

**Clean Energy Production Technologies**  
*Series Editors:* Neha Srivastava · P. K. Mishra

Manish Srivastava  
Maqsood Ahmad Malik  
P. K. Mishra *Editors*

# Green Nano Solution for Bioenergy Production Enhancement

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## **Series Editors**

Neha Srivastava, Department of Chemical Engineering and Technology, IIT (BHU)  
Varanasi, Varanasi, Uttar Pradesh, India

P. K. Mishra, Department of Chemical Engineering and Technology, IIT (BHU)  
Varanasi, Varanasi, Uttar Pradesh, India

The consumption of fossil fuels has been continuously increasing around the globe and simultaneously becoming the primary cause of global warming as well as environmental pollution. Due to limited life span of fossil fuels and limited alternate energy options, energy crises is important concern faced by the world. Amidst these complex environmental and economic scenarios, renewable energy alternates such as biodiesel, hydrogen, wind, solar and bioenergy sources, which can produce energy with zero carbon residue are emerging as excellent clean energy source. For maximizing the efficiency and productivity of clean fuels via green & renewable methods, it's crucial to understand the configuration, sustainability and techno-economic feasibility of these promising energy alternates. The book series presents a comprehensive coverage combining the domains of exploring clean sources of energy and ensuring its production in an economical as well as ecologically feasible fashion. Series involves renowned experts and academicians as volume-editors and authors, from all the regions of the world. Series brings forth latest research, approaches and perspectives on clean energy production from both developed and developing parts of world under one umbrella. It is curated and developed by authoritative institutions and experts to serves global readership on this theme.

Manish Srivastava • Maqsood Ahmad Malik •  
P. K. Mishra  
Editors

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Springer

*Editors*

Manish Srivastava  
Dept of Chemical Engineering & Tech  
Banaras Hindu Univ, Indian Inst of Tech  
Lanka, Varanasi, Uttar Pradesh, India

Maqsood Ahmad Malik  
Department of Chemistry  
King Abdulaziz University  
Jeddah, Saudi Arabia

P. K. Mishra  
Dept of Chem Engineering and  
Technology  
Indian Institute of Technology BHU  
Varanasi, India

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# Chapter 1

## Biomass Based Materials for Green Route Production of Energy



Amit Kumar Tiwari, Nirupama, Amar Nath Mishra, Sunder Lal Pal,  
and Dan Bahadur Pal

**Abstract** To fulfil the energy requirement the exploitation of fossil fuels is now converted as a continuous process that has led to the uncontrolled depletion of our natural resources. In view of the loss of natural resources and their preservation, there is a necessity for the up-gradation and distension of renewable sources of energy presently. Furthermore, the negative effects of the exploitation of natural resources and fossil fuels on the change of climate and environment, global warming, as well as overall pollution, etc. should be studied and taken care of concomitantly. The availability of plenty of biomass materials from different sources and its wonderful possibilities as a renewable reserve makes it the best choice for the conversion, production, and storage of energy. Various methods such as gasification, pyrolysis, etc. are useful thermal treatments for the generation of materials such as biochar, bio-oil, syngas, etc. from the biomass, these products are the perfect sources of green and clean energy. In the trans-esterification process, pyrolysis and production of syngas, biochar is widely used as the main catalyst. Biochar-based other materials are also used in the technological manufacturing of batteries, fuel cells, and super-capacitors. Therefore, biomass and its derived materials can help us in the generation of power, conversion and its storage. The better use of biomass material would also help us in the reduction of environmental pollution global warming and reduced exploitation of natural resources, including secure sustainable development and energy security.

**Keywords** Carbon sequestration · Energy security · Global population · Global warming · Syngas · Technological manufacturing

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A. K. Tiwari · Nirupama · A. N. Mishra · D. B. Pal (✉)

Department of Chemical Engineering, Birla Institute of Technology, Ranchi, Jharkhand, India

S. L. Pal

Department of Chemical Engineering, Maulana Azad National Institute of Technology, Bhopal, Madhya Pradesh, India

