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

Manish Srivastava
Neha Srivastava
Rajeev Singh *Editors*

Bioenergy Research: Biomass Waste to Energy

Springer

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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.

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

Rajeev Singh
Department of Environmental Studies,
Satyawati College
University of Delhi
Delhi, India

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Foreword

A powerful and sustainable alternate fuel option is mandatory to protect the environment from the harmful impact of fossil fuel as well as the society from its crises. Bioenergy is the most sustainable, renewable, and green option to overcome the adverse effects of fossil fuels. Though there are some tremendous and potential bioenergy options to replace fossil fuels for a long term period, but due to limited research and limitations in practical goals, it is not opted commercially at a global scale. These re bioenergy options include bioethanol, biodiesel, biogas, bio-methane and biohydrogen, biobutanol, biomethanol and algal biofuels which have tremendous potential, but roadmap of these biofuels are still needs rigors improvement for commercial implication of these bioenergy options.

Publication of the book entitled "Bioenergy Research: Biomass Waste to Energy" is one of the efforts by the editors of the book to enhance the quality and sustainability of bioenergy options. This book *discusses more common and close to commercialization issues and options related to* bioenergy production technologies. This book is discussed about, how far this bioenergy options are which are close to commercialization in present scenario.

I am completely satisfied while writing this message and want to congratulate editors of this book as efforts of this book is put a milestone for the researchers, academician and industries working in this area. The book has kept 10 potential and well-explained chapters along with possible sustainable solutions to vanish the existing technical hurdles. Additionally, this book also covers recent insight in the research of various existing potential bioenergy options from their basic to future prospects only in terms of improving this option at commercial scale. The book will be definitely an asset for the people involved in academic, research, and industries.

I appreciate the efforts of *Dr. Manish Srivastava, Dr. Neha Srivastava,* and *Dr. Rajeev Singh* for bringing out this book entitled "Bioenergy Research: Biomass Waste to Energy".

College of Natural Resources and Environment,
Northwest A&F University
Yangling, Shaanxi, China

Mukesh Kumar Awasthi

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Contents

About the Editors

Manish Srivastava is currently working as SERB-Research Scientist in the Department of Chemical Engineering and Technology, IIT (BHU), Varanasi, India. He has worked as DST INSPIRE faculty in the Department of Physics and Astrophysics, University of Delhi, India. He has published over 50 research articles in peer-reviewed journals, edited 10 books for publishers of international renown, authored several book chapters, and filed one patent. He received his PhD in physics from the Motilal Nehru National Institute of Technology, Allahabad, India. Presently, he is working on the synthesis of graphene-based metal oxide hybrids and their applications as catalysts. His areas of interest are synthesis of nanostructured materials and their applications as catalyst for the development of electrode materials in energy storage, biosensors, and biofuels production.

Neha Srivastava has received PhD in biotechnology from Department of Molecular and Cellular Engineering, SHIATS, India in the area of bioenergy. She is working as Research Scientist, Department of Chemical Engineering and Technology, IIT (BHU) Varanasi, India. She has published more than 37 research articles in peer-reviewed journals of SCI impact factor and has filed 3 patents, 1 technology transfer, and 14 published books and two book series of international renowned publisher. She is working on bioprocess technology and biofuels production (microbial screening and enzymes, production and enhancement, biohydrogen production from waste biomass, bioethanol production).

Rajeev Singh is Head, Department of Environmental Studies, Satyawati College, University of Delhi. He is working in the area of environmental and reproductive health. He is founder secretary of Bioelectromagnetics Society of India. He is recipient of Young Scientist Award of Federation of European Microbiological Societies (FEMS), Gold Medal for best oral presentation, etc. He is member of Faculty of Science, Delhi University, and Expert, Board of Studies, Amity Institute of Environmental Science. He has participated in several national and international conferences and delivered invited lectures. He has published more than 60 research papers, chapters in books, and conference proceedings of international repute.

Advancements in Biofuel Production

1

Javaria Bakhtawar, Hira Arshad, Sobia Faiz, Muhammad Irfan,
Hafiz Abdullah Shakir, Muhammad Khan, Shaukat Ali,
Shagufta Saeed, Tahir Mehmood, and Marcelo Franco

Abstract

Due to environmental effects, health concerns, and global warming, utilization of fossil fuels has become unsustainable day by day. Biofuels are promising alternatives to fossil fuels to attain sustainable energy and to resolve the problems caused by fossil fuels. Certain advances are needed for significant production of biofuel to meet its future requirement. Co-culturing of cellulolytic microbes, genome shuffling, and microbial consortia construction are being used to obtain biofuel from renewable resources. Directional heredity rebuilding for microorganisms is also being applied for the cultivation of better and valuable strains for significant hydrogen production. A broad range of chemical or biological additives are being used to enhance biogas production. Advanced separation techniques are also being applied for in situ continuous recovery. Biofuel advanced technologies are the conversion methods which are still under examination and development.

J. Bakhtawar · H. Arshad · S. Faiz · M. Irfan (✉)
Department of Biotechnology, University of Sargodha, Sargodha, Pakistan
e-mail: irfan.ashraf@uos.edu.pk

H. A. Shakir · M. Khan
Department of Zoology, University of the Punjab new campus, Lahore, Pakistan

S. Ali
Department of Zoology, Government College University, Lahore, Pakistan

S. Saeed · T. Mehmood
Institute of Biochemistry and Biotechnology, University of Veterinary and Animal Science, Lahore, Pakistan

M. Franco
Department of Exact Sciences and Technology, State University of Santa Cruz (UESC), Ilhéus, Brazil

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Keywords

Global warming · Biofuels · Co-culturing · Genome shuffling · Microbial consortia · Additives

1.1 Introduction

The industrialization and the growing global population are accelerating energy requirements in the world that have led to many problems, including contamination of the atmosphere, fossil fuels exhaustion, and lack of electric energy supplies which must be accommodated and properly resolved. The first priority is to restrain the atmosphere and discourage toxic chemicals from being used for the manufacture of gasoline. So ecofriendly measures are appropriate to meet energy requirements and to effectively address these problems to achieve a sustainable competitive advantage. In fact, such problems have often benefited from the production and full utilization of renewable resources, especially biomass (Uzoejinwa et al. 2018).

The methods for enhancing the production of renewable, safe, and efficient fossil fuel sources of energy depends on the fluctuations of world oil markets, protection of energy supplies, global climate change and the emergence of new agricultural possibilities. These are the key drivers of biofuel production, which have emerged as one of the main encouraging alternative resources, and these factors establish a proper a renewable resource network (Chu et al. 2007; Nogueira 2011). Biofuel history started in 1970 when Austria studied about biodiesel in 1970 and used rapeseed oil for annual 500 ton of biodiesel production (Du et al. 2016; Paul et al. 2020). Biofuels, along with the biodegradable materials, are considered to have diverse benefits: no carbon dioxide (CO_2) effluents have been seen in the surrounding environment; during processing, less harmful composites are emitted into atmosphere; further, animals and plants that generate biomass then consume much of the emitted CO_2 (Voloshin et al. 2019; Surriya et al. 2015; Razzak et al. 2013). Global energy supply percentage in 2017 can be seen in Fig. 1.1.

