase, reaching 11 billion liters in 2019.

Also, feedstock composition in global biodiesel production has varied over time. Use of vegetable oils has increased and is anticipated to grow up to 30.7 billion liters through 2019 (OECD 2010). Jatropha and other biomass feedstock for biodiesel production make a considerably smaller share; however, their use has increased over time and is anticipated to remain at this level in the future as well.

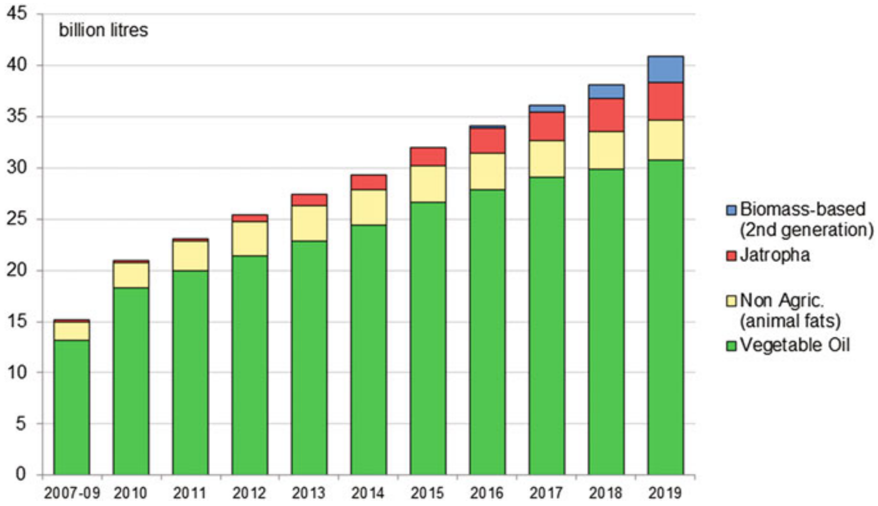

Fig. 4 Global biodiesel production by feedstock—projections (2007–2019). *Source* OECD (2010)

Production of biodiesel from animal fats has remained rather stable over time and is anticipated to reach the level of 3.9 billion liters by 2019 (Fig. 4).

On the US biofuels market, a significant increase in cellulosic ethanol production was sparked by the 2007 Energy Independence and Security Act that enacted Renewable Fuel Standards (RFS) as a mandate to expand the total quantity of renewable fuels blended into transport fuel from 9 billion gallons (34.07 billion liters) in 2008 up to 36 billion gallons (136.27 billion liters) in 2022. These totals were also divided into specific categories, with a requirement that each category of renewable fuel emits less GHG than petroleum fuel it replaces. Accordingly, starting in 2015, out of the total 36 billion gallons only 15 billion gallons (56.78 billion liters) can be provided on the market from conventional ethanol. The remaining volume needs to be produced from advanced feedstocks. In April 2010, the EPA announced the RFS2 that specified minimum quantities from specific feedstocks or biofuel types that need to be met toward the total mandate (FAPRI 2010a; Ziolkowska et al. 2010) (Fig. 5). Thus, the production of cellulosic ethanol is mandated to increase gradually and reach 16 billion gallons (60.5 billion liters) in 2022 (US EPA 2010) (Fig. 5).

Past and current developments indicate that cellulosic ethanol (and other biomass fuels, e.g., from algae feedstock) will play an increasingly important role in the future. However, at the same time, the economic feasibility of both cellulosic ethanol and algae-based fuels is still unfavorable for a large-scale market commercialization, especially in times of low prices of conventional fuels (i.e., gasoline). According to Colye (2010), production costs of cellulosic ethanol equal to $2.65/gal, which is $1 more than costs of corn ethanol (Fig. 6). High costs of

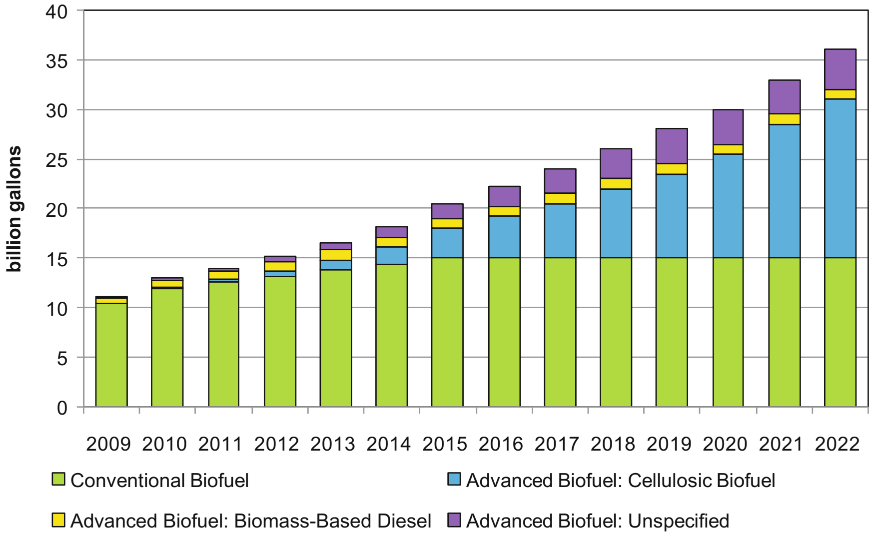

Fig. 5 Renewable Fuel Standard in the US (2009–2022). *Source* US EPA (2010)

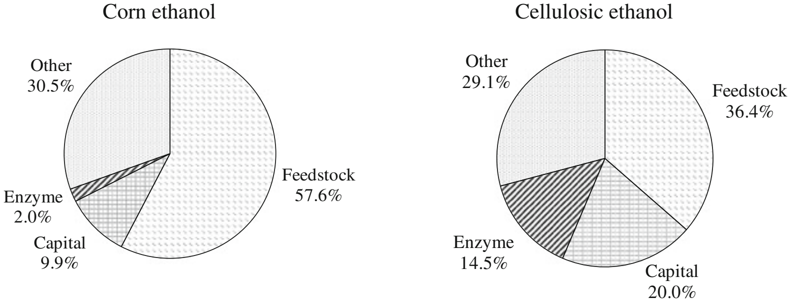

Fig. 6 Production costs of corn-based and cellulosic ethanol. *Source* Coyle (2010); Ziolkowska and Simon (2011)

enzymes needed to break down cellulose are among the main driving cost components in production of the cellulosic ethanol.

For algae-based fuels, economic feasibility presents even a bigger challenge. According to US Department of Energy (2008), the price for algae-based fuels produced on a large scale amounts to more than \$8/gal (compared to \$4/gal for soybean-based fuel). However, it needs to be mentioned that long-term cost trends over the past 30 years (and normalized to 2009 price values) indicate a decrease in production costs from \$6.09 in 1982 (Benemann et al. 1982) to \$2.41 in 1996 (Benemann and Oswald 1996; Gallagher 2011; Ziolkowska and Simon 2014).

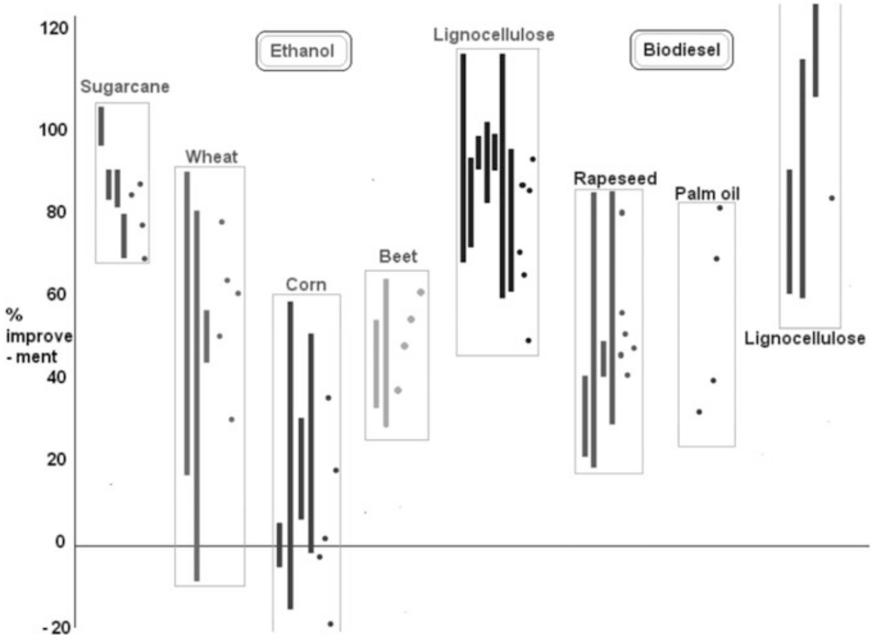

Fig. 7 Net life relative cycle GHG emission improvement of selected biofuels pathways as compared to gasoline and diesel fuels (without land use change). Legend: Bars and dots shown in the graph indicate the range and point estimates of improvements in net GHG emissions as elaborated from the data found in the reviewed studies. *Source* OECD (2008); Ziolkowska and Simon (2010)

Considering environmental concerns, the ecological footprint of cellulosic ethanol is significantly lower than of traditional gasoline or even conventional biofuels. According to OECD (2008), lignocellulosic ethanol can reduce GHG emissions in the range between 50 and 110% compared to gasoline and diesel fuels (w/o LUC—land use change), while lignocellulosic biodiesel can generate an environmental effect of 60% and more GHG reduction (Fig. 7). Also, algae-based fuels offer a number of environmental benefits that make them a desirable product on the biofuels market. Environmental footprint of algae has been described as negative (i.e., carbon neutral) as algae biomass requires 2 g of CO_2 for every g biomass generated (Pienkos and Darzins 2009), while one ton of CO_2 can be converted into 60–70 gallons of algae-based ethanol (Hon-Nami 2006; Hirayama et al. 1998). In addition, algae do not compete for freshwater as they can be grown by using waste/saline water, while they do not require productive land either (Ziolkowska and Simon 2014).

Given the economic challenges and environmental potentials of advanced (cellulosic and other biomass-based) biofuels, nanotechnology has been studied as a possible solution to reduce production costs and thus lower environmental footprint as described above. However, most recent studies indicate that nanotechnology can also bear other health and environmental risks that have not been considered comprehensively in the discussion of biofuels yet. Section 3 will provide more insights into both new advances nanotechnology offers for biofuels production and potential short and long-term risks associated with its application.

3 Potentials and Risks of Nanotechnology for Biofuels Production

Scientific metric classification describes the “nano” unit as one billionth part of the factor of 1. Thus, for instance, 1 nanometer (nm) equals 10^{-9}m (0.000000001 m).

Nanotechnology (from the Greek word “nano”, i.e., dwarf) aims at manipulating materials at the atomic and molecular levels to create new molecular structures known as “nanomaterials”. Nanomaterials have unique and new characteristics that differ from characteristics of the original materials they are derived from, while their structured components are of at least one dimension less than 100 nm. As a comparison, the size of atoms is in the range of 0.1–1 nm, viruses are between 10 and 100 nm small, and bacteria between 1 and 10 micrometers (μm) (=1,000–10,000 nm) (Warad and Dutta 2007). Thus, nanotechnology is able to “see” and control individual atoms and molecules (NNI 2016). It is important to emphasize that at the nanoparticle level, changes in electrical, chemical, magnetic, mechanical or biological properties of materials can occur that differentiate them from the bulk material, albeit with no change in chemical composition. Consequently, nanotechnology generates new (in many instances enhanced) characteristics related to, e.g., material flexibility, strength, conductivity, surface tension or color (Molins 2008).

Although nanotechnology has been successfully applied in many disciplines to solve complex environmental problems (e.g., oil spill cleanups) (Avila et al. 2014), this section will focus on nanotechnology in advanced biofuels production only.

The major question raised frequently is about ways and approaches how nanotechnology could be utilized to improve efficiency of biofuels production. According to Wegner and Jones (2009), nanotechnology can be applied in the following ways:

(1) To manipulate nanoscale cell walls structures (also referred to as a nanofibril) within trees and plant materials to facilitate an easier disassemblement into constitutive materials for biofuels production (either through fermentation, gasification, or catalysis).
(2) Through application of nanocatalysis to break down cellulose that makes 15–25% of the carbohydrate part of wooden materials.
(3) Through application of engineered nanoscale enzymes or systems of enzymes (e.g., glycol hydrolases, expansins, and lignin-degrading enzymes) to improve conversion efficiency of cellulose into sugars. Also, in addition to the first approach, tree biology could be engineered for enzymes and enzyme systems to

be created and stored/sequestered in the living tree until harvest and then be activated for engineered woody biomass self-disassembly.

(4) To create new symbiotic nanoscale biological systems which would work together to create ethanol or other biofuels.

In recent years, nanotechnology has been described as a technology of the future, research in this field has boomed to determine cons and pros of each of the abovementioned approaches, while public research funding and private investments in laboratory experiments increased considerably. This strong support for nanotechnology results from the many advantages this technology promises as well as the consecutive (currently yet unknown) advances as a spillover effect.

In regard to cellulosic ethanol, the mainstream of traditional material science with treating cellulose, hemicellulose, and lignin has been through breaking materials down to particles to regenerate them or create new materials. Enzymes have been applied to convert cellulose into simpler sugars that can further be fermented by bacteria to ethanol. Nanotechnology has been introduced as advancement to this traditional practice as it provides a potential to build materials through a designed arrangement of atoms into nanostructures of various types. This is possible as lignocellulosic biomass is made up of nanometer-size building block units that provide valuable properties to wood and other types of renewable lignocellulosic and cellulosic biomaterials. Accordingly, nanoparticles can immobilize beds of expensive enzymes that can be used over and over again to break down the long chain of cellulose polymers into simpler fermentable sugars for ethanol production (LTU 2009). Savings estimates range between $32 million for each cellulosic ethanol plant and $7.5 billion given that the RFS goal of 16 billion gallons of cellulosic ethanol is achieved (LTU 2009). For biodiesel production, nanocatalysts can be used for transesterification of fatty esters from vegetable oils or animal fats into biodiesel and glycerol (Lin et al. 2007).

Laboratory experiments triggered consecutive research and continuous development of nanotechnology. An increasing number of research studies unveiled new approaches for cellulose conversion (Munasinghe and Khanal 2010; Jiang et al. 2009), while economics, sustainability and renewable energies have been among driving research issues (Raman et al. 2015; Cacciatore et al. 2012; Serrano et al. 2009). While the number of research studies on nanotechnology for biofuels has increased over years (Li et al. 2016; Kizling et al. 2016; Babadi et al. 2016; Guo et al. 2012), many questions still remain open (Bhatia 2014; Guerin 2009).

In regard to algae-based fuels, research in nanotechnology has also raised scientific interest (Gavrilescu and Chisti 2005) to solve current challenges related to algal biomass. Those challenges have been identified by Pattarkine and Pattarkine (2012) as follows: (a) lack of consistent industrial-scale algae production, (b) high costs of algae harvesting and production, and (c) energy intensive lipid extraction. Nanotechnology could help with: (a) mitigating the existing limitations related to gas transfer, mixing, illumination, and biomass yield, (b) improving efficiency, lipid extraction and yield of algal biofuels (also through genetic engineering), and (c) improving harvesting technologies. As emphasized by Pattarkine and Pattarkine

(2012), application of silver nanoparticles for improved photoconversion, calcium oxide nanocrystals in transesterification, and mesoporous nanoparticles in biofuel separation would help with achieving those goals.

In addition, the new “nanofarming” technology can facilitate oil extraction from algae more efficiently as it supports a continuous process of “milking algae” for up to 70 days instead of destroying their cell and biomass structure as suggested by traditional material science (Vinayak et al. 2015; Chaudry et al. 2016; Ziolkowska and Simon 2014). Commercialization of this new technology has been discussed between the US Ames Laboratory and Catilin (a nanotechnology-based company specializing in biofuel production) with the aim to reduce costs and energy consumption of non-food source biofuels feedstocks. The pilot project of “nanofarming” has been funded by the US DOE (Office of Energy Efficiency and Renewable Energy Industrial Technology Program), Catilin company, and Iowa State University (Lin et al. 2009).

In summary, the application of nanotechnology in biofuels production has been evaluated as a promising approach to (1) reduce transportation costs of feedstocks, (2) break down the feedstock more efficiently, and (3) improve biofuels production efficiency, which would help lower prices of advanced biofuels. Despite those promising advantages, on the one hand, nanotechnology has raised concerns about potential short and long-term economic and environmental issues, on the other hand.

One of the major concerns is missing knowledge about potential impacts and side effects of nanotechnological modifications (Renn 2006), as well as effects and implications for living organisms (including ecosystems and humans), as many nanomaterials entering the environment might remain in it indefinitely (Colvin 2004). Once deposited on soils, nanoparticles can traverse several soil strata and leak into aquifers, while drinking water filtering systems might not be capable of filtering them out (Alargova and Tsujii 2001). Unlike nanoparticles originating as byproducts of combustion engines, manufactured nanoparticles do not agglomerate as much and thus could remain more reactive for longer periods of time. There is a risk that due to their very small size, they could enter the human bloodstream via the lungs after inhalation, the digestive tract, and the skin if applied or deposited on it. As consequences and impacts of nanoparticles in human body are unknown, more research is needed to be able to assess advantages and disadvantages of nanotechnology in general and for any kind of application, including biofuels production (Justo-Hanani and Dayan 2015; Hull and Bowman 2014). Also, policy regulations are needed that would establish a well-grounded oversight and monitoring procedure (Colvin 2003; Molins 2008).

In addition to traditional examples and applications of nanotechnology in biofuels production as described above, also experiments have been undertaken to explore utilization of bacteria and plant enzymes to break down cellulose and lignin (Ziolkowska 2014b). For instance, the US Department of Energy (DOE), the BioEnergy Science Center, and the University of California researchers developed the *Clostridium celluloyticum* bacteria capable of breaking down cellulose and enabling the production of isobutanol in one inexpensive step (Casey 2012a, b).

In addition, DOE also found engineered strains of the *Escherichia coli* bacteria to be able to break down cellulose and hemicellulose contained in plant cell walls, e.g., switchgrass (Ziolkowska 2014b). Also, a method has been developed at the University of Central Florida to break down cellulose and refine ethanol from orange peels by means of a tobacco enzyme. The tobacco enzyme is derived by cloning genes from fungi and bacteria. This process was found to be considerably less expensive than using synthetic enzymes (Casey 2012a, b). Combining nanotechnology with those processes might yield even higher economic benefits by limiting carbon footprint of biofuels production. However, environmental and health concerns remain and will require basic research and potentially policy regulations in the years to come.

4 Conclusions and Outlook

Biofuels technology has experienced a considerable progress in the past decades, expanding its scope from conventional to advanced feedstocks with lower environmental footprint and higher energy efficiency. This process revealed several key challenges, especially for advanced biofuels: cellulosic ethanol and algae-based fuels that face economic challenges related to breaking down cellulose and lignin, and extracting lipids, respectively.

Nanotechnology can potentially provide solutions to some of those challenges that have hindered and delayed commercialization of advanced fuels at a large scale. It can help with reducing transportation costs of feedstocks, breaking down the feedstock, extracting oils more efficiently, and improving biofuels yields and production efficiency, which could ultimately help with reducing biofuels prices. Even though nanotechnology provides promising potentials, uncertainties exist among scientists and regulatory agencies about the safety of nanotechnology both for humans and the environment, as some nanomaterials can be toxic. As nanotechnology is not regulated yet, and no rules exist for its application, there is a valid question of unknown potential long-term environmental and social impacts that could theoretically be irreversible.

Furthermore, as nanotechnology is a new approach, more research is necessary to discover and understand its potentials, also for biofuels applications, while minimizing any potential risks to the environment and humans. Governmental and environmental regulations are needed for companies producing nanomaterials as well as a clear monitoring and enforcement system. Also, the potential combination of new technologies (nanotechnology and genetic engineering) to reduce production costs of advanced biofuels might bring new developments and changes to the biofuel market in the long term.

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Nanotechnology: A New Tool for Biofuel Production

Sachin K. Mandotra, Rohit Kumar, Santosh K. Upadhyay and Pramod W. Ramteke

Abstract Rapid depletion of fossil fuel reserves has posed a serious challenge to meet future energy requirement. Biodiesel with low carbon footprint has emerged as a potential candidate that can replace the need of fossil fuels. Biofuel derived from algae offers best alternative due to their high lipid content, robust nature, and noncompetitive nature toward food crops. The downstream production of biodiesel from feedstock is, however, facing challenges due to energy-intensive nature and higher production cost. A new and rapidly emerging field of nanotechnology has given a choice to built robust nanobiocatalytic systems with long-term stability and low input cost. Earlier studies reported that the addition of nanomaterials in algal culture system improved microalgal growth as well as induced lipid accumulation. Moreover, with the application of nanomaterials, the lipid extraction efficiency could also be enhanced. This chapter is aimed to review the current and significant applications of nanotechnology in the field of algal biodiesel production. Development of innovative technologies dealing with nanotechnological application in algal cultivation, lipid accumulation, harvesting, and transesterification has been critically reviewed.

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1 Introduction

The energy requirement is increasing with the increase in worldwide population. Global fossil fuel uses has increased in such a way that its consumption rate is 10^5 times faster than its creation by nature (Satyanarayana et al. 2011); with the current consumption rate, the utilization of primary energy sources will double by 2035 and triple by 2055 (UNDP 2000). It has been estimated that by the year 2050, all the known sources of fossil fuels will be completely exhausted (Demirbas 2009). Global warming due to increase in greenhouse gases (GHGs) and economic concerns are other major issues associated with the use of fossil fuels (Zhang et al. 2010). Therefore, the focus has been shifted toward the exploitation of renewable fuels such as biodiesel, biohydrogen, bioethanol, biogas, etc. They have gained huge attention in recent years due to their low GHGs emission, reduced carbon footprint, and more importantly because of their sustainable nature (Hussein 2015).

There are several sources that can be used for the production of biodiesel such as various oil crops (sunflower, soybean, mustard, canola, etc.), animal fat, and lipid extracted from algae. Biodiesel is fatty acid methyl or ethyl ester made from plant oils, animal fats, and recycled cooking oil. Besides their renewable nature, the use of biodiesel in conventional diesel engines results in reduced carbon dioxide (CO_2) and carbon monoxide (CO) emission. Higher content of hydrogen and oxygen in biodiesel is an advantage; moreover, higher lubricity of biodiesel improves the fuel injection system and enhances the life of sliding metallic components of the engine (Hussein 2015). Microalgae, due to its higher growth rate and lipid content, have emerged as better option for biodiesel feedstock. Unlike other oilseed crops, algae have the ability to grown in saline or wastewater, and they not compete for arable land with other food crops. Furthermore, the growth conditions of algae can be altered for higher biomass and lipid content, which is not in the case of other oil-producing plants (Mandotra et al. 2016, Upadhyay et al. 2016). In this way, algal offers a great potential as a feedstock for biofuel. To develop a cost-effective commercial biofuel, however, the algal biofuel system should overcome a number of challenges particularly the cost factor associated with it. Modifications in photobioreactor design are in practice to improve illumination, mixing, and biomass yield of the algae. Harvesting is an energy-intensive process; advanced harvesting technologies with improved biomass separation significantly improve the cost-effectiveness at industrial scale. Apart from this, lipid extraction from wet biomass using various solvents systems and its transesterification into biodiesel in the presence of enzymes at low temperature is highly appreciable for the process to be cost-effective (Pattarkine and Pattarkine 2012).

Nanotechnology is an emerging science that has gained considerable attention in the recent years. At present, a number of engineered nanoparticles are being used in various industries such as cosmetics, drug delivery, food, coating, crop production, bioremediation, photonic crystals, and material science (Lopez-Serrano et al. 2014, Lee et al. 2015). The emerging field of nanotechnology is offering potential solutions to various challenges in algal biodiesel production to reduce the cost of downstream processing. The following sections deal with recent advancements in the field of nanomaterials for improved algal biofuel production including algal cultivation, harvesting, extraction, and separation of biofuel.

2 Nanomaterials and Their Advantages

Nanotechnology is a technique to fabricate and apply material with the molecular precision at dimensions of 100 nm or smaller (The Royal Society and The Royal Academy of Engineering [RS/RAE], 2004). Figure 1 illustrates the natural and fabricated structure and their relative size with nanomaterials. They provide many times more surface area to volume ratio in comparison to the same weight of other material. It has been observed that the physical properties of several materials change at their nanoscales, for example, physical properties of carbon nanotubes are significantly different from plain carbon material. Various properties such as electrical, optical, mechanical, magnetic, and chemical properties are different for same material at different dimensions (Zhang et al. 2010). Change in these properties is attributed to the surface area and the quantum effects. At nanoscale, quantum effects play a significant role, as it is seen in the case of silver which is nonmagnetic at macroscale but shows magnetic nature at nanoscale due to electronic interactions (Johnson 2003). Currently, for industrial biotechnological applications, various nanomaterials such as nanofibers, nanoparticles, nanosheets, nanotubes, nanopores, and nanocomposites are being used. Their high surface area can be used for higher amount of enzyme to be immobilized; as a result, better biocatalytic activity and stability could be achieved. An enzyme immobilized on nanoparticle offers low mass transfer resistance in comparison to macro scale matrices, which result in enhanced stability and activity of an enzyme. Moreover, magnetic nanomaterials allow quick and efficient removal by the use of magnet that facilitates the quick separation of enzyme from the product. Unlike other

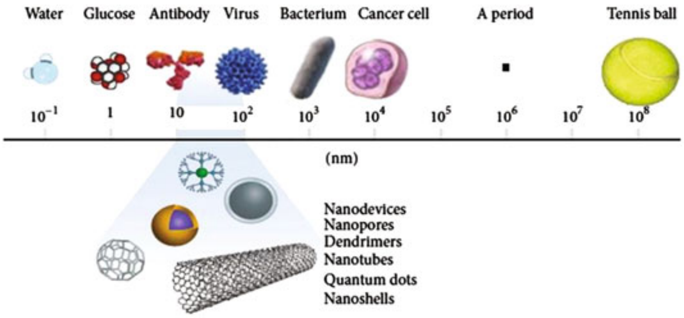

Fig. 1 Relative size of nanomaterials in comparison to natural and man-made material (Amin et al. 2014)

conventional methods (centrifugation and filtration) that lead to enzyme instability due to mechanical shearing, the use of magnetic nanoparticles provides an efficient and economic option for this process (Ren et al. 2011, Yiu and Keane 2012).

3 Nanotechnology for Algal Biofuel

3.1 Application of Nanotechnology in Algal Cultivation and Lipid Induction

One of the preliminary requirements for culturing algae is illumination. Considerable research has been done in the field of innovative nanomaterials for the manufacturing of light emitting diodes (LEDs) (Pattarkine and Pattarkine 2012, Pompa et al. 2006). Most recent technology is the use of metallic nanoparticles together with localized surface plasmon resonances (LSPR). Higher quantities of nanoparticles in algal culture medium may adversely affect the growth of algae by hindering required amount of light. Therefore, metal nanoparticles are used to amplify light at specific wavelength outside of closed photobioreactor (PBR). LSPR technology is based on the combined oscillations of free electrons at a metallic dielectric interface (Torkamani et al. 2010). Resonant interactions between photons and surface plasmons ensure selective absorption and scattering of light at specific wavelength. In an experiment with *Chlamydomonas reinhardtii* and *Cyanothece* 51142 in PBR, 30% higher cell growth was observed by strong backscattering of blue light from silver nanoparticles suspension (Torkamani et al. 2010). In another study, light uptake efficiency of *Chlorella vulgaris* has been improved significantly via increased accumulation of chlorophyll and carotenoid pigments by using spheroidal silver nanoparticles and gold nanorods (Eroglu et al. 2013). The biggest advantage of using nanoparticle suspension is that it can be used for the growth of specific microalgal species as well as to avoid photoinhibition by changing the size and concentration of the nanoparticles (Lee et al. 2015).

Adequate mixing is as important as illumination for algal to sufficiently provide carbon dioxide (CO_2) and various nutrients in the culture medium. A study conducted by Zimmerman et al. 2009 on nano- and microbubbles in an airlift loop bioreactor (ALB) may be used to increase the algal biomass production. Nanobubbles provide uniform stirring motion that stirs suspended algal cell toward the wall of ALB so as to expose every cell with sufficient light intensity to carry out photosynthesis for bulk biomass production (Zimmerman et al. 2009).

Besides the indirect use of nanotechnology, as in case of illumination and bubbling culture media, there are quite a few reports where the direct addition of nanoparticles nutritionally supplemented the algal culture medium. A study performed with green microalga *Chlorella vulgaris* supplemented with $MgSO_4$ nanoparticles and organic carbon source revealed enhanced photosynthetic efficiency with a significant reduction in glycerol consumption (Sarma et al. 2014).

Increased photosynthetic efficiency was due to increase in chlorophyll content, which was an adaptation to utilize low light intensities as a result of $MgSO_4$ induced flocculation. The study also revealed hike in lipid yield of the alga (Sarma et al. 2014). In another study, Kadar et al. (2012) supplemented three microalgae (*Pavlova lutheri*, *Isochrysis galbana*, and *Tetraselmis suecica*) with synthetic nanoscale zero-valent iron nanoparticles (nZVI); as a result, two algae, viz., *Pavlova lutheri* and *Tetraselmis suecica*, accumulated higher lipid content in comparison to the cultures supplemented with standard Fe-EDTA. Higher lipid accumulation in algae was in response to the oxidative stress caused by nZVI generated reactive oxygen species. San et al. (2014) reported an increased cell growth of green microalga *Chlorella vulgaris* incubated with 38–190 nm sized laser-ablation-prepared silica nanoparticles. Yet another study performed on *Chlorella vulgaris* UTEX 265 found a slight increase in lipid content with the supplementation of 0.1 g/L TiO_2 nanoparticles under UV treatment. The growth of alga, however, decreased at 2.5 and 5.0 g/L TiO_2 nanoparticles, demonstrating the negative effect of the higher concentration of TiO_2 nanoparticles in the presence of UV radiation (Kang et al. 2014).