## 1.1 Introduction

The continuous rise in the human population is a big challenge for natural resources, it is noticed that in the previous two centuries, it has been increased around seven times. According to Van Bavel (2013), in the year 2011, the total population was approx 7 billion (70,000 Lakhs) and it is expected it will add around 2 billion (20,000 Lakhs) more in the coming 25 years. This population growth has created an extra burden on the global environment. Natural resources suffering from a high level of unexpected stress and are also exploited in an improper manner. Therefore, the conservation and maintenance of these resources should be done on a priority basis; which is necessary for the sustenance of the life and planet (Cropper and Griffiths 1994). The continuous growth of the population is directly associated with industrial development and urbanization, due to these developments; the requirement of energy became a fundamental need of the society. Nowadays, over lifestyle is changed and even most of the peoples are the user of technology and modern equipment frequently; for which it is required to continuous production, storage, and distribution sufficient amount of energy to fulfil the energy requirement. According to Nakicenovic et al. (2007), the consumption of energy will increase by around 1.1% per year; by 2030, this consumption might be increase up to  $7.5 \times 10^{20}$  J. The huge demand, consumption, and requirements of energy are always responsible for the reduction of natural resources especially fossil fuels. Tergin (2006) also stated that the reduction in fossil fuel reserves (e.g. coal, oil, and gas) that are used for energy production, which is now a big challenge for energy security. In addition, when fossil fuels are burnt for different purposes they release a lot of harmful gases and unwanted particles in the air, which is responsible for generating air pollution and global warming due to which changes in climate can be noticed (Jain et al. 2019). Nowadays, the reduction of fossil fuels due to overutilization created the big problem of energy security which is directly associated with global geopolitical issues. Uncontrolled utilization of available fossil fuel reserves is responsible for the depletion and it is very important to reduce and preserve the depletion of fossil fuel resources. According to Lund (2007), proper utilization and preservation of these resources can help to develop a wide range of alternatives of environment-friendly and economical renewable energy. These alternatives are sunlight, air (wind), earth, water, and biomass, etc. Production of energy is not the only solution to the problem, we should also think about the storage of converted energy which will help us to improve the production, storage, and capability to produce and store energy. Liu et al. (2010) also suggested that a better result can be obtained by developing systems for the storage of energy from eco-friendly, economical, and efficient materials and distribute it so that it can be easily utilized for the said purpose. Biomass such as bio-oil, ash, and biochar, which are derived from carbon-rich materials, have huge potential for the production and storage of energy (Saleh et al. 2020). Various previous research reports are available on the generation and storage of energy that includes storage of hydrogen (Zhang et al. 2017), catalysts for the fuel cells, batteries electrodes, and super-capacitors

(Su et al. 2013). Apart from this, activated carbons carbon and nanotubes have also been found to be strong materials for the storage of energy. These materials are useful for the production of nanomaterials, also utilized in different applications in medical sciences (Zhang and Zhao 2009). The production of energy from these materials requires additional processes that require extra cost investments due to which it is not too much encouraged. McCarl et al. (2012) also suggested that the production cost of commercially produced activated carbons is six-time greater than the biochar. Similar kind of information provided by Ahmad et al. (2012), because the biochar production can be done at low temperature and it does not require an activation process; therefore, additional energy is not needed which help to reduce the cost of biochar production. These cost benefits associated with biochar production are good examples of economical production processes, which could help in sustainable process development. As suggested by Shaikh et al. (2020), biochar having few extra advantages such as non-carbonized fraction, high cation exchange capacity, etc., and these properties of biochar helping it in the removal of metallic and organic contaminants. Due to these properties biochar is found suitable for the elimination of metallic contaminants from the contaminated samples (Mondal et al. 2018). As per the suggestion of Bhattacharya et al. (2013), biochar could also be used for the treatment of polluted soil, water bodies, and groundwater. Apart from that, soil fertility can also be enhanced by the application of biochar because it acts as a microbial growth promoter and provides food and condition for multiplication of microbes in the soil (Pietikainen et al. 2000; Lehmann et al. 2011), it helps to increase the water retention capacity of the soils (Yu et al. 2013). Ventura and Yue suggesting that biochar helps to reduce the discharge of nutrients from the soil and enhancing the nutritional status. Therefore, on the basis of the above findings, we can say that biomass is an uncomplicated, economic, and environment-free stuff, which can give better options for energy security. Biochar is a product that is obtained from different biomasses such as wasted wood, agricultural and kitchen waste, sludge, and algal materials, etc. after passing it through a specific process known as “pyrolysis” and it is a highly porous and carbonaceous material, (Nautiyal et al. 2016), these biomasses are abundantly available in earth (Bar-On et al. 2018). Biomass having wide-ranging applications due to its different remarkable physio-chemical properties such as enhanced porosity, good surface area, high stability, appreciable water holding capacity, excellent carbon content, and cation exchange capacity (Zhang et al. 2013). According to Barkat et al. (2020), biochar having a good amount of nutritional components and has an alkaline nature. Nowadays biochar is more popularized for the treatment of polluted water and soil (Zhang et al. 2013), sequestering carbon substances (Manyà et al. 2018), production of energy (Titirici et al. 2012), waste treatment and management (Hossain 2016), and used as a material for the production of super-capacitors, batteries, and fuel cells in the energy sector (Cha et al. 2016). Presently, biotechnological research is also involved in energy production using the immobilization of enzymes (nanotechnology) that are too much costly activity which commonly used for biofuels production (Srivastava et al. 2019). Apart from that, several nano-biocatalysts such as nanofibers, nanoparticles, nanotubes, etc. have been shown the capacity to enhance