1.2 Environmental Effects of Fossil Fuels

Fossil fuels are the main power generating systems in many countries (Caetano et al. 2017; Sugiawan and Managi 2019). Although it has many attributes, such as strong thermal management processes, their utilization has various issues. Several studies have investigated and discussed those issues (Pillot et al. 2019; Savvidis et al. 2019). These concerns, including the impacts on the atmosphere, production cost, dearth and price fluctuations, placed nonrenewable energy sources at the focal point of the development toward sustainable energy economies. It has been noticed that there is a close association among air contamination, energy utilization, water availability, and greenhouse gas emission (Khan et al. 2016). The consumption of fossil fuels causes serious environmental concerns such as thermal pollution, greenhouse gas emission

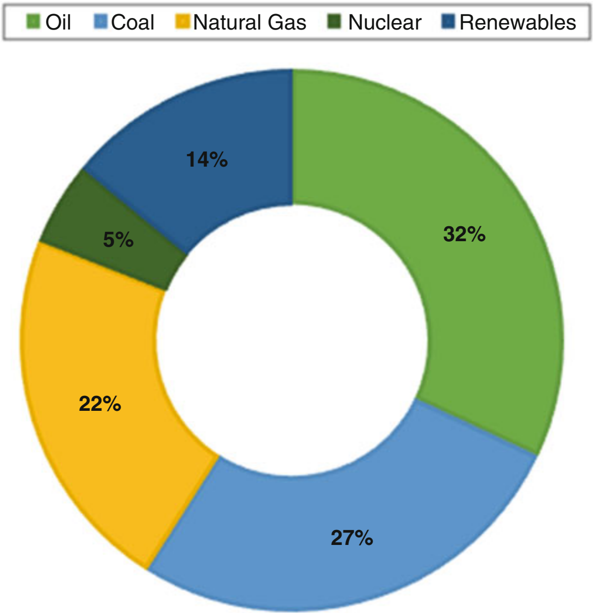

Fig. 1.1 Global energy supply percentage in 2017. Retrieved from World Bioenergy Association (WBA) 2019

and chemical and particulate emission, which lead to health complications and impact population standards of life (Lott et al. 2017). In addition to public health concerns, fossil fuels are disproportionately spread, which raises energy protection challenges as they play a crucial part in energy generation processes at present (Narula 2019). A number of political discussions and environmental issues are on the raise due to fossil fuel production and utilization. It has been reported that burning of fossil fuels cause about 98% of carbon pollution (Aransiola et al. 2012). Fossil fuels relate to a significant part of global energy consumption as can be seen in Fig. 1.2.

1.3 Need for Alternative of Fossil Fuels

Due to environmental effects, health concerns, and global warming, the utilization of fossil fuels has become unsustainable day by day. Biofuels are the promising alternatives to fossil fuels to attain sustainable energy and to resolve the problems caused by fossil fuels (Schenk et al. 2008; Hossain et al. 2008). This theory was first formulated and established by Rudolf Diesel during the late nineteenth century, when bio-fuels were widely looked to as the fuel of the future. Biofuels have been utilized mostly in the transportation industry since its inception, because of its ability to substitute petrol and diesel. Breakthroughs in the sector have demonstrated, however, that biofuel would be utilized for processing, cosmetics, medicinal, heating, and agricultural practices, as well as its usage as a renewable vehicle fuel (Bringezu 2009).

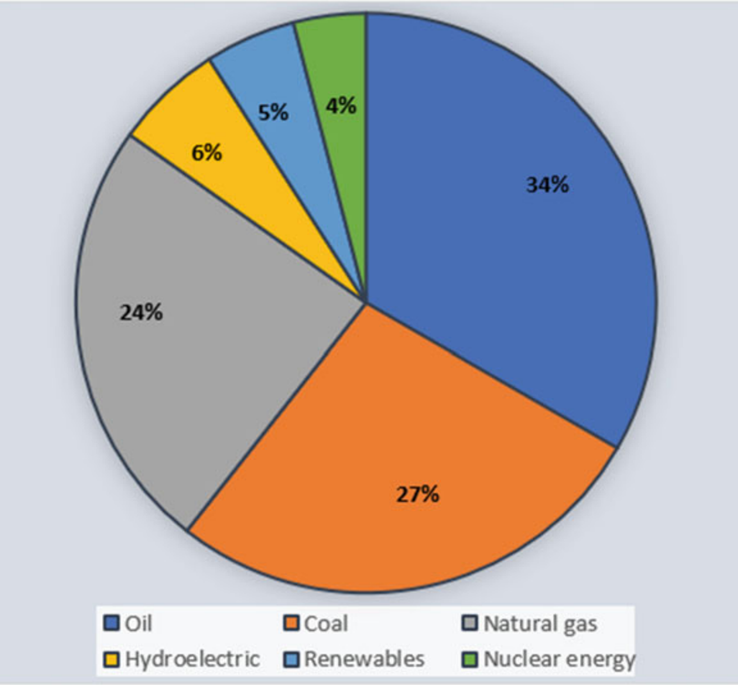

Fig. 1.2 Statistical percentage of global energy consumption 2019. Modified from Forbes (2020)

However, considering the clearly defined consumer opportunities and environmental advantages, there have been ongoing discussions regarding the use of agricultural-fuels in fossil fuels. The observers posed concerns about the effects of biofuel on the economy and the atmosphere and enquired about its sustainability and prosperity. Despite this, studies and research are being conducted in biofuel development, and much of the underlying problems have been mitigated. Appropriate advanced projects have been initiated by governments, industry actors, and civil societies to establish standards for effective biofuel development (Bringezu 2009).

1.4 Production of Biofuels

Biofuel production consists of the following main steps. Certain modifications are needed for significant production of biofuel, including grinding, enzyme treatment of substrates, which is followed by further bioconversion techniques (Arifin 2009). Transesterification is a widely used technique to manufacture biofuel which involves catalyzed chemical process that is beneficial in changing oil viscosity (Demirbas 2008). Biofuel production process steps are shown in Fig. 1.3.

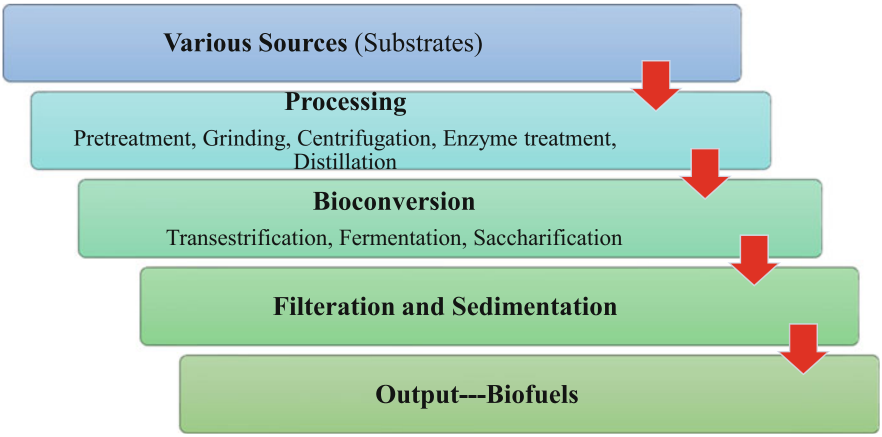

Fig. 1.3 Biofuel production process steps modified from Kapasi et al. (Kapasi et al. 2010)

1.5 Advancement in Biofuel Generations

The production of biofuels began in the late nineteenth century, when bioethanol was extracted from maize and Rudolf Diesel's initial engine was based on peanuts oil. The fall of CO_2 emission in the transport sector has turned into a particularly important catalyst to obtain biofuels in addition to energy protection and sustainable agriculture issues. In general, biofuels can be divided into first, second, third, and fourth generation biofuels (1G, 2G, 3G, and 4G) as shown in Fig. 1.4. However, the same fuel can be classified in a different way, depending on either technological maturity, on balance of greenhouse gas emission, or by the nature of feedstock resource (Berni et al. 2013). A few of the biofuel producing feedstocks are listed in Table 1.1.