3.2 *Algal Harvesting Using Nanoparticle*

Algal biodiesel is a potential candidate for the replacement of fossil fuels. The major challenge is, however, downstream process technologies. Algal biomass harvesting from aqueous phase accounts for more than quarter of the total production cost of overall process from cultivation to biofuel production (Pienkos and Darzins 2009; Wang et al. 2015). Among various technologies such as centrifugation, magnetophoretic separation, membrane-based filtration, flocculation, and electrolysis, flocculation is considered as one of the most economical and viable methods for harvesting algae (Farooq et al. 2013; Vandamme et al. 2013; Uduman et al. 2010). Moreover, except flocculation, harvesting smaller algal cells with the size range of 2–4 μm is difficult and still remains a major challenge for efficient harvesting technologies (Hu et al. 2013; Ríos et al. 2012). Recently, magnetic flocculation has emerged as one of the most efficient technologies for microalgal harvesting. Harvesting process with magnetic nanoparticles is quick, inexpensive, and energy efficient. During this process, magnetic nanoparticles are coated with target cells and under the influence of external magnetic field, separation takes place followed by detachment of microalgal biomass from magnetic nanoflocculant for recycling. At present, magnetic iron oxide nanoparticles are being used in fishponds and freshwater bodies for algae removal. In several places, they have been used for the last 40 years for the removal of algae from lakes (Bitton et al. 1975, Toh et al. 2012, Liu et al. 2013, Wang et al. 2013). Figure 2 shows algal harvesting using Fe_3O_4 nanoparticles. To study the harvesting efficiency, Seo et al. (2016) incubated *Chlorella* sp. with CTAB-decorated Fe_3O_4 nanoparticles; as a result, 96.6% of microalgae harvesting was achieved at a dose of 0.46 g particle/g cell. After one

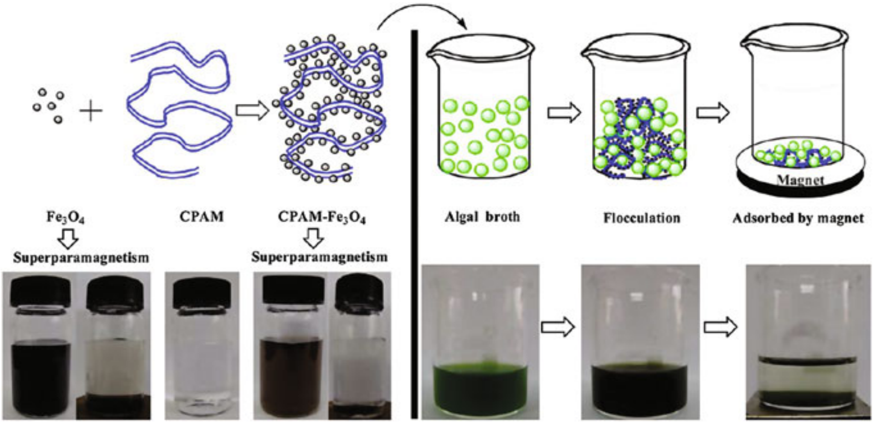

Fig. 2 Algal harvesting using Fe_3O_4 nanoparticles (Wang et al. 2013)

cycle of harvesting, 80% reuse efficiency was recorded by detached CTAB-decorated Fe_3O_4 nanoparticles.

In another study with microalga *Nannochloropsis maritime,* the recovery efficiency of Fe_3O_4 nanoparticles was as high as 95% at a dose of 120 mg/L within four minutes. The study revealed that neutral and alkaline conditions resulted in cell aggregation that improved algal cells harvesting (Hu et al. 2013). Wang et al. (2013) supplemented Fe_3O_4 nanoparticles with microalgae *Botryococcus braunii* and *Chlorella ellipsoidea*; as a result, the recovery efficiency of 95% at a dose of 25 mg/L and 120 mg/L, respectively, was achieved.

3.3 Nanotechnology for Lipid Extraction

For biodiesel production from microalgae, lipid extraction part contributes one of the major portions of the entire cost. It is because of the reason that the cell wall of the algae is composed of complex carbohydrates and glycoprotein which provide algae with a wide range of chemical resistances and high mechanical strength (Kim et al. 2013, Lee et al. 2015). Currently, the most common approach of extracting lipid from algae is the use of different solvents (chloroform, methanol, hexane, etc.). They are used either individually or in combination in different proportions. It has been observed that the lipid yield of algae significantly varies with the use of different solvent combinations. Moreover, the extraction conditions such as homogenization, ultrasonication, and irradiation could affect the overall lipid yield. For an optimized extraction protocol with higher lipid yield, all of these factors should be considered which may add to the overall cost of the downstream processing for biodiesel production (Zhang et al. 2013, Cheng et al. 2009, Vicente et al. 2009, Pernet and Tremblay 2003). Recent development in the field of nanotechnology has given reliable, safe, and cost-effective alternatives. Apart from their higher percentage of oil extraction efficiency, unlike solvents, nanomaterials offer non-toxic approaches of lipid extraction. Moreover, the solvent–lipid separation step in the conventional extraction process which is tedious and adds cost to the overall process can be eliminated with the use of nanomaterials (Zhang et al. 2013).

Lin et al. (2009) reported the use of sphere nanomaterial that can be used for lipid extraction from microalgae without harming algal cell which could be used continuously for lipid accumulation; hence, re-cultivation cost of algae could be reduced. A study conducted with *Chlorella* sp. KR-1 revealed that in the presence of aminoclay nanoparticles, the oil extraction efficiency greatly enhanced with increase in microalgae harvesting efficiency. The improved extraction could be explained by the fact that, apart from weekending cell wall of the algae, cationic charged aminoclay nanoparticles decrease the water layer between cell wall and hydrophobic solvent; as a result, higher amount of solvent comes in contact with cell wall for the release of internal oil (Lee et al. 2013a). In another study, oil extraction from disrupted cells was done by OH free radicals which were generated by Fe-based aminoclay in the presence of hydrogen peroxide (H_2O_2) (Lee et al. 2013b). Lee et al. (2014) demonstrated the application of aninoclay-TiO_2 nanocomposite in the presence of UV irradiation (365 nm) for simultaneous harvesting and algal cell disruption. Razack et al. (2016) reported the increase in the oil content of *Chlorella vulgaris* from 8.44 to 17.68% with the increase in the concentration of silver nanoparticles (AgNPs) from 50 to 150 µg/g. Figure 3 shows the scanning electron microscope (SEM) image of *Chlorella vulgaris* cells before and after treatment of AgNPs.

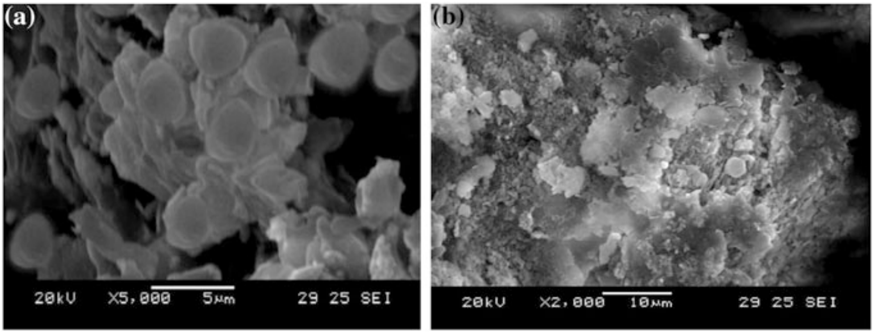

Fig. 3 SEM images of *Chlorella vulgaris*: **a** intact cells before treatment and **b** disrupted cells after treatment with AgNPs (Razack et al. 2016)

3.4 Transesterification by Nanomaterials Application

Transesterification is a chief process of conversion of oil into biodiesel. During this process, oils derived from algae, plant, animal, and other microorganism source react with alcohol to produce fatty acid methyl esters (FAME) which are also called as biodiesel (Fig. 4). For the production of biodiesel, currently, transesterification is carried out mainly through four types of catalysts, viz., enzyme, acid, base, and heterogeneous catalysts (Zhang et al. 2013, Kumar et al. 2016).

In acid-catalyzed reactions, generally, HCL and H_2SO_4 are used as a catalyst; however, the use of acid catalyst involves additional concern, and besides this, the process requires higher amount of methanol which itself makes the process costly. On the other hand, base catalyze transesterification reaction requires higher amount of base due to soap formation. Unlike acid and base catalyst, enzymatic transesterification by the use of lipase is more efficient and environmentally friendly. Chief problem associated with enzyme-catalyzed transesterification is the higher cost and mainly the enzyme denaturation. During transesterification process, the enzymes are inactivated by substrates and by-products (Kumari et al. 2009). The biocatalytic activity of the enzyme is decreased in the presence of methanol, which is used as an acyl acceptor. Recently, researchers find out a way to reuse lipase by immobilization it on carriers and other porous materials. It has been found out that the activity and stability of recycled lipase remain constant (Zhang et al. 2013, Vicente et al. 2009, Ullah et al. 2009, Du et al. 2004, Noureddini et al.2005, Jegannathan et al. 2008).

The advantage of using nanomaterials is their large surface to volume ratio which provides a large surface area for lipase immobilization. Moreover, the active sites of lipase are offered with high reactant diffusion rate due to small pore size in nanomaterials (Zhang et al. 2013). Shah et al. (2007) carried out transesterification of ethyl butyrate by immobilizing lipase onto carbon nanotubes (CNTs); as a result, as high as 97% activity of lipase was retained. In another study, 80% activity of lipase encapsulated by polymer nanogel was retained in comparison to 10% activity of free lipase (Ge et al. 2009). Magnetic nanoparticles, on the other hand, offer a great convenience and low-cost alternative due to their easy recovery from reaction mixture and enhanced thermostability (Verma et al. 2013). In a study, 90%

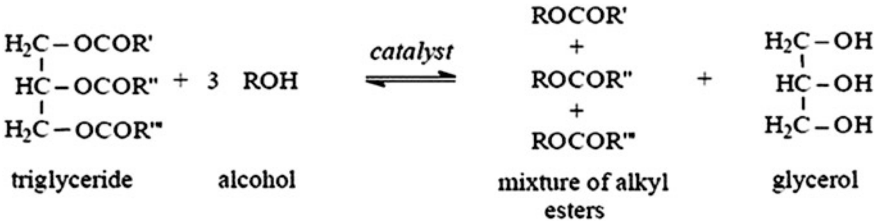

Fig. 4 General reaction of transesterification where triglyceride reacts with alcohol in the presence of catalyst to produce FAME and glycerol is produced as by-product

biodiesel conversion efficiency was achieved with the application of covalent attachment of *T. lanuginosus* lipase with amino-functionalized magnetic nanoparticles (Xie and Ma 2010). Wang et al. (2009) reported full percent conversion of oil into biodiesel with the application of *P. cepacia* lipase (PCL) immobilized on Fe_3O_4 magnetic nanoparticles. In another study, Sakai et al. (2010) carried out butyl biodiesel production in the presence of electrospun polyacrylonitrile nanofiber bound PCL; as a result, 94% butyl biodiesel production was achieved.

4 Conclusion

This chapter gives a comprehensive understanding of the application of nanotechnology to improve the overall process of algal biofuel production. Algal culture supplementation with nanoparticles could significantly enhance the CO_2 accumulation and biomass production capacity. Harvesting of biomass from culture system is one of the cost- and energy-intensive as well as time-consuming processes; with the application of magnetic nanomaterials, biomass harvesting could be improved with higher efficiency and low-cost input. Nanoparticles possess a unique ability to weaken and rupturing the algal cell wall for maximum lipid recovery. Moreover, the use of nanotechnology offers a stable and tolerant enzyme system that can sustain the adverse effects of various solvents used during biodiesel production. In this way, the combination of biodiesel technology and nanotechnology provides a promising opportunity that can improve the economic production of biodiesel in future.

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Introduction of Nanotechnology in the Field of Biofuel Production

Afifa Qidwai, Shashi Kant Shukla, Rajesh Kumar, Anand Pandey and Anupam Dikshit

Abstract Nanotechnology has an increasingly large impact on a wide range of industries, but its current use in the production of electricity and heat from biomass is limited. The potential impact of nanotechnology on bioenergy production through a literature review and interviews with industry members. Current technologies and methods in use were reviewed, with a focus on fuel handling and combustion systems. Areas in which problems existed were identified and nanotechnologies with properties relevant to those problems were examined. Basic economic analyses were also performed to determine the conditions for the economic viability of the nanotechnology solutions. Biodiesel can be used as a substitute for fossil fuels and successful studies have been carried out in different applications. Butchery wastes were used for the production of hydrocarbon gases and biodiesel. The economics of this novel process is much more cost competitive due to the cheap raw material (butchery waste) that contains high levels of fatty acids. Photocatalysis gave hydrocarbons of prime importance. The study reported an interesting finding that butchery waste could be used for not only the production of biodiesel but also for hydrocarbons. This technology differs from others in that it uses low energy input, cheap and reusable catalyst, with low sulfur and nitrogenous waste gases than petro-diesel and is environment-friendly.

The inadequacy of fossil fuels is a matter of concern of the problem worldwide. As all the development concerns regarding the environment, economics, and energy security resulting from disproportionate dependency on petroleum and its restricted accessibility are compelling the world to search for alternatives in the form of biofuels like bioethanol and biodiesel (Rai et al. 2016). The use of biofuels is a

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boon to the pressure on depleting energy across the world, for Otto cycle engines, ethanol, pure or in a mixture with gasoline, is an alternate successfully applied in countries like Brazil and USA. Biodiesel is another significant alternative fuel, used in diesel engines owing to its technical, strategic, and environmental advantages (Benavides et al. 2007). Furthermore, biodiesel is a petroleum-derived diesel fuel and requires essentially no changes in the fuel distribution infrastructure. An advantageous property of biodiesel is that it provides a reduction of most exhaust emissions, higher flashpoint, biodegradability, inherent lubricity, and of domestic nature (Stachett et al. 2007). Biofuels are produced from animal fats, vegetable oils, and carbohydrates by transesterification and fermentation. However, its production faces the high production expenditures and other technical barriers. Considering the high-cost production, environmental and economic issues, and involvement of nanotechnology seems to be a viable solution. Nanoparticles have advantageous properties for the production of second-generation ethanol or transesterification of oils and fats to produce biodiesel. It is beneficial for recovery and reuse of catalysts. The present chapter discusses the role of nanotechnology in the fabrication of biofuel (Aguilar et al. 2011) (Fig. 1).

Nanotechnology, a new emerging and concerning field of science is currently applied in many areas. It has great application as the discipline of fabricating machines/devices on the scale of molecules. Nanoparticles (NPs) are commonly accepted as materials with at least two dimensions between 1 and 100 nm (Singha

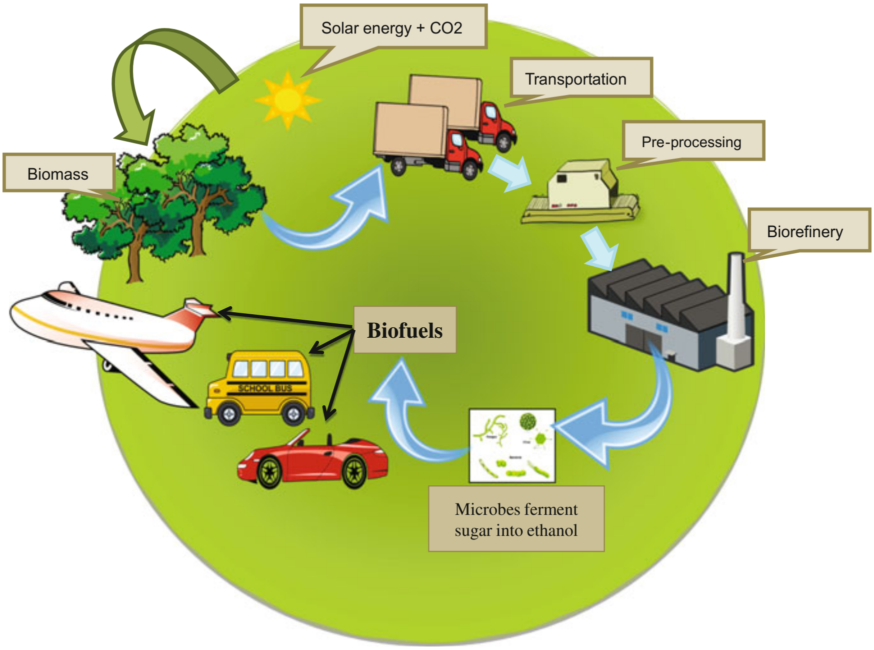

Fig. 1 Applications of biofuels in current scenario

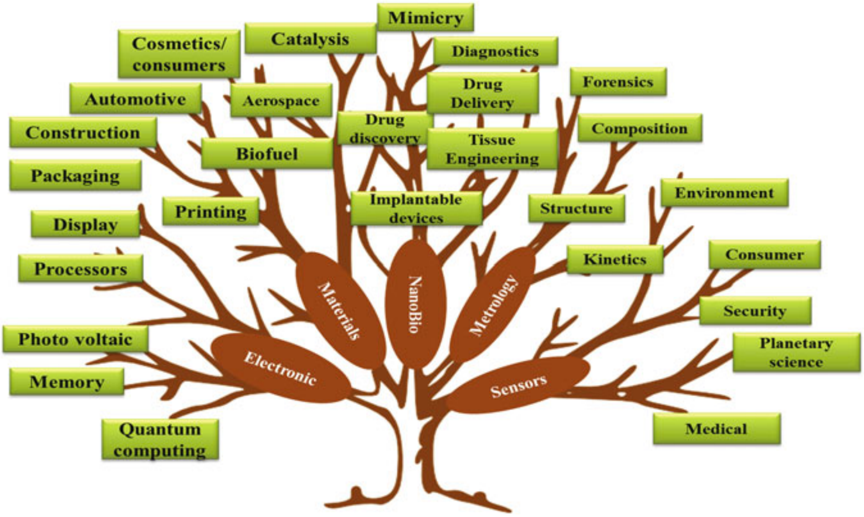

Fig. 2 Application of nanotechnology in the possible fields

et al. 2015). NPs fall in a transitional zone between individual molecules and the corresponding bulk materials, and therefore hold unique properties which are peculiar from their molecular and bulk counterparts (Rai et al. 2016). Unique properties of NPs include very large specific surface area, high surface energy, and quantum confinement (da Silva et al. 2005).

The characteristic feature of NPs may result in different environmental fate and behaviors than their bulk counterparts. Figure below shows some practical applications of nanotechnologies and confirms the vastness of their domain (Singha et al. 2015) (Fig. 2).

Nanotechnologies instigate nanofabricated polymers, its applications can be found in the sustenance of diagnostics and therapy, manufacturing processes, pharmaceuticals applications, medical and dental prosthesis, and thin films for surface treatment. The main chemicals involved in nanostructured polymers are polyacrylates, polyoxides, polysaccharides, polyvinylics, and polyethylenes. The main materials incorporated into polymer nanomatrices are silicon, chromium, and carbon (Sergio 2010).

1 Role of Algae in the Production of Biofuels

The algae-derived biofuels offer a great promise in reference to the probable high yields and smaller area requirements. Further, algae play a significant role in carbon alleviation, as growing algae should feed them carbon dioxide (CO2), in addition to water and sunlight. Algae can be fed other substrates as well cost-effectively, on carbon dioxide there would be a requirement of concentrated sources of the gas, like that are found in combustion off-gases from fossil-fueled power plants (Hannon et al. 2010).

Oil can form up to 50% of the algae mass, in comparison to the best oil-bearing plants (oil palm trees) with less than 20% of the biomass. Algae carbohydrates can also be prepared into ethanol and gasified to biogas, hydrogen, or methane (Borschiver et al. 2005). However, there are a number of challenges for algae culture to overcome for fabricating commercial biofuels. As algae also need water to propagate, development of algae culture production may create a problem of water versus fuel. Further, the low natural carbon dioxide concentration in the atmosphere also pose a challenge, hence the concern of additional sources of carbon supply for algal growth in commercial biofuels system emerges. These problems give way to the use of nanotechnology to turn algae into biofuels. The Quantum Sphere Company received a grant from the California Energy Commission to cultivate a nanocatalyzed algae biogasification (Fig. 3). Whereas in California, the Salton Sea receives huge amounts of agricultural overspill, which sometimes build up large algae blooms. These algae biomass have been converted experimentally into methane, hydrogen, and other gases (Benemann 2003).

The use of nanoparticles is escalated as no-harm poses to the harvesters of biofuel oils from algae, which results in extracting the oil without harming the algae. Maintaining the algae alive can intensely reduce fabrication costs and the generation cycle (http://biomassmagazine.com/articles/2354/dudek-catalyx-nanotech-to-build-landfillfacilities).

2 Role of Nanotechnology in the Landfill Facilities

The organic matter in landfills tends to undergo anaerobic fermentation yielding methane and carbon dioxide (http://journalstar.com/news/local/article_6d5b6a34-e86f-11df-ae58-001cc4c002e0.html), which if naturally expelled into the atmosphere that complements to the greenhouse emissions that would warm the climate. The methane has 25 times larger climatic effect than that of carbon dioxide for a time horizon of 100 years (http://en.wikipedia.org/wiki/Global_warming_potential). Therefore, there is a need to confiscate the carbon present in landfill methane. Nanocatalysts can break down methane into their elemental part, i.e., carbon and hydrogen. The carbon can be formed in high-purity nanographite for use in automobile, aerospace, batteries, etc. This method of handling methane can significantly recover the economics of landfills as well as of anaerobic digester plants that generate electricity from biogas.

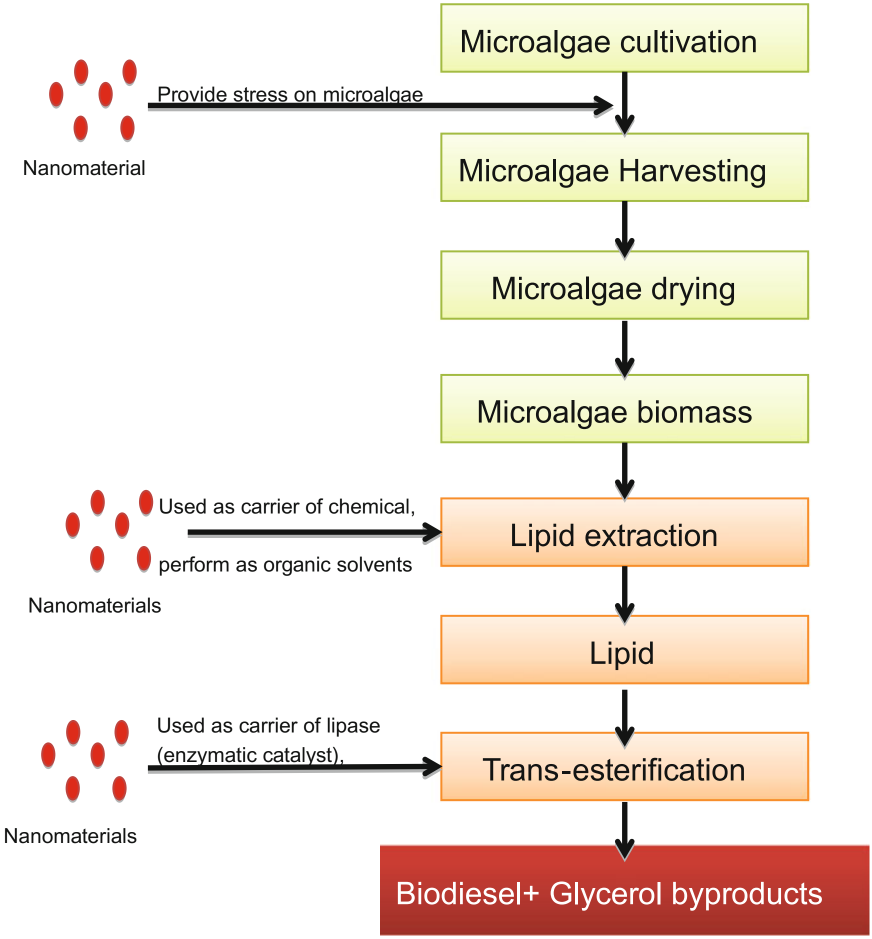

Fig. 3 Flowchart presenting the role of nanoparticles in the bioprocessing of biodiesel production

3 Role of Nanotechnology to Convert Biomass into Biofuels

The biofuels production from food crops is an essential condition to develop the scale of the market diffusion of biofuels globally Here, the potential lies in nanoparticles used as immobilizing beds for expensive enzymes that can be used repeatedly to break the long chain cellulose polymers into simpler fermentable sugars (Louisiana Tech University 2009). Enzymes used in the hydrolysis of agro wastes for production of fermentable sugar and transesterification for the production of biodiesel from various plant oils and algae. The incorporation of nanoparticles significantly escalates the surface area for immobilization and hence nanostructures have high loading power of enzymes (Fig. 4).

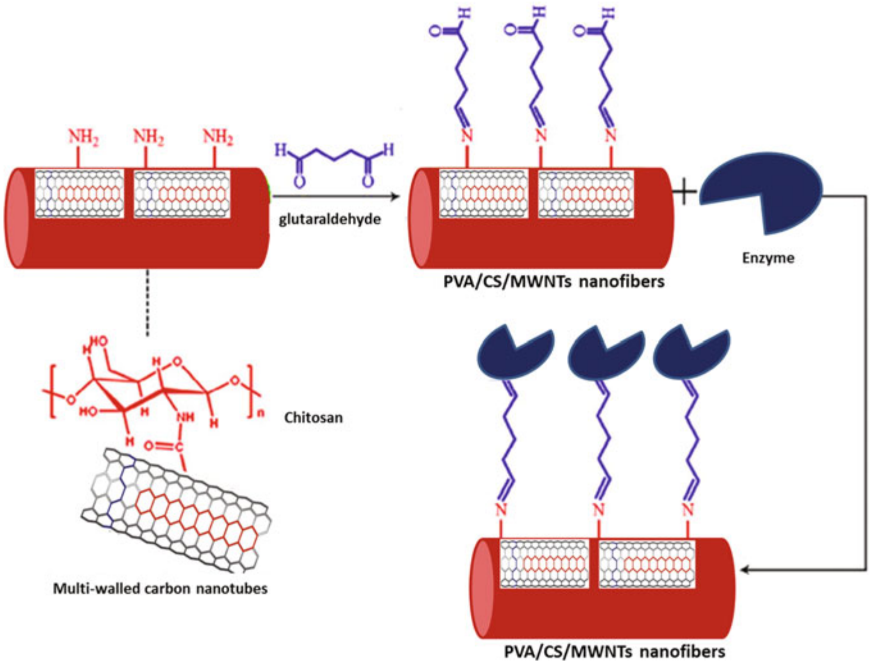

Fig. 4 Schematic illustration of enzyme (laccase) immobilization on PVA/CS/MWNTs nanofibrous membranes via activation

4 Immobilized Enzymes Used During Biofuel Production

1. **Laccase**: it is an extracellular enzyme used in the pretreatment of agro wastes, which reduces various cellulosic materials and yields sugars and various other phenolic byproducts. There are various laccase enzymes that are produced by various bacterial and fungal sources. Laccase is currently immobilized with various nonmaterials. It displays the rise in stability and half-life of the enzyme (Xu et al. 2015). Investigation shows that the enzyme loading and laccase activity on various carbon nanoparticles, fullerene (C60), multi-walled carbon nanotubes (MWNTs), oxidized-MWNTs (O-MWNTs), and graphene oxide (GO). The activity of laccase on various nanomatrices using 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTs) as a substrate decreased in the following order:

$$\mathrm{GO} > \mathrm{MWNTs} > \mathrm{O} - \mathrm{MWNTs} > \mathrm{Fullerene\ C} - 60$$

2. **Lipase**: these are extracellular or intracellular enzymes used in various processes such as in detergent industries, biofuel productions. Extracted lipase and some lipase-producing microorganisms (mostly fungi) are immobilized in biomass support particles and used as catalytic beds to obtain persistent use. The Louisiana Tech University is one of the organizations worldwide engaged in this industry, (Yücel et al. 2012). The emphasis is on nonedible cellulosic biomass, such as wood, grass, stalks, etc. This method to produce ethanol can reduce GHG emissions by some 86% in comparison to fossils fuels.

5 Nanotech Liquid Additives

All the preceding demonstration referred to solid nanoparticles playing a catalytic role for the procurement of biofuels from algae, biomass, and landfill methane that examine the proficient prospects for liquid nanoparticles or droplets (Cleaner diesel engines 2010). The rate of treatment for lubricity is influenced by the concentration of adsorption saturation. Provided the improved detergency and water co-solvency is acquired by the creation of nanoemulsions. Also, the efficient combustion and subsequent fuel proficiency increase depends on the behavior of nanodroplets formed by the surfactant action of the additive in the formulation of fuel and due to water existence in all commercial fuel systems, usually due to evening condensation.

The nanoemulsions, which the authors call microemulsions, (Putzbach and Ronkainen 2013) are shown by studies of Wulff et al. (2008) with fuel (biofuel included most likely), water and surfactant. These are thermodynamically stable, microscopically isotropic, and nanostructured (thus, nanoemulsions). The use of these nanoemulsions is proficient in breaking the usual exchange between reductions of NOx and soot emissions

The interpretation offered for the behavior of stable diesel (and most likely biodiesel)-water-surfactant nanoemulsions is as follows (Strey et al. 2007):

1. The surfactant components (nitrogen-containing compounds (amines) and oleic acid) dissolve promptly in biodiesel and bind water to it readily.
2. The nanosize of water droplets helping to stabilize the emulsion
3. The resultant “liquid sponge” can be stored indeterminately without risk of phase separation
4. The obtained formulation, when burnt results in the approximately complete combustion elimination of soot, and a decrease up to 80% in NOx emissions

6 Public Concerns over Nanotechnology: Security, Health and the Environment

With the emergence of new technologies, there may emerge the concern of all the positive and negative health and the environmental impact. The Woodrow Wilson Center carried out a Nanotechnology project (http://www.loe.org/shows/segments.htm?programID=05-P13-00050&segmentID=3) from 2005 which state that “manipulating materials at the atomic level can have astronomic repercussions, both positive and negative, the problem is no one really knows exactly what these effects may be.” This was the inspiration for the Project on Emerging Nanotechnology at the Woodrow Wilson Center. Another initiative came from the International Risk Governance Council—IRGC’s Nanotechnology project (http://www.irgc.org/-Nanotechnology-.html) to frame out the risks and benefits of nanotechnology. A division was made between the nanotechnologies of the Frame One (passive or classical technology assessment) and Frame Two (active or the social desirability of innovation). Risks are often not unambiguously mentioned but there is always a concern for unpredicted side effects (Fig. 5). There is a hidden concern about industry, science and politics building a coalition against public interest. And one negative occurrence could have a devastating impact on public attitudes” (http://www.yasni.ch/ext.php?url=http%3A%2F%2Fwww.irgc.org%2FIMG%2Fpdf%2FOrtwin_Renn_Nanotechnology_Frame_1_Policy_Implications_.pdf&name=Ortwin+Renn&cat=document&showads=1).