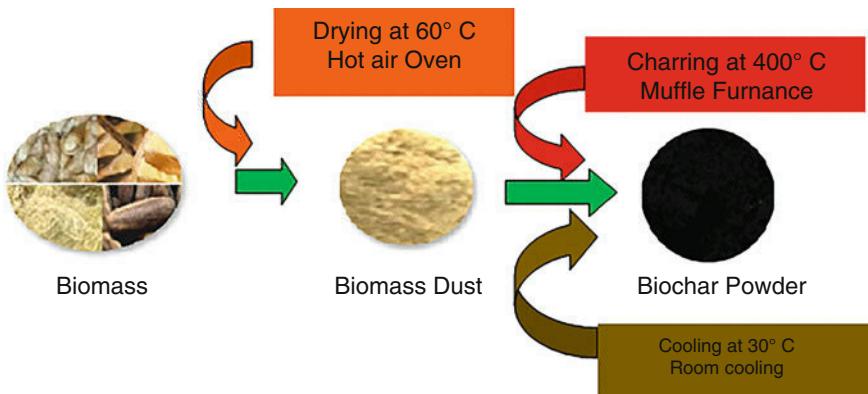
the production of biofuels. Therefore, it can be expressed that the biomass waste materials that could be utilized for the production of biochar can be applied for the production and storage of energy in the recent future.

## 1.2 Biomass and Bio-Energy Parameters

All kinds of agricultural wastes and kitchen wastes can be consumed for the preparation of biochar, syngas, and bio-oil which further helps in reducing impact on the environment by reducing landfill areas, enhancing sanitation, proper waste management, and achieving multiple sustainable developments. However, inconsistency, processing cost, and regulatory restriction limits its utilities (Kuppusamy et al. 2016; Tripathi et al. 2016). Agricultural bio-wastes considered as a pocket of solar energy; as these captures solar energy and consume CO<sub>2</sub>. During the photosynthesis, carbon atoms are produced and stored in it. Upon pyrolysis, these stored carbon releases energy (Lian et al. 2011). For proper utilization of biomass, it must contain moisture less than 30%, this may be obtained using natural or air drying (Bryden and Hagge 2003). Thermal processes such as tor-refraction (low temperature pyrolysis), carbonization, and hydrothermal carbonization: Heat treatment of wet biomass at elevated pressure and temperature), gasification, combustion (heating in the presence of oxygen, less efficient methods), and pyrolysis is being efficiently used to convert biomass materials into products such as biofuels, bio-energy, etc. With the gasification process syngas produces in abundance while produces lower quality biochar and bio-oil. On the basis of heating rate pyrolysis can be slow or fast process. Slow pyrolysis process produces more char while fast pyrolysis produces high yield of bio-oil. Other factors on which pyrolysis of biomass depends are vapour residence time, high surface area, particle size, porosity, ash content, and heating techniques such as heating by electricity or burning process (Asensio et al. 2013; Lee et al. 2017; Wang et al. 2018; Liao and Thomas 2019). The biomass for the generation of bio-energy has been shown in Fig. 1.1.

## 1.3 Steps and Parameters in Bio-Energy Production

Biomass availability and its renewability makes it a sustainable source for the production of the energy. It can be utilized to produce of gaseous, liquid, or solid fuel using various methods, e.g. thermal techniques (Bridgwater and Peacocke 2000). Quality of the energy produce can be affected by the properties of the biomass. These properties include its structural constituents, moisture content, decomposition temperature, etc. By using biomass for production of energy is pollution free and also reduction of CO<sub>2</sub> release into the atmosphere. Now the commercialization and automobile, a large amount of sulphur oxides, nitrogen oxides, and methane releases into the atmosphere can also be reduced with the



**Fig. 1.1** Thermal process: biomass to biochar

utilization biomass for energy production. This reduction of methane and sulphur and nitrogen release in atmosphere could help to reduce the cost of pollution abatement measures. In addition, this helps in the reduction of the greenhouse gases and temperature increase. Hence, the agricultural waste material based fuels would, gives several of repayment (Guruviah et al. 2019).

Now-a-days, biomass extensively used for the production of liquid fuel and syngas using pyrolysis techniques (Lehmann et al. 2006). Pyrolysis treatment with lower temperature, less vapour residence, and extended heating rate produces liquid fuel like ethanol. However, pyrolysis techniques with elevated temperature, extended gas residence, and slow rate of heating produces fuel in the form of gas which is known as syngas. This gas is a mixture of CO and H<sub>2</sub> along with trace of CH<sub>4</sub>, H<sub>2</sub>O, and CO<sub>2</sub>. In addition to bio-oil and syngas, pyrolysis of biomass also produces huge amounts of heat which could be utilized in number of purposes in the industries such as steam generation (Baker et al. 2013).