1.6 First Generation (1G) Biofuels

Biofuels obtained by using starch-based or edible sources are considered as first generation (1G) biofuels (Zabed et al. 2014; Sadia et al. 2020). The conventional biofuels are liquids or gas fuels generated from various biomasses. Biofuels of 1G include ethanol and biodiesel, which are closely connected to biomass from an edible source. Ethanol is obtained as a result of fermenting the sugar obtained from sugar beet or sugar cane, or sugar extract of starch found in maize kernels or other starch-filled crops, and biodiesel is obtained from vegetable oils (Dupont 2007; Berni et al. 2013). The main drawback of 1G is the utilization of agricultural sources like sugar, vegetable oil, starch, and animal fats that puts an undesirable pressure on production of food. Moreover, increased carbon emission threatens our food supply due to high supply demand of these resources. Crops are used to extract oil in the

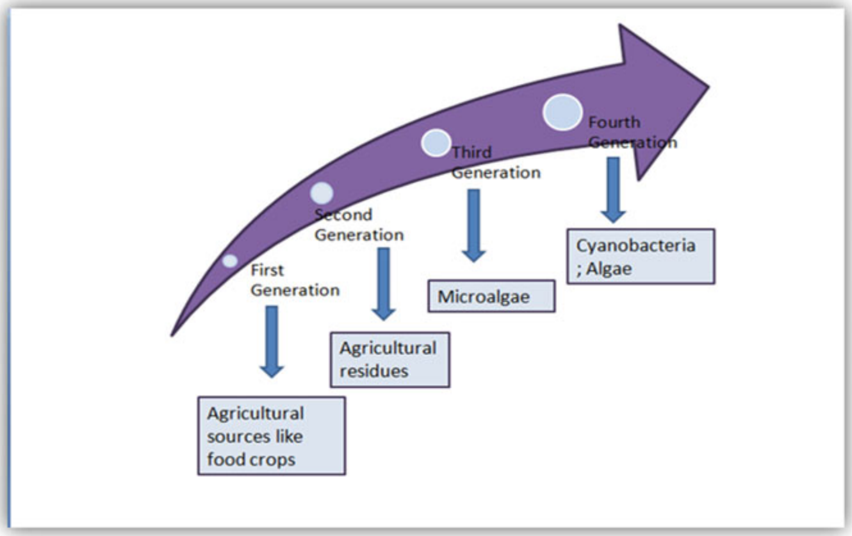

Fig. 1.4 Different generations of biofuels on the base of their feedstocks

form of bioethanol and biodiesel by carrying fermentation process (Rajee et al. 2014).

Most of the biofuels belonging to 1G releases more CO_2 than their feedstocks. Hence, it is a long-lasting debate that whether they reduce greenhouse gases and carbon emission or not. However, the most debatable thing of 1G biofuel is the issue of food. Increased demand of fuel tends to increase the production of food crops, as a result of which food prices are inflating worldwide (Rajee et al. 2014).

For instance, consider the production data of 1G bioethanol—bioethanol is a grain alcohol which can be used in motor vehicles by blending it with gasoline. The overall production of 1G bioethanol was almost 51 billion liters (L) in 2006, obtained from Brazil (using sugar cane) and United States (using maize), both contributed about 35% of the total production (Renewable Fuels Association 2008). United States in 2007 was estimated to have produced almost 34 billion L of ethanol yield by utilizing 27% of its corn crop (Collins 2007). The maximum ethanol production obtained in main countries during 2019 is shown in Fig. 1.5. As seen in 2019, US by generating 15.8 billion gallons achieved maximum ethanol production all over the world. Brazil was ranked next with almost 8.6 billion gallons.

1.7 Second Generation (2G) Biofuels

Second generation (2G) of biofuels is being produced to prevail over the issues faced due to 1G. The use of food crops in 1G can be addressed in 2G by using non-food resources, such as agricultural residues. Unlike 1G biofuels this generation utilizes

Table 1.1 Biofuels produced from different resources

Serial no.	Type of biofuel	Resource/ substrate	Microbe	Reference
1	Ethanol	Avicel	*T. saccharolyticum*	Argyros et al. (2011)
2	Ethanol	Cellulose	*C. thermocellum*	He et al. (2011)
3	Bioethanol	Diatom	Diatoms	Wang and Seibert (2017)
4	Bioethanol	Green microalgae	Not available	Lakatos et al. (2019)
5	Ethanol	Glucan	*K. marxianus*	Jiang et al. (2019)
6	Bioethanol	Sugarcane molasses	Not available	Aguilar et al. (2002)
7	Butanol	Barley-straw hydrolysate	*Clostridium beijerinckii* P2960	Qureshi et al. (2014)
8	Butanol	Lettuce leaves	*Clostridium acetobutylicum* DSMZ 792	Khedkar et al. (2017)
9	Butanol	Waste of mango peels	*Clostridium acetobutylicum* NCIM 2878	Avula et al. (2015)
10	Butanol	Glucose	*E. coli* strain BuT-8 L-ato	Saini et al. (2015a)
11	Butanol	Alkali extracted corn cobs	*C. thermocellum*	Wen et al. (2014)
12	Butanol	Cassava flour	*C. beijerinck*ii	Lépiz-Aguilar et al. (2011)
13	Biobutanol	Cheese whey (lactose)	*C. acetobutylicum* (immobilized)	Napoli et al. (2010)
14	Biobutanol	Sago starch	*C. saccharobutylicum* DSM 13864	Kumar and Gayen (2011)
15	Butanol	Cassava bagasse	*Clostridium acetobutylicum*	Lu et al. (2012)
16	Butanol	Rice bran	*C. saccharoperbutylacetonicum* N1-4	Visioli et al. (2014)
17	Butanol	Glycerol	*C. pasteurianum*	Khanna et al. (2013)
18	Biogas	Green microalgae	–	Sakarika and Kornaros (2019)
19	Biogas	Diatom	Chaetoceros spp	Syvertsen (2001)
20	Biogas	Crude sunflower oil	Not available	Bambase et al. (2007)
21	Biodiesel	Oilseeds	–	Leung et al. (2010)
22	Biodiesel	Vegetable oils and animal fat	–	Dias et al. (2008)

(continued)

Table 1.1 (continued)

Serial no.	Type of biofuel	Resource/ substrate	Microbe	Reference
23	Biodiesel	Crop residues	–	Dhanker and Tiwari (2020)
24	Biodiesel	Cyanobacteria	Cyanobacterial strains	Anahas and Muralitharan (2015)
25	Biomethane		Actinomycetes	Maurya et al. (2019)
26	Methanol oil	Waste cooking oil	*Pseudomonas aeruginosa*	Ali et al. (2017)
27	Biohydrogen	Miscanthus	Clostridium species	Zhang et al. (2013)

feedstock from plants, may be residual material, which serves as a solution to the problems of increased demand in producing foodstuff and reuse of the waste released into landfills (Ralph et al. 2009; Rajee et al. 2014).

Biofuels of 2G can be generated by using waste substances generated from industrial manufacturing units, agriculture or agro forestry. It includes alternatives to decrease the price of production of biofuel and to reduce the competitiveness with food. These biofuels do not utilize edible resources as raw matter. For more than three decades, bioethanol is being produced by employing lignocellulosic biomass from a variety of nonedible resources, by means of all the ingredients of biomass (Forster-Carneiro et al. 2010; Furimsky 2013). Since 2G biofuels use diverse bioconversion pathways, it seems that they stay away from the dilemma of “fuel against food.” Yet, they are capable of competing for the usage of agricultural soil that is utilized for food crops cultivation (Rathmann et al. 2010).