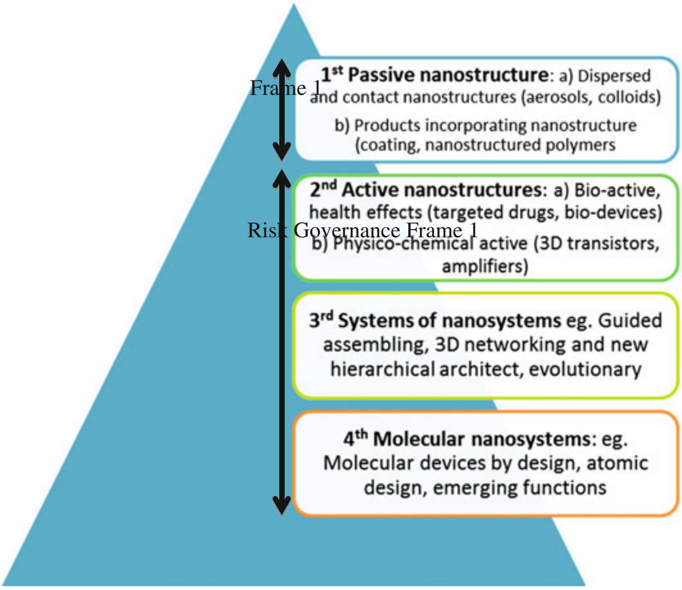

Fig. 5 Frames of reference of nanotechnology generations

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Nanocatalyst for Biofuel Production: A Review

Khaled Saoud

Abstract The demand for renewable and alternative types of energy has taken a new dimension; the primary reason is traceable to the climate change effects that fossil-based fuels have in the earth atmosphere. Bioenergy is one of the many arrays of renewable forms of energy that have taken centre stage in replacing the conventional fossil-based energy sources. Biofuel is the liquid or gaseous fuel derived from biological processes such as agriculture (biomass) or anaerobic digestion (solid or liquid wastes) or a combination of both, rather than geological processes that are known with the traditional fossil-based counterparts. Biomass energy is readily available and environmentally friendly, because it does not lead to a net increase in carbon dioxide levels and produces low amounts of sulphur. An effective implementation of biomass in the current energy scheme would involve the development of new technologies for the large-scale production of biofuel. The two primary methods for converting biomass to biofuels are thermochemical and biochemical processes. Thermochemical conversion is a major path for producing products such as bioethanol, biodiesel, bio-oil, bio-syngas and biohydrogen. It includes fast pyrolysis, liquefaction, combustion and gasification. Liquefaction of biomass to bio-oils involves two main routes which are hydrothermal and catalytic liquefaction. Catalytic liquefaction is very similar to hydrothermal liquefaction; however, a catalyst is used to reduce the residence time, operating temperature and pressure thereby increasing the quality of liquid products. Thermochemical biofuels are getting much more attention lately as these biofuels offer several technical and strategic advantages, such as highly developed industrial infrastructure and the biofuels can be produced from virtually all sorts of available biomass in a reasonable timeframe without significant modification in the overall process. At lower reaction temperatures, thermal processing of biomass with catalytic methods offers the possibility of selectively yielding a narrow range of products and reducing the energy requirements of the transformations. In terms of catalysts used, for biodiesel production, heterogeneous catalysts in comparison to homogeneous catalysts

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provide more effective separation steps for products and catalysts, eliminate quenching process, and offer conditions for the continuous production process. The objective of this review is to discuss the trends, recent advances in heterogeneous catalysts and expected contribution to knowledge, specifically in nanocatalysts for biofuel production, such as metal oxide catalysts (e.g. ZnO), metal supported by metal oxide catalysts (e.g. Au–ZnO), Alloy (e.g. Cu–Co), Metal oxide supported by metal oxide (e.g. KF–CaO–Fe_3O_4). Our focus will be on heterogeneous catalysts.

Keywords Renewable energy · Biodiesel production · Biomass Thermochemical processes · Catalysis · Nanocatalysts · Heterogeneous catalysts

1 Introduction

Availability of cost-effective and reliable energy sources is considered one of the important characteristic of modern society. Unfortunately, most of the societies in the world continues to rely heavily on fossil fuels such as oil, natural gas and coal. The production of fossil fuels have a significant societal and environmental impact varied from production to utilization which affects water, air and earth temperature that leads to global climate change. Alternative energy sources such as nuclear and renewable energy (wind, solar and biomass) can offer new cost-effective solutions to the energy production. These sources can increase the energy efficiency and help to reduce the environmental impacts.

The world energy demand has continued to take an upward trend. The primary reason for this increase is not unconnected with the world population and our methods of energy consumption. Despite the recent reduction in crude oil prices, fossil-based fuels remain energy sources that must eventually be replaced worldwide due to the diminishing fossil fuel reserves along with climate change effects caused due to constantly increasing levels of greenhouse gases in the earth atmosphere (Matthews et al. 2016). Bioenergy has been touted as one of the best alternative sources of energy to replace fossil-based fuels eventually. Biofuel is the term denoted to liquid or gaseous fuels derived from biomass, and a transition from fossil-based fuels to biofuels is assumed to reduce emissions of climatic gases (Berg 2013). The primary alternative sources of energy systems that can replace fossil fuels are water, wind, solar energy and biomass. Biomass energy is readily available and environmentally friendly because it does not lead to a net increase in carbon dioxide levels and produces low amounts of sulphur (Akia et al. 2014). A major hindrance to the growth of biomass energy is the competition on food/feed versus fuel. This can be overcome by using non-food biomass sources. Lignocellulosic biomass such as agri-residues, agri-processing byproducts and energy crops which do not compete with food and feed can be used for biofuel production (Munasinghe and Khanal 2010). However, for potential replacement of crude oil by biomass, it is important to note that the petrochemical industry currently consumes three-quarters of the crude oil to cover the demand for liquid hydrocarbon fuels of the

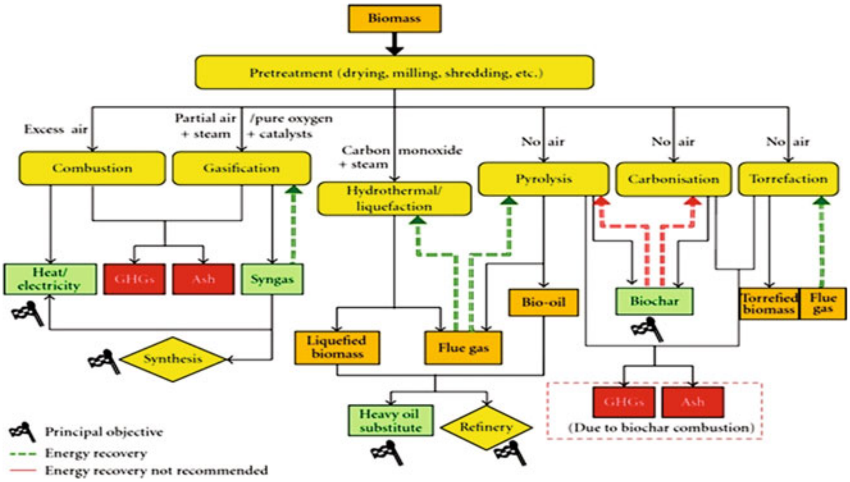


Fig. 1 Biomass thermochemical conversion pathways (Verma et al. 2012)

transportation sector, whereas only a small fraction of the petroleum is utilized in the synthesis of industrial chemicals and other derivatives. Consequently, an effective implementation of biomass in the current energy system will necessarily involve the development of new technologies for the large-scale production of biofuel (Serrano-Ruiz and Dumesic 2011). Presently, 4.7% of liquid transportation fuel production originates from renewable sources (Matthews et al. 2016). The two primary methods for converting biomass to biofuels are thermochemical and biochemical processes. Thermochemical conversion is a major path for producing products such as bioethanol, biodiesel, bio-oil, bio-syngas and biohydrogen. It includes fast pyrolysis, liquefaction, combustion and gasification as seen in Fig. 1. Fast pyrolysis is used for pyrolysis processes with a very short residence time of intense thermal treatment from 0.5–3 s at 400–600 °C. The shorter duration of heat exposure of the biomass in fast pyrolysis process results in increased heat and mass transfer, along with phase transition with chemical reaction kinetics. Long residence times (few minutes to hours) and lower temperature range (200–350 °C) favour charcoal formation (Verma et al. 2012). Liquefaction of biomass to bio-oils involves two main routes, which are hydrothermal and catalytic liquefaction. Hydrothermal liquefaction is based on the superior properties of water at higher temperatures and pressures. The reactivity of biomass is considerable in water, especially under hydrothermal conditions. Water is used as both reactant and solvent in the liquefaction, which prevents any polymerization and prevents the formation of solid products, such as coke and char. Catalytic liquefaction is very similar to hydrothermal liquefaction, however a catalyst is used to reduce the residence time, operating temperature and pressure thereby increasing the quality of liquid products. It was seen that the crude bio-oils produced from catalytic liquefaction flowed easily and were much less viscous than the bio-crude of noncatalyzed liquefaction (Akia et al. 2014). Gasification typically involves the partial oxidation of biomass into fuel gases at high temperatures (>800 °C). It is usually carried out with air or steam to generate a mixture of CO, H_2, CO_2, and some light hydrocarbons. Gasification processes take place with or without catalysts (Du 2013). Torrefaction is the thermal pretreatment of biomass in an oxygen-free atmosphere over a temperature range of 200–300 °C and has been recognized as an effective method to upgrade biomass into more energy dense and hydrophobic solid fuels. It can be classified into three different severities: light (200–235 °C), mild (235–275 °C) and severe (275–300 °C) torrefaction (Kumar et al. 2017). Combustion of biomass in the presence of air at high temperatures (>800 °C) converts the chemical energy into hot gases. A major drawback is a need for standardized pretreatment processes, such as Sun/drum/vacuum/freeze-drying, grinding, centrifugation and settling, so it is cost intensive. It is employed mostly for biomass with less than 50% of moisture (Kumar et al. 2017).

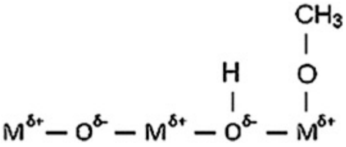
Biochemical conversion pathway produces liquid or gaseous fuels through fermentation or anaerobic respiration (Akia et al. 2014).The general biochemical conversion pathways consist of five process steps, namely a biomass pretreatment process, a biomass-to-gas conversion process (anaerobic digestion or gasification), a gas cleaning process, a gas-upgrading process, and a the Fischer–Tropsch synthesis (gas-to-liquid process) (Berg 2013). Thermochemical biofuels are getting much more attention lately as these biofuels offer several technical and strategic advantages such as highly developed industrial infrastructure and the biofuels can be produced from virtually all sorts of available biomass in a reasonable timeframe without significant modification in the overall process. In addition, the thermochemical transformation is virtually independent of environmental conditions for production purposes (Verma et al. 2012). At lower reaction temperatures, thermal processing of biomass with catalytic methods offers the possibility of selectively yielding a narrow range of products and reducing the energy requirements of the transformations (Li et al. 2016). Compared with homogeneous catalysts, heterogeneous catalysts can provide clean and recyclable catalyst systems (Guo et al. 2012). The aim of this review is to discuss recent advances in catalysis, specifically nanocatalysts for biofuel production. Metal oxide catalyst (e.g. ZnO), metal supported by metal oxide catalyst (e.g. Au–ZnO), alloy (e.g. AuCu), metal oxide supported by metal oxide (e.g. KF–CaO–Fe_3O_4). Our focus will be on heterogeneous catalysts.

2 Metal Oxide Nanocatalyst for Biofuel Production

A nanocatalyst is a substance or material with catalytic properties that has at least nanoscale dimension, either externally or in terms of internal structures. Nanocatalyst has a large surface-to-volume ratio, and this results in enhanced performance of the catalyst since there is more surface to react with the reactants. Based on the existence of a catalyst in the same phase as the substrate, they can be classified into two broad groups, heterogeneous catalyst and homogeneous catalyst. Biofuels can be grouped into bioethanol and biodiesel. Bioethanol is the most common biofuel, accounting for more than 90% of total usage. Using sugar and starch biomass as feedstock, it can be produced based on the enzymatic conversion of starchy biomass into sugars, and fermentation of 6-carbon sugars with final distillation of ethanol to fuel grade. While using lingocellulosic materials as feedstock, bioethanol production includes biomass pretreatment to release cellulose and hemicellulose, hydrolysis to release fermentable 5- and 6-carbon sugars, sugar fermentation, separation of solid residues and non-hydrolyzed cellulose and distillation to fuel grade. Biodiesel production is based on transesterification of vegetable oils and fats through the addition of methanol (or other alcohols) and a catalyst, giving glycerol as a co-product. Catalyst plays a major role in the production of biodiesel as it enhances the reaction rate of transesterification process and aids in producing high yields of biodiesel (Hashmi et al. 2016). In recent years, heterogeneous catalysis for biofuel production has been widely studied. Many metal oxides have been examined for the transesterification process of oils and have emerged as potential heterogeneous catalysts; these include alkali earth metal oxides, transition metal oxides, mixed metal oxides, and supported metal oxides (Refaat 2011). The structure of metal oxides is made up of positive metal ions (cations), which consists Lewis acid and negative oxygen ions (anions) which possess Bronsted base as seen in Fig. 2. ZnO is attractive because it is abundant. The use of nanostructures has been proved to improve the catalytic performance of ZnO.

In a thesis, Molina (2013) synthesized ZnO nanorods using a solution approach. The nanorods were used as catalysts to produce biodiesel from olive oil. The nanorods achieved conversions of 94.8% at 150 °C for reaction times of 8 h. They also demonstrated better catalytic performance, which was attributed to their increased degree of crystallinity than conventional ZnO (Molina 2013). Levy et al. (2006) synthesized ZnO nanomaterials in supercritical water (SCW)using a flow-type apparatus and a batch reactor. $ZnAl_2O_4$ was also successfully synthesized with a high specific surface area. Zinc-based oxides were used as catalysts for the conversion of glucose into H_2. For the application of the catalytic reaction by the metal oxide catalysts, biomass conversion in subcritical water was studied to produce H_2. Glucose and H_2O_2 were used as model biomass and oxidant, respectively. Sınağ et al. (2011) studied the effect of ZnO and SnO_2 catalysts on the conversion of cellulose to biofuel as shown in Fig. 3. He presented the contribution of nano ZnO on cellulose conversion at 300 °C and 600 °C and nano SnO_2 was an effective catalyst for cellulose conversion at 400 °C and 500 °C. The lower H_2 production

Fig. 2 Surface structure of metal oxides (Zabeti et al. 2009)



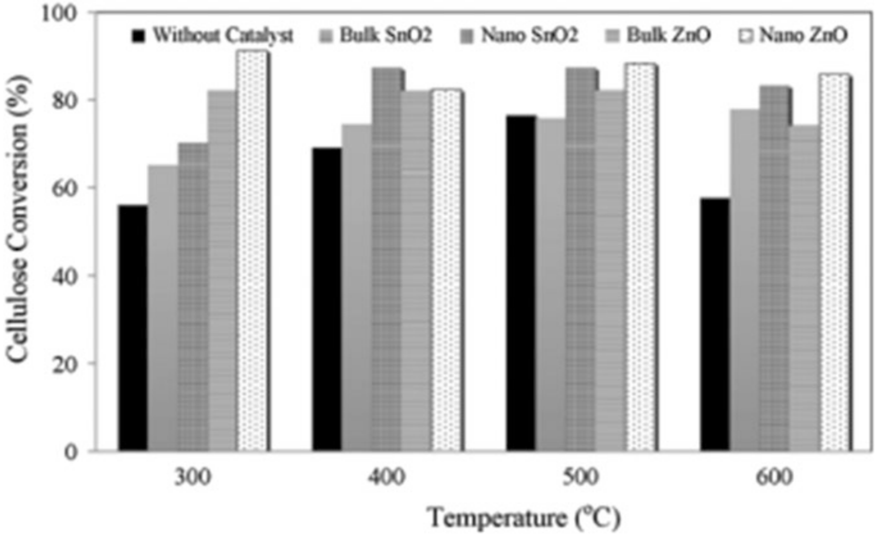


Fig. 3 Effect of nano and bulk ZnO and SnO_2 particles on the conversion degree of cellulose

using the ZnO catalyst synthesized in a flow-type apparatus compared with those in the batch reactor could be explained by the presence of sulphate on the surface of the grain, which is an active poison for the catalyst (Levy et al. 2006).

Wen et al. (2010) prepared a KF–CaO solid base nanocatalyst from KF and CaO with impregnation method and used this to convert Chinese tallow seed oil to biodiesel. The catalyst had a porous structure with the particle size of 30–100 nm. Under the optimal conditions, the biodiesel yield was 96.8% in the presence of as-prepared KF–CaO catalyst (Wen et al. 2010). A promising route for the production of biodiesel via transesterification of soybean oil (SBO) and poultry fat with methanol in quantitative conversions (Fig. 4) at room temperature has been developed (Venkat Reddy et al. 2006) using nanocrystalline calcium oxides as catalysts with high yields. Under the same conditions, laboratory-grade CaO gave only 2% conversion in the case of SBO, and there was no observable reaction with poultry fat (Venkat Reddy et al. 2006).

The catalytic activity for the production of biodiesel with three morphologically different nanocrystalline MgO materials prepared using simple, green and reproducible methods was investigated by Verziu et al. (Verziu et al. 2008) The nanocrystalline samples studied were MgO nanosheets (MgO (I)), conventionally prepared MgO (MgO (II)) and aerogel prepared MgO (MgO (III)). The methods to produce the catalysts include the following:

- 4-methoxy-benzyl alcohol-templated sol-gel process followed by supercritical drying and calcination in air at 773 K (MgO (I)),
- from a commercial MgO that was boiled in water, followed by drying at 393 K, and dehydration under vacuum at 773 K (MgO (II)), and

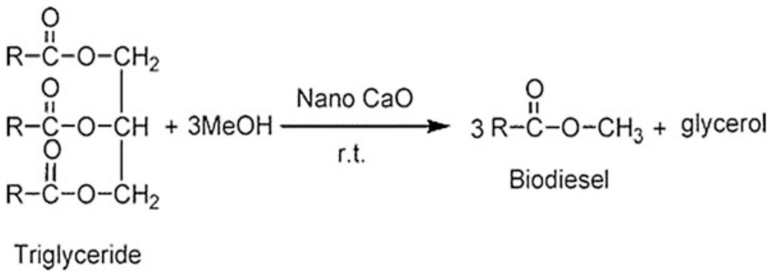


Fig. 4 Synthesis scheme for biodiesel production from soybean oil (Venkat Reddy et al. 2006)

- via hydrolysis of $Mg(OCH_3)_2$ in a methanol–toluene mixture, followed by supercritical solvent removal with the formation of a $Mg(OH)_2$ aerogel that was dehydrated under vacuum at 773 K (MgO (III)).

These catalysts were tested in the transesterification of sunflower and rapeseed vegetable oils at low temperatures, under different experimental conditions; autoclave, microwave and ultrasound. Working with these materials under microwave conditions provided higher conversions and selectivity to methyl esters compared to autoclave or ultrasound conditions. Under ultrasound, a leaching of the magnesium was evidenced as a direct consequence of a saponification reaction. These systems also allowed working with much lower ratios of methanol to vegetable oil than reported in the literature for other heterogeneous systems. Also, these preparations are very green, involving nontoxic reagents and synthesis routes. These metal oxides are active, recyclable heterogeneous catalysts and can be used for transesterification of vegetable oils at low temperatures, as it has been demonstrated for sunflower and rapeseed oils. Thus, these investigations show that nanostructured MgO can be used effectively as a heterogeneous catalyst system for biodiesel transesterification (Verziu et al. 2008). Li et al. (2008) studied the preparation of nano-NiO particles and their applications as catalysts in biomass pyrolysis (an important step in biofuel production). First, nano-NiO particles were prepared via precursors, which were obtained by homogeneous precipitation involving an aqueous solution of nickel nitrate hexahydrate and urea. The formula of the precursor was identified as $NiCO_3{\cdot}2Ni(OH)_2{\cdot}nH_2O$, and it could be completely translated into NiO nanoparticles below 360 °C under an air atmosphere. Furthermore, the catalytic activity of nano-NiO particles in pyrolyzing three biomass components (cellulose, xylan and lignin) was preliminarily investigated, and the results were compared with those of micro-NiO particles under the same conditions. Nano-NiO particles demonstrated a more efficient catalytic effect in biomass pyrolysis over micro-NiO particles. The results indicated that the NiO catalyst could affect the pyrolysis process significantly, with the primary reaction of decomposition to occur at a relatively lower temperature and a marked decrease in the final yield of char as well as the activation energy of biomass pyrolysis (Li et al. 2008).

3 Metal Oxide Supported by Metal Nanocatalyst for Biofuel Production

Calcium oxide (CaO) has been widely used as a solid base nanocatalyst due to its low cost and high activity. Kouzu et al. (2009) found that this high activity was caused by calcium ions leaching into polar phases. These dissolved Ca ions, therefore, act as homogeneous catalysis in the transesterification reaction, leading to an additional cost for post-treatment and a short catalyst lifetime. To improve the catalyst lifetime and stability, metals such as zinc and lanthanum have been used to modify CaO for transesterification reactions. The catalytic activity and catalyst lifetime were dramatically improved by doping with these elements (Yu et al. 1868). Studies by Gurunathan and Ravi (2015) suggested that transesterification reaction could be optimized by using copper-doped zinc oxide (CZO) nanocatalyst for biodiesel production from neem oil as seen in Fig. 5. They synthesized the CZO nanocatalyst by chemical co-precipitation which could be recycled and observed a highly porous and non-uniform surface, which led to the aggregation of CZO nanoparticles in the form of multilayered nanostructures. Biodiesel yield of 97.18% was obtained in 60 min reaction time at 55 C using 10% (w/w) CZO nanocatalyst and 1:10 (v:v) oil: methanol ratio (Gurunathan and Ravi 2015). The heterogeneous solid copper-doped zinc oxide nanocatalyst synthesized by chemical co-precipitation was found to be effective for the production of biodiesel from neem oil. In work done by Baskar et al. (2017) Manganese-doped zinc oxide was used as a heterogeneous catalyst for the production of biodiesel from mahua oil. The synthesized manganese doped zinc oxide nanocatalyst. The SEM and XRD results confirmed the hexagonal structure of the catalyst with the particle size of 24.18 nm. The 8% (w/v) catalyst concentration, 1:7% (v/v) of oil to methanol ratio, 50 min of reaction time and 50 °C of reaction temperature were found to be the optimum

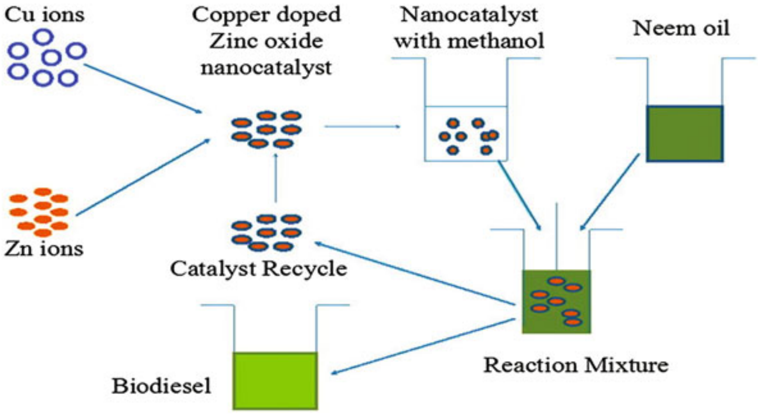


Fig. 5 Biodiesel production from neem oil using copper-doped zinc oxide heterogeneous nanocatalyst (Gurunathan and Ravi 2015)

process condition for the maximum biodiesel yield of 97%. The presence of methyl esters in biodiesel was confirmed by FTIR and GC-MS analysis (Baskar et al. 2017). In the study done by Feyzi et al. (2013), Cs–Al–Fe_3O_4 nanocatalysts were prepared and used for the biodiesel FAME (fatty acids methyl ester) production. This research investigated the effects of different Cs–Al and Cs–Fe molar ratio and calcination conditions on the catalytic performance of Cs–Al–Fe_3O_4 catalysts. Results obtained showed high catalytic activity for biodiesel production and the biodiesel yield reached 94.8% under the optimal conditions (Feyzi et al. 2013). Lithium-impregnated calcium oxide has been prepared by wet impregnation method in nanoparticle form and was examined by Kaur and Ali (2011). Calcium oxide impregnated with 1.75 wt% of lithium was used as a solid catalyst for the transesterification of *karanja* and *jatropha* oil, containing 3.4 and 8.3 wt% of free fatty acids, respectively. The complete transesterification of *karanja* and *jatropha* oils was achieved in 1 and 2 h, respectively, at 65 °C, utilizing 12:1 molar ratio of methanol to oil and five wt% (catalyst/oil, w/w) of catalyst (Kaur and Ali 2011). Iron–tin (ISnO) oxide nanoparticles were used as catalysts for the transesterification of soybean oil as well as esterification of soybean oil fatty acids in the study done by Alves et al. (2014). High yields, ca. 84%, were achieved, after 1 h reaction time at 200 °C. The oxide was magnetically recovered and reused four times without loss of its activity. ISnO also demonstrated catalytic activity for *macauba* oil, a highly acidic substrate. Mixed iron–cadmium (ICdO) and iron–tin (ISnO) oxides were prepared and tested as catalysts in biodiesel production through hydrolysis, esterification and transesterification reactions using soybean oil. The surface area of the ICdO catalyst was twice that of ISnO. Despite this difference in a surface area, no significant catalytic activity difference was observed in the esterification reaction (Alves et al. 2014).

In the study done by Montero et al. (2010), caesium incorporation via co-precipitation on nanocrystalline MgO under supercritical conditions generates $Cs_2Mg(CO_3)_2$nanocrystallites. Wet impregnation proved less effective for modifying MgO nanocrystals. A strong synergy between Cs and Mg components in the co-precipitated material dramatically enhanced the rate of tributyrin transesterification with methanol about undoped MgO and homogeneous Cs_2CO_3 catalysts. Caesium was an effective promoter of MgO solid base catalysts for the transesterification of tributyrin with methanol. Doping via co-precipitation under solvothermal regimes promoted the formation of $Cs_2Mg(CO_3)_2$ nanocrystallites with significantly enhanced base site densities and polarizabilities compared with undoped MgO nanocrystals (Montero et al. 2010).

4 Alloy

Cu–Co bimetallic nanoparticles coated with carbon layers have been developed through direct heating treatment of bimetallic oxide precursors incipiently deposited with polyethene glycol (Chen et al. 2017). The simultaneous formation of carbon layers over the nanoparticles protects them from oxidation and deactivation. The nanocatalyst performed excellently in the chemoselective hydrogenolysis of 5-hydroxymethylfurfural (HMF) to 2, 5- dimethylfuran (DMF). DMF is a biofuel that can be produced through selective hydro-de-oxygenation of a platform molecule from cellulose (5-hydromethylfurfural, HMF).The yield of DMF reached approximately 99.4% and exceeded the results of supported noble metal catalysts. The catalyst showed good recyclability and recoverability in a six-run recycling test. This work provides a novel and insightful strategy to develop low-cost and high-performance hydrotreating catalysts based on base metals for industrial organic process and valorization of renewable biomass (Chen et al. 2017). Hybrid nanocatalysts containing enzymes and metallic nanoparticles have also been used for biodiesel production. In work done by Xie and Ma et al. (2010), lipase was covalently immobilized onto magnetic Fe_3O_4 nanoparticles by using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC) as an activating agent, and the bound lipase was used to catalyze the transesterification of vegetable oils with methanol to produce fatty acid methyl esters. It was determined that the immobilized lipase exhibited better resistance to temperature and pH inactivation in comparison to free lipase. The conversion of soybean oil to methyl esters reached over 90% in the three-step transesterification when 40% immobilized lipase was used. Moreover, the lipase catalyst could be used for three times without a significant decrease in the activity (Xie and Ma 2010). Bimetallic gold–silver core–shell nanoparticles (Au–Ag) were synthesized at room temperature, where gold nanoparticles served as seeds for continuous deposition of silver atoms on its surface. The catalytic activity of these nanoparticles towards biodiesel production from sunflower oil through transesterification was studied by Banerjee et al. (2014), and a yield of 86.9% biodiesel was attained. The fuel properties of the synthesized biofuel were at par with standard biofuel. Further, the catalyst showed sustained activity for three cycles of transesterification (Banerjee et al. 2014). Deng et al. (2011) synthesized hydrotalcite-derived particles with Mg/Al molar ratio of 3/1 by a co-precipitation method using urea as precipitating agent, subsequently with (MHT) microwave-hydrothermal treatment, and followed by calcination at 773 K for 6 h. These particles were micro-sized mixed Mg–Al oxides as characterized by SEM and AFM. But actually, they were nanosized according to the calculations from XRD data. Because of their strong basicity, the nanoparticles were further used as a catalyst for biodiesel production from *jatropha* oil after pretreatment. At the optimized condition, biodiesel yield of 95.2% was achieved. The catalyst can be reused for eight times. The catalyst was only 7.3 nm by calculation, but according to AMF analysis, they congregated to form a layered structure with size as large as 0.941 mm width and 381 nm thickness. The main reasons for catalyst deactivation were the surface absorption of by-product glycerol as well as the collapse of the layered structure. After removing the glycerol on the surface, the catalyst was reused for eight times (Deng et al. 2011).