A wide variety of biomasses are available in abundance which may be a probable feedstock for the fabrication of biofuels. These biomasses include kitchen waste, municipal solid waste, and paper wastes (Berge et al. 2011). These materials are mainly composed of carbohydrates, proteins, lipids, cellulose, lignin, and hemicelluloses. Due to compositional difference in the biomass feedstock, produced bio-oil may have diverse constituents in different quantities. These constituents can be alcohols, acids, aldehydes, and derived products from the hemicellulose and lignin of the raw biomass. In comparison to remnant fuels, bio-oil is recognized as a green energy source due to negligible release of the SO<sub>2</sub> and NO<sub>2</sub>. Still, bio-oil utilization is lacking behind because of its change in physical and chemical parameters. Notwithstanding, there are a variety of technologies are developed for the production of biofuels and it is used which supported its utility in areas like transportation (Xiu and Shahbazi 2012).

Different steps are involved in the heat treatment of biomass; in the thermal processing of biomass, in the first step the conversion of biomass into gaseous form

is performed follow by a condensation process to convert gaseous into a liquid material i.e., oil. After passing the biomass form different stages, this bio-oil is used for the production of syngas. Viscosity of bio-oil is an important property which decides the flow-ability, the viscosity of bio-oil is generally depends on the type and properties of biomass, used and independent of the reactor type (Sundaram and Natarajan 2009). It is already reported that the biomass which is smaller in size is producing highly viscous fuel than the bigger size biomass (Park et al. 2004). Lu et al. (2008) stated that if the biomass is processed at low temperature, then the produced bio-oil will have more viscous. Compared to other process parameters, the heating rate has least effect on the viscosity of the oil during production. An electrostatic precipitation and condensation system was designed by Yin et al. (2013) to study the boosted heating rate and its effect on bio-oil production with no effect on the viscosity of the oil. The biomass which has high moisture content at initial stage of bio-oil production will produce bio-oil with elevated amount of moisture which is not a good characteristic of bio-oil (Wildschut et al. 2009). Therefore, it is required to eliminate the initial moisture from the waste material before further processing. The excess moisture can be removed by using various drying and dehydration processes such as sun-drying, hot air-oven drying, or air drying. pH of bio-oil is an important factor of quality of final product, the raising of pH can be minimized by the process of Dehydroxygenation can be done to increase the bio-oil quality (Guruiah et al. 2019). To enhance the production in prospect of efficiency and worth, chemical catalysts can be applied in the biofuels production process.

In the production of energy and conversion of biomass into economical useful products temperature plays an important role. Pyrolysis is a temperature based process by which we can convert biomass into different type of products such as biochar, syngas, and bio-oil, etc. from biomass materials. The conversion process or pyrolysis depending on different treatment factors such as heating temperature, heating rate, and vapour residence, etc. Different chemical and physico-chemical processes occur during pyrolysis of materials; these processes are decomposition of biomass, formation of new functional groups, volatilization and devolatilization, etc. Biochar production requires slow pyrolysis process; whereas for the production of gaseous product like syngas requires comparatively higher temperature (Goyal et al. 2008) and best quality biofuels may be formed by fast pyrolysis process. Process parameters like high temperature, extended time of vapour and reduced temperature are the more efficient factors for increased bio-oil yield (Onay and Kockar 2003). Another pyrolysis process (Flash-pyrolysis) yields highly viscous bio-oil which has properties that are very similar to commercially available diesel. Chemical catalysts can be used in pyrolysis process for the production of biofuels through fast heat exchange. In the production of energy and conversion of biomass into economical useful products temperature plays an important role. Pyrolysis is a temperature based process by which we can convert biomass into different type of products such as biochar, syngas, and bio-oil, etc. from biomass materials. The conversion process or pyrolysis depending on different treatment factors such as heating temperature, heating rate, and vapour residence, etc. Different chemical and physico-chemical

processes occur during pyrolysis of materials, these processes are decomposition of biomass, formation of new functional groups, volatilization chemical catalyst are required during thermal treatment of biomass materials because they plays an important role in the quality of obtained products and their formation. They also minimizing the solid product formation, due to which the maximum liquid and gaseous products can be achieved (Balat et al. 2009). Alkali metals, nickel-based catalysts are the widely used chemicals required for catalysing the gasification. Various nanocatalyst such as  $\text{CaO}$ ,  $\text{TiO}_2\text{-ZnO}$ , hydrotalcite, and  $\text{Cs/Al/Fe}_3\text{O}_4$  are been utilized in thermal treatment of biomass during production of bio-energy (Madhuviilakku and Piraman 2013).