Biomass conversion is carried out by means of two broad techniques: thermo-chemical decomposition together with gasification, liquefaction, biocarbonization, pyrolysis and biological-digestion, basically referring to microorganism’s digestion, and fermentation. A few biofuels cannot be allocated to an exact “generation” (like biomethane), whereas other products claim to exist as real third generation (3G) (fuel obtained from CO_2 fixating bacteria). Hydro-treated vegetable oils are not an absolute 2G since the raw material is (presently) 1G biofuels (Bridgwater 2012; Berni et al. 2013).

Biofuels belonging to 2G are produced by using lignocellulosic (LG) biomass. Switchgrass and corn stover are the main biofuel producing significant sources due to low cost and easy availability (Kim et al. 2011; Saini et al. 2015b; Bakhtawar et al. 2020). Conventional bioethanol and cellulosic ethanol are chemically the same component; yet, raw materials for 2G are made of cellulose, while in 1G, simple sugars are straightaway fermented to bioethanol. Since 2G biofuels use dissimilar bioconversion pathways so they avoid food versus fuel choice. However, they fight for the agricultural land utilization which is used for the purpose to grow food crops (Rathmann et al. 2010).

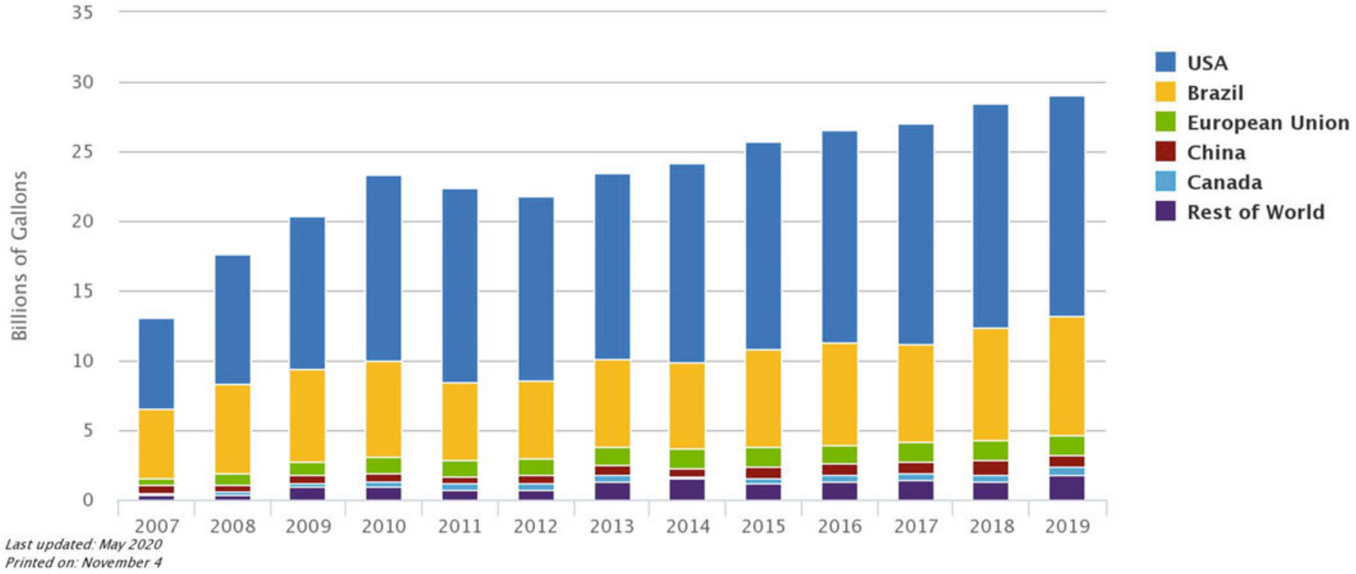

Fig. 1.5 Global ethanol production all across the world in 2019

In short, 2G biofuels are more competent and climate friendly as compared to their 1G predecessors. Their requirement of farmland for feedstock harvesting is not so much as they use plants and their residual material as well. Hence, the uneatable plant elements can be engaged to produce biofuel by reducing the food competition that is primary issue (Rajee et al. 2014).

1.8 Third Generation (3G) Biofuels

Biofuels of 3G come from algae along with hydrogen produced from lignocellulosic (LG) biomass. Production technologies employ catalytic improvement methods to convert starch, sugar and all types of lignocellulosic materials into required short-chained carbon compounds. The technologies used for 3G biofuel production are still in the progress state and their large-scale production is predicted in medium to long term (Kotay and Das 2008).

Microalgae have significant growth rate and advanced photosynthetic efficiency, so it is a possible way to produce 3G biofuel (Berni et al. 2013). Moreover, microalgae are rich in oil, and with favorable conditions microalgae can grow at a fast rate and doubles its biomass in almost 24 h (Patnayak and Sree 2005; Rajee et al. 2014). Algae cultivation requires a small area so its competition to food crops is almost negligible. Moreover, its production is completely reliant on non-arable ground and requires less water so it is preferred as compared to 1G and 2G biofuels (Hannon et al. 2010). While considering water practice in algal cultivation, a high water percentage could be recovered that can be used latter, which reduces water usage. Algae also have the ability to treat wastewater, and as a result, the released water has a better quality than the initial water used (Hannon et al. 2010). Furthermore, due to lessened dependence on arable land, algal cultivation results in less deforestation that is main contributor of carbon release in environment (Ryan et al. 2009). The total oil yield resulting by treating algae is almost 20 times greater than that of the yield from oil seed crop (Darzins et al. 2010).

Microalgae can be employed to obtain biodiesel by harvesting, dewatering, and drying after their growth. Algal oil is obtained from two steps: by extraction and transesterification or by in situ algal oil transesterification into biodiesel. Chemical, enzymatic, and thermochemical conversion methods and four major catalysts—acid, alkali, lipase and heterogeneous catalysts—are being used to obtain algal biodiesel. Drawback of this method is methanol requirement that causes an increase in cost and affects glycerol that is a byproduct used in many industries. Heterogeneous catalysis is also in debate; but it is not easy to predict that as it could displace the main conversion method of homogenous acid catalysis. Lipase is a biological catalyst that has also been reported to synthesize biodiesel, but its cost does not allow a large-scale biodiesel production (Daroch et al. 2013; Berni et al. 2013).

Fermentation of microalgae into bioethanol and in situ transesterification of microalgal biomass to obtain biodiesel are the most effective ways to produce biofuel until now. However, advanced downstream processing is required for both these, which is the main barrier to commercialize the algal biofuel production

(Uduman et al. 2010; Berni et al. 2013). Thus, metabolic engineering of photosynthetic organisms proved to be a great breakthrough in producing biofuels that assures a significant simplified downstreaming process (Daroch et al. 2013; Berni et al. 2013).

Strain selection and its growth play a main role in biofuel production through fermentation of algal feedstock. Two approaches are being used to overcome this issue. Either macroalgae feedstock of a natural locality can be used or microalgal strain can be properly grown under artificial conditions. Comminution is needed for macroalgae processing, as, in the case of cellulosic ethanol, before the sugar fermentation algae have to undergo pretreatment and saccharification by mean of chemical, physical and enzymatic means. However, algae lack lignin, so its biomass can easily be transformed into simple sugars. In addition to cellulose and hemicelluloses, numerous algal species have a reserve material in the form of starch (Mussatto et al. 2010; Daroch et al. 2013).