5 Metal Oxide Supported by Metal Oxide Nanocatalyst for Biofuel Production

Biodiesel is mainly composed of ethyl esters and fatty acid methyl esters (FAEE and FAME) and is taken to be one of the clean and environmentally friendly sources of energy. Biodiesel is produced from fats and oils via esterification and transesterification in the presence of homogeneous or heterogeneous acid–base catalysts (Basumatary 2013). Heterogeneous catalysts are preferred because they are much easier to separate, have lower production cost and display environmentally friendly features when compared with homogeneous catalysts (Borges and Díaz 2012). Traditional heterogeneous catalysts (for example, zeolites, single-metal oxides, hydrotalcite and supported alkali metal/metal ion) have been widely demonstrated to have high efficiency for biodiesel production. However, there are some drawbacks with these catalysts; they show weak strength, expensive and complex to prepare, have relatively small surface area, low catalytic performance, have little resistance to atmospheric CO_2 and water pollution, require high temperature and pressure and alcohol–oil ratios (Chang et al. 2014). These are the reasons why biodiesel is not produced in large scale when these traditional catalysts are employed. To remove the drawbacks mentioned above, the deployment of solid mixed metal oxide catalysts as heterogeneous catalysts have stimulated substantial interest recently for the production of biodiesel. Solid mixed metal oxide catalysts typically refer to those comprising of two or more metal oxides in their makeup. For example, base mixed metal oxide catalysts and acid-based bifunctional mixed metal oxide catalysts.

- **Base mixed metal oxide catalysts for biodiesel production**

Base mixed metal oxide catalysts are typically doped with MgO or CaO to boost their catalytic performance. These types of catalysts are very active for the transesterification reaction in the production of biodiesel. In these catalytic processes, the used raw materials (fats or oils), with a certain amount of free fatty acid content are considered to be necessary; otherwise, it will cause base catalyst poisoning and affect the quality of the biodiesel. Some research works carried out on mixed metal oxide catalysts are detailed in Tables 1 and 2.

CaO- and MgO-based mixed metal oxide catalysts have stimulated interest in research community due largely to their exceptional catalytic performance. However, these catalysts usually show poor recyclability and poor resistance to water and acid (Chang et al. 2014). Thus, these forms of catalysts are mostly used in the transesterification of oil-bearing low acid and water contents. On the other hand, acid mixed metal oxide catalysts prepared from corresponding transition metal salts could simultaneously catalyze the esterification and transesterification reactions though harsh reaction conditions are required such as high temperatures, high alcohol/oil ratios, and longer reaction times (Chang et al. 2014).

Table 1 CaO-based mixed metal oxide catalysts

S/N	Catalyst	Oil	Catalyst amount (wt %)	Alcohol/oil ratio	Reaction temp (°C)	Reaction time	FAME (%)	Ref
1	CaO–NiO	*Waste cottonseed oil*	5	15:1	65	4 h	>99	Kaur and Ali (2014)
2	CaO–CeO_2	*Refined palm oil (acid value< 0.4* $mg_{KOH}g^{-1}$*)*	5	20:1	85	3 h	95	Thitsartarn and Kawi (2011)
3	CaO–ZrO_2 (molar ration: Ca–Zr = 0.5)	*Waste cooking oil*	10	30:1	65	2 h	92.10	Dehkordi and Ghasemi (2012)
4	CaO–Al_2O_3	*Palm oil*	6	12:1	65	5 h	98.64	Zabeti et al. (2010)
5	CaO–La_2O_3	*Jatropha curcas oil 13.60* $mg_{KOH}g^{-1}$	4	24:1	65	6 h	86.51	Teo et al. (2014)
6	CaO–MgO(Mg/Ca = 0.5)	*Jatropha curcas oil*	3	25:1	120	3 h	90	Taufiq-Yap et al. (2011)
7	CaO–ZnO	*Sunflower oil*	3	12:1	60	45 min	>90	Rubio-Caballero et al. (2009)
8	CaO–La_2O_3	*Well-refined soybean oil*	5	20:1	58	1 h	94.30%	Yan et al. (2009)
9	CaO–ZnO	*Sunflower oil*	2	10:1	60	4 h	97.50	Kesić et al. (2012)
10	CaO(16 wt%)–ZnO	*Sunflower oil*	1.3	12:1	60	2 h	>90	Alba-Rubio et al. (2010)
11	KF–CaO–Fe_3O_4	*Stillingia oil*	4	12:1	65	3 h	>95	HusY (2011)

Table 2 MgO-based mixed metal oxide catalysts

S/N	Catalyst	Oil	Catalyst amount (wt%)	Alcohol/oil ratio	Reaction temp (°C)	Reaction time	FAME (%)	Ref
1	MgO–ZnO	*Jatropha curcas oil*	3	25:1	120	3 h	83	Lee et al. (2013)
2	TiO_2–MgO	*Waste cooking oil*	5	30:1	150	6 h	>85	Wen et al. (2010)
3	LaMgO	*Cottonseed oil*	5	54:1	65	20 min	96.00	Mutreja et al. (2014)
4	MgAlCe	*Soybean oil*	5	9:1	67	3 h	>90	Dias et al. (2012)
5	20-Sr–MgO	*Refined palm oil*	3	6:1	60	75 min	96	Faungnawakij et al. (2012)

- **Acid Mixed Metal Oxide catalysts for Biodiesel Production**

In order to address the high free fatty acid content in raw oils used for biodiesel production, different acid mixed metal oxide catalysts have been developed. Table 3 shows some of the works carried on the production of biodiesel using acid mixed metal oxide catalysts.

6 Synthesis and Characterization of Nanoparticles for Biofuel Production

- **Green synthesis of nanoparticles**

Metal nanoparticles have been studied extensively due to their exceptional electrical, optical and catalytic properties (Coe et al. 2002; Bruchez et al. 2013). For the optimization and utilization of nanosized particles' physical or chemical properties, great research efforts have been focused on how to control their shapes and sizes which are needed in the modification of their optical and physicochemical properties (Bar et al. 2009). For the synthesis of metal nanoparticles, different techniques have been explored which are mainly divided into physical and chemical means. The methods include electrochemical reduction (Liu and Lin 2004), heat evaporation (Smetana et al. 2005), chemical reduction (Yu 2007), photochemical reduction (Mallick et al. 2005), etc. Mostly, to prevent nanoparticles from aggregation, surface passivator reagents are employed (Bar et al. 2009). However, a large number of surface passivators (mostly organic) such as mercapto acetate, thiourea, thiophenol, etc., are toxic to the environment when a large number of nanoparticles are produced (Bar et al. 2009). In order to address this drawback, green biosynthesis of nanoparticles is gaining traction in nanoparticles research community due to the need to produce environmentally friendly alternatives. For example, research efforts have been put into the production of biosynthetic inorganic materials (e.g. metal nanoparticles) synthesized from microorganisms (Shahverdi et al. 2007; Basavaraja et al. 2008).

Rao and Pennathur (2017) discussed the green and environmentally friendly method of synthesis of cadmium sulphide (CdS) nanoparticles from the aqueous cell-free extract of *Chlamydomonasreinhardtii*. From morphological analysis by electron microscopy, the authors (Rao and Pennathur 2017) observed the presence of spherical particles measuring roughly 5 nm under HRTEM. From structural analysis using X-ray diffraction and FTIR, the authors (Rao and Pennathur 2017) confirmed the cubic CdS nanoparticles that were capped with algal proteins. Optical analyses of the nanostructures showed an increase in the band gap to 2.93 eV. Photoluminescence spectrum of CdS nanoparticles revealed emission peaks at 430 nm and 470 nm. The nanoparticles were found to be stable in solution with a zeta potential of −30.7 mV. The authors (Rao and Pennathur 2017) thus concluded that the one-step strategy employed with algal cell-free extract to produce CdS

Table 3 Production of biodiesel with acid mixed metal oxide catalysts

S/N	Catalyst	Oil	Catalyst amount (wt%)	Alcohol/ oil ratio	Reaction temp (°C)	Reaction time (h)	FAME (%)	Ref
1	SO_4^{2-}–ZrO_2–TiO_2	Oleic acid	5	16:100	65	6	Esterification: 42.2 transesterification: 88	Shao et al. (2013)
2	Fe_2O_3–SiO_2	Crude Jatropha oil	15	218:1	220	3	Transesterification >99	Suzuta et al. (2012)
3	SnO_2–SiO_2	Soybean oil	5	24:1	180	5	Transesterification: 81.7 esterification: 94.6	Xie et al. (2011)
4	WO_3–SnO_2	Soybean oil	5	30:1	110	5	Transesterification: 79.2	Xie and Wang (2013)
5	SO_4^{2-}–TiO_2–SiO_2	Waste soybean oil	10	20:1	120	3	Transesterification: 88	Shao et al. (2013)

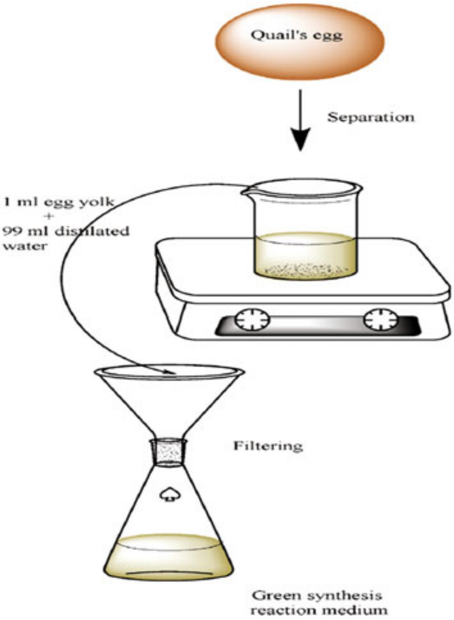


Fig. 6 The processing for the green reaction medium (Nadaroglu et al. 2017)

nanoparticles is an environmentally friendly and feasible economical approach for the large-scale synthesis of CdS nanoparticles for deployment in photocatalysis.

Nadaroglu et al. (2017) used quail egg yolk (shown in Fig. 6) for the synthesis of platinum nanoparticles of 7–50 nm. The authors (Nadaroglu et al. 2017) employed the high protein and vitamin contents of the yolk for green synthesis in the reaction medium without addition of any chemical reducing agent. Reaction conditions and parameters (pH, temperature, time and concentration) were controlled in order to attain the optimal reaction conditions to obtain platinum nanoparticles. The results obtained showed that the maximum platinum nanoparticles were synthesized at 20 °C, pH 6.0 for 4 h. Also, the optimal concentration of metal ions was established as 0.5 mM. For the characterization of the platinum nanoparticles, the authors (Nadaroglu et al. 2017) employed UV–Vis spectroscopy, XRD and SEM (shown in Fig. 7). The analysis showed that the synthesis of platinum nanoparticles was performed based on direction, morphology and quantity characterization. Synthesized platinum nanoparticles have a wide range of applications catalysis, electrocatalysis, nanotechnology, pharmaceutical and chemical processes.

Bar et al. (2009) effectively synthesized silver nanoparticles from $AgNO_3$ using an environmentally friendly green resource latex of *Jatropha curcas* as capping as well as reducing agent. For the characterization of the synthesized nanoparticles, the authors (Bar et al. 2009) used X-ray diffraction, HRTEM and UV–Vis absorption spectroscopy. X-ray diffraction analysis showed that the nanoparticles were of the face-centred cubic structure. A comparison of the radius of nanoparticles obtained from HRTEM image with the optimized cavity radius of the cyclic peptides present

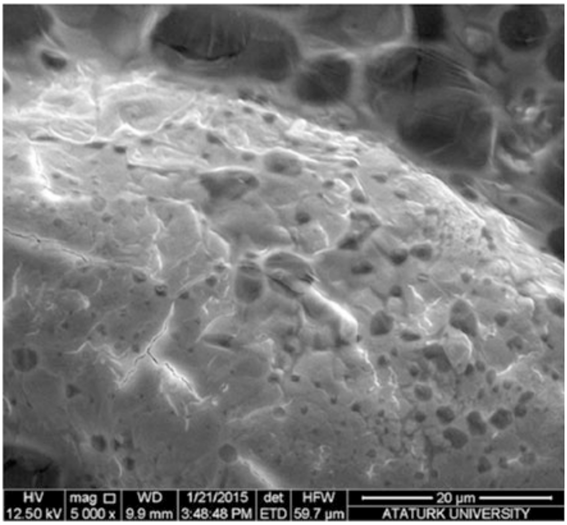


Fig. 7 SEM micrographs of synthesized platinum nanoparticles (Nadaroglu et al. 2017)

within the latex revealed that the particles having radius 10–20 nm are mostly stabilized by the cyclic peptides. Also, HRTEM and UV–Vis spectroscopy showed that there are two major distributions of particles size; the smaller particles are majorly stabilized by the cyclic octapeptide (curacy cline A) and cyclic nonapeptide (curacy Cline B). However, the larger and irregular shaped particles are majorly stabilized by the curcain, the enzyme found in the latex. The authors (Bar et al. 2009) thus recommended further experiment for size-selective synthesis of silver and gold nanoparticles using cyclic peptide found in the latex.

In the field of nanotechnology, synthesis of metal nanoparticles via eco-friendly route is gaining momentum (Sharmila et al. 2017). Sharmila et al. (2017) presented an environmentally friendly biogenic synthesis of palladium nanoparticles (PdNPs) using leaf extract of *Filiciumdecipiens*. For characterization, the synthesized PdNPs were studied by TEM, UV–Vis spectroscopy, FTIR and XRD. The PdNPs formation was established by UV–Vis spectrophotometer and spherical-shaped PdNPs with a size range of 2–22 nm was detected in TEM analysis. Energy dispersive X-ray spectroscopy (EDS) analysis established the presence of palladium in the synthesized nanoparticles. XRD pattern confirmed the crystalline nature of PdNPs. The phytochemicals and proteins were identified by their functional groups in FTIR spectrum and revealed the amide and amine groups present in *Filiciumdecipiens* which could have been involved in the bio-reduction reaction for PdNPs synthesis (Sharmila et al. 2017).

Wang et al. (2016) prepared $S_2O_8^{2-}$–ZrO_2 (solid superacid catalyst), by one-pot method (a new synthesis route), treated with $(NH_4)_2S_2O_8$ (ammonium persulfate) through vapour phase hydrolysis to increase biodiesel production with expired soybean oil as a reactant. For the synthesized catalyst characterization, the authors (Wang et al. 2016) used TEM, XRD and NH3-temperature programmed desorption

(NH3-TPD) to determine the optimal pretreatment conditions and to understand the role of the active sites for transesterification. At 500 °C, $S_2O_8^{2-}$–ZrO_2 calcined was seen to compose of tetragonal phase ZrO_2 microcrystallites TEM examination and showed an amorphous phase by XRD characterization. The microcrystallites which anchored more $S_2O_8^{2-}$ had abundant super acid and displayed high catalytic activity in the transesterification under mild reaction conditions. The reaction parameters over the catalyst were optimized and both the conversion of soybean oil and selectivity of biofuel reached 100% under the conditions of 4 h of reaction time, 110 °C of reaction temperature and 20:1 of methanol-to-oil molar ratio. The author (Wang et al. 2016) observed the catalyst to show high stability in the reactions and during cyclic utilization, no sulphur leaching was found in the biodiesel products.

- **Non-green synthesis of nanoparticles**

Banerjee et al. (2014) synthesized bimetallic gold-silver core–shell nanoparticles (Au@Ag NPs) at room temperature, in which pre-synthesized gold nanoparticles (AuNPs) served as seeds for continuous deposition of silver atoms on its surface. For the characterization, the core–shell structure of the nanoparticles was analyzed by TEM (shown in Fig. 8), UV–Vis spectroscopy and energy dispersive X-ray (EDX). The authors (Banerjee et al. 2014) further studied the catalytic activity of the nanoparticles towards biodiesel production from sunflower oil through transesterification. The confirmation for biofuel synthesis was performed with FTIR spectroscopy. The fuel properties were determined by standard ASTM (American Society for Testing and Materials) protocols. The authors (Banerjee et al. 2014) observed that at a certain temperature, reaction time and catalyst concentration, 86.9% (highest yield) of biodiesel was achieved. On further analysis, it was discovered that the properties of the synthesized biofuel are the same with conventional biofuel. Furthermore, the catalyst sustained its activity for three cycles of transesterification processes.

Chen et al. (2017) synthesized Cu–Co bimetallic nanoparticles coated with carbon layers through direct heating of bimetallic oxide precursors. Polyethene glycol over the precursors acts as the reductant for metal species and carbon sources of carbon layers. The as-synthesized nanocatalyst performed well in chemoselective hydrogenolysis of 5-hydroxymethylfurfural to 2, 5-dimethylfuran yielding up to 99.4% of dimethylfuran, which surpassed the results obtained when supported noble metals catalysts were used. The Co-based catalysts exhibit higher performance than Cu-based catalysts. For the characterization, the synthesized bimetallic nanocatalysts were characterized in details by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The results obtained showed that the bimetallic nanoparticles were encased in carbon shells, capable of protecting them deactivation and oxidation. The authors (Chen et al. 2017) carried out the six-run test, and the synthesized catalyst showed excellent recoverability and recyclability. The authors (Chen et al. 2017) thus concluded that the method employed provides an insightful and novel approach to

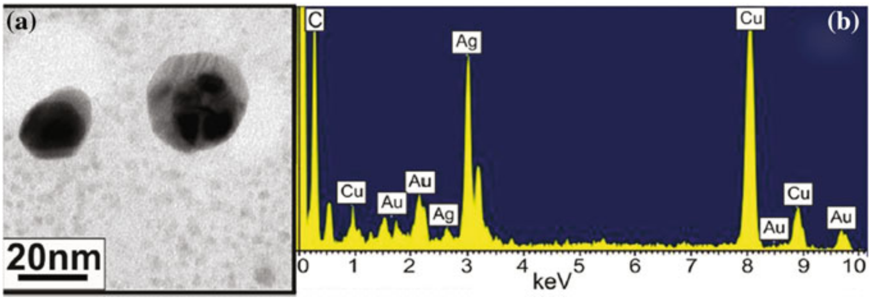


Fig. 8 Typical TEM image (**a**) and EDX spectrum (**b**) confirming the presence of both gold and silver in the Au–Ag core–shell bimetallic NPs Banerjee et al. (2014)

developing high-performance and low-cost hydrotreating catalysts based on base metals for deployment in renewable biomass.

Lapin et al. (2016) synthesized cerium oxide nanoparticles in water, ethanol and ethanol-water solution for the first time by the use of laser (fundamental harmonic of nanosecond Nd: YAG) ablation of bulk metallic cerium target. The authors (Lapin et al. 2016) obtained nanocrystalline powders of cerium oxide from the dispersion of average crystallite size of 17–19 nm. For the characterization, Raman spectroscopy and XRD were used for the phase composition of the nanoparticles. Carbon impurity (0.3–0.5% by weight) was discovered to be present on the surface of CeO2 particles which would probably have appeared during the drying of the dispersion. The authors (Lapin et al. 2016) thus recommended that further studies of nanocrystalline ceria should be carried out by laser ablation in the liquid phase that would include the study of surface properties and composition, as well as the study of their functional characteristics for subsequent use catalytic applications (Fig. 9).

Table 4 gives a summary of some of the articles reviewed on nanocatalysts for biofuel production; it shows the oil used, the catalyst size, the synthesis method and the conversion obtained.

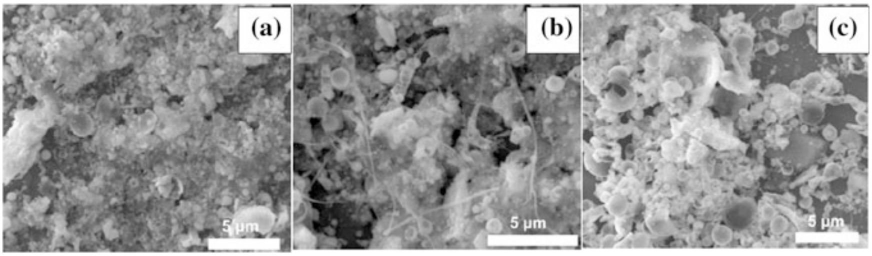


Fig. 9 Morphology of CeO_2nanopowders (the SEM image): from water (**a**), water-ethanol (**b**) and ethanol dispersion (**c**) (Lapin et al. 2016)

Table 4 Nanocatalysts used for biofuel production with their sizes and methods of synthesis

S/N	Oil	Catalyst size (nm)	Synthesis method	Conversion (%)	Recyclability (cycles)	Catalyst type	REF
1	*Olive oil*		Solution approach	94.80		ZnO	Molina (2013)
2	*Chinese tallow seed oil*	30–100	Impregnation method	96.80		KF–CaO	Wen et al. (2010)
3	*Soybean oil*	20	Purchased	99	4	CaO	Venkat Reddy et al. (2006)
4	*Sunflower oil*	50–200	Sol-gel	99	5	MgO	Verziu et al. (2008)
5	*Neem oil*	40.62	Chemical co-precipitation	97.10	6	Cu–ZnO	Gurunathan and Ravi (2015)
6	*Mahua oil*	24.18	Co-precipitation	97	5	Mn–ZnO	Baskar et al. (2017)
7	*Sunflower oil*	30–35	Precipitation	94.80	4	Cs–Al–Fe_3O_4	Feyzi et al. (2013)
8	*Karanja and jatropha oil*	50–70	Wet impregnation	99	0	Li–CaO	Kaur and Ali (2011)
9	*Soybean oil*	34.8	Co-precipitation	84	4	Fe–SnO	Alves et al. (2014)
10	*5-hydromethylfurfural*	Oct-60	Direct heating treatment	99.40	6	Cu–Co	Chen et al. (2017)
11	*Soybean oil*	11.2	Co-precipitation	90	3	Fe_3O_4	Xie and Ma (2010)
12	*Sunflower oil*	28	Deposition	86.90	3	Au–Ag	Banerjee et al. (2014)
13	*Jatropha oil*	7.3	Co-precipitation	95.20	8	Mg–Al	Deng et al. (2011)

7 Conclusion

This work has reviewed the literature on nanocatalysts for biofuel production. The review carried out focused on heterogeneous catalysts such as metal oxide (e.g. ZnO), metal supported by metal oxide (e.g. Au–ZnO), alloy (e.g. Cu–Co), metal oxide supported by metal oxide (e.g. KF–CaO–Fe_3O_4); their synthesis and characterization (with much emphasis on green production). This is to highlight what has been done and the stage reached, in order to give researchers a clear idea of an expected contribution to knowledge in nanocatalysts for biofuel production.

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Nanoadditives: Propitious Alternative For Increase Biofuel Performance

Shanti Bhushan Mishra

Abstract In spite of the limited sources of fossil fuels, energy demand has been considerably increased since the last century. The problems associated with global warming due to rising atmospheric greenhouse gas levels and scarcity of fossil fuels makes it imperative to reduce our heavy dependency on fossil fuels. These reasons forced countries throughout the world to search for new fuel alternatives. Biofuel has gathered considerable attention due to their inherent benefits, like lower greenhouse gas emission, renewability, and sustainability. Commercially, biofuels are produced from vegetable oils, animal fats, and carbohydrates by using transesterification and fermentation. However, biofuel production suffers from high production costs and other technical barriers. Considering the environmental and economic issues, use of nanotechnology seems to be a viable solution. Nanoparticles have a number of interesting properties for the production of second-generation ethanol or transesterification of oils and fats to yield biodiesel. In this chapter highlighting the various available edible as well as nonedible vegetable feedstocks for biodiesel production, metal-based additives along with the variations in physiochemical properties.

Keywords Biodiesel · Biofuel · Nanometallic additives · Nanotechnology
Renewable resources

1 Introduction

Fuels are playing a major role in the economy of every country of this world and majority of the world energy needs are supplied by the petrochemical resources, coal, and natural gases, with the exception of hydroelectricity and nuclear energy (Shiu et al. 2010; Dennis et al. 2010). Among these mineral oils, petroleum plays a major role in the development of industrial growth, transportation, agricultural

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sector, and to meet many other basic needs of human being (Basha et al. 2009). Since 1970s, mineral-based fuel oil (i.e., petroleum, diesel, kerosene, natural gas, etc.) prices are increasing day by day due to depletion of fossil fuel reserves and rapid consumption of mineral oils. The main reason that caused the fast diminishing of energy resources is due to rapid population and industrialization growth globally (Lam et al. 2010). Moreover, petroleum-based fuels are creating negative impact on the ecosystem and burning of these fuels leads to emission of pollutant gases like CO_2, HC, NOx, SOx (Shahid and Jamal 2008). Due to the above and following reasons like rapidly increasing prices, uncertainties concerning petroleum availability, increased environmental concern and effect of greenhouse gases from industries have stimulated the search for alternative sources for petroleum-based fuel including diesel fuel (Balat and Balat 2008).

As a result, biodiesel and ethanol have been known as biofuel to substitute petroleum-derived cetane and octane fuel, respectively. These fuels have been attracting the attention since use of these oxygenated fuels in the engines clearly reducing the exhaust emission of greenhouse gases, particulate matters, unburned hydrocarbons, poly-aromatics, and oxides of sulfur (Lin et al. 2009).

Biodiesel, a processed fuel is derived from the vegetable oils and animal fats through the esterification and transesterification reactions of free fatty acids (FFAs) and triglycerides, respectively, that occur naturally in renewable biological sources (Clayton et al. 2008). In other words, we can define biodiesel as a mixture of alkyl esters of long-chain fatty acids, which are synthesized through esterification and transesterification of free fatty acids (FFAs) and triglycerides (TG) (Dennis et al. 2010; Clayton et al. 2008; Murugesan et al. 2009). The major feedstocks available for biodiesel are rapeseed, palm, canola, and soybean oils, though the process to grow nonfood grade oil is under process in the developing nations in tropic and subtropics. Many biodiesel industries have been set in the last decades worldwide, whereas most of these are not operational throughout the year due to the scarcity of cheap vegetable oils as feedstock for economic production of biodiesel.

In the production of biodiesel, more than 95% of feedstocks come from edible oils since they are mainly produced in many regions of the world and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute. Use of such edible oil to produce biodiesel is not feasible in view of a big gap in demand and supply of such oils as food and they are far expensive to be used at present, and obviously, the use of nonedible vegetable oils compared to edible oils is very significant. Moreover, biodiesel does not contain any compounds like sulfur or aromatic compounds and burning of biodiesel results in the lower emission of hydrocarbons, carbon monoxides, and particulate matters (Karmakar et al. 2010; Shu et al. 2010). Since the cost of raw materials accounts about 60–80% of the total cost of biodiesel production, so choosing a right feedstock is very important and properties of biodiesel produced from different feedstocks would be quite different (Dennis et al. 2010). However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel; moreover, it will cause deforestation in some countries because more and more forests have been felled for plantation purposes. In order to overcome these disadvantages, many researchers, scientists, technologists as well as industrialists are interested in nonedible oil source which are not suitable for human consumption because of the presence of some toxic components in the oils. Furthermore, nonedible oil crops can be grown in wastelands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high yield without intensive care (Dennis et al. 2010; Balat and Balat 2008; Qian et al. 2010). However, most nonedible oils contain high free fatty acids. Thus, they may require multiple chemical steps or alternate approaches to produce biodiesel, which will increase the production cost, and may lower the ester yield of biodiesel below the standards.

Some of the common methods followed for improving the performance of diesel engine are engine modification, fuel modification, and exhaust gas retreatment. Fuel modification is carried out by adding catalysts or additives with the base fuel to optimize its physiochemical properties. The fuel additives are mixed thoroughly with diesel fuel for improving both performance and emission.

2 Importance of Additives

Biofuel is one of the best substitutes for petroleum diesel fuel. Biodiesel, mono-alkyl esters of long-chain fatty acids which are nontoxic in nature, nonexplosive, less flammable, and more importantly, it is biodegradable. Biodiesel is produced from various available natural sources namely palm, Jatropha, Pongamia, grape seed, mahua, castor, cotton seed, tobacco seed, rubber seed, rice bran, neem, coconut, sunflower oil, etc., Neat oil produced from these natural sources are chemically processed by “transesterification”, in which the alcohol is added to the neat oil under mild condition in presence of a base catalyst. During esterification process, the triglycerides present in the oil get transformed into alkyl esters and glycerol. The transesterification process is carried out in the temperature range of around 50–80 °C with the addition of methanol or ethanol. The base catalysts commonly used are sodium hydroxide (NaOH) and potassium hydroxide (KOH). The methods used for biodiesel production are ultrasonic reactor method, supercritical process, lipase-catalyzed method and batch reactor method. Generally, the vegetable oil feedstock for biodiesel is categorized into two, namely edible and nonedible sources. Some of the prominent edible and nonedible feedstock available in India are as follows.

3 Edible Feedstocks

Corn belongs to the family of Poaceae with Zea mays as species name. Corn oil is extracted from the germinated maize. It is usually seen in tropical climates having a slow and sluggish growth upto a height of 6 m. With an oil content of around 40%, solvent extraction process using n-hexane or 2-methyl pentane extracts 85% of corn germ oil from its kernels. Soybean belongs to the family of Fabaceae with annuals as species. Soy is a leguminous and bushy plant producing beans for food and oil industry. It has of 18–20% of lipid and oil, 40% of protein along with minimal quantity of cellulose, glucose, ash, and fiber. Percolation extraction technique in the presence of n-hexane is used to extract oil from Soybean. *Brassica napus* (Canola) is capable of producing 75–240 gallons of oil in every hectare of cultivation. With oil content between 35 and 42%, solvent extraction method is widely adopted to extract oil.