## 1.4 Green Route for Energy Production

### 1.4.1 *Biomass for Energy Production*

The pyrolysis is the one of the best methods to extract useful energy from the waste biomass. Pyrolysis of biomass yields to provide various useful products such as energy rich bio-oil, syngas, and biochar. Biochar is a carbonaceous product which left behind after the pyrolysis process. Sometimes, energy released during pyrolysis of biomass is higher than the combustion process (Nanda et al. 2016). This is because efficiency of retaining the carbon in pyrolysis is very long. Peters et al. (2015) carried out life cycle assessment in order to define application of biochar for energy production. They observed that these biochar can be utilized in number of application such as adsorption of pollutants from soil and water enhancement, activated carbon for biomaterial production, and for sorption of toxins and drugs in pharmaceutical industry (Nanda et al. 2016). Biochar is also an important substitute for coal in power plant industries. This is because coal leads to the production of environmental pollutants during combustion as well as during its mining. Whereas utilization of biochar eliminates these problems. A good amount of gases like carbon monoxide and hydrogen and heat produced during the biochar formation, which are collected and used as fuel. Pyrolysis of biomass also decreases the release of air pollutants (Peters et al. 2015). In addition, biochar act as an admirable source of carbon sequestration. During pyrolysis of biomass, carbon content in it get stabilized. Carbon is dependent on to biochar. These biochar are highly stable with a mean residence time of about 1600 years (Singh et al. 2012). Liu et al. (2015) checked carbon contained in the biochar and found that yearly  $\text{CO}_2$  emissions is about 0.3 billion tons. Windeatt et al. (2014) reported carbon dioxide of about 0.50 billion tons could be sequestered every year if annually 339.4 tonnes of biochar is being produced.

The surplus porosity and high surface area of biochar helps to capture carbon dioxide using physisorption, surface functional groups interaction, formation of polar bond, and Van der Waals interaction (Creamer et al. 2014). By conversion to fuel this carbon dioxide can be utilized to exact energy. This carbon dioxide can be

used for conversion of various valuable products such as hydrocarbon, methanol, dimethyl ether, syngas, etc. (Centi and Perathoner 2009).

### ***1.4.2 Bio-catalyst for Energy***

Municipal waste biomass can be used for the generation of energy, i.e. biogas aerobically (Proll et al. 2007). Shen et al. (2015) reported anaerobic digestion of biomass generates mainly 50–70% methane and 30–50% carbon dioxide. In addition to methane and carbon dioxide it also generates significant quantity of NH<sub>3</sub>, H<sub>2</sub>S, N<sub>2</sub>, H<sub>2</sub>, and O<sub>2</sub>. However, excess NH<sub>3</sub> generation is problem (Mumme et al. 2014). Luo et al. (2014) reported that the anaerobic digestion if done in extremely acidic conditions, it will have antagonistic effects on the microbial community.

Biologically synthesized nanoparticles (NPs) show catalytic characteristics only due to the high surface area and volume. From leaf extract biomass for the production of palladium nanoparticles for the dye removal (Petla et al. 2012). The soluble bio-based products coated NPs efficiently adsorb dye from dye degradation. The outcome of pH on the dye degradation using NPs was also studied by conducting sorption experiments in the laboratories and it was observed and reported that at every increase in pH there was an increase in the % dye removal. In the soil, the use of biochar support microbial activity and reduces the generation of the NH<sub>3</sub> and CO<sub>2</sub> (Mumme et al. 2014). This is possible due to its alkaline nature. Also, alkaline metals such as K, Ca, and Mg helps to dissolve and improve biomass digestion (Shen et al. 2015). Shen et al. (2015) observed an increase in CH<sub>4</sub> generation, during anaerobic digestion of biochar. It was being noticed that during the anaerobic digestion CO<sub>2</sub> might be converted to bicarbonates and carbonates. This will further improve the digestion mechanism stability and maintains alkaline nature of the system (Stams and Plugge 2009). Luo et al. (2014) reported increased CH<sub>4</sub> production, because of high electrical conductivity of biochar, which accentuates interspecies electron transfer.

### ***1.4.3 Biomass for Trans-esterification***

In the recent years, production of biodiesel gained considerable attention. This is because of the utilization waste biomass which are non-toxic, eco-friendly, biodegradable and reduces CO<sub>2</sub> emissions (Shahzad et al. 2017). Trans-esterification process (involving chemical changes) can be accentuated by homogeneous or heterogeneous catalyst (Gardy et al. 2017). However, generally heterogeneous catalysts are preferred because they can be reused without neutralization, can be easily separated, low cost and non-polar nature favours (Li et al. 2014; Kastner et al. 2012). Heterogeneous catalysts are made through biochar sulphonation and are used for trans-esterification of fats (Dehkhoda et al. 2010). Sulphonated biochar can be

excellent catalyst for trans-esterification. Also, it improves biodiesel production. Feedstock which contain higher amount of free fatty acid like cooking oil can improves the biofuels fabrication (Li et al. 2014).