Microalgae as compared to macroalgae are currently being utilized as a feedstock to obtain high biodiesel yield. Until now, reported macroalgal biodiesel are very low than microalgal biodiesel production (Daroch et al. 2013). The main reason of this production difference is microalgal carbohydrates (cellulose, hemicelluloses, and starch hydrolysis). Microalgal carbohydrates are related to those of global harvests, and the yields acquired for their processing are elevated. Furthermore, by the progress of novel enzymes for lignocellulosic saccharification, the gap among conversion efficiencies of both macroalgal and microalgal feedstocks are predicted to enhance. On the other side, usage of wasted macroalgae biomass demands consideration for bioethanol yield that transfers biofuel production to the idea of biorefinery, which is being considered as a long-lasting sustainable key for biomass energy (Berni et al. 2013).

During oil and residue conversion procedure, all gases and wasted heat are reused by using low cost co-products, for example, selected acids, biomass residue, and glycerol. The toxicity, number, and usage of these products will decide the environmental impact it will have. Furthermore, gases, such as methane, can burn up like a fuel to produce electrical energy (Liang et al. 2012). In future perspectives, it is predicted that the concept of systems metabolic engineering will produce algal strains having improved capacity to produce hydrogen, alkanes, alcohols, and diesel. There are established corporations trying to advertise algal fuels in the Israel, NZ (New Zealand), and US (United States) (Jang et al. 2012; Berni et al. 2013).

1.9 Fourth Generation (4G) Biofuels

Biofuels of fourth generation (4G) gets an advantage of synthetic biology of cyanobacteria and algae that is a new but strongly developing field of research (Berla et al. 2013; Scaife et al. 2015; Aro 2016). Cornell University (n.d.) has reported that plants allowing simple cellulosic breakdown or of great yield is preferred in 4G biofuels. Moreover, they are planted on a land that is unfit for other agricultural purposes, so any biomass destruction is not warranted. An alternative fuel that is replacing fossil fuel should have a great environmental benefit, have an affordable cost and should be produced in enough quantity to put a significant influence on energy requirement. Moreover, the net energy obtained from feedstock should be greater than its production demand (Meng et al. 2009; Rajee et al. 2014).

Recently scientists have designed eucalyptus trees having capability to accumulate three times greater CO_2 which has been proved a major breakthrough to solve the current issue of greenhouse gases and global warming. Moreover, microorganisms because of having a short life cycle, fewer labor supplies, and enhanced production are being considered as another source of traditional feedstock to obtain biofuel yield (Li et al. 2008; Rajee et al. 2014).

Microbial oil can also be produced by using autotrophic microalgae that relies on natural sunlight and does not demand for variation in light intensity (Chisti 2007). Oil accumulation is also influenced by some other environmental factors like temperature, minerals, acidity, salinity, and nitrogen source (Li et al. 2008). These microbial species are Chlorella vulgaris, Dunaliella primolecta, Neochloris oleoabundans, Phaeodactylumtricornutum, Tetraselmissueica, Botryococcus braunii, Crypthecodinium cohnii, Navicula pelliculosa, Monallanthussalina and Scenedsmusacutus (Liang et al. 2006; Rajee et al. 2014). On the other side, heterotrophic microalgae as well, can be transformed into autotrophic via genetic engineering modification or changing the environmental conditions during its cultivation; these species can truly use natural carbon instead of sunlight (Li et al. 2008). Chlorella protothecoides that is an autotrophic microalgae relies on natural carbon source that is cost efficient and has the ability to produce four times more bioethanol (Miao and Wu 2004; Rajee et al. 2014).

1.10 Recent Advancements in Biofuel Production

Biofuel production reduces greenhouse gases emission as well as the demand for fuel based on petroleum. Biofuel comprises of bioethanol, biomethanol, biodiesel, biohydrogen, and biogas (Balat 2008). Studies of the last 15 years declare that biofuel has replaced diesel and gasoline and reduced the emission of greenhouse gases—ethanol reduced the emission by 71%, bioethanol by 31% and biodiesel by 54% (Koh and Ghazoul 2008). Bioethanol that can easily be produced by using renewable resources is the most promising fuel among all these and is also being commonly used in transportation industry (Tamburini et al. 2011). Advanced technologies for biofuel production are the conversion methods which are under study and progress presently; these include extracting hydro-treated vegetable oil from animal fats and plant oil, biofuels produced from lignocellulosic biomass (like cellulosic ethanol), liquid diesel and bio-synthetic gas from biomass; biofuels based on algae and the transformation of simple sugar into diesel like biofuels by means of biological or chemical catalysts (Nigam and Singh 2011).

1.11 Bioethanol

Biofuel production including biodiesel, biobutanol, and bioethanol has gathered considerable interest (Karmee and Lin 2014; Jiang et al. 2017). Bioethanol is a carbon natural liquid fuel used in transportation, so it is most important among all (Carroll and Somerville 2009; Jiang et al. 2019). It is a non-toxic biodegradable renewable source and has a great potential to reduce the particulate transmission in compression–ignition engines (Hernández and Kafarov 2009; Balat 2009).

Bioethanol can be obtained by using LG biomass, starch, and sugar (Coppola et al. 2009). Sucrose is derived from sugar harvests, for example, from, sugar cane, sweet sorghum, sugar beet, and then fermented via yeast to form ethanol, which also creates additional metabolic byproducts, like CO_2 (Berni et al. 2013). Third generation bioethanol production takes place by using algal feedstock. Due to high rate of productivity, low lignin percentage, and high fermentable sugar content, bioethanol production from algal feedstock has a significant potential as compared to other feedstocks (Moore 2009). Biorefinery approach is necessary to obtain ethanol by using LG biomass in order to make the process economically affordable. Some other valuable products along with ethanol can also be produced by using lignocellulosic biomass. Biorefinery is the coproduction of some chemicals, bioenergy, and biofuel, and resembles petroleum-based refinery, in which many types of products along with the main fuel are obtained (Kamm 2007).

The most current advancements in ethanol production are the use of Saccharomyces cerevisiae after its genome shuffling and the overall transcription machinery engineering (Mussatto et al. 2010). Solventogenic yeasts, like Saccharomyces cerevisiae, and a few bacteria, like Termoanaerobacter species, are broadly used to produce ethanol (Hon et al. 2017; Jiang et al. 2019). A synthetic E. coli binary culture was made for straight conversing hemicelluloses into ethanol. The ultimate concentration of ethanol was obtained 2.84 g/L that was 55% of the hypothetical yield (Shin et al. 2010a, b).

Still, the feedstock range is restricted to a few starch-based resources (Dürre and Richard 2011). Lignocellulosic biomass is economically more reasonable alternative as compared to grain-derived feedstocks due to its easy availability and affordable cost (Jiang et al. 2019). Co-culturing of cellulolytic microbes in the company of ethanol producing microbe is a suitable and flexible advancement to make ethanol from lignocelluloses (Jiang et al. 2019). Other important advances in fermentation field are the use of lignocellulosic hydrolysates as feedstock, implementing a high gravity technology, and high-cell-density continuous process application (Berni et al. 2013).

1.12 Biobutanol

Biobutanol is regarded as an advanced biofuel as compared to bioethanol. It is a straight chain of four carbons and has high heating value, low heat of vaporization, low corrosivity, high viscosity, and improved inter-solubility (Jiang et al. 2019).

About 20 g/L of biobutanol concentration inhibits the growth of microorganisms (Knoshaug and Zhang 2009). Moreover, clostridium cultures are anaerobes, and their conditions require to be adjusted prior to fermentation, and reactors have to be closed throughout the process (Visioli et al. 2014).