Arachis hypogaea (Peanut also known as groundnut or goober) is widely grown in tropical and subtropical regions with a higher yield in light, sandy loan soil with pH between 5.9 and 7 and soil temperature of 20 and 35 °C. The oil content is estimated to be between 45 and 52% of which nearly 50% is extracted by pre-pressing and the remaining oil is extracted through solvent extraction method. *Chamaerops humilis* (Palm), a feedstock to extract edible oil from the mesocarp of the fruit, is usually seen in warm and tropical climates. The oil content is estimated to be between 48 and 52% along with high level of β-carotene. The oil extraction is based on screw pressing technique. *Cocos nucifera* (Coconut) belonging to the family of Arecaceae is widely grown in the coastal regions with hot and humid climatic conditions. The oil is extracted from the dried kernel (copra) of the coconut. The oil content is found to be between 65 and 72% and it is extracted by employing rotary chucks and oil expellers. Extract from grape seed of *Vitis vinifera* (Grape) is rich in polyunsaturated fat of about 69.6%. *Oryza sativa*, a type of Asian rice widely found in Asian countries including India is rich in carbohydrates. The oil extracted from the outer hard layer of rice husk is called rice bran oil. It mainly contains oleic acid which is used for edible purpose. Solvent extraction method is adopted to extract oil from the rice bran. *Helianthus Annuus* (Sunflower) belonging to the family of Asteraceae is a native of North America and presently widely cultivated as ornamental plant as well as food crop. The kernels of sunflower contain 44–50% of oil rich in oleic acid. Compression technique is used to extract oil from seeds of sunflower.

4 Nonedible Feed Stocks

Madhuca indica (Mahua), an origin of central and north India, belongs to the family of Sapotaceae. It is one of the most important tree species of Central India producing huge quantity of oleaginous seeds. The oil content of the seed is estimated around 33–43%. *Ricinus communis* (Castor) belonging to the family of Euphorbiaceae is a nonedible, high oil yielding crop mainly found in tropical regions. The castor bean is estimated to contain 40–50% of oil which is extracted through high-pressure continuous screw press technique with n-heptane as solvent. *Millettia pinnata* (Pongamia) of Fabaceae family is a semi-deciduous, drought-resistant, midsized tree found mainly in tropical and subtropical Asia. It is capable of growing in a wide range of soil and climatic conditions. It contains 30–40% of oil which is extracted through expeller and cold pressing, and solvent extraction method. *Jatropha curcas* (Jatropha) belonging to the family of Euphorbiaceae is a tropical and drought-resistant plant-producing seeds with oil content around 37–40%. Recently, Temasek life sciences laboratories and JOil Pte Ltd, Singapore developed strains of *Jatropha curcas* with 75% of oleic acid thereby making it as a more suitable biofuel. The oil is extracted by using mechanical press expeller as an oil extraction technique.

Azadirachta indica (Neem) of Meliaceae family, originated from India is found in all agro-climatic zones with soil pH value of 10 except in cold regions. Mechanical pressing, steam pressing, and solvent extraction techniques are used to extract 30–50% of oil from the seeds of neem. *Simmondsia chinensis* (Jojoba) belonging to the family of Simmondsiaceae is a species capable of growing in arid, semiarid with minimal water and extreme conditions but not suitable for soil prone to flooding and heavy waterlogging. The seed contains nearly 50% oil which is extracted using mechanical pressing followed by leaching and solvent extraction method. Nicotiana (Tobacco) belonging to Solanaceae family is a nonedible, green leafy plant grown in warm climates with its seed containing oil between 17 and 26%. Oil from the tobacco seed is extracted through solvent extraction and steam distillation methods. *Hevea brasiliensis* (Rubber tree) belonging to the family and subfamily of Euphorbiaceae and Crotonoideae have their nativity to African and Brazilian countries. Presently, it is widely cultivated in Southern Peninsular India. The rubber seed oil mainly contains linoleic and oleic acid which are extracted through mechanical expeller followed by soxhlet process. The various edible and nonedible biodiesel feedstock are shown in Fig. 1. Potential nonedible oil seeds plants of India have been mentioned in Table 1 and their physicochemical properties are described in Table 2.

5 Fuel Additives and Its Importance

Additives are organic based or metal-based substances which are easily soluble in fuel and its main purpose is to improve, maintain, and provide beneficial characteristics to the fuel without affecting the performance and combustion parameters. The fuel additives are added in smaller quantities ranging from 100 ppm to several thousand ppm. The fuel additives are broadly classified as refinery products, distribution system products, and automotive performance enhancement products. They are again subdivided into following categories namely antioxidants, cetane improvers, antiknocking agents, antifreezing agents, stability improvers, additives to prevent corrosion, cold flow improvers, fuel borne catalysts, antiwear agents, etc.

Fig. 1 Various edible and nonedible biofuels feedstock

6 Antioxidants

Biodiesels are fatty acid methyl esters produced by transesterification process which are ready to react with oxygen by the process called auto-oxidation. To avoid auto-oxidation of biodiesel in the diesel blend, additives like BHT (Butylated hydroxytoluene), TBHQ (Tert-butyl hydroquinone), BHA (Butylated hydroxyanisole), PG (Propyl gallate), and PA (Pyrogallol) are mixed with diesel–biodiesel blends.

7 Oxygenated Additives

To improve the burning characteristics of fuel with more ignition delay, chemical compounds having more oxygen content are added to that fuel at a trivial quantity. Oxygenated components like ethanol, methanol, biodiesel, dimethyl ether, dimethyl

Table 1 Potential nonedible oil seed plants in India

Botanical name	Common name	Distribution	Potential (metric/ annum)	Oil %	Use
Cyanobacteria	Algae	Few places in India	157.4–629.8	20–40	Human nutrition, animal feed, aquaculture, biofertilizer, source of polyunsaturated fatty acids, and recombinant proteins, etc
Ricinus communis	Castor	All over India	790,000	46–55	Adhesives, coatings, soaps, lubricant, paints, and dyes, etc
Gossypium hirsutum	Cotton	All over India	851,000	18–25	Dairy cattle feeding, alternative biofuel source, etc
Jatropha curcus	Jatropha	All over India	15,000	40–60	Biodiesel, manufacture of candles, soap, and cosmetics
Simmondsia chinensis	Jojoba	Few places in India	–	45–55	Cosmetics, skin softeners, lubricants
Pongamia pinnata	Karanja	Maharashtra, Karnataka, Assam	200,000	30–40	Tanning leather, soap, lubricant and pesticides
Garcinia indica	Kokum	Western Ghats region, Andaman and Nicobar	55,000	–	Ideal feedstock for biodiesel
Linum usitatissimum L.	Linseed	Few places in India	150,000	35–45	Textiles, oil crops, stem fibers, geotextiles, filters, absorbents
Madhuka indica	Mahua	Maharashtra, Gujarat, West Bengal, Tamil Nadu, Orissa	520,000	35–40	Ointments, rheumatism, lighting, soaps, etc
Moringa oleifera	Moringa	Himalayan regions	_	33–41	Skin diseases
Mesua ferra	Nahor	North-eastern state of India	_	58–75	Production of biodiesel, boat buildings, mine props, tool handles
Azadirachta indica	Neem	All over India	500,000	35–45	Preservation of stored grains, Ayurvedic medicines, Unani and Homeopathic medicines
Erythea salvadorensis	Palm	_	<70,000	20–21	Cosmetics, soaps, lubricant for biodiesel engine

(continued)

Table 1 (continued)

Botanical name	Common name	Distribution	Potential (metric/ annum)	Oil %	Use
Simarouba glauca	Simarouba	Gujarat, Maharashtra, Tamil Nadu	1.1–2.2 oil/ha yr	55–65	Manufacture of soap, vegetable, fat lubricant, paints, polishes
Sapindus mukurossi	Soapnut	Andhra Pradesh, Karnataka, Delhi	6.61	51.8	Medicinal soap, surfactant, fabric, bathing
Citrullus colocynthis	Tumba waste cooking oil and animal fats	Few places in India, Restaurants and household	21,000 tons 1,135,000	_	Medicinal biodiesel production

carbonate, diethylene glycol diethyl ether, sorbitan monooleate, etc., which easily mixes and blends with diesel are used as an additive.

8 Additives to Improve Cold Flow Behavior

During cold conditions, the wax content present in the biodiesel begins to freeze and results in crystal-like structure which affects the cold filter plug point (CFPP). This situation may be avoided by using additives like ethylene vinyl acetate copolymer, glycerol ketals, glycerol acetates, phthalimide, and succinimide copolymers which improves the cloud point property of the fuel.

9 Additives to Improve Cetane Number

Cetane number is one of the major factors which determines the fuel quality by representing the ignition capability of the fuel. Fuels with high cetane number provide better performance with respect to compression ignition engine. Nitrates, nitroalkanes, nitro carbonates, peroxides, etc., are used as additives which improve the cetane number of the fuel.

Table 2 Physiochemical properties of biofuel feed stocks

Chemical properties	Castor oil	Cotton seed	Jatropha	Jojoba	Karanja	Kokum	Linseed	Mahua	Moringa	Nahor	Neem	Palm	Rice bran	Simarouba	Soap nut	Tumba	Waste cooking
Unsaponifiable matter(w/w)	–	–	–	–	3.3	–	–	1	–	2.7	–	–	–	0.40	–	–	–
Specific gravity	0.96	0.9148 at 15°c	0.912 at 15°c	0.8635–0.8640 at 40°c	0.882 at 15.5°c	0.895 at 40°c	0.931–0.938 at 15.5°c	0.856 at 15°c	0.907	0.92 at 30°c	–	0.9180 at 15°c	0.92 at 30°c	–	–	0.924–0.927 at 28°c	0.925
Kinematic viscosity at 30° c (mm^2/s)	29.7	33.5 at 38°c	29.4	11.82 at 40°c	27.8	–	22.2 at 40°c	24.5 at 40°c	43.4 at 38°c	4.1 at 40°c	50.3	5.7	36.68 at 40° c	–	–	–	36.4 at 40°c
Calorific value MJ/kg	39.5	39.648	39.23	42.17	34.000	–	–	38.863	–	36	–	36.510	39.500	–	–	–	–
Iodine value (g/I2/100gm)	88.72	104.7	108.4	82–89	29.9	25–38	156.74	58–70	73	89.4	65–80	35–61	90–108	53.8	64.5	118–122	141.5
Acidic value (mg KOH/g)	–	0.16	28	–	5.06	–	–	38	1.194	34	–	6.9	0.45	–	–	–	0.15
Saponification value (mgKOH/g)	191	198.5	200.8	92-167	188.5	187–192	187.6	190.5	199.7	190.6	209.66	208.6	201.27	191	195	172–174	188.2
Flash point (°c)	260	234	225	292	205	–	241	232	–	172	–	164	316	–	–	–	212
Aniline point (°c)	–	–	–	52.9	–	–	–	–	–	–	–	–	–	–	–	–	–
Cetane no.	42.3	54	61–63	–	60–61	65.6	34.6	56.61	56.66	54.6	57.83	62	50.1	59.32	59.77	–	49
Pour point (°c)	–32	258 k	2	6	–3	–	–15	15	–	–1.2	–	–31.7	1	–	–	–	11
Carbon residue (wt%)	0.21	0.42	0.44	–	0.71	–	<0.001	0.42	–	–	–	–	0.6	–	–	–	0.46
Moisture content (wt%)	0.15–1.30	–	–	–	19%	–	–	1.6	7.9 ± 1	0.1	–	0.02	0.02	–	–	–	0.42

10 Metal-Based Additives

The burning characteristics of the fuel can also be improved by the addition of metals and metal oxides to the fuel in the range of micro- or nanosizes through ppm or percentage by weight ratios. Metals like iron (Fe), aluminum (Al), magnesium (Mg), manganese (Mn), silver (Ag), gold (Au), copper (Cu), boron (B), graphene, silica (Si), etc., and metal oxides like aluminum oxide (Al_2O_3), cobalt oxide (Co_3O_4), cerium oxide (CeO_2), titanium oxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO) etc., are used as additives to improve the fuel physiochemical properties. Alloys of metals like magnalium (Mg-Al), Carbon nanotubes (CNT) are also used as metal-based additive which improves the performance of fuels by changing its physiochemical properties. Figure 2 shows some of the metals and metal oxides nanoadditives used as performance enhancers.

After several studies, researchers have found that the modification of fuel with respect to its physiochemical properties yields better results in enhancing the engine performance and controlling the exhaust emissions rather than carrying out engine modifications. With reduced exhaust emissions, ignition delay, cold flow characteristics, etc., along with comparable performance characteristics, using biodiesel as fuel is found to be favorable. A few literature also reported about the reduction in lifespan using biodiesel as fuel which can be overcome with the use of fuel additives.

The main focus of this chapter is to comprehend the knowledge and information related to fuel modification by the addition of metal and metal oxide nanoadditives to improve the performance and reduce the emissions of the diesel engine. There are

Fig. 2 Metal and metal oxide nanoadditives as a performance enhancer

the outcome of several studies carried out by various researchers on the impact of nanofuel additives on fuel properties, its effect on performance and exhaust emissions at different operating conditions.

11 Effect of Nanometallic Additive on Fuel's PhysioChemical Properties

Attia et al. (2014) investigated the effect of B20-Jojoba methyl ester with the addition of aluminum oxide nanoparticle on properties of fuel, performance, and emission characteristics of the diesel engine. The result showed that there was a considerable change in fuel properties. It was also noticed that the addition of Al_2O_3 reduced the kinematic viscosity of the fuel along with an increase in density and cetane number. Arockiasamy and Anand (2015) mentioned that the addition of 30 ppm Al_2O_3 and CeO_2 with Jatropha methyl ester improved the kinematic viscosity, density, and calorific value as 4.25 Cst, 875 kg/m3 and 38.9 MJ/kg for JBD30A blend. JBD30C blend was found to have similar fuel property values as 4.30 Cst, 876 kg/m3, and 38.7 MJ/kg, respectively. The addition of alumina with Jatropha biodiesel improved the fuel properties. Aalam and Saravanan (2015) also obtained similar improved fuel properties for B20-Mahua biodiesel by adding aluminum nanoparticles.

Syed Aalam et al. (2015) evidently exhibited the enhancement in ZJME 25 fuel properties with the addition of alumina nanoparticles. AONP 50 gave better results with ZJME 25 than AONP 25 blend with increased flash point and cetane number. Shaafi and Velraj (2015) used alumina, ethanol, and isopropanol as a fuel additive for B20-Soybean biodiesel. They mixed 100 mg/l of AONP in D80SBD15E4S1 blend and noticed a drastic decrease in viscosity and calorific value along with an increase in cetane number. Anbarasu et al. (2016) and Bharathiraja et al. (2015) studied the effect of blending AONP with Canola methyl ester emulsion and straight diesel, and noticed a significant increase in flash point, density along with a significant decrease in viscosity.

Sadhik Basha and Anand (2013) compared the fuel properties of JME with and without the presence of AONP and CNT. The result indicated that the addition of CNT with JBD yielded better results with enhanced fuel properties. The flash point of CNT-blended Jatropha biodiesel was lowest when compared with neat JBD- and AONP-blended JBD.

Balaji and Cheralathan (2015) and Singh and Bharj (2015) mentioned that the addition of CNT with biodiesel resulted in increased flash point, viscosity, calorific value, and cetane number. The values were found to be increasing with increase in the amount of CNT concentration. Tewari et al. (2013) discussed about the change in properties of HOME with the addition of CNT. The author concluded that HOME + 50 ppm CNT showed better results than HOME + 25 ppm CNT.

Sadhik Basha and Anand (2014) studied the CNT-blended JME water emulsion and found that flash point for 100 CNT blend was 1220C, which was lowest among all the blends. With the increase in CNT concentration, viscosity, density, calorific value, and cetane number also showed an increased trend.

Karthikeyan et al. (2014a) mentioned that the addition of ZnO with B 20-Grape seed oil methyl ester increased the flash point, fire point, density, and viscosity.

Rao and Rao (2015) and Karthikeyan et al. (2014b) showed that the addition of ZnO and CeO_2 nanoparticles with straight diesel and B20-Pomoline stearin wax biodiesel resulted in increase of calorific value and decrease in flash/fire point.

Gan et al. (2012) investigated the burning characteristics of various nanoparticles at dilute and dense concentrations. Iron nanoparticle spherical in shape of size 15–80 nm (coated with thin layer of carbon between 2 and 6 nm) and boron nanoparticle nonspherical in shape of size 80 nm were studied.

Kannan et al. (2011) highlighted about the addition of FBC ($FeCl_3$) in waste cooking palm oil biodiesel which decreased the flash point, fire point, and density values, whereas the kinematic viscosity, calorific value, and cetane number showed a significant increase. Banapurmath et al. (2014), found that the addition of AgNP with HOME decreased the flash point value, whereas it increased the viscosity, density, and calorific values. HOME + 50 ppm of Ag showed good results compared to properties of HOME.

Vishwajit et al. (2015) found that the addition of graphene NP improved the properties of HOME. Among all the blends, HOME + 50 ppm graphene showed an enhanced properties.

Ansari et al. (2014) elaborated the recent trends in nanofluids, its preparation, and its applications. Nanofluid synthesis was classified into two types as one-step process and two-step process.

Bafghi et al. (2015) studied the performance and emission characteristics of a single-cylinder four-stroke air-cooled diesel engine fuelled with nanoceria added diesel–biodiesel extracted from waste fried oil. CeO_2 of size 10–30 nm were mixed with diesel–biodiesel blends in the range of 5–25 ppm.

Sharma et al. (2015) discussed about the addition of CeO_2 and CNT in JME + TPO blend and found that CeO_2 addition decreased the viscosity and density, whereas the same was increased with CNT addition.

Caynak et al. (2009) found that the addition of Mn (12 µmol/L) in B25 of pomace oil reduced the viscosity by upto 20.37% and flash point by upto 7%. The pour point got reduced from 0 to −15 °C.

Studies by Ayhan (2002) and Jayed et al. (2009) also showed the importance of adding nanometal additives in biodiesel and its effect in improving the physio-chemical properties of the nanometal-blended biodiesel.

12 Change in PhysioChemical Properties upon Addition of Nanometal Additives

Addition of CuO and Al_2O_3 nanoparticles with neat diesel increased the flash point and cetane number, whereas ZnO and CeO_2 reduced the values of flash point (Bharathiraja et al. 2015; Rao and Rao 2015). Addition of nanoparticles to the emulsified fuel increased the values of viscosity, density, calorific value, and cetane number (Singh and Bharj 2015; Sadhik Basha and Anand 2014). Addition of CeO_2, Al_2O_3, CNT, Al, Ag, and graphene nanoparticles with neat biodiesel reduced the flash point values, whereas the same increased the viscosity and density values [14, 20, and 29]. Calorific value of neat biodiesel increased with the addition of FBC, CNT, graphene, and Al nanoparticles [21, 29, and 30]. Addition of ZnO nanoparticles increased the flash point, viscosity, density, and calorific value of the fuel. Mn, Mg, and aluminum nanoparticles in diesel–biodiesel blends reduced the flash point values [15, 38, and 39].

The reason for adding metal-based nanoadditives to the diesel/biodiesel is to enhance the performance of the engine by improving the properties of the fuel. The addition of nanoparticles with diesel/biodiesel blends increased the calorific value and cetane number of the fuel. In some cases, it also reduced the sulfur content present in the fuel. Addition of CuO and Al_2O_3 with neat diesel reduced the sulfur content (Gumus et al. 2016). Aluminum nanoparticle with mahua methyl ester reduced the flash point and increased the calorific value and cetane number Aalam and Saravanan (2015). Addition of ZnO with biofuel blends increased the flash and fire point, calorific value, and cetane number (Karthikeyan et al. 2014a, c). Addition of fuel-borne catalysts also reduced the flash and fire point of the fuel (Arockiasamy and Anand 2015; Aalam and Saravanan 2015; Sadhik Basha and Anand 2013). ZnO with neat diesel reduced the flash and fire point values (Rao and Rao 2015). The calorific value increased with the addition of ZnO in all the cases. Addition of CNT with emulsified fuels improved the properties of fuels, whereas Al_2O_3 with emulsified fuels increased the flash and fire point and decreased the calorific value (Singh and Bharj 2015; Sadhik Basha and Anand 2014). Graphene nanoparticles gave better fuel improvements in HOME compared to silver nanoparticles (Vishwajit et al. 2015).

13 Conclusion

It is understood that the addition of nanoparticles plays a major role in improving the fuel properties and enhancing the performance of CI engine as well as reducing the exhaust emissions. Addition of nanoparticles increases BTE which depends upon the base fuel used, amount of nanoparticle added, how well they are mixed with the base fuel, and operating condition of the CI engine. Nanoparticles like Al_2O_3, Al, CNT, and CeO_2 show good results as additives with diesel and biodiesel blends in all aspects. ZnO also gives better results, but more amount of ZnO should be added than other nanoparticles to get an equivalent performance and the use of ZnO as fuel additive increases the cost of fuel. The performance enhancement cannot be achieved with every amount of nanoparticle addition. Therefore, selecting optimal range of nanoparticles addition is key to get good results on enhanced performance and reduced emission in a CI engine. Some nanoparticles give good results with every base fuel with which it is added, but in some cases, it fails to improve neither performance nor emissions. Size of the nanoparticle is also a criterion to be considered in using nanometal additives for improving the fuel properties. Therefore, selecting the nanoparticles based on the properties of the fuel to be improved.

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Strategies of Porous Carbon Materials for Future Energy

Kelvii Wei Guo

Abstract Carbon materials mostly involved in new alternative clean and sustainable energy technologies have been playing more and more significant role in energy storage and conversion systems, especially for the carbon porous materials, because carbon porous materials with structures can provide large surface areas for reaction, interfacial transport, or dispersion of active sites at different length scales of pores and shorten diffusion paths or reduce diffusion effect. Therefore, the soft-, hard-templated and hierarchically ordered strategies employed to fabricate porous carbon materials are marked along with the relevant advantages and disadvantages aim to provide the vital information about the growing field for future energy to minimize the potential environmental risks. Carbon porous materials with attractive structures as ideal candidates for the versatility and feasibility of application to energy storage and conversion should not only be realized, but also much effort has to be devoted to systematic studies on the relationship between physicochemical properties of these materials and their performances in energy conversion and storage to more efficiently stimulate further developments in this fascinating area, alongside eco-technologies that will ensure minimal environmental impact.

Keywords Carbon porous materials · Hard-templated porous carbons
Soft-templated porous carbons · Hierarchically ordered porous carbons

1 Introduction

Technologies in an urgent attempt to alleviate fossil fuel usage and CO_2 emissions, fuels, heat or electricity must be economic, energetically efficient, environmentally friendly, and not competitive with food production due to unsustainability of the current fossil fuel usage and its successive greenhouse gas production. Carbon

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materials, especially for porous carbon materials and nanostructured materials, with hierarchically ordered porosity and structures have been heavily involved in newly developed energy storage and conversion systems. With meticulous design and ingenious hierarchical structure of porosities by mimic nature, hierarchically structured porous carbon materials can provide large surface areas for reaction, interfacial transport, and dispersion of active sites at different length scales of pores to shorten the diffusion lengths as well as to increase the diffusion rate. It can be also widely used in energy storage devices such as supercapacitor and lithium ion battery.

To date, several researches on state-of-the-art carbons and porous carbon materials with well-controlled porosity including micropore, mesopore, and macropore have wide variety of applications in environmental remediation (separation science and water purification), heterogeneous catalyst supports, sensing devices, and the developing areas of electrochemical energy conversion and storage devices.

Moreover, a tremendous wave of interest in elucidating the relationship between performance and their physicochemical properties including surface area, porosity, surface property, electrical conductivity, and chemical stability has been illustrated. It shows that the porous structure of porous carbon materials can play a crucial role in determining and optimizing the performance in the abovementioned applications. It is also noteworthy that the required disruptive improvement in energy and environmental science has motivated the design of the structure, porous architecture, and surface functionality/polarity of porous carbon materials through the aid of suitable templates (soft templates and hard templates) and pore surface modification.

2 Synthesis Strategies for Ordered Porous Carbons

2.1 Soft-Templated Porous Carbons

The porous material can be defined as a solid matrix permeated by an interconnected network of pores such as cavities and channels being deeper than their width. Three classes of porous materials are defined according to their pore sizes, namely microporous (pore size < 2 nm), mesoporous (2 nm < pore size < 50 nm), and macroporous (pore size > 50 nm) (Gogotsi et al. 2009). Porous carbon materials of designed porosities and tunable properties, with high surface area, tunable porosity and surface property, good electrical conductivity, high chemical stability have attracted intense interests in separation science and water purification, stationary phase materials, heterogeneous catalyst supports, sensing devices, and energy generation and storage applications (fuel cells, batteries, solar cells, and supercapacitors) (Stein et al. 2009; Xia et al. 2010; Nishihara and Kyotani 2012; Inagaki et al. 2016; Salinas-Torres et al. 2016).

According to the requirements of disruptive improvement in energy and environmental science, the design of the pore architecture and surface functionality/polarity of porous carbon materials is therefore proposed with the aid of suitable templates (soft templates, hard templates), along with the pore surface modification.

Templating is one of the most frequently used methods for the synthesis of uniformly and hierarchically porous carbon materials. In the templating synthesis of materials, the template plays the most important role in controlling the types of porous networks as well as the sizes and shapes of pores (Borchardt et al. 2012; Wang et al. 2015). The templates in the broader sense can be classified into two categories. The first one is the common "soft template" in which the organic molecules or supramolecular aggregates are used as soft templates to impart structural features to the porous carbons. The second type of templates uses porous solids as templates (hard templates) to structure the porous carbon, often being inverse replicas of the template. The soft and hard templates can come in a variety of forms including organic molecules, ionic surfactants, block copolymers, nanoparticles, colloids, colloidal crystals, and even biological materials.

Generally, the use of ordered mesoporous silicates as the hard template makes the procedures complicated, time-consuming, and unsuitable for mass production. Moreover, a toxic chemical of hydrofluoric acid is needed for the removal of silicates.

Therefore, soft-templating techniques using surfactants and biomolecules as the templates have been developed for the production of ordered mesoporous carbon materials. It is well known that one of the major advantages of soft-templating method is the use of all commercially available and low-cost raw materials to prepare the highly ordered mesoporous carbon materials (Borchardt et al. 2012; Esposito et al. 2004; Acevedo and Barriocanal 2015).

Unfortunately, some mesoporous carbon materials cannot offer any macropore character (pore size > 50 nm), and soft-templating process is a versatile method and the selection of soft templates is often flexible but is also complicated and unpredictable. The obtained mesostructures from the self-assembly of soft templates are highly dependent on many parameters such as temperature, solvent, concentration, hydrophobic/hydrophilic properties, interface interaction, and ion strength. Astonishingly, a significant progress in soft-templating method has been achieved on the direct synthesis of ordered mesoporous carbon materials proposed by Liang et al. (2004) with self-assembly of copolymer molecular arrays and carbon precursors to realize the efficient synthesis of mesoporous carbons with controllable pore structures. It first reported the preparation of highly ordered and well-oriented mesoporous carbon thin films through the carbonization of a nanostructured phenolic resin and polystyrene-b-poly(4-vinylpyridine) (PS-P4VP) composite as shown in Figs. 1 and 2. Two important roles of the block copolymers in the synthesis are: (1) directing the formation of the phenolic resin nanostructure and (2) serving as templates for nanopores. Resorcinol monomers interact with the P4VP segment of the copolymer via hydrogen bonds, and are preorganized into well-ordered mesostructured films assisted with amphiphilic PS-P4VP self-assembly through spin coating and solvent annealing followed by in situ polymerization to form the

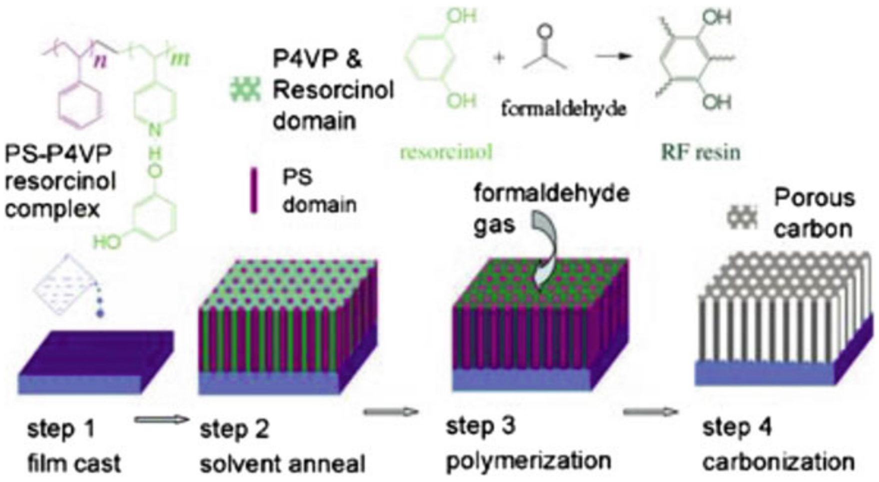

Fig. 1 Schematic representation of the synthesis protocol used to prepare well-defined carbon nanostructures

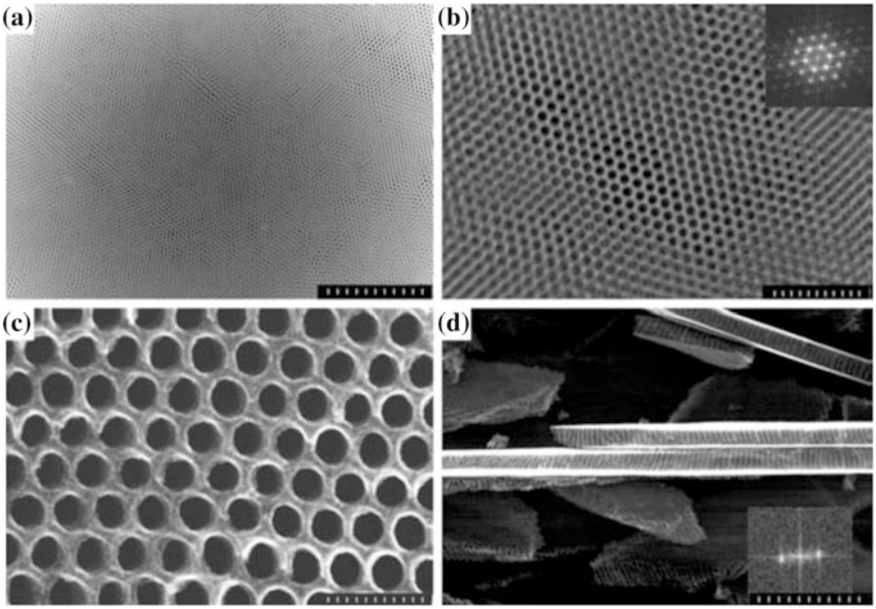

Fig. 2 Electron microscopy images of the carbon film

carbon precursor in the presence of formaldehyde vapor. After carbonization under N_2 atmosphere, ordered mesoporous carbon films with a hexagonal structure and large pore size of *ca.* 34 nm were obtained.