#### ***1.4.4 Bio-catalyst for Pyrolysis***

Plastics, which become the part of our live from small household thing to sophisticated equipment, are now made by the plastics. But these plastics have many disadvantages; one major disadvantage is that it takes millions of years for its degradation. Nowadays, only about 20% of the total plastic wastes are recycled (Miandad et al. 2017; Nizami et al. 2016). These plastic wastes can be used for the production energy using pyrolysis techniques as it contains carbon-hydrogen bonds (Miandad et al. 2016, 2019). Biochar can be used as catalysts which can helps to improve thermal process. Krerkkaiwan et al. (2015) reported that the biochar can be excellent catalyst for the degradation of the plastics in pyrolysis process. Biomass helps in degradation process due the occurrence of Si, Al, and aluminium-hydroxides in it. These biochars can also be utilized as a sorbent for the pollutant removal in the post-treatment process which helps in improving biofuels quality. During pyrolysis process, carcinogenic polycyclic aromatic hydrocarbons are produced such as polyethylene. These carcinogens can be removed by biochar sorbents (Budhwani 2015). Also, biochar is having porous structure and high surface area which aids in the polycyclic aromatic hydrocarbons elimination (Yargicoglu et al. 2015).

#### ***1.4.5 Biomass Gasification for Syngas***

Gasification of biochar is slower than the gasification of biomass. Biomass gasification continues with about 80% removal of mass, which is mainly due to the volatilization of the gases (Di Blasi 2008). CO<sub>2</sub> generated in the gasification acts as a gasifying agent. Furthermore, during biochar pyrolysis it produces tar which causes crack on the char. This crack might collect carbon causing slow gasification process (Nanda et al. 2016). Due to the presence of alkaline metals, the biochar reactivity improves during gasification process (Li et al. 2006). Alkaline metals such as Na, K, Ca, and Mg act as a catalyst in gasification process which causes either increase or decrease reactivity. Catalyst sorbs gasifying agents and increasing the active sites causing improvement in the gasification process. Another parameter that can affect the gasification process is the surface and structure variability (Asadullah et al. 2010). In the power plant, biochar is used as a gasifying agent which is a better substitute of coal. Gasification process if done without catalyst then produces loose biochar. Whereas, catalyst based gasification produce biochar with cross-linked structures (Li et al. 2006). During biochar gasification, it generates syngas, which

can be utilized in the production of hydrogen, alkane, and alcohol (Rostrup-Nielsen 2001). Biochar catalyst can also accelerate the production fuels (Huber et al. 2006).

#### **1.4.6 *Biomass Materials for Fuel Cells***

Biomass may be used in the fuel cell like PEMF cell, microbial fuel cells, and direct carbon fuel cells are very promising for the electrical energy production using  $H_2$  and  $CH_3OH$  (liang et al. 2013). In carbon fuel cells, biochar can be directly used (Jafri et al. 2018). Because biochar properly interact with the molten carbonate electrolyte, it will help in biochar diffusivity for the reaction. In biochar, carbon oxidizes to its oxides which initiates electron transports. Transportation of electrons helps in the electricity production. Biochar have high electrical conductivity which favours its utility in the fuel cells. Furthermore, biochar's disordered carbon structure improves the biochar reactivity (Cao et al. 2007). Although poor crystal structure of biochar inhibits the electrical conductivity and reactivity (Cherepy et al. 2005). Also, porosity and high surface area of biochar helps in improving reactivity and, thereby, improves fuel cell performance. Li et al. (2009) reported surface functional groups helps in chemisorbing oxygen molecules during fuel cell functioning which leads to the improvement in its performance. Li et al. (2006) reported the presence of magnesium oxides, calcium oxides, and iron oxides acts as a catalyst in the fuel cell, whereas aluminium oxides and silicon has an inhibitory effect. Thus, it is important to optimize the percentage of inorganic material and ash content in the biochar in order to better fuel cell efficiency. These MFCs are promising for non-chemical and sustainable technology. MFCs are the promising technology for the future and can be used in wastewater treatment, organic compound degradation, and bio-energy generation. In the recent years, when global warming and depletion of the fossil fuels increasing tremendously. These MFCs are also used in the power generation, bio-hydrogen production, water desalination processes, and other useful chemicals. MFCs transform pollutants and nutrients present in wastewater into electricity using microorganism (Liu et al. 2004). Energy generated by MFC is utilized for energy compensation during wastewater treatment. In MFC biomass is used as a cathodic catalyst due to its benefits such as good durability, low cost, and high reactivity. Huggins et al. (2014) found that the power generation by biochar addition is comparable to activated carbon. Other benefits of biochar which makes it preferable in MFCs are its high porosity and surplus surface functional groups. Doping with nitrogen and phosphorus to biochar will improve oxygen reduction catalysis. In the MFC for longer run, biochar cathode biofouling must be taken into consideration (Janicek et al. 2015). Biofilm growth that reduces biofouling and upsurge their operability must be disinfected.