Butanol synthesis is more complex than ethanol production (Pfromm et al. 2010). Normally, butanol synthesis is carried out through ABE fermentation (acetone–butanol–ethanol) by using solventogenic Clostridium sp. (Shanmugam et al. 2018; Sun et al. 2018). ABE fermentation is the second principal mode of fermentation and the most complicated process (Bharathiraja et al. 2017; Agarwal et al. 2020). Still, most Clostridium sp. are not able to directly use lignocellulose like polysaccharides, because of in-expression of polysaccharide-decomposing enzymes (Jiang et al. 2018). So, microbial consortia construction was significantly used to produce direct butanol by using renewable feedstocks. For instance, C. beijerinckii and C. thermocellum were co-cultivated to produce butanol directly by using lignocellulose material (Wen et al. 2014). C. thermocellum hydrolyzed the reducing sugars and were metabolized by Clostridium beijerinckii simultaneously to produce butanol. Meanwhile, sugar utilization enhanced the feedback-inhibition and improved degradation capacity of alkali-extracted corn-cobs through thermocellum (Jiang et al. 2019). Introducing butanol synthesis module to *Escherichia* coli can trouble the metabolic stress, while dividing butanol synthesis into two steps—butyrate producing and converting module—in a co-culture is a more possible way. The quantity of butanol production obtained by using co-culture is also higher than that of pure culture (Saini et al. 2015a).

Plants for biofuel production are sensitive to price variations and depends over price of feedstock (Green 2011), thus, product price depends on feedstock price, and costly feedstock leads to costly fuel. Substrate prices during biobutanol production creates an economic competition with petroleum industry (Napoli et al. 2010). Agricultural remains are confirmed as cheaper sources (Taylor 2008); however, their hydrolysis produces fermentation inhibitors (Qureshi et al. 2007).

In butanol production, 70% of the total cost represents feedstock. In the beginning, substrates based over starch sugar were used for butanol production, but they were too expensive and the process was not feasible. Use of cheap or low-cost renewable stock like lignocellulosic biomass is the key to overcome the production cost. Alcohol production by using lignocellulosic material involve: pretreatment, hydrolysis, and finally fermentation (Visioli et al. 2014). It has been reported that barley straw can also be employed as a feedstock to produce butanol, but some inhibitors are also present in this substrate that requires a pretreatment for efficient fermentation. After pretreatment, the butanol thus obtained by using glucose was higher. Hydrolysates of corn stover and switchgrass were also proved as efficient substrates for butanol synthesis (Qureshi et al. 2007). Butanol production by using corn stover hydrolysates was same as that of barley (Visioli et al. 2014).

Butanol production has another main requirement concerning the separating methods and their applications, mostly for in situ continuous recovery (Mariano et al. 2012). Distillation is a major separation technique used for separating aqueous solution from butanol but an azeotrope is formed in this process that increases energy cost and low concentration of butanol is recovered (Vane 2008; Zheng et al. 2009; Mariano et al. 2011). For cheap and efficient separation, some alternative methods are also reported. Moreover, mathematical models are also made to design and stimulate the process on industrial scale to avoid optimization of operational requirements of the reactor (Liu et al. 2009; Visioli et al. 2014).

It has been accounted that butanol can be recovered from fermentation broth by using the technique of adsorption, ionic liquids, pervaporation, gas stripping, liquid-liquid extraction, aqueous two-phase separation, flash fermentation and supercritical-extraction (Ezeji et al. 2012; Secuianu et al. 2004; Visioli et al. 2014). Butanol can be easily separated from aqueous media of fermentation broth by using adsorption. Butanol over water is significantly selected by using hydrophobic adsorbents (Knoshaug and Zhang 2009). Some companies have tended to start butanol fermentation commercially (Cheng et al. 2012). In future, it is expected that companies working on butanol fermentation will increase globally and will also increase the butanol yield by developing new technologies (Pfromm et al. 2010).

1.13 Biodiesel

Biodiesel is an ecofriendly biofuel that can supply immense, robust, and durable energy supply (Lai 2014; Mata et al. 2010). It is made up of renewable materials and does not emit much of greenhouse gases as compared to petroleum and diesel, and thereby, reduces health risks related to air pollution (Lippke et al. 2012). Biodiesel production has become significant worldwide due to reduction of CO_2 emissions and oil independence (Chaker Ncibi and Sillanpaa 2013).

Commonly oleaginous algae are being used as biodiesel producers (Singh and Olsen 2011), but its slow growth rate, lipid accumulation, and commonly inappropriate nature of biomass restrains its further applications (Sharma et al. 2012; Li et al. 2011). So the co-cultivation of fungus and algae is an alternative source of biodiesel synthesis. Aspergillus awamori that is an oleaginous fungus was co-cultured by Chlorella minutissima and Cocculinella minutissima respectively. These two consortia have obligate heterotrophic fungi and photoautotrophic green algae. This system has the capability to use glycerol as an alternative to glucose that reduces the cost of biodiesel production. Moreover some major fatty acid composites were also obtained by using this co-culture technique indicating that the system can be significantly used to produce biodiesel (Dash and Banerjee 2017; Jiang et al. 2019).

In biodiesel production, feedstock comprises of 85% of its total cost (Haas et al. 2006; Zhang et al. 2003). A broad range of feedstock can be employed for biodiesel production including rapeseed and soybeans in US (Mekhilef et al. 2011). Jatropha is a nonedible oil and is being used to produce biodiesel (Fan and Burton 2009). Additionally, algae-based biodiesel are also a topic of interest in recent times (Aresta et al. 2005). Still, for the survival of biodiesel, low cost bioresources are being preferred which include grease, waste cooking oil and soap stocks (Keskin et al. 2008; Fan and Burton 2009).

Oil from algal and vegetable source is composed of triglycerides (having saturated and unsaturated fatty acids of varying molecular weights). Biodiesel production is influenced by the chemical properties such as cetane number, viscosity, and density of these fatty acids (Chaker Ncibi and Sillanpaa 2013). In general, reactivity, low volatility, and high viscosity of unsaturated fatty acid chains are unfavorable for biodiesel (Saka and Kusdiana 2001). Reduced reactivity and low cetane number of unsaturated fatty acids are the reasons for partial biodiesel combustion that causes coking of engines and, ultimately, trumpet formation. Moreover it is also the reason for the formation of gum, thickening, and gelling of the lubricating oil which causes deterioration and contamination when mixed with vegetable oil (Priya and Thirumarimurugan 2020). High viscosity problem can be sought out by microemulsions of the fuel with a solvent that may be alcohol, with an ionic or nonionic amphiphiles of nanoscale size replacing the direct/blend fuels. Emulsions of vegetable oil were done by alcohols; ethanol, methanol, butanol, and propanol were employed (Ziejewski et al. 1984). This vegetable oil emulsification lowered the fuel viscosity and also exhibited improved spray patterns throughout combustion (Leung et al. 2010).

Combustion quality of biodiesel is improved by increasing the cetane number, which is achieved by increasing the chain length and saturation of used fatty acids. High cetane number can also be obtained by using monounsaturated as well as high saturated fatty acids (Van Gerpen et al. 2004). So it can be supposed that high saturated and monounsaturated fatty acid contents are reliable standards to produce biodiesel with high quality. Suitable feedstock with high cetane number, such as Mahua, Karanja, microalga Chlorococcum humicola, jatropha and rapeseed are the most appropriate for high quality biodiesel production (Chaker Ncibi and Sillanpaa 2013).

Process optimization is the key endeavor concerning to biodiesel production. Main troubles faced due to vegetable oil usage are reactivity of unsaturated hydrocarbons, high viscosity, less volatility, and high content of free fatty acids which leads to deprived combustion in traditional diesel engines. These difficulties can be overcome by diverse techniques and numerous chemical steps like pyrolysis, dilution, catalytic cracking, microemulsification, and transesterification (Demirbas 2009).