To date, the ordered mesoporous carbons can be fabricated using solvent evaporation-induced self-assembly (EISA) synthesis procedure in the presence of resol and copolymers. Low-molecular-weight and water-soluble resol, which is from the polymerization of phenol and formaldehyde under an alkaline condition, was first mixed with PEO-PPO-PEO triblock copolymer in an ethanol. The homogenous solution is poured into dishes to evaporate the solvent. It induces the organic–organic self-assembly of phenolic resin with amphiphilic block copolymers by hydrogen-bonding interaction to form ordered mesostructure. The polymerization of phenolic resins is carried out at 100 °C. Due to the difference in chemical and thermal stability between the phenolic resin and the triblock copolymer, the template can be removed either by pyrolysis at 350 °C under an inert gas atmosphere or by extraction with sulfuric acid solution, and results in the formation of ordered mesoporous polymers. Heating at a high temperature above 600 °C under N_2 or Ar atmosphere can transform the polymer into corresponding carbon frameworks. The family members include two-dimensional hexagonal (space group, *p6m*), three-dimensional bicontinuous (*Ia3d*), body-centered cubic (*Im3m*), and lamellar mesostructures, which can be controlled through simply adjusting the ratio of phenolic resin/template or choosing different block copolymers. The carbon mesostructures are highly stable and can be retained at temperatures up to 1400 °C under nitrogen atmosphere.

2.2 Hard-Templated Porous Carbons

In the hard-templating process, a liquid or a fluid material is poured into a template, which contains a hollow cavity of the desired shape, and is then allowed to solidify. Templating is most frequently used for making complex shapes that would be otherwise difficult or uneconomical to produce by other methods (Wilson et al. 2015).

The hard-templating process mainly includes three steps: (1) impregnation of carbon precursor (monomer and polymer) into solid template of mesoporous silica, (2) polymerization followed by carbonization of the precursor in the pore system resulting in a carbon-silica composite, and (3) removal of mesoporous silica template via chemical reaction. Various carbon precursors such as sucrose, furfuryl alcohol, phenolic resin, benzene, poly-vinyl chloride, pitches, acenaphthene, propylene, and acetonitrile can be utilized as the carbon precursors. The mesopore structures of the hard template acting as a nanoreactor have a significant influence on the size and structure of resultant cast replicas. Theoretically, replicated mesostructures with different symmetries can be obtained by choosing proper templates. The pore connectivity of the hard templates directly affects the structures of mesoporous replicas. When the template consists of a fully continuous solid phase and a connected pore channel system, 3D pore structures of resulting materials can be easily retained.

2.2.1 Ordered Mesoporous Silica-Templated Ordered Porous Carbons

Conventionally, mesoporous carbons are usually prepared by catalytic activation and carbonization of organic gels (carbon aerogel) with high mesoporosity. In 1986, Knox et al. (1986) first synthesized the rigid mesoporous carbon materials which exhibited unique retention characteristics in liquid chromatographic separation using spherical solid silica gel with controlled pore structure as the template and a phenol-formaldehyde resin as the carbon precursor. However, the concept of nanocasting in mesoporous materials was proposed after more than 10 years (Göltner and Weißenberger 1998). After that, many unique carbon materials with disordered structures have been synthesized by the hard-templating approach using silica as template. Unfortunately, the mesopores are still not well organized in an ordered form. But with exhilarating news, only after one year, the hard-templating mesoporous carbon with an ordered pore structure was synthesized successfully (Ryoo et al. 1999).

Since then, various studies have been carried out to synthesize ordered mesoporous carbon with different mesopore structures. Until now, it is well accepted that the structure of the resultant mesoporous carbon is indeed determined by that of the parent template. In the cases of preparing cubic phase mesoporous carbons, MCM-48 silica was first used as a template. The polymerization of sucrose in the pore space of MCM-48 silica catalyzed by sulfuric acid and carbonization leads to the formation of mesoporous carbon of CMK-1 type after the removal of the silica. Interestingly, the structure of the mesoporous carbon replica can be easily be tuned by varying the filling amount of carbon precursor. Up to now, the ordered mesoporous silicates as hard templates with the nanocasting strategy for the synthesis of ordered mesoporous carbons have been applied successfully.

2.2.2 Colloidal-Crystal-Templated Ordered Porous Carbons

Ordered macroporous carbons are prepared via the replication of ordered array structures, which are assembled by spherical and monodispersed colloidal spheres of sub-micrometer size including silica and polymer latex (e.g., polystyrene (PS) and poly(methyl methacrylate) (PMMA)) (Stein 2001; Stein and Schroden 2001; Cong and Yu 2011). The pore size of the ordered macroporous solid is controllable by tuning the size of the spherical silica or polymer latex. The hard-templating approach is illustrated in Fig. 3. It can be seen that the colloidal crystals are first formed by packing uniform spheres into arrays, then the interstitial voids of the colloid crystals are filled with liquid precursor, and subsequently converted into a solid skeleton. Removal of the colloidal spheres leads to the

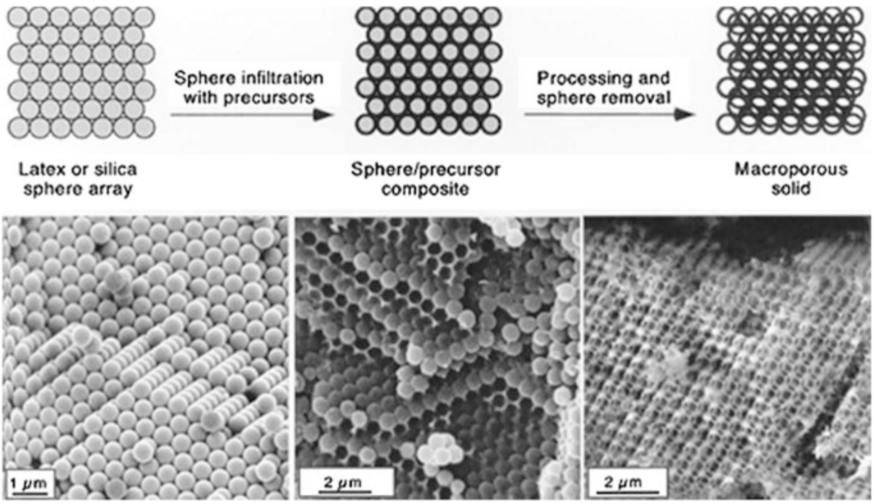

Fig. 3 General synthesis scheme for periodic macroporous solids and the corresponding SEM images for a PS/Silica system prepared with TEOS

generation of a solid skeleton in the location of the former interstitial spaces and interconnected voids where the spheres are originally located. It also shows that the morphology of macroporous carbon materials is actually largely dependent on the extent of void infiltration of template.

Besides spherical silica, organic polymer microspheres (e.g., PS or PMMA) are also been used as the templates for the synthesis of ordered macroporous carbon materials with mesoporous windows. The use of polymer beads as templates may eliminate the dissolution step, which is an indispensable step when inorganic templates (silica sphere) are used, because of the ready thermal decomposition of the polymer beads along with the carbonization of the carbon precursors.

2.2.3 Zeolite-Templated Ordered Porous Carbons

The major approaches to prepare microporous carbons are the pyrolysis of carbon precursor (such as glucose) (Shi et al. 2015) and the modification of existing pore structures of microporous carbons by chemical vapor deposition (CVD) (Almasoudi and Mokaya 2014), and the carbide-derived carbons (CDC) produced by high-temperature chlorination of metal carbides. Xie et al. (2011) explored nitrogen-doped, microporous carbon materials using zeolite EMC-2 as a hard template and acetonitrile as the carbon source by chemical vapor deposition (CVD) in the temperature range 700–950 °C. Figure 4 illustrates carbons prepared at 700–900 °C

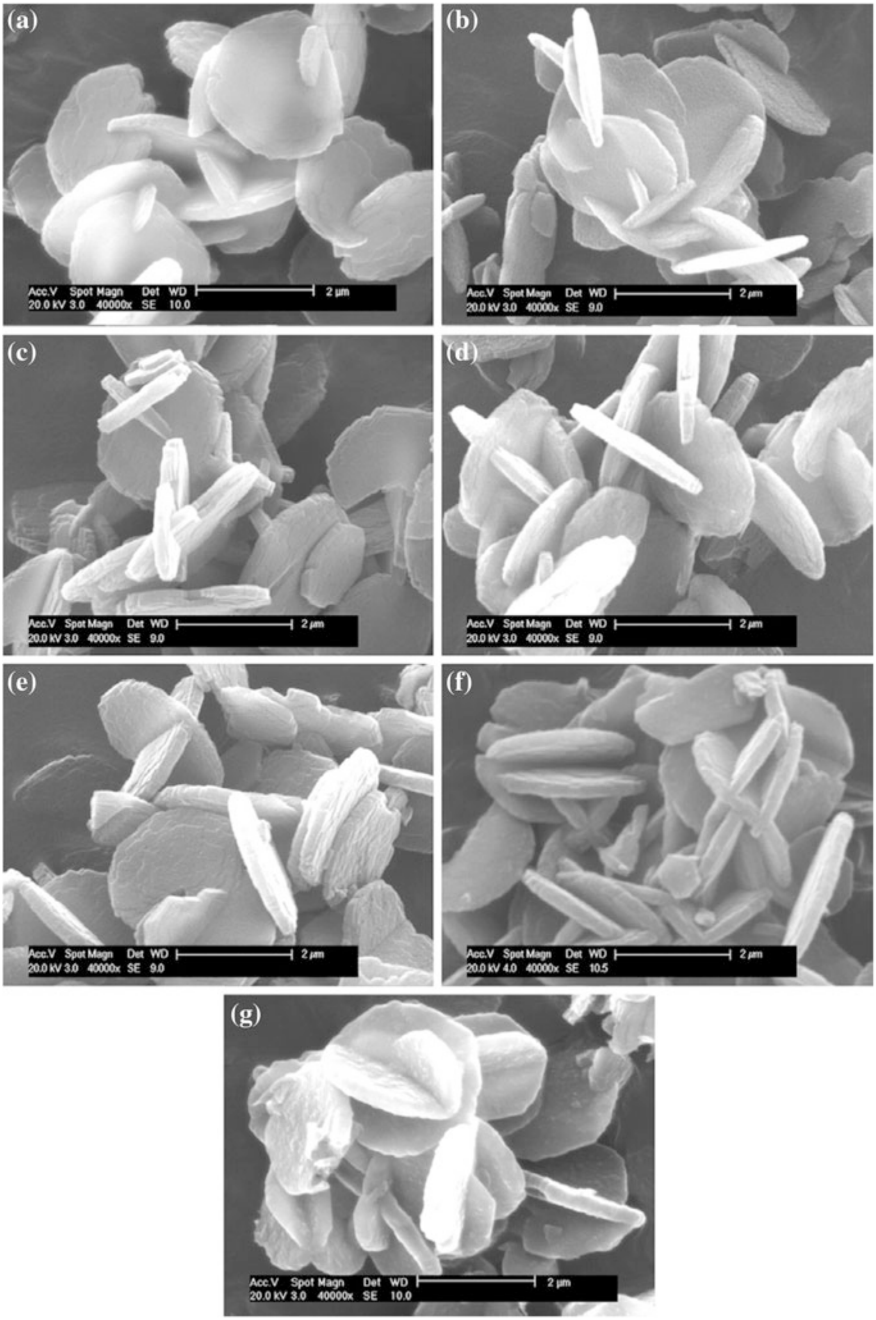

Fig. 4 Representative SEM images of zeolite EMC-2 (**a**) and zeolite-templated carbons prepared at **b** 700 °C (CEMC700), **c** 750 °C (CEMC750), **d** 800 °C (CEMC800), **e** 850 °C (CEMC850), **f** 900 °C (CEMC900) and **g** 950 °C (CEMC950)

display solid core disc-like particles, while the sample prepared at 950 °C exhibits broken hollow sheet-like particles. The morphology of the zeolite EMC-2 template was clearly transferred to the carbon materials, which is consistent with a templating mechanism whereby the carbon is predominantly nanocast either within the pore channels of the zeolite EMC-2 (700–900 °C) or on the surface of the zeolite particles (CEMC950).

In principle, the specific surface area of colloidal-crystal-templated macroporous carbon structures is relatively low due to the presence of large pores. However, macroporous carbons with high surface area are usually desirable when these materials are designed for serving as adsorbents, catalyst supports, and electrode materials. To create a high surface area and maintain their pores in an ordered structure, a solution method is normally used to generate secondary porosity in the macropore frameworks (Chai et al. 2004).

The advantage of hard template is that the synthesis process is more easily controlled and predicted, because the hard-templated structures are already fixed by nanoscale pore architectures. Therefore, the framework and morphology of the replicas are under control. However, the use of ordered mesoporous silicates as hard templates makes the procedures complicated and time-consuming, and the mesopore size obtained from the hard templating is relatively small, which is not easily tunable. It is noteworthy that the hard templates are actually produced from the soft-templating process, which means that hard-templating method would be unsuitable for mass production. In addition, toxic chemical such as hydrofluoric acid (HF) is needed for removal of silicates templates and HF itself is very toxic and harmful to the human body.

3 Hierarchically Ordered Porous Carbons

The soft-templating methods have been proven to successfully prepare both the ordered macroporous and mesoporous carbons. However, the surface area of ordered macroporous carbon is usually lower than that of ordered mesoporous carbon. Therefore, the porosity in macroporous carbon materials can be tuned by introducing micro- and mesoporosity into the macropore wall to increase the specific surface area. The use of dual-templating strategy, which combines multiple hard- and soft-templating approaches, to synthesize three-dimensional hierarchically porous carbon materials with designed porosity on multiple length scales has been explored. In this case, the two templates play different roles: the hard template is used to control the macroscopic structures, while the other which may be hard or soft template is employed for self-assembly of structurally ordered mesopores (Israel et al. 2015).

3.1 Polymer Sphere/SiO_2 Sphere for Ordered Porous

Chai et al. (2004) proposed a dual-templating method by coprecipitation of colloidal crystals (polystyrene sphere and silica particles) with ordered arrays for fabrication of hierarchically porous carbon as shown in Fig. 5. The 3D ordered interconnected macropores were generated from the PS spheres, and the matrix was composed of silica particles. After impregnation of divinylbenzene together with free-radical initiator (azobisisobutyronitrile) into voids of matrix followed by polymerization, carbonization, and HF etching, the ordered macro-/mesoporous carbon materials containing 330 nm of macropores and 10 nm of mesopores were obtained. The specific surface area of the ordered macro-/mesoporous carbons could be up to 465 m^2g^{-1} with the pore volume of 1.32 cm^3g^{-1}. Although the synthesis of hierarchical carbon materials is more complicated, time-consuming, and more expensive, the morphology can be easily tailored, especially compared with the traditionally nanocasting mesoporous carbons.

A one-pot synthesis of hierarchically ordered porous carbons with interconnected macropores and mesopores has also been proposed by an in situ self-assembly of colloidal polymer and silica spheres with sucrose as the carbon source (Zhang et al. 2010). Compared with the other techniques, this procedure is simple, environmentally friendly, and can be used for the mass production of hierarchically ordered porous carbon. Neither pre-synthesis of the macropore/mesopore or crystal templates nor additional infiltration is needed, and the self-assembly of polymer spheres into the crystal template as well as the infiltration can be completed in the same system. The sizes of macropores and mesopores can be independently tuned by simply selecting the sizes of polymer (280–475 nm) and silica spheres (9–50 nm), respectively.

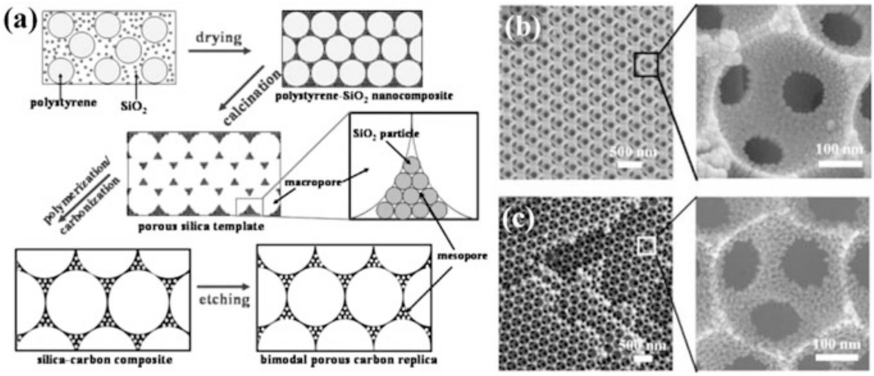

Fig. 5 **a** Schematic illustration of the synthesis of a periodically ordered macroporous carbon framework with mesoporous walls. SEM images at different magnifications of **b** the silica template composed of silica nanoparticles in the walls and macropores of about 330 nm, and **c** the resulting bimodal porous carbon replica composed of macropores of about 317 nm connecting with small mesopores of about 10 nm

3.2 Polymer Sphere/Triblock Copolymer for Ordered Porous

In addition to the inorganic SiO_2, organic polymers such as poly(methyl methacrylate) (PMMA) and polystyrene can be used as the templates for macropores. Wang et al. (2008) also found that hierarchically ordered macroporous polymer and carbon monoliths with walls containing face-centered cubic or 2D-hexagonal mesopores could be synthesized via a facile dual-templating technique using both PMMA colloidal crystals and amphiphilic triblock copolymer surfactants F127 as templates. A bimodal mesostructure could be conveniently controlled by the concentration ratio of F127 and phenolic resin. Starting from the PMMA templates, four processing stages including precursor infiltration, solvent removal, thermal curing, and carbonization were involved in preparing the bimodal porous carbon materials. A two-step thermal curing method was utilized to improve the robustness of the products. The growth of mesopores was significantly influenced by the confinement effect of the colloidal crystal template. Both spherical and cylindrical mesopores were aligned parallel to the surface of PMMA spheres. Therefore, the obtained mesostructures exhibited apparent curvatures near the surface of macropore walls. On the basis of nanoindentation measurements, it demonstrates that the carbon products were mechanically more stable than that of hierarchically porous carbon monoliths synthesized by nanocasting method, and the product with the cubic mesopore structure was even more stable than 3D-ordered macroporous carbon lacking of any templated mesopores in the wall skeleton. Compared with the conventional nanocasting strategies, this method avoids the use of hazardous hydrofluoric acid required to remove a silica template, and therefore the synthesis procedure is more environmentally benign.

3.3 Hierarchical Ordered Porous Structure from Biological Templates/Triblock Copolymer Templates

Compared with traditionally artificial templates, the attractive characteristics of biological templates are generally abundant, renewable, inexpensive, and environmentally benign. Biological templates are not only inherently hierarchical and complex, but also different from species to species, even within the same biology, making it possible that the obtained biomimetic materials have unique multilevel structures and morphologies (Zhou et al. 2011). Liu et al. (2010) have used a natural crab shell, which contains a number of relatively uniform ellipse-type macropores with dimensions of *ca.* 1×0.5 μm, as a confined space for Pluronic P123-templated self-assembly of phenolic resin. The obtained mesoporous carbon nanofiber arrays (MCNAs) retained an interpenetrated ordered array that was replicated from the crab shell hard template and all the carbon nanofibers were composed of ordered mesopores with close to 2D hexagonal structures. MCNAs contained three types of pores in the materials, namely, 11 nm mesopores originated from P123 templates, 70 nm void pores formed between the nanofibers, and 1 μm macropores between nanofiber arrays. The unique structure consisting of ordered mesopores, macroporous voids, and partially graphitic framework provides a more favorable path for electrolyte penetration and transportation, good electronic conductivity as well as a large specific surface area (1270 m^2g^{-1}) and more vacancies or defects in a graphite plane, which facilitates uniform distribution of metal nanoparticles and a synergistic effect between the nanoparticles and MCNAs for serving as a promising electrocatalytic support for Pt in direct methanol fuel cells.

4 Conclusion

The advantages of soft-templating strategy are that the templates can be of low cost, and the procedure is relatively easy and can be carried out under mild conditions, and various mesoporous structures are possible, depending on synthesis parameters such as mixing ratios, solvents, and temperatures. The self-assembly between templates and carbon precursor plays a key role in the success of soft-templating synthesis. In addition to the ability of self-assembly between templates and carbon precursors, two key requirements should be concerned: (1) the stability of the template that can sustain at the temperature required for polymerization of carbon precursor but will be readily decomposed during carbonization and (2) the ability of the carbon precursor to form a highly cross-linked polymeric material that can retain its porous structure during the removal of templates. At present, block copolymers are the dominant templates used in the soft-templating strategy for ordered mesoporous carbon. Pursuing the suitable templates for self-assembly holds promise for controlling the uniform mesopore size in the range of 2–50 nm as well as for diversification of soft-templated mesoporous carbons. Moreover, soft templating offers the chance to synthesize porous carbon materials with particular structures such as nanospheres, vesicles, and hierarchical structure, which are difficult to fabricate through the hard-templating method.

The success of the hard-templating method lies in its simplicity and fidelity in replicating the porous-structured templates. The corresponding microporous, mesoporous, and macroporous structures can be controlled by choosing inorganic solids such as zeolite, ordered mesoporous silicas, and colloidal silicas as hard templates. However, it is still complicated because several processes including the complete filling of pore in the template by liquid impregnation, carbonization in the template channels, and separation of the obtained carbon from template by costly chemical etching using dangerous reagents HF are essential. This is not desirable for a large-scale production of ordered porous carbon. In addition, the ordered structure in the carbon cannot be retained after removal of the template when the filling of carbon precursor is not enough. Furthermore, few undesired chemical reactions between silica templates and carbon occur during the carbonization at high temperature, such as the formation of SiC or SiOC. Besides the inorganic solids, some organic polymers such as PS and PMMA spheres have been used as hard templates for the synthesis of ordered macroporous carbons with pore sizes ranging from 50 nm to several hundred nanometers. These templates can be removed by dissolution with organic solvent or thermal decomposition along with the carbonization of carbon precursor.

Ultimately, the use of dual-templating strategies, which combine multiple hard- and soft-templating approaches, to synthesize three-dimensional hierarchically porous carbon materials with designed porosity on multiple length scales will be an impressively exciting research area in the near future, especially coupled with the nanotechnology.

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Nanotechnology Applied for Cellulase Improvements

Gustavo Molina, Gustavo Pagotto Borin, Franciele Maria Pelissari and Fabiano Jares Contesini

Abstract The biotechnological potential of cellulases has been demonstrated in various industrial segments including food, animal feed, pulp and paper, and several others. Among them, one of the most important applications of cellulases is the bioethanol production from lignocellulosic biomass. Despite the great potential of this enzyme in cellulosic biofuel production and also the interest in such products, expansion has been limited by relatively high production costs and other drawbacks. In this sense, several strategies have been proposed to overcome these obstacles and major challenges, such as the utilization of nanotechnology. This technique has raised the interest of research and can be considered a potential candidate to boost the biofuel refineries aimed at new developments in the area. In this approach, the main goal of this chapter is to conduct a broad and recent review of the potential of nanotechnology to improvements in cellulase production and hence to drive advances in the production of second-generation ethanol. The material will cover the main microbial sources used for the production of cellulases and their applications in different industrial segments. Finally, the applications of nanotechnology for cellulase improvements in bioprocesses will be addressed.

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1 Introduction

Human and industrial activities have been considerably intense over the years. Problems associated with the large-scale use of fossil fuels and oil reserves are in the fact that these resources are depleting very fastly, implying in serious future limitations. Besides that, they can also be considered as the major contributors for emission of harmful gases, with negative impacts in loss of biodiversity, climate change, rise in sea level, among others (Agarwal 2007).

In this perspective, considering the increased depletion of nonrenewable resources and also the greenhouse effect, bioconversion of renewable lignocellulosic materials into biofuel, biochemicals, and other value-added products is of great significance in replacing traditional fossil fuel (Sánchez and Cardona 2008; Han et al. 2017; Bischof et al. 2016; Kumar et al. 2016).

Lignocelluloses, composed of cellulose (ranging from 35 to 50%), hemicelluloses (25–30%) and lignin (from 25 to 30%) (Behera and Ray 2016), are one of the most worldwide available and renewable biomass resources, reaching the production rate of 200 billion tons biomass per year (El-Bakry et al. 2015). Among them, cellulose is a key structural component of plant cell walls and is the most abundant source of renewable carbon on Earth (Greene et al. 2015).

Several cellulosic biomass materials such as agricultural and forestry residues, agricultural by-products, and woody biomass are produced abundantly worldwide (Zhang et al. 2017) and arouse much interest for the future of the bioprocess industry. These materials are essentially potential raw materials for the production of fermentable sugars, which are fundamental for various industrial products such as biofuels, biodegradable plastics, biosurfactants, enzymes, etc. (Pandey et al. 2000).

Biofuels technology presents several advantages over the conventional petroleum fuels, such as a much more sustainable process chain, their biodegradable property besides being more environmental friendly (Gaurav et al. 2017). Thus, one important example is that the biological conversion of the stored potential energy in cellulose to biologically derived biofuels has gained much attention over the past few decades as the drive to shift human energy dependence from fossil fuels to renewable sources continues (Greene et al. 2015).

Ethanol production from lignocellulosic biomass is a complex process, however it can be briefly summarized in the main steps: pretreatment of lignocelluloses, hydrolysis of cellulose and hemicellulose, sugar fermentation, and distillation of ethanol (Sánchez and Cardona 2008). The economic feasibility of second-generation bioethanol relies mainly on the substrate and the enzymes which are the two major cost factors. In this way, it becomes essential to select a cheaper, abundant, and easily hydrolyzable material to be used as substrate, playing a critical role for an economical production of fermentable sugars (Gomes et al. 2016).

Similarly, the selection of an enzyme complex that displays satisfactory performance, capable of withstanding the process conditions, and presenting broad spectrum of activity and efficiency in the presence of lignocellulosic materials substrates is essential. In this context, the biological depolymerization of cellulose found in lignocellulosic biomass is primarily achieved from the action of synergistic cellulases (Greene et al. 2015), increasing considerably the potential of these enzymes.

Cellulase is a general term for cellulolytic enzymes (Kuhad et al. 2016) of which three classes are recognized on the basis of the mode of enzymatic actions and the substrate specificities: endoglucanases (EC3.2.1.4), exoglucanases (EC3.2.1.74 and EC3.2.1.91), and β-glucosidases (EC 3.2.1.21) (Molina et al. 2016). They are members of the glycoside hydrolase families of enzymes, according to the CAZy database (www.cazy.org), with the capability of hydrolyzing oligosaccharides and/or polysaccharides (Teeri 1997). Cellulases are capable of breaking down insoluble crystalline cellulose into soluble sugars that can then be fed to ethanologens to produce bioethanol or other engineered microorganisms to produce other fuel precursors (Wen et al. 2013).

Cellulases have been commercially available for more than 30 years for both research and industrial applications, and have demonstrated their biotechnological potential in various industries including food, animal feed, pulp and paper, brewing and winemaking industries, and also in agriculture, biomass refining, textile (Cherry and Fidantsef 2003; Ferreira et al. 2014), wastewater treatment (Fitzpatrick et al. 2010), and most importantly for bioethanol production from lignocellulosic biomass (Chapple et al. 2007).

Various methods have been reported for the cellulase-catalyzed hydrolysis of cellulose-producing biofuels (Singhvi et al. 2014). However, it is well known that to produce biofuels effectively, the key step is improving the efficiency of converting lignocellulose to fermentable sugars using cellulases (Sun and Cheng 2002). The performance of cellulase mixtures in biomass conversion processes depends on several of their properties including stability, product inhibition, specificity, synergism between different enzymes, productive binding to the cellulose, physical characteristics as well as the composition of cellulosic biomass (Heinzelman et al. 2009).

Despite the great potential of this enzyme group in cellulosic biofuel production and also the interest in such products, expansion has been limited by relatively high production costs (Cherry and Fidantsef 2003). This is linked to a series of process drawbacks, such as low enzymatic hydrolysis efficiency that is one of the main factors that restrict the industrialization of the second-generation bioethanol (Saini et al. 2016). Low rates of enzymatic hydrolysis efficiency were reported as one of the most critical issues due to the nonproductive adsorption of cellulase on the lignin in substrates (Lin et al. 2016; Saini et al. 2016), which decreased the effective concentration of cellulase in enzymatic hydrolysates (Cai et al. 2017).

Other important factors of bioalcohol production are related to the rate-limiting enzymatic saccharification step due to the challenges of degrading complex mixtures present in plant cell walls (Greene et al. 2015) and limited solubility of lignocellulose in traditional aqueous phase (Bose et al. 2010). Currently, the cellulose saccharification by cellulases remains costly, thus hindering the commercial bioethanol production process (Banerjee et al. 2010). Hence, bringing many challenges to understanding the overall process involving the use of this enzyme system (Kuhad et al. 2016).

Therefore, the enzymatic hydrolysis of the cellulose component has been acknowledged as one of the bottlenecks for the biorefinery of lignocellulosic biomass (Liu et al. 2013). This fact drives efforts in the research and development of numerous techniques to make improvements in the process.

In this sense, several strategies have been proposed to overcome these obstacles and major challenges, such as the enhancement of cellulase productivity that has been studied through strain modification and bioprocess improvement strategies (Kuhad et al. 2016). Aiming to reduce enzyme costs, cellulase recycling seemed as a promising strategy (Wang et al. 2016) and the use of low-cost substrates, such as sugar mixture (Li et al. 2016) and cornstarch hydrolysate (Zhang et al. 2017) were proposed. Several approaches were conducted for improvements in bioethanol production using cellulases, such as genetic engineering tools (Greene et al. 2015), new immobilization systems (Salem et al. 2016), application of ionic liquids (Xu et al. 2016b; Mihono et al. 2016) and modulation of cellulase activity by charged lipid bilayers (Mihono et al. 2016), and purification techniques (Yang et al. 2017). Process developments were studied by using solid-state fermentation (Ray and Behera 2017), use of nutrient limitations (Callow et al. 2016), repeated fed-batch fermentation (Han et al. 2017), and residues and by-products as alternative substrates (Gomes et al. 2016), among several others.