### 1.4.7 *Biomass Derived Products for Batteries*

In the recent years, Li and Na ion batteries are extensively used due to its efficiency and high energy density (Bachman et al. 2016). Porous biochar with active functional groups and surface area may be utilized in the batteries. These biochar acts as ion diffuser, which helps to improve electrolyte interface, that are very important for the conquer electrochemical result (Wang et al. 2016). The storage capacity of the batteries can be improved by increasing biochar's porosity and surface area. Storage capacity can also be improved by the tuning the electrode conductivity. Nitrogen doped biochar improve the storage capacity by inserting chemically active defects, hence increases the active site as well as conductivity (Yan et al. 2017). The carbon's electro-negativity can also be improved by nitrogen doping, which helps in facilitating the more active sites for ion storage. It also helps in improving the electrochemical stability and electronic conductivity of the biochar. Highly porous biochar helps in promoting creditable cycle performance. Nitrogen doping also helps in reducing inner resistance and enhancing specific capacity of biochar. Cobalt oxides, iron oxides, and manganese oxides can be added in biochar so that it can be used as an anode electrode in batteries (Wang et al. 2015). Zhu and coauthors also showed the biochar can be able to summarize S and polysulphides in the Li-ion batteries that improves the battery stability by suppressing the active materials. However, biochar is not able to prevent polysulphides diffusion from the cathodes that causes adverse effects. Metal doping with cerium oxides, lanthanum oxides, and magnesium oxides on the biochar improves the cycling stability as well as ability of the batteries.

## 1.5 Advanced Technologies for Energy Production

Sun et al. (2018) prepared graphene nanosheet with 3D vertically aligned arrays using waste biomass. Nanosheet was prepared using hydrothermal carbonization technique followed by potassium hydroxide chemical activation to spruce bark. They found the 3D interconnected structures. These 3D structures have high surface area and pore volume. When these nanosheets are used in super-capacitors it found out with high capacitance and energy density. Using garlic skin, Zhang et al. (2018) synthesized 3D hierarchical porous graphitic carbon materials. Garlic skin first carbonized and then chemically activated with potassium hydroxide. When these nanosheets utilized for super-capacitors to observe with superior electrochemical properties. Microspores which developed in the material help in improving capacitance performance, reducing the offered resistance, and energy storage efficiency. Peng et al. (2018) synthesized hierarchical high capacitance 3D porous carbon material using *Moringa olifera* and suggested to use as electrode materials in super-capacitors. Zhou et al. (2016) synthesized graphitic carbon nanosheets using biomass waste (wheat stalk) and suggested to use these materials in Li-ion batteries to provide quick transport of Li ions and electrons. They employed hydrothermal

process followed by graphitization treatment for the synthesis of the material. Graphitization treatment helps to reduce the voltage hysteresis which shows a promising alternative for electrochemical storage. Yuan and coauthors also showed the carbon materials from peanut residue and suggested to use as anode materials to lithium-ion battery. They used carbonization along with chemical activation by potassium hydroxide. They observed graphene-like structures and high degree of graphitization in the developed material. This material revealed rapid transfer of electron and intercalation/deintercalation of lithium ions. Li et al. (2020) have done a comprehensive review on the porous material utilization with the special focus on the metal-organic for energy and storage, solar and electrochemical energy conversion, challenges, and opportunities for advanced energy technologies. Sun et al. (2020) also reviewed about the lithium-ion and lithium-ion batteries used for energy storage with special focus on electrode materials and electrolytes. Guo et al. (2020) prepared alloy-based catalysts with silicon oxide/nitrogen doped bamboo leaves material.

## 1.6 Summary

Increasing energy demand and fossil fuel depletion created a status quo of energy security, which must be taken care sustainably. Biomass waste which is available in abundance grasps huge potential for the energy production. Biomass is a renewable and sustainable source. Thermal techniques such as gasification and pyrolysis were used to extract energy from the biomass. There are various parameters such as pyrolysis temperature, biomass type, vapour residence time, and heating rate which must be optimized in order to get higher yield. Biomass have various advantages which includes high electrical conductivity, high porosity, large surface area, and low production cost makes which make it appropriate candidate for the energy conversion and storage devices. Furthermore, nanoparticles, hetero atoms, and metal oxides doping to biochar will improve its fitness in the energy conversion and storage devices. Biomass is also used as catalyst in various applications such as pyrolysis, energy production, and syngas generation.

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# Chapter 2

## Green Synthesized Bimetallic Nanomaterials for Bioenergy Applications



D. H. A. G. K. Perera, J. P. Usliyanage, U. A. D. Y. S. Perera,  
S. A. K. K. Samaraweera, and G. Thiripuranathar

**Abstract** A novel class of materials, “bimetallic nanoparticles” (BNPs), for catalysis have intensively investigated by integrating two different metals, which offer synergistic or novel features surpassing that of monometallic nanoparticles (MNPs). The green route of synthesizing BNPs is attracted immensely as a substitute to vanquish the drawbacks in conventional physical and chemical routes as the green route appears eco-friendly, inexpensive, and less time-consuming to synthesize. Among them, employing plants toward the synthesis of BNPs is emerging as advantageous compared to microbes. The application of BNPs as catalysts is a widespread, providential area considering their larger surface area, and thus utilizing the catalytic properties in altering the biomass into biofuel is a potential area to achieve maximum economic and environmental benefits. Hence, this chapter is a comprehensive contribution of the green synthesis of BNPs, the parameters that affect the synthesis of BNPs, characterization, practical applicability, and their application in bioenergy production.