1.14 Biohydrogen

Fossil fuels cannot be regenerated, and thus, increasing consumption will deplete the fossil fuel resources with time. Hydrogen fuel is a sort of energy with plentiful reserves that does not rely on fossil fuels. Beside this, hydrogen energy fulfills the worldwide energy requirement so more attention is being paid to this. Hydrogen can be produced in bio-system by two ways, namely anaerobic fermentation and light drive method. Light drive process is supposed to be a suitable process because of converting solar energy into hydrogen by directly using photosynthetic bacteria. But this is not practically applicable due to complexity in designing reactors and less consumption effectiveness of light. Anaerobic fermentation is carried out by using hydrogenogens, which are simple, rapid, easily handled, and renewable and organic waste resources for hydrogen production (Xing and Zhang 2005). As compared to light drive process, anaerobic fermentation is easy to carry and is appropriate for the requirement of sustainable growth strategy, but hydrogen production rate and yield are still low.

With the technological progress of molecular biology, directional heredity rebuilding for microorganisms has become an emerging research field that can completely alter biological characteristics of microbes as well as its metabolic means for cultivation of better and valuable strains for hydrogen production at low cost and with efficient pathway for the utilization and popularization of hydrogen energy resources (Liu et al. 2008).

Biohydrogen is being considered as an upcoming fuel due to its sustainability. Biohydrogen can be used for fats hydrogenation in food industry, in reformulating and desulfurizing of gasoline in refineries, in chemical synthesis and in steel processing. It also has some drawbacks as well. It is very complicated and expensive to store hydrogen gas (Kotay and Das 2008; Kırtay 2011; Berni et al. 2013). A diverse range of photosynthetic along with non-photosynthetic microbes such as anoxygenic photosynthetic bacteria, unicellular green algae, cyanobacteria, nitrogen-fixing bacteria, and obligate anaerobic are capable of producing biohydrogen, but still they have low efficiency (Jang et al. 2012; Berni et al. 2013).

1.15 Biogas

Global industrialization and population across the globe are the reasons for increase in solid waste quantity (Srivastava and Ramanathan 2018). Organic material of this solid waste can undergo anaerobic digestion and can be converted into biogas (Srivastava 2020). Biogas production through anaerobic digestion is significant as compared to other bioenergy production processes. Actually, biogas has been proved as energy-efficient and eco-favorable technology for bioenergy production (Deublein and Steinhauser 2011). Degradation process is carried out through hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In all these phases diverse clusters of facultative or obligatory anaerobic microbes are concerned (Horváth et al. 2016).

Anaerobic digestion is a complicated and multistep microbial route where microorganisms have a mutually supporting and synergistic association with each other. Information of the microbial community is necessary to have a significant approach to digestion process, its optimization, and development. There are a range of molecular methods to identify bacterial and archaeal communities from anaerobic digestion, such as combinations of 16S ribosomal RNA gene clone library sequencing (Chouari et al. 2005), fluorescence in situ hybridization (Cirne et al. 2007), terminal restriction fragment length polymorphism (Ike et al. 2010), real-time polymerase chain reaction (Shin et al. 2010a, b), dot blot hybridization (Maurya et al. 2019), and denaturing gradient gel electrophoresis (Bialek et al. 2012), which have all been accounted to asses microbial community structures and their shift during anaerobic fermentation of different residues.

Omics method is a very supportive molecular biology technique to identify anaerobic digesters (Ma et al. 2016) and is uses a combination of metagenomics, metaproteomics, and metatranscriptomics (Karthikeyan et al. 2016). Anaerobic digestion may be affected by disturbance in process, lack of quality raw materials, unintentional organic loading, and accidently adding up of toxic substrate (Karthikeyan et al. 2016). Therefore, consistent monitoring and organized technologies for efficient process is necessary. Anaerobic digestion is an analytical deal carried out with a highly developed monitoring procedure through chemometric multivariate data analysis and spectroscopic and electrochemical measurement principles (Madsen et al. 2011; Maurya et al. 2019). Highly developed technologies like electrochemical arrays and multivariate sensor technologies have contributed in the development of monitoring tools (Karthikeyan et al. 2016).

Biogas produced by anaerobic digestion has CO_2, hydrogen sulfides, siloxanes, water vapor, hydrogen and ammonia; CO_2 is thought to be a major gas among all these contaminated gases. Only hydrogen and methane can be utilized for energy among all these. If biogas is used without purification then contamination can harmfully affect appliances; for instance, hydrogen sulfides are corrosive for engines and pipelines, so concentrating techniques need to be developed. Biogas upgrading is carried out by some traditional methods like Pressure Swing Adsorption, Solvent Scrubbing, Membrane Technology, Chemical Scrubbing, and Water Scrubbing (Maurya et al. 2019). Cryogenic upgrading and in situ enrichment are some new technologies that are being studied widely to be applied in near future (Kadam and Panwar 2017).

Biogas has wide range of application, but it depends on its production source. It can be directly utilized to produce heat by combustion, produce electrical energy by micro-turbines or fuel cells and as a fuel for vehicle. The most significant constriction of biogas conversion into thermal or chemical energy is low calorific value (Hosseini and Wahid 2013; Kadam and Panwar 2017).

Biogas production and plant efficiency can be enhanced by improving microbial activities by mean of a range of chemical or biological additives in diverse operating conditions. Additives are frequently used to supply ideal nutrient state for microorganism; still its optimal amount depends on biocenosis and observation of a research team (Chen et al. 2008; Demirel and Scherer 2011). Magnesium and calcium salts used as additives enhance methane production and minimize slurry foaming (Sreekrishnan et al. 2004). Additives to reduce hydrogen sulfide and ammonia concentration and to stabilize variable pH are also being used (Kuttner et al. 2015). Biological additives are also being used to improve biomethane and biogas production and latter stored for 7 weeks as compared to raw sample (Vervaeren et al. 2010; Prasad et al. 2017).

1.16 Conclusion

Biofuel is the most promising fuel of the present, fulfilling all energy requirements with a very low cost. With the technological development biofuel production can be enhanced to meet all energy demands globally, by replacing the costlier petrochemical-based fuel types. Many industrial countries are trying to replace traditional fuels with biofuel production, which can lead to an economically ideal energy source. Recent advancements in biofuel production lead to the utilization of nonedible feedstock sources for the purpose of valuable fuel production.

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Bioenergy: Sustainable Renewable Energy

2

Meenal Jain, Meenakshi Mital, and Puja Gupta

Abstract

Bioenergy is one of the major renewable sources of energy, originating from sunlight and produced via photosynthesis. It is one of the many different resources available to human beings for meeting their energy requirements. Bioenergy is one among different renewable sources of energy. It is derived from living organic materials known as biomass. Looking at the increasing energy demand in the country, bioenergy is a significant energy source for meeting future energy requirements. At the same time, it is an efficient and green source of energy, thereby helping curb the greenhouse gas emissions. Bioenergy can be utilized in a number of ways namely heat, electricity, or as biofuels, and can be obtained from varied sources ranging from agricultural crops to animal, human, and industrial wastes. Similarly, there are different technological options for producing bioenergy, depending on the type and source of biomass. This chapter will throw light on the benefits, challenges, and need of bioenergy as a source of sustainable renewable energy. Further, it will discuss the various technologies for biomass conversion like combustion, gasification, pyrolysis, and anaerobic digestion. Various possible uses of biofuels as sustainable renewable energy will also be thrown light on.