More recently, nanotechnology has been raised the interest of research and can be considered a potential candidate to boost the biofuel refineries aimed at new developments in the area. The use of nanotechnology has increased broadly over the last years in several areas of knowledge, including medicine, robotics, chemical engineering, biology, and advanced materials. In this context, some efforts have been made to combine nanotechnology with biomass degradation and second-generation ethanol (Chandel et al. 2015).

In this approach, the main goal of this chapter is to conduct a broad and recent review of the potential of nanotechnology for cellulase improvements and hence to drive advances in the production of second-generation ethanol. The material will cover the main microbial sources used for the production of cellulases and their applications in different industrial segments. Finally, the applications of nanotechnology for cellulases improvements in bioprocesses will be addressed.

2 Cellulase-Producing Microorganisms

Lignocellulosic material is the main component of plant cell walls and is found worldwide, mainly in the composition of several agro-industrial residues. Lignocellulose is generally composed of cellulose, hemicellulose, and lignin. Cellulose is the most abundant organic polymer on earth (Klemm et al. 2005) and is composed of linear chains of β (1 → 4) linked D-glucose units. These linear chains are compacted among each other through hydrogen bonds what results in the intense recalcitrance of this polymer in plant cell wall. In addition, cellulose is the most abundant component of lignocellulosic biomass and is considered the most interesting candidate for the substitution of either fossil fuels or oil refineries through the utilization biorefineries, due to its high abundance in agro-industrial residues.

Cellulose degradation is very interesting to produce high quantities of glucose that can be used for the production of second-generation ethanol through fermentation by yeasts, among other applications. One of the most efficient strategies for the hydrolysis of cellulose is by the action of enzymes produced by microorganisms known as degraders of lignocellulosic material. Cellulose is hydrolyzed by cellulases that correspond to a group of enzymes that act in different parts of cellulose cleaving β (1 → 4) bonds among glucoses. Cellulases are classified as endoglucanases (EC 3.2.1.4) that cleave random β (1 → 4) bonds of the amorphous region of cellulose, exoglucanases, or cellobiohydrolases (EC 3.2.1.91) that hydrolase (1 → 4)-beta-D-glucosidic linkages in cellulose, releasing cellobiose from the free chain ends. The cellobiose released is degraded into glucoses by the action of β-glucosidases (EC 3.2.1.21) (Segato et al. 2014).

Cellulolytic microorganisms share their ecological niche with other cellulolytic and non-cellulolytic fungi and bacteria. Interestingly, the degradation of lignocellulose is performed by different sets of microorganisms and enzymes, since cellulose is commonly coated by other polymers, such as lignin and hemicellulose, resulting in a great variation of structural and chemical arrangement and therefore recalcitrance. In nature, the degradation of cellulose results in the formation of cellobiose that is inhibitory to the cellulase system of fungi and bacteria. However, due to the presence of several other saccharolytic microorganisms, the excess of cellobiose is utilized, allowing the continuity of the degradation of cellulose. In return, these saccharolytic strains help to neutralize toxic effects of lignin-degrading fungi, as well as providing vitamins and other nutrients assimilated by cellulolytic strains. Therefore, the complex machinery of cellulase system and nature of enzymes have been coordinated by the evolution of these organisms (Bayer et al. 1994).

2.1 Bacteria as Producers of Cellulases

Both fungi and bacteria have been studied for cellulase production. Although, the former have been more studied, lately bacteria have received more attention due to their higher growth rate than fungi and the fact that they produce more complex and multi-enzymatic complexes (Sadhu and Maiti 2013). Several bacteria produce cellulases, including species from *Cellulomonas*, *Clostridium*, *Bacillus*, *Erwinia*, *Ruminococcus*, *Thermomonospora*, *Bacteriodes*, *Microbispora*, *Streptomyces*, and *Acetovibrio* (Bisaria 1991).

There are works focused on the optimization of the production of cellulases by bacteria. (Manfredi et al. 2016) studied the production of endoglucanases by the strain *Bacillus* sp. AR03 in the peptone-based broth supplemented with 10 g/L

CMC (carboxymethyl cellulose) and 10 g/L sucrose after 48 h cultivation at 30 °C reaching 3.12 ± 0.02 IU/mL of enzyme activity. In a study carried out by Sethi et al. (2013), three bacteria capable of producing cellulase were isolated from soil and identified as *Escherichia coli, Pseudomonas fluorescens*, *Serratia marcescens*, and *Bacillus subtilis*. The optimal conditions for cellulase production were found at 40 °C, pH 10, using glucose and ammonium sulfate as the carbon and nitrogen source, respectively. In addition, coconut cake induced cellulase production. The author observed that *Pseudomonas fluorescensis* was the best producer of cellulase among the other four strains.

In the early 1980s, a multifunctional, multienzyme complex, capable of solubilizing cellulose, called cellulosome, was discovered in the cellulolytic thermophilic anaerobe *Clostridium thermocellum* (Lamed et al. 1983; Bayer et al. 1983). This complex is produced by some anaerobic cellulolytic bacteria, since the energy level generated by anaerobic bacteria limits the production of enzymes. Cellulosomes are remarkably efficient, organized, cell surface enzymatic system (Bayer et al. 2004) that result in enzyme recycling and direct assimilation products. Moreover, this complex can have a better access to cellulose surface because it physically separates cellulose microfibrils (Resch et al. 2013; Ding et al. 2012).

Cellulosomes are composed of dockerin-containing enzymes or different types of ancillary protein, and cohesin-containing structural proteins, termed scaffoldins. These two main blocks are bound to each other since they are complementary modules. Interestingly, these multienzyme complexes can be released as cell-free cellulosomes or attached to the bacterial cell surface (Hamberg et al. 2014; Xu et al. 2016b).

Cellulosomes are produced by different anaerobic bacteria such as different species of *Clostridium* and *Ruminococcus* and *Acetivibrio cellulolyticus.* In addition, there are different types of enzymes in cellulosomes system depending on the bacterial producer, including cellulases, hemicellulases, and pectinases (Artzi et al. 2016).

2.2 Fungi as Producers of Cellulases

In nature, there are innumerous fungi capable of producing different lignocellulolytic enzymes, including species from ascomycetes (i.e., *Trichoderma reesei* and *Aspergillus niger*), basidiomycetes including white-rot fungi (i.e., *Phanerochaete chrysosporium*), brown-rot fungi (i.e., *Fomitopsis palustris*), and a few anaerobic species (i.e., *Orpinomyces* sp.) The last group corresponds to fungi found in gastrointestinal tracts of ruminant animals (Ljungdahl 2008; Kim et al. 2007).

Filamentous fungi are well-recognized decomposers in nature and present important role in the decomposition of lignocellulosic material. Among the most interesting fungi cellulase producers, one can cite species from *Aspergillus, Trichoderma, Penicillium* and *Schizophyllum* (Sternberg 1976; Duff and Murrayh 1996).

Taking into consideration the high costs of enzyme obtainment, different strategies have been applied to optimize cellulase production, including fermentation optimization and the use of molecular biological tools. The first focuses on the optimization of bioprocesses and includes the selection of the best media that can be used for submerged fermentation (SmF), or solid-state fermentation. In this context, the use of agro-industrial residues can be of great relevance, since they are low-cost and have high nutritional value. The composition of the cultivation medium, as well the fermentation condition, including temperature, pH and agitation must be optimized for a maximum cellulase production, using different techniques, for instance, response surface methodology. In the work of Pirota et al. (2016), the best conditions for the production of different cellulases, including endoglucanases and β-glucosidases were 28 °C, with an initial substrate moisture content of 70%, 80% of inlet air humidity and 20 $\mathrm{mL.min^{-1}}$ of airflow rate. Matkar et al. (2013) isolated and identified a strain of *Aspergillus sydowii*. The cellulase production was optimized showing that endoglucanase (1.32 IU/ml), exoglucanase (3.99 IU/ml), and β-glucosidase (cellobiase 9.24 IU/ml) were optimal on the 6th day under SmF using 10% (v/v) inoculum with 0.1% Tween-20 at 40 °C, pH 5.5, and 120 rpm. In addition, the best carbon source was lactose.

Besides the optimization of fermentation for protease production, there are several techniques of molecular biology applied to increase production of specific cellulases or cocktails. Ascomicetes are not only recognized as excellent cellulase producers but also efficient hosts for the secretion of heterologous proteins that can be native or engineered. They include *Aspergillus* species, such as *A. nidulans*, *A. oryzae*, and *A. niger*, and *T. reesei* (Zoglowek et al. 2015). These techniques include the use of constitutive promoters to improve enzyme secretion (Bando et al. 2011) and deletion of genes involved in different pathways (Schuster et al. 2012). Different strategies are also used like the work of Patyshakuliyeva et al. (2016) that applied adaptive evolution in *A. niger* generating a mutant that showed a five times higher production when compared to the parental strain. The authors observed that the expression of *noxR* gene was reduced in the mutant strain, what was proved after the obtainment of *noxR* knockout strains.

Secretomic analysis of both *T. reesei* and *A. niger* cultivated in sugarcane bagasse showed that, since 6 h of cultivation, these ascomicetes were capable of secreting enzymes involved with deconstruction of polysaccharides from sugarcane cell walls. Although *A. niger* produced more enzymes, quantitatively and qualitatively, both fungi secreted important cellulases, including cellobiohydrolases, endoglucanases, and β-glucosidases, as well as some other hemicellulases. In addition, the authors concluded that a combination of enzymes from both fungi could be interesting to increase saccharification processes (Borin et al. 2015).

Trichoderma reesei is probably the most important producer of cellulases being used for industrial production of cellulolytic cocktail. The strain *T. reesei* QM6a that has been engineered through classical mutagenesis for the last three decades resulted in the industrial strain *T. reesei* RUTC30 that has a massive capability in producing a combination of cellulases. This engineered strain showed a surprisingly high number of mutagenic events, leading to the loss of more than 100 kb of genomic DNA that was related to 43 genes that are involved in nuclear transport, secretion/vacuolar targeting, mRNA stability, metabolism, and transcription (Le Crom et al. 2009).

3 General Applications of Microbial Cellulasesin Industrial Sectors

Due to the enzymatic complexity of cellulases, these microbial enzymes can have a wide spectrum of application and have shown their biotechnological potential in several industrial processes (Kuhad et al. 2011; Cherry and Fidantsef 2003; Ferreira et al. 2014). Among them, the main industries that seek the use of cellulase enzyme complex are the food, detergents, and the pulp and paper industries. In order to extend the understanding of the potential of application of these enzymes, with exception of lignocellulose conversion and bioethanol, this chapter briefly presents more information on these processes.

3.1 Application of Microbial Cellulases in the Food Industry

In the food industry, clarification of fruit juices is one of the main focuses of enzyme application. The process of juice production results in the disruption of cell wall and the generation of insoluble particles that interfere with the final appearance of the juice. In this context, cellulases have been applied in combination with other enzymes, mainly pectinases and hemicellulases. It improves filtration, clarification, and stabilization of the juice (Kuhad et al. 2011). A study characterized and applied immobilized pectinases–cellulases for grape juice clarification. Enzymatic preparations were tested for turbidity reduction in grape juice, resulting in a decrease of 50% in 1 h (Magro et al. 2016). In a different work, the combination of xylanase, pectinase, and cellulase was studied for the clarification of pineapple juice, resulting in a 90.2% yield and 80.9% clarity (Pal and Khanum 2011).

Cellulases have also been studied for the extraction of different industrially relevant compounds. The extraction of water-soluble polysaccharides from pumpkin (*Cucurbita moschata*) has been investigated. The authors observed that optimal conditions of extraction were determined as 40 min, 55 °C, pH 4.5, and 4000 U/g of cellulose. After polysaccharide purification and pulverization, it had high antibacterial activity against *Escherichia coli, Bacillus subtilis,* and *Staphylococcus aureus* at the concentration of 100 mg/mL (Qian 2014). Cellulases have also been applied in the extraction of water-soluble fiber diary from apple pomace that presents functional properties. In comparison with other methods, cellulase presented the best results (Li et al. 2014).

Secoisolariciresinol, the main flax seed lignin, is converted into enterodiol by human intestinal microbiota. This compound is related with the reduction of mammary and prostatic tumors. The extraction of secoisolariciresinol from seed hulls and whole seeds of flax has been studied using an enzymatic step with cellulase R10 from *Trichoderma reesei*. The best conditions were found using 1 unit ml^{-1} of cellulase R10 in 0.1 M citrate–phosphate buffer pH 2.8 at 40 °C for 6 h (Renouard et al. 2010). On the other hand, pigments are important compounds that can also be extracted using cellulases. In the study of Zuorro et al. (2011), tomato skins were pretreated by a food-grade enzyme preparation with cellulolytic activities and pectinolytic and subjected to hexane extraction. An 8- to 18-fold increase in lycopene recovery was obtained when compared to the untreated plant material.

In wine and beer industry, cellulases are applied mainly in the maceration process for the extraction of relevant compounds that provide sensorial or functional properties for the product. In the work of Bautista-ortín and Jiménez-pascual (2013), the combination of cellulases and polygalacturonase was important to the degradation of seed cell walls, resulting in the diffusion of proanthocyanidins located in the peels and seeds of grapes. These compounds interfere with the astringency, bitterness and color stabilization of red wines. Regarding brewing, Sensidoni et al. (2011) investigated the addition of cellulases from *Aspergillus* spp. in beer production and observed that after the enzymatic treatment the levels of β-glucan, maltotriose and maltose were reduced, while the levels of glucose and fructose increased. Consequently, the flow rate during filtration increased to 21.97 L/h/m^2 compared to the non-treated beer (8.1 L/h/m^2) and resulted in better filtration.

3.2 Application of Microbial Cellulases in Detergent Industry

Besides, the industrial applications already mentioned of cellulases, these enzymes are also used in detergent formulations along with protease, lipase, and amylase enzymes. The most used cellulases for this application are cellobiohydrolase CBH1 and endoglucanase EGIII, being the filamentous fungi, *T. reesei, T. viride, T. harzianum,* and *A.niger* being some microbial sources of these enzymes. Cellulases from *Humicola insolens* and *H. grisea* var. *thermoidea* are also employed in washing powders and detergents because of their particular properties of being enzymes active under mild alkaline condition and at high temperatures. These cellulases are reported to improve the color brightness, dirt removal, and protuberances in cotton industries, making a step named biopolishing. Alkaline cellulase along with lipase and protease are able to remove the oil from interfiber space of clothes and enhance the cleaning potential of a detergent (Kuhad et al. 2011; Sukumaran et al. 2005; Kottwitz and Schambil 2005; Karmakar and Ray 2011; Gaubert et al. 2016). Nowadays, little is known about this subject and further studies are necessary aiming to investigate cellulases and their role on boosting the activity of detergents.

3.3 Application of Microbial Cellulases in the Pulp and Paper Industry

The interest in the application of cellulases in the pulp and paper industry has increased considerably during the last years (Kuhad et al. 2011), along with xylanase, laccase, and lipase that display important applications in this area (Demuner et al. 2011). In the process chain of the pulp and paper industry, cellulases can be employed in different segments including enhancement of drainage, deinking, and mainly in fiber modification (Tolan 2010; Kirk and Jeffries 1996).

Enzyme treatments improve drainage by removing the fines or peel off fibrils on the fiber surface and dissolved and colloidal substances, which often cause these problems in paper mills and impact on the production rate (Bhat 2000). Cellulases have also been reported to enhance the bleachability of softwood kraft pulp resulting in a final brightness grade comparable to that of xylanase treatment (Singh et al. 2007). It was shown that cellulases used alone or combined with xylanases are beneficial for deinking of different types of paper wastes (Singh et al. 2007). Mechanical pulping process can also be improved with cellulases and other enzymes providing energy savings which may vary from 20 to 40%, due to the lower energy input of these enzymes (Karmakar and Ray 2011).

Cost-effectiveness is essential for enzymatic treatment of dissolving pulp toward industrial application. In this perspective, the strategy of cellulase recycling with fresh cellulase addition was demonstrated. This technique resulted in decreasing the viscosity (470 mL/g) and increasing the Fock reactivity (80%) of the dissolving pulp. Thus, cellulase recycling should be considered as a promising strategy to reduce enzyme cost (Wang et al. 2016).

Besides that, cellulases can have several other applications in the pulp and paper industry, such as to reduce chlorine requirement, to improve fiber brightness and strength properties, and also can be used during the production of biodegradable cardboard, paper towels, and sanitary paper (Kuhad et al. 2011). Some other specific applications of cellulose in this industry were well reviewed in the literature conducted by Kirk and Jeffries (1996) and Bhat (2000), among others.

4 Nanotechnology and Cellulases for Bioethanol Production

The use of nanotechnology has increased broadly over the last years in several areas of knowledge, including medicine, robotics, chemical engineering, biology, and advanced materials. The miniaturization trend and the development of more precise equipment have allowed a great range of different applications for nanotechnology and attracted increasing attention due to the possibility of optimizing and improving the productivity of processes, such as nanoimmobilization of enzymes and development of nanomaterials of industrial interest (Mamalis 2007; Verma et al. 2016; Cipolatti et al. 2016). In this context, some efforts have been made to combine nanotechnology with biomass degradation and second-generation ethanol. Therefore, nanotechnology has been elected as a potential candidate to boost the biofuel refineries (Chandel et al. 2015).

Over the past years, the increasing global demand and dependence for fossil fuels has emerged as one of the main environmental concerns due to the emission of greenhouse\gases and the climate change associated and depletion of fossil fuels reserves (Goldemberg 2007; Banerjee et al. 2010). Thus, it is of paramount importance to replace the petroleum and other fossil fuels by biofuels produced from sustainable energy sources, such as the lignocellulosic feedstocks (agricultural residues and industrial wastes, for instance). Bioethanol is one of the promising alternatives among the biofuels to replace fossil fuels and it might be obtained through the fermentation of sugars released from vegetal cell wall degradation, conversely to the sugarcane sucrose and cornstarch used by the major producers United States and Brazil, respectively, for the production of first-generation ethanol (Jørgensen et al. 2007; Agbor et al. 2011; Kubicek and Kubicek 2016).

Lignocellulose is basically composed of three elements: cellulose, hemicellulose, and lignin. All these components are arranged in a robust and recalcitrant network that must be deconstructed in order to make sugar monomers available from lignocellulose to microbial fermentation and bioethanol production. Thus, briefly the lignocellulose requires physical/chemical pretreatments to have its backbone more accessible to the enzymes of the hydrolysis step. The list of enzymes used for lignocellulose deconstruction is vast, but the main ones are the cellulases cellobiohydrolases, endoglucanases, β-glucosidases and the hemicellulases xylanase, β-xylosidase, β-arabinofuranosidase, xyloglucanase, and esterases. Cellulases sources have been already discussed previously, and it is well known that filamentous fungi are superb producers and secretors of this type of enzyme in nature and their cellulases mixtures are employed in diverse commercial cocktails (Cannella and Jørgensen 2014; Van Den Brink and De Vries 2011; Kim et al. 2015). However, one of the major drawbacks of the bioethanol production still is the economic viability due to the high cost associated with enzyme production, purification, and concentration (Jönsson et al. 2013; Chandel and Singh 2011; Cannella and Jørgensen 2014). Therefore, one alternative to overcome this challenge is the reuse of the enzymes to hydrolyze the lignocellulose components by immobilization in nanomaterials.

Enzyme immobilization is an interesting method used to optimize industrial processes fixing a biocatalyst (an enzyme, for example) in a biocompatible and inert support (Romo-Sánchez et al. 2014). It offers several advantages compared to free biocatalyst, such as improvement of enzyme loading and activity, better thermal and pH stability, recovery of desired products with high purity degree, and biocatalyst reusability (Eş et al. 2015; Ansari and Husain 2012; Abraham et al. 2014a). Enzyme nanoimmobilization is a particular immobilization method that uses materials at nanoscale having higher surface area and superior physical properties (like strength, chemical reactivity, and conductivity) than conventional materials. These nanomaterials reduce the diffusion limitations, maximize the functional surface area to improve the enzyme loading, and provide a strong cross-linking immobilization through covalent bonds (Abraham et al. 2014a; Chandel et al. 2015). An improvement on the stability of proteins adsorbed onto nanomaterials in denaturing conditions was also observed (Dordick et al. 2012).

Several different nanostructures for immobilization, such as nanoparticles, nanofibres, nanopores, nanocomposites, nanotubes, nanorods, and nanosheet (Verma et al. 2013a, b, 2016) have been reported, however, the most used nanostructures related to lignocellulose hydrolysis and bioethanol production are magnetic (MNPs), gold, and silica nanoparticles (Table 1) (Dwevedi 2016; Verma et al. 2016). Adsorption and covalent binding were the attachment approach of most of them to immobilize cellulases and each method has cons and pros based on the enzymatic biocatalyst, nanomaterial, and substrate. Adsorption of cellulase is supported by van der Waals forces, hydrogen bonding, and hydrophobic interactions between the enzyme and the nanostructures. It presents lower costs and is relatively a nontoxic method. For covalent binding immobilization, the surface nanomaterials have to be modified, however, this attachment is the safest method to reduce protein desorption (Gokhale and Lee 2012).

Enzyme reusability is one of the key factors for industrial processes, because it has impact directly on the cost production of a desired product, making the production economically viable or not. Thus, it is necessary that the nanoimmobilized enzyme has an efficient recovery, does not suffer much leaching, and still retains high residual activities after several recycles and purification steps (Miletić et al. 2012). Among all the studies presented, it is quite difficult to compare the best results and nanoimmobilization methods because of the differences between the growth conditions, strains, and substrates used, and also due to different methodologies applied. However, it is worth to mention the interesting results obtained by Verma et al. (2013a, b). In this study, the authors immobilized a β-glicosidase from *A. niger* in iron oxide MNPs by covalent binding method. Using the synthetic substrate pNPG and a temperature of 60 °C, the nanoimmobilized enzyme retained more than 80% of its residual activity after eight recycles of 10 min each. Furthermore, immobilized β-glicosidase was able to hydrolyze more than 90% of cellobiose within 5 h incubation, while the free enzyme reached the same cellobiose conversion only after 16 h (Table 1) (Verma et al. 2013a, b).

Besides MNPs, silica nanoparticles have also been used for cellulase immobilization and ethanol production. Lupoi and collaborators adsorbed a cellulase from *T. viride* in 40 nm silica nanoparticles and observed a greater ethanol production (>10 mg ethanol) on simultaneous saccharification and fermentation (SSF) compared to free enzyme (4 mg ethanol) using a temperature of 35 °C, cellulose as substrate and a time incubation of 96 h. In addition, the cellulose conversion yielded 1.6 times more glucose by nanoimmobilized cellulase than free enzyme at pH 4.8 and 35 °C (Table 1) (Lupoi and Smith 2011).

Although there are various types of characterized nanoparticles and different attachment methods for nanoimmobilization, further efforts are needed to optimize the conditions of enzymatic hydrolysis and ethanol production yield in order to overcome the lignocellulose hydrolysis bottleneck using this approach.

Nanotechnology has also progressed on the discovery of new materials and methods. Qi and collaborators, for example, reported high glucose concentration from permeate after an enzymatic hydrolysate being filtrated on polyamide membranes (NF90 and NF270 from Dow Filmtec™). Steam exploded wheat straw

Table 1 Cellulase nanoimmobilization studies using different nanoparticles and substrates

Nanoparticles	Nanoparticles size	Cellulase and microbial source	Substrate	Optimum pH and temperature	Km, Vmax	Reusability (percentage relative to the original activity)	Reference
SiO2-coated Fe3O4	–	Commercial cellulase (Runyang Ltd Co., China)	CMC	–	–	77% after 7 cycles	Tao et al. (2016)
MNP	40 nm	β-glucosidase from *A. niger* (Sigma)	pNPG	6.0, 60 °C	4.3 mM, 0.89 U/mg	>80% after 8 cycles	Verma et al. (2013)
β-cyclodextrin-Fe3O4	6.2 and 4.5 nm	Cellulase from *A. niger* (Sigma)	Rice straw	–	–	44.15% after 16 cycles	Huang et al. (2015)
PMMA[a]-Fe3O4	150 nm	Endoglucanase from Thielavia terrestris (Cellusoft CR, Novozymes, Brazil)	CMC	5.0–6.0, 55–65 °C	–	69% after 8 cycles	Lima et al. (2016)
Silica modified gold	6.3–9.6 nm	Cellulase complex from T. reesei (Sigma, USA)	Waste bamboo chopsticks powder	8.0, 50 °C	–	>99% after 6 cycles	Cheng and Chang (2013)
Nanogold-coated PU[b]spheres	35 ± 7 Å[e]	Endoglucanase from *Fusarium* sp.	CMC	5.0, 70 °C	–	43% after 5 cycles	Phadtare et al. (2004)
MNP-PMAA[f]shellparticles	100 nm (MNP), 30 nm (PMAA[f])	Cellulase mixture from *T. reesei* (Celluclast 1.5 L, Novozymes)	Avicel	–	–	–	Kamat et al. (2016)

(continued)

Table 1 (continued)

Nanoparticles	Nanoparticles size	Cellulase and microbial source	Substrate	Optimum pH and temperature	Km, Vmax	Reusability (percentage relative to the original activity)	Reference
Sílica	40 nm	Cellulase from T. viride (Sigma)	Avicel	–	–	–	Lupoi and Smith (2011)
PMMA[a] core-shell	80–120 nm	Cellulase from *Aspergillus* sp. (Sigma)	CMC	7.0, 50 °C	–	–	Ho et al. (2008)
TiO2	<25 nm	Commercial cellulase (Sisco Research Labs)	CMC	–	3.35 mg, 4.02 µmol/min (physically immobilized); 0.67 mg, 2.68 µmol/min (covalently immobilized)	<10% after 5 cycles (physically immobilized); 60% after 5 cycles (covalently immobilized)	Ahmad and Sardar (2014)
PAA[c] polymer-silica	25 nm (PAA), 100 nm (silica)	Cellulase from *T. reesei*, β-glucosidase from *A. niger* (Novozymes)	Filter paper, solka-floc cellulose, cellobiose	–	–	–	Samaratunga et al. (2015)
PAA[c] polymer-silica	25 nm (PAA), 100 nm (silica)	Cellulase from *T. reesei*, β-glucosidase from *A. niger* (Novozymes)	Solka-floc cellulose, cellobiose	4.4, 50 °C	–	–	Samaratunga et al. (2015)

(continued)

Table 1 (continued)

Nanoparticles	Nanoparticles size	Cellulase and microbial source	Substrate	Optimum pH and temperature	Km, Vmax	Reusability (percentage relative to the original activity)	Reference
MAPS [d]covered enzyme particle	3 nm (polymer layer); 5–30 nm (polymer layer + enzyme)	Celluclast BG enzyme from *T. reesei* (Novozymes)	Filter paper	7.0–12.0, 70 °C	–	–	Hegedüs et al. (2012)
MNP-magnetosome system	75 nm	Endoglucanase and β-glucosidase from *C. thermocellum*	CMC	–	–	>70% after 5 cycles	Honda et al. (2015)
MNP	40 nm	Cellulase from *T. reesei* (Sigma)	CMC	4.0, 60 °C	2.6 mg/mL, 2.0 mg/mL/min	70% after 3 cycles	Abraham et al. (2014b)

[a]PMMA: poly(methyl methacrylate); [b]PU: polyurethane; [c]PAA: poly(acrylic acid); [d]MAPS: 3-(trimethoxysilyl) propyl methacrylate; [e]Gold nanoparticle diameter; [f]PMAA: Poly(methacrylic acid)

(SWES) was hydrolyzed by a commercial cellulase (Genencor Bio-Products) at 50 °C and then a nanofiltration step was used to recover the soluble sugars from the hydrolysis and the water for recycling. Thus, a glucose concentration of 110.2 and 70.6 g/L using the NF270 and NF90 was found, respectively, operated at 13.3 L/ m^2h, versus 30.2 g/L of glucose from the non-nanofiltrated hydrolysate. Along with this strategy, a previous filtration step was able to recover the cellulases from the hydrolysate to recycling, showing the feasibility of using this combination of filtration methods to improve the bioethanol production process (Qi et al. 2012).

Finally, Zhao and collaborators introduced a real-time assessment of morphological changes of cellulose promoted by a sodium chloride (NaCl) treatment using atomic force microscopy (AFM) imaging. Shortly, they fixed microcrystalline cellulose powder on a nanomechanical sensor named microcantilever, previously rinsed in a polyvinylamine (PVAM) solution and were monitoring the differences of cellulose roughness using an increasing NaCl concentration (0.1, 0.5 and 1 M). PVAM layer was used to improve the adhesion of the 10–20 nm cellulose layer and the microcantilever surface. The authors observed that 1 M of NaCl was enough to cellulose having 43% increase in roughness, what suggests the correlation between the bending of microcantilever and the morphological changes on the cellulose (Zhao et al. 2010). A few years later, the same leading researcher published a work showing that the addition of 0.15 μM of cellobiohydrolase CBH1 from *T. reesei* induced microcantilever bending and this change was related to cellulose deconstruction (Xi et al. 2013). Despite some efforts have been made, this field of nanotechnology has to be more explored in order to better understand the breakdown of cellulose at molecular level. This real-time technique could be improved to use other enzymes and substrates, broadening its applications. The combination of structural analysis of lignocellulose and the assessment of molecular changes is also a valuable tool to get insights of the cell wall recalcitrance and its deconstruction (Chandel et al. 2015).

5 Concluding Remarks

The wide complexity of cellulase system boosts their research and industrial potential. In this way, the understanding of its activity and its application in a suitable industrial process are essential for bioethanol production from lignocellulosic biomass. Despite the significance in substituting traditional fossil fuel and usual technologies, the ethanol production from lignocellulosic biomass is a complex process. This technology presents a massive potential for the future of the industry but has still faced several technological challenges that directly impact the adoption of an industrial scale.