**Keywords** Green synthesis · Bimetallic nanoparticles · Phytochemicals · Microbes · Catalyst · Bioenergy

### Abbreviations

Ag	Silver
Al	Aluminum
Al <sub>2</sub> O <sub>3</sub>	Aluminum oxide
As	Arsenic
ATP	Adenosine triphosphate
Au	Gold

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D. H. A. G. K. Perera · J. P. Usliyanage · U. A. D. Y. S. Perera · S. A. K. K. Samaraweera · G. Thiripuranathar (✉)  
College of Chemical Sciences, Institute of Chemistry Ceylon, Welikada, Rajagiriya, Sri Lanka  
e-mail: [tgobika@ichemc.edu.lk](mailto:tgobika@ichemc.edu.lk)

Bi	Bismuth
BNCs	Bimetallic nanocomposites
BNMs	Bimetallic nanomaterials
BNPs	Bimetallic nanoparticles
C	Carbon
Cd	Cadmium
Ce	Cerium
CeO <sub>2</sub>	Cerium oxide
CH <sub>4</sub>	Methane
Co	Cobalt
CO <sub>2</sub>	Carbon dioxide
Cu	Copper
Cu(OH) <sub>2</sub>	Copper(II) hydroxide
Cu <sub>2</sub> O	Copper(I) oxide
CuO	Copper(II) oxide
DLS	Dynamic light scattering
DMF	2, 5-Dimethylfuran
DNA	Deoxyribonucleic acid
EDS	Energy dispersive X-ray spectroscopy
Fe	Iron
FTIR	Fourier-transform infrared spectroscopy
H <sub>2</sub>	Hydrogen
HMF	5-hydroxymethylfurfural
HRTEM	High-resolution transmission electron microscopy
Ir	Iridium
La <sub>2</sub> O <sub>3</sub>	Lanthanum oxide
MALDI-TOF	Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
MDT	Magnetic drug targeting
MFH	Magnetic fluid hyperthermia
Mg	Magnesium
MNNMs	Monometallic nanomaterials
MRI	Magnetic resonance imaging
Ni	Nickel
NMR	Nuclear magnetic resonance spectroscopy
NMs	Nanomaterials
NPs	Nanoparticles
Pb	Lead
Pd	Palladium
PDI	Polydispersity index
PET	Positron emission tomography
Pt	Platinum
Pt(acac) <sub>2</sub>	Platinum(II) acetylacetone
Ru	Ruthenium

SEM	Scanning electron microscopy
SERS	Surface-enhanced Raman spectroscopy
Si	Silicon
SiO <sub>2</sub>	Silicon dioxide
Sn	Tin
SPR	Surface plasmon resonance
STEM	Scanning transmission electron microscope
TEM	Transmission electron microscopy
TGA	Thermo gravimetric analysis
TiO <sub>2</sub>	Titanium dioxide
UV	Ultraviolet
UV-Vis	Ultraviolet-visible spectroscopy
VA	Vinyl acetate
XAS	X-Ray absorption spectroscopy
XCT	X-Ray computed tomography
XPS	X-Ray photoelectron spectroscopy
XRD	X-Ray diffraction
Zn	Zinc
ZrO <sub>2</sub>	Zirconium dioxide

## 2.1 Introduction

Nanotechnology has existed since the dawn of time, and has constantly been utilized by nature to produce molecular assemblies in the body, such as lipids, proteins, carbohydrates, and enzymes. However, the formal discovery of nanotechnology is largely credited to Dr. Richard Phillips Feynman, an American physicist, and Nobel Laureate (Subramani et al. 2019; Toumey 2009). Nanotechnology is the reconstruction of matter at the molecular and atomic levels, within the 1–100 nm size range (Subramani et al. 2019; Bhushan 2016). At the nanoscale, the matter has distinct properties than the matter at a larger scale, hence the principles of quantum chemistry nor classical physics hold true in this nanoscale domain (Klabunde 2001). When a material's dimensions are reduced from the usual large scale, the characteristic properties remain constant initially, however, minor changes occur gradually, and finally, substantial changes occur in the characteristics properties as the size of the particle becomes less than 100 nm (Bhushan 2016). Nanometer-sized particles display peculiar features allowing nanotechnology to pervade essentially every industry and aspect of our lives, serving as the foundation for incredibly effective and affordable computers, novel technologies for diagnostic and therapeutic purposes that could help humans live longer and healthier (Taraifdar et al. 2013; Iqbal et al. 2012). The present nanotechnology research can be classified into three comprehensive categories: nanotools, nanomaterials (NMs), and nanodevices (Iqbal et al. 2012).