Therefore, nanotechnology can be considered as a potential candidate to boost the biofuel refineries aimed at new developments in the area, offering new improvement with cellulases as a new technological tool. Some of the advances include efficient recovery of cellulase enzymatic complexes through nanoimmobilization and the cost reduction associated with their reuse. Nanotechnology has also progressed on the discovery of new materials and methods, opening up many future prospects in this area.

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Nanotechnology in Bioethanol/Biobutanol Production

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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.

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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)

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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

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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.

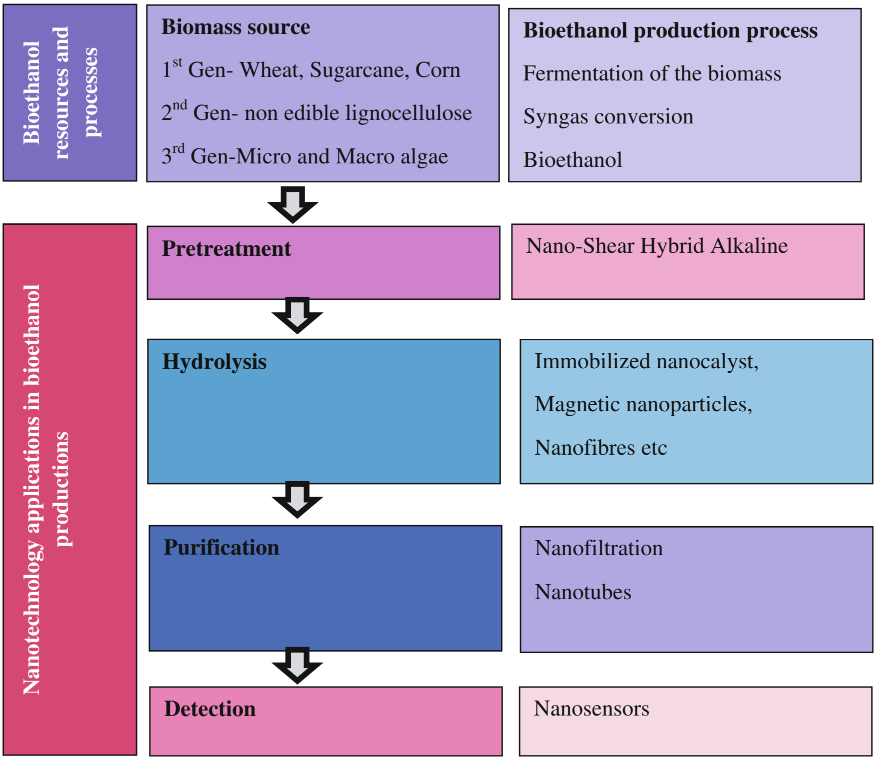

Fig. 1 An overview of various nanomaterials used in various process of bioethanol production

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Exploring Application of Nanoparticles in Production of Biodiesel

Sharad Kumar Tripathi, Rajesh Kumar, Shashi Kant Shukla, Afifa Qidwai and Anupam Dikshit

Abstract In spite of the limited sources of fossil fuels, energy demand has been considerably increased since the last century. The problems associated with global warming due to rising atmospheric greenhouse gas levels and scarcity of fossil fuels make it imperative to reduce our heavy dependency on fossil fuels. These reasons forced countries throughout the world to search for new fuel alternatives. Biofuel have gathered considerable attention due to their inherent benefits, like lower greenhouse gas emission, renewability, and sustainability. Commercially, biofuels are produced from vegetable oils, animal fats, and carbohydrates by using transesterification and fermentation. However, biofuel production suffers from high production costs and other technical barriers. Considering the environmental and economic issues, use of nanotechnology seems to be a viable solution. 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. To improve the biodiesel production rate nanocatalysts and nanomaterial bound microbial enzymes are used and on the other hand, several types and kinds of nanomaterial additives are used to increase the biogas production yield. On the basis of various review studied, it was found that the lipase enzyme from *Pseudomonas cepacia* were relatively more efficient in the production of biodiesel.

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1 Nanotechnology and Nanomaterials

Nanotechnology is a science of atomic-scale phenomenon and mostly deals with particles ranging from 100 to 0.1 nm. It has now become possible to handle individual atoms; pick them up or place them from one place to another. Nanoparticles now have endless uses and applications like manufacture of fogless car mirrors, fabric which does not absorb ink, nanojacket, nanosensors, carbon nanotubes, etc. (Fig. 1). This multidisciplinary scientific field involves creation and utilization of materials, devices, or systems which has enabled the development of an amazing variety of methods for fabricating nanoparticles in recent years.

Nanotechnology provides essential improvement potentials for the development of both conventional energy source (fossil and nuclear fuels) and renewable energy sources like geothermal energy, sun, wind, water, tides, or biomass. Nanocoated, wear-resistant drill probes, for example, allow the optimization of lifespan and efficiency of systems for the development of oil and natural gas deposits or geothermal energy and thus the saving of costs.

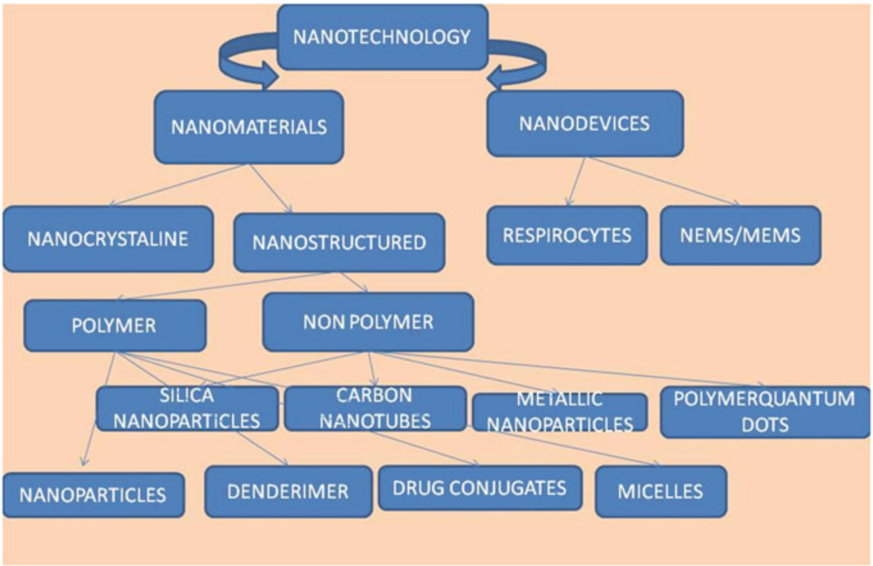

Fig. 1 Classification of nanoparticles

2 Need of Nanoscience for Energy

The worldwide energy demand is continuously growing and according to forecasts of international energy agency, it is expected to rise by approximately 50% until 2030. Currently, over 80% of the primary energy demand is covered by fossil fuels. Although their reserves will last for the next decades, they will not be able to cover the worldwide energy consumption in the long run. In view of possible climatic changes due to increase in the atmospheric CO_2 content as well as conceivable scarcity of fossil fuels, it becomes clear that future energy supply can only be guaranteed through increased use of renewable energy source. Nanotechnology as key and cross-sectional technologies exhibit the unique potential for decisive technological breakthroughs in the energy sector, thus making substantial contributions to sustainable energy supply. The range of possible nanoapplication in the energy sector comprises gradual short- and medium-term improvements for a more efficient use of conventional and renewable energy source as well as completely new long-term approaches for energy recovery and utilization.

A smart future of oil refining would be to increasingly utilize margins to finance a transition away from oil towards future alternative providers of mobility, in particular biofuels. Future scenarios of liquid biofuels involve the market penetration of second and further generations of technologies and the continuous improvement of first-generation processes. On the other hand, nanotechnologies are among the candidate technologies for the biofuels of the future. The nanotechnology field is vast and its applications unbound. This is followed by a brief review of nanotechnology developments, especially as they apply to liquid particles, beyond the more common solid particle applications. Algae growth, harvesting and conversion are presented and discussed, given the immense potential of their contribution towards an energy future where biofuels play a significant role. Most of the current effort in second-generation conversion to liquid biofuels is based on biomass cellulosics to ethanol and biodiesel. Likewise, the presently used processes to convert oils and animal fat into biodiesel are based on transesterification with methanol or ethanol, which inevitably generates glycerol, which must find a market or get disposed properly. Nanoprocesses may be useful in addressing this issue. Speculative considerations are made about the role of liquid nanoparticles of fuel additives in enhancing the performance of additized biofuel/fuel blends, in connection with surface and combustion effects.

Public concerns over the impacts of nanotechnologies on security, health and the environment are also mentioned and discussed. But a cautionary optimistic view is presented on the huge benefits of a careful penetration of nanotechnologies in the realm of biofuels and fuel additives, and in many more applications, especially those dealing with human health.

3 Why Biodiesel?

The enormous global daily consumption of liquid fuels is of the order of 80 million barrels/day (equivalent of 12.7 million m3/day). The sugar cane area required to produce the same volume of ethanol is about 700 million hectares, assuming a yield of 6.5 m3/ha/year of ethanol. This area is equivalent to 100 times the sugar cane cultivated area in Brazil, the second largest bioethanol producer in the world. Biofuels definitely face an issue of scale. In 2010, fuel ethanol and biodiesel combined displaced a mere 3% of oil in the world.

A bone of contention in the development of the biofuels industry is the present competition for feedstocks between the food and fuel industries. In the case of biodiesel, all commercial vegetable oils that are used in preparing food are also convertible to biodiesel. A similar situation exists with respect to fuel ethanol, especially for the starch-based feedstocks (corn and wheat). Since the cost of biofuels is dominated by feedstocks cost, access to feedstocks in the required amounts, timing and at adequate prices is key to the success of the biofuels economy. The combination of the food versus fuel conundrum with the need to have reliable and economic access to feedstocks is shifting the industry towards non-food feedstocks and to the market penetration of second-generation technologies to convert cellulosic biomass into liquid biofuels.

Concern in important consuming markets about the sustainability of biofuels producing systems is putting pressure on suppliers to abide by sustainability protocols subject to certification. The sustainability of biofuels is actually linked to freer international trade, which would tend to phase out unsustainably produced biofuels in favour of regions of the world that can meet sustainable production requirements. A valuable discussion on this matter was hosted by the Rockefeller Foundation in 2008 at its Bellagio Centre and produced a sustainable biofuels consensus. The objective was to understand the many drivers for sustainable trade, consumption and production of biofuels, and the comparative advantage of supplying regions combined with demand and technology from consuming regions.

4 History of Biodiesel

Biodiesel has been around for a very long time from 1900. Lin et al. (2011) described the study of various biodiesel productions and the experimentation of biodiesel in engine since 1893. In 1893, Rudolf Diesel for the first time used the peanut oil for running the diesel engine. Later in 1937, Chavanne, a Belgian scientist, found the concept of running the engine with vegetable oil called to be “Biodiesel”. However, it has not been widely used or widely manufactured till recent years. The reason that biodiesel cannot withstand long production run because Petroleum was cheaper and more widely available than biodiesel for many decades. However, the main problem of not using biodiesel commonly is the high

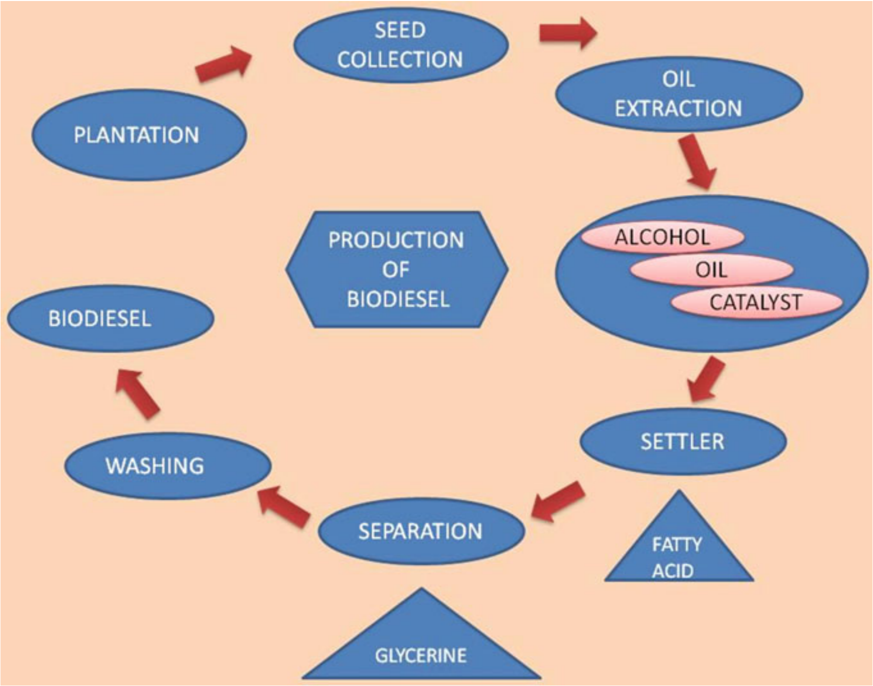

Fig. 2 Layout of biodiesel production

NOx emission. According to OECD-FAO agriculture outlook report 2011–2020, crude oil prices were assumed to increase in 2012 and continuous to show a rapid price rise by $107/barrel by 2020. The estimated biodiesel production is compared with the biodiesel trade around the world by 2020 as shown in Fig. 2. In order to go for a better alternative fuel and for replacing petroleum, many scientists have an eye on improving the qualities of biodiesel with some other blends and with nanoparticles to minimize the NOx (Prabu and Anand 2012).

5 Biodiesel from Butchery Waste Using Nanotechnology

Energy plays a pivotal role in socio-economic development by raising the standard of living. Biomass has been used as an energy source for thousands of years by humankind. In this study, solid fatty butchery waste of animal origin was converted into biofuels like biodiesel and hydrocarbons. Nickel is a widely distributed metal that is industrially applied in many forms. Evidence shows that Ni nanoparticle posses many new characteristics, which include a high level of surface energy, high magnetism, low melting point, high surface area and low burning point. Therefore, it can be widely used in the catalytic decomposition in modern industries. Pyrolysis is the thermal decomposition of solid biomass at high temperature and pressure (Navarro et al. 2009). The thermal decomposition produces hydrocarbons at 1000 °C and absence of air. The catalytic pyrolysis decreases reaction temperature up to 650 °C. The simplest type of decomposition is the fixed bed countercurrent decomposition. The major advantages of this type of decomposition are its simplicity, high charcoal burnout, and internal heat exchange that lead to low gas-exit temperatures and high decomposition efficiencies (Quaak et al. 1999).

6 Use of Biodiesel

Biodiesel can be used as a substitute for fossil fuels, and successful studies have been carried out in different applications. The advantages with biodiesel are lower bulk, higher energy density, as well as more transportable and storable capability. We used butchery waste for the production of hydrocarbon gases and biodiesel. For this purpose, we used nanocatalyst and anatase form of titanium dioxide photocatalyst at room temperature. In the first experiment, butchery waste was cracked into low melting point oil, solid residue, and hydrocarbon gases. In the second experiment, cracked oil was transesterified to biodiesel with NaOH at room temperature and atmospheric pressure. The results yielded best quality biodiesel. The economics of this novel process is much more cost competitive due to cheap raw material (butchery waste) that contains high levels of fatty acids. Photocatalysis gave hydrocarbons of prime importance. This study reports an interesting finding that butchery waste could be used for not only the production of biodiesel but also for hydrocarbons. This technology differs from others in that it uses low-energy input, cheap and reusable catalyst, with low sulphur and nitrogenous waste gases than petrodiesel and is environment-friendly.

Energy is a major need for the development of country, and the increase in population needs more energy for both economic and social development. The petroleum products and fossil fuels are a predominant source of energy but the scarcity of those items and the environmental pollution caused by petroleum fuels are the major uncertainties in the challenging world. Biodiesel is considered to be an alternative fuel to petroleum-based fuel resulting in numerous environmental, economic and social benefits. Biodiesel benefits include biodegradable, non-toxic, free from sulphur (<0.001%) and 60% less net carbon dioxide emissions. In addition, it has high flash point (greater than 160 °C) which helps biodiesel by transportation and storage. The important quality that biodiesel posses is that it decomposes more easily when they expose to environment and most importantly they can be produced easily compared to petrol and diesel. Another advantage of using biodiesel is that it eliminates the compound such as polycyclic aromatic hydrocarbons (PAH) and nitrated PAH that causes cancer in humans. The lubrication property of biodiesel dominates more when compared to the diesel fuel and increases the engine life. Biodiesel causes less emission of carbon dioxide (CO_2), hydrocarbon (HC) and particulate matter (PM), which are the dominant factors while compared with diesel. A long-run endurance test has been conducted by researchers around the world and proved that it can be easily used in compression ignition engines without any modification. The only drawback in the case of biodiesel such as NOx emission is to be reduced. Many researches are in process for reducing the NOx during and after the combustion process.

7 Biodiesel Cultivation, Harvesting Techniques

Biodiesel is produced by plantation of trees and shrubs such as *Jatropha*, *Pongamia*, Mahua, etc. The jatropha biodiesel has advantages of low fatty acid composition and the low phospholipids content. The cultivation and production of edible and non-edible plants depends on high oil yielding plant, saline soil, high yield of fruiting and fast growing plants. For harvestation, a plant seed with short gestation period has to be selected for production of biodiesel. For getting a high yield of oil, the seeds should be grinded properly after harvestation. Achten et al. (2010) carried out the life-cycle assessment of jatropha biodiesel in rural India. They highlighted the cultivation techniques of nursery practices such as polybag, water, fertilizer and harvestation techniques. The technique such as polybag, fertilizers, plantation and oil extraction is described briefly by Pandey et al. (2011). They experimented with jatropha biodiesel by polybag technique in which a black-coloured polyethylene bag containing equal quantity of humus, sand and soil weighing 10 g per bag is used. The mixer is well mixed and left for growing with seeds and cutting in the nursery. Later for 3 days, it is watered properly for obtaining good quality of about 70% germination seed rate. They carried out plant density of 2500 per hectare in which 25 kg of urea was used as fertilizer in the mixer. Irrigation was carried out with the pipe attached to water tankers. Weeding, pruning and harvesting were carried out after 3 months of grow. For oil extraction, process such as decortication, seed pressing, filtering and oil processing were carried out. The total energy utilized for the process from plantation to transesterification was 22 GJ for 4126.8 kg. Prueksakorn et al. (2010) compared jatropha oil production for both perennial and annual in Thailand. The perennial plantation (20 years) gives energy balance of 4720 GJ per hectare with net energy ratio of 6 which is focussed on biodiesel production only, whereas the annual plantation gives a net energy balance of 9860 GJ per hectare for a net energy ratio of 7.5 focussed on both wood and biodiesel production. So type of plantation has to be selected based on the energy and coproducts.

8 Biodiesel Production Techniques

The oil obtained by vegetables cannot be used directly to the engine due to high-density fatty ester, and it has to be converted into more compatible fuels for engines operation. Generally, biodiesel is produced by transesterification method. Transesterification is the process of converting vegetable oils into biodiesel, where the process involves triglyceride reaction with three molecules of alcohol in the presence of a catalyst, produces an end product of fatty acids and glycerol. The transesterification is carried out by new methods such as supercritical methanolysis, ultrasonically assisted transesterification and microwave oven-assisted transesterification. The process of supercritical methanolysis is carried out in a reactor with a blender, preheater, condenser and funnel. An electric thermostat is used to control the temperature of the reactor. Both water and vegetable oil are undergone hydrolysis in a reactor 1 and separated by water phase treatment and made to undergo esterification reaction in a reactor 2 where the methanol recovery is done along with separating biodiesel. Song et al. (2008) performed transesterification using supercritical methanolysis in palm oil. The experiments were conducted by varying temperature between 200 and 400 °C and the mole ratio of methanol to palm oil between 3 and 80 under operating reaction time of (0.5–20 min). Under 300 °C, fatty acid methyl ester (FAME) is affected by thermal decomposition, which was analysed by gas chromatography. They resulted that transesterification by supercritical methanolysis was optimum at 350 °C. Jachmanian et al. carried out experimental work in soybean oil by supercritical methanol and ethanol without catalyst. Water concentration of 0 and 10 wt% used for oil to alcohol ratio was 1:40 at 20 MPa, and the temperature was in the range of 250–350 °C. Among the two levels, 10 wt% concentration results in higher ester content and triacylglycerol depletion. The reacting condition of water level at 10 wt% increases the reaction rate and reduces the degradation of fatty acids in both methyl and ethyl ester content. The maximum yield of methyl ester and ethyl ester was obtained for a flow rate of 1.5 ml/min and 2 ml/min at 350 °C for 10% water, respectively.

Ultrasonication method is used to increase the reaction speed and conversion rate in the biodiesel production. This method works under pressure of 1–3 bar gauge pressure by a feed pump and an adjustable back-pressure valve. This process of producing biodiesel is costly because of its apparatus cost. Armenta et al. carried out transesterification in fish oil by ultrasonic energy method with KOH as catalyst at 0.5, 0.75 and 1% with respect to fish oil. Fish oil of approximately 0.05 mol (45 g) was taken in three 250 ml in Erlenmeyer flasks and sonicated for 30 min in case of both indirect and direct sonications at a frequency of 35 and 20 kHz for 20 °C. Later, 2% citric acid was added and mixed for 30 min to neutralize the catalyst. The mixture was allowed to get glycerol settled and washed with water to separate FAME.

Hydrogen Agilent 6890 GC System with a flame ionization detector (FID) and a FAME wax Column (Inner diameter of 0.32 mm, 30 m of length and a film thickness of 0.25 μm) was used for testing the transesterified samples (Shakinaz et al. 2010). Reported in detail about the production of biodiesel using microwave technique. They compared the yield of biodiesel with both microwave and catalyst techniques of biodiesel production. By this way of production of biodiesel by microwave technique, scientific microwave with advanced vessel technology was used. It contains a fast vessel in which heat is distributed among the oven homogeneously throughout the cavity. The microprocessor was used to control the microwave power output up to 1200 W. A pressure glass reactor measuring 500 ml flask and a reflux condenser was placed inside the oven. The oven is controlled by a colour touch screen controller for varying storage time, temperature and power. The oil was preheated to 65 °C using the microwave controller, and temperature was maintained at 65 °C. Then, mixture of alcohol and catalyst was then kept in the flask, and the mixture was irradiated under reflux for various reaction times as 1, 2, and 3 min. They compared the microwave technique of obtaining biodiesel with base-catalysed transesterification, and the biodiesel they used for comparison of the yield is jatropha biodiesel. They used methanol as alcohol and KOH as catalyst in two loading of 1 and 1.5 wt% KOH and three alcohols to oil molar ratios (4.5:1, 6:1 and 7.5:1). The result obtained in the yield % with that of reaction time given in the graph with highest yield of biodiesel up to 97.4% was obtained for 2 min reaction time. The maximum yield in case of methanol as alcohol and KOH as catalyst in two loading of 1 and 1.5 wt% KOH and three alcohols to oil molar ratios (4.5:1, 6:1 and 7.5:1) was carried out for 60 min but the maximum yield obtained in the microwave technique was 2 min; hence, the microwave technique of producing is much easier compared to the transesterification process.

9 Role of Nanoparticles in Biodiesel Production

Sadhik Basha and Anand (2011a, b, c) carried out the systematic experiment on performance and combustion characteristics of a diesel engine using alumina nanoparticle additive in water–diesel emulsion fuel diesel in a constant speed of 1500 rpm in single-cylinder CI engine. Two surfactants namely span 80 (Sorbitan monooleate) and Tween 80 (Polyoxyethylenesorbitanemonooeate) were used as bridging agent along with D2S5 W (93% diesel, 2% surfactants and 5% water), D2S5 W25Al (68% diesel, 2% surfactants and 5% water and 25% alumina nanoparticle), D2S5 W50Al (43% diesel, 2% surfactants and 5% water and 50% alumina nanoparticle) and neat diesel. The brake thermal efficiency obtained for alumina nanoparticle for D2S5W, D2S5W25Al, D2S5W50Al and neat biodiesel was 25.8%, 25.9%, 27.7% and 25.2%, respectively, and the NOx emission obtained for D2S5W, D2S5W25Al, D2S5W50Al and neat biodiesel was 1046, 1012, 978 and 1340 ppm. The maximum reduction of CO emission decreases at full load obtained for D2S5W50Al is 0.19% vol; similarly, for HC emission 76 ppm is obtained for D2S5W50Al. The same team (Sadhik Basha and Anand 2010) carried out the experiment with addition of nanoadditive in the range of 25, 50 and 100 ppm with jatropha biodiesel by 83%, 15% water and 2% surfactants such as span 80 and tween 80. They used alumina as nanoparticle in biodiesel. The same team (Sadhik Basha and Anand 2010) performed the experimental investigation of CNT (Carbon nanotubes) with diesel emulsion fuels. They carried out the experiments in three phases by the order of one by neat biodiesel, two by water diesel emulsion fuel and three by CNT blended with water diesel emulsion fuel. The emulsions they carried out for this experiment was Span 80 and Tween 80 in the mass fraction of 25 and 50 ppm. The advantage of using nanoparticle is that it enriches the surface area-to-volume ratio; results more fuel to get combustible easily. The research group (Sadhik Basha and Anand 2011b) extended the experimental investigation by carrying out alumina–CNT biodiesel fuels with 25 ppm CNT and alumina blended with jatropha biodiesel. This paper highlights the combined use of nanoparticle such as alumina and CNT at 25 ppm level which results in a good solution by both performance- and emission-wise. Selvan et al. (2009a, b) carried out the experimental investigation of using biodiesel as addictive in diesel and alcohol mixture under various compression ratios such as 15, 17 and 19. They carried out the experiment in a computerized single-cylinder DI variable compression ratio constant speed four-stroke CI engine. The lowest HC of 110 ppm obtained for D85E5B10 was at compression ratio of 19. The lowest NOx emission obtained at compression ratio of 19 for neat diesel was 250 ppm, whereas the lowest smoke absorption coefficient obtained for E25 blend at 15 as compression ratio was 2.1 m−1 K (Selvan et al. 2009b). They resulted in the lowest SFC of 0.33 kJ/kWh for neat diesel at the compression ratio of 19, and brake thermal efficiency was higher for compression ratio.

Sajith et al. (2010) carried out the experimental investigation using cerium oxide as nanoparticles in biodiesel. After the addition of nanoparticles in the biodiesel, there was no change in the cloud point and pour point of the modified biodiesel at 40 ppm dosing level. The engine performance increases brake thermal efficiency by 1.5% when the dosing level was between 20 and 80 ppm. 25–40% reduction in HC was obtained when the ppm range was between 40 and 80 ppm. The reduction of NOx by 30% was obtained for the dosing level of 80 ppm. Hadirahimi et al. (2009) carried out the environmental fuel additive for reducing the emissions and performance. They used diesetrol addictive with a combination of diesel fuel (D), biodiesel (B) and ethanol (E). They prepared bioethanol from waste potato in the vapour phase of 3A Zeolite and the biodiesel with sunflower biodiesel. The flash point was reduced by 16% with the addition of 3% bioethanol to diesel and sunflower methyl ester. The transesterification of sunflower oil was carried out with 1.8 g KOH and 33.5 cc methanol, and the yield percentage obtained was 80–85%. They classified the fuel blends of biodiesel with addictives at various levels of composition. CO emission decreases for various blends because of more oxygen concentration in the blends, and HC emission also decreases by 3% for bioethanol and 2% for sunflower methyl ester at 60 ppm. Qi et al. (2011) carried out experimental investigation to validate the effects of diethyl ether and ethanol as additives to biodiesel and on various diesel blends. Different blends such as B30 (30% biodiesel and 70% diesel in vol.), BE-1 (5% diethyl ether, 25% biodiesel and 70% diesel in vol.) and BE-2 (5% ethanol, 25% biodiesel and 70% diesel in vol.)

were used in a DI diesel engine. The result shows that the BSFC of B30 is slightly higher than that of BE-1 and equal to that of BE-2. They mentioned that due to the higher volatile character of diethyl ether and ethanol, the mixing velocity of air/fuel mixture improves both combustion and efficiency. The NOx concentration of blends increases due to its highest oxygen content in ethanol. The order of increase in NOx was BE1, BE30 and BE2. For CO emission, the BE30 is high when compared to the other blends. The characteristic curves are shown in Fig. 2.

10 Production of Biodiesel from Plants Biomass

Biodiesel production from plants particularly food crops is a utmost condition to explore the scale of the market value of biofuels globally. Among these, the inherent resistance of cellulosic feedstocks to conversion to simpler sugars that can be fermented into ethanol is prone to interest. Here, the promise lies in nanoparticles used as immobilizing beds for expensive enzymes that can be used over and over again to break down the long-chain cellulose polymers into simpler fermentable sugars as suggested by Sadhik Basha and Anand 2010. The attention is on non-edible cellulosic biomass, such as wood, grass, stalks, etc., to be converted into ethanol. The broader field of nanotechnology research into converting biomass into biofuels is growing fast.

Moreover, Berkeley had used nanotechnology in research for cost-effective solar panels. Another relevant application of nanotechnology is the use of nanocatalysts for the transesterification of fatty esters from vegetable oils or animal fats into biodiesel and glycerol. The nanocatalyst spheres replace the commonly used sodium methoxide (Selvan et al. 2009a, b). The spheres are loaded with acidic catalysts to react with the free fatty acids and basic catalysts to react with the oils. This approach eliminates several production steps of the conventional process, including acid neutralization, water washes and separations. All those steps dissolve the sodium methoxide catalyst so it cannot be used again. In contrast, the catalytic nanospheres can be recovered and recycled. The overall result is a cheaper, simpler and leaner process.

11 Conclusion

Overall, the process claiming for biodiesel production by nanotechnology would be economical, recyclable, to react at mild temperatures and pressures, with both low and high free fatty acid (FFA) feedstock, producing cleaner biodiesel and cleaner glycerol, greatly reducing water consumption and environmental contaminants, and can be used in existing facilities.

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