Keywords

Bioenergy · Sustainable energy · Biomass conversion technologies · Sustainable energy

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M. Jain (✉) · M. Mital · P. Gupta
Department of Resource Management & Design Application, Lady Irwin College, University of Delhi, New Delhi, India

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2.1 Introduction: Bio Energy—A Sustainable Energy Source

Energy is critical for the growth and development of countries. This is especially true for a country like India given its fast pace of development and a huge population base. Most of the world's energy requirements (approximately 80%), however, are fulfilled by fossil fuels, which are the leading causes of greenhouse gas (GHG) emissions. The challenge therefore today for most nations, especially the developing nations, is to improve energy availability and access to modern and clean energy sources for all its citizens. These clean energy sources have to be financially affordable and sustainable, should address energy security, and minimize GHG emissions.

The United Nations Framework Convention on Climate Change (UNFCCC) signed the Paris Agreement in 2016 to bring the nations together to reduce their GHG emissions by setting individual targets. The aim of this agreement was to limit the rise in global temperature to below 2 °C at the earliest. However, only a handful of nations are likely to achieve their NDCs (Nationally Determined Contributions) owing to lack of commitment on the one hand and lack of sustainable alternatives to fossil fuels on the other. This need for sustainable alternatives has lead to the discovery and production of bioenergy.

Bioenergy is produced from biomass or the organic matter derived from plants and animals. The primary source of bioenergy is sunlight, which is a major driver for photosynthesis. Bioenergy is classified as a renewable energy source. The technologies used for production of bioenergy range from as simple as burning of wood to generating thermal energy for heating and cooking, to as complex as advanced generators for production of liquid biofuels. Bioenergy is one of the primary sources for world energy supplies and is the most widely used renewable energy globally.

The energy derived from biomass can be further converted into heat, electricity, or biofuels like bioethanol. Biofuel is a green source of energy that comes from organic matter or biomass or wastes. It is a safe alternative that not only emits less carbon dioxide (CO_2) but is also an advantage to the struggling economy by creating an industry and providing more jobs. It is a sustainable fuel that reduces the dependence on petrol, diesel, or other fossil fuels.

To make biofuels, several materials may be used, including maize, sugarcane, wood waste, grasses, algae, animal waste, wastewater sludge, or other plant matter that would be unusable otherwise. Today, most biofuels are made from crops and are referred to as conventional biofuels. Newer technologies for creation of fuels from waste, inedible crops, and forest products are called second-generation biofuels or advanced biofuels and are considered to be more sustainable as compared to the former. Two biofuels namely bioethanol and biodiesel are already being used commercially in the transportation sector.

Biogas can potentially be used for electricity generation and also as an alternative to compressed natural gas (CNG) which is a fossil fuel based energy source. In 2018, the global production of biogas and biomethane production has been estimated to be approximately 35 Mt. Overall, the use of biofuel for transport has been increasing gradually with figures showing an increase of 6% on yearly basis in 2019.

Although biofuels are a positive move toward sustainable energy, the contemporary economic conditions do not favor the biofuels industry. The production of bioenergy at large scale has been found to be expensive and thus, researches are underway to bring down the costs. As per estimates, it was forecasted that by the year 2024, the production of biofuel will increase by 25%; however, the global COVID-19 pandemic decreased the fuel demand, in turn suppressed the crude oil prices. Biodiesel manufacturers, however, did not witness much impact of the pandemic due to increased e-commerce activities which required transportation. In the foreseeable future, clean and green energy sources are bound to play a key role in reducing global warming, halting climate change, and reducing dependence on fossil fuels which are fast depleting.

2.2 Biomass

Biomass is any living or recently dead matter from animals and/or plants, excluding fossilized fragments of organisms. Thus, all the living matter comprises of biomass. Biomass energy includes those products which can be used for energy generation in place of fossil fuels. Biomass utilizes carbon dioxide for photosynthesis and gives it back when it is used for generating energy. The process leads to a carbon-neutral cycle preventing the increase in GHG concentration.

Burning of biomass along with fossil fuels can be used as an economically cheaper method for mitigating GHGs. About 80% of potential energy from biomass can be efficiently tapped by combined heat and power (CHP) operations. In these systems, the waste heat from bio power production operation is tapped and used for heating or cooling purposes. Biomass is also helpful in producing transportation fuels for reducing the usage of petroleum products and decreasing GHG emissions. Presently two most prominently used biofuels are ethanol and biodiesel. Further, researches are under way to create a number of advanced second-generation biofuels made from non-food biomass feedstock, such as municipal organic waste, wood shavings, and algae. These fuels are composed of cellulosic ethanol, biobutanol, methanol, and synthetic gasoline/diesel equivalents. Thus, biofuels are a significant source for clean transportation fuel.

2.2.1 Biomass Feedstock

As discussed earlier, biomass is derived from plants and animals and thus, wherever these two are present, biomass can be produced. Agricultural crops, animal and plant wastes, and other organic wastes are all sources of biomass. The type of biomass regulates the kind and amount of bioenergy that can be produced from it as well as the technology that should be used for the generation process. For instance, the agricultural crops like corn and canola are suitable for producing liquid biofuels such as ethanol and biodiesel, whereas moist biomass are more appropriate to produce biogas through anaerobic digestion. This biogas can further be combusted to generate power and heat or upgraded into a transport fuel namely biomethane.

Every geographical region has its own biomass feedstock from agriculture and forest, agro industries, and urban sources. Besides, most of the biomass feedstock thus generated has the potential utility for making liquid fuels, heat and electric power along with other bio-based products. Thus, biomass is a flexible and extensively available source that can be used to generate energy to meet local needs and purposes. Some of the most common (and/or most promising) biomass feedstock are:

- grain crops like wheat and corn; starch crops like sugar cane, and sweet potatoes;
- agricultural waste in the form of rice and wheat straw;
- food waste from food processing industries, from catering units, restaurants, etc.;
- forestry waste in the form of forest thinning, stump wood, branches, crests, residues, etc.;
- animal byproducts like animal remains, fish oil, wastes, and manure;
- energy crops like soybean, rapeseed, sunflower, and cotton seed;
- urban waste products such as municipal solid wastes (MSW), sludge, wood wastes, and waste cooking oil.

2.3 Biomass and Land Use

Biomass is a significant renewable energy resource like wind and solar, and has a favorable effect on our atmosphere. It declines our reliance on climate change-causing fossil fuels. Biomass energy, however, is unique and differs from other renewable sources of energy as its production is related to the organic waste from farms, forests, and other ecologies from which the raw material namely biomass is obtained. The use of biomass for biofuels has both environmental and social impacts. They affect water resources, soil system, biodiversity, and local communities both positively and negatively. These impacts, however, differ depending on the types of biomass being used, as well as the time and method of their procurement. Therefore, it is essential that biomass is produced and harvested as sustainably as possible. Here, sustainability implies selecting those management practices which curtail negative impacts and help in achieving local land-management objectives like soil preservation, sustainable forest stewardship, sustainable food production, and wildlife management.

One of the debates regarding land use and biomass is the “food-vs-fuel” debate. This issue often arises as a result of conflict between food production and bioenergy, as a number of conventional food crops like sugar and corn are also most commonly used bioenergy feedstock. A number of times, agricultural lands are used for producing dedicated energy crops, which has certainly contributed to increased prices for many of these supplies. To reduce the problems arising from agricultural lands being used for biomass, other alternatives can be used like increased use of agricultural and forestry wastes, food wastes, and use of marginal lands for growing bioenergy crops.

Another problem largely linked with biomass production is the emission of GHGs especially CO_2, CH_4, and N_2O, emerging from land management and land use change. These emissions can be divided into direct and indirect sources. Direct emissions emerge from clearing of land, use of fertilizers, practices undertaken while growing or harvesting a biomass crop, etc. On the other hand, indirect emissions emerge as a result of market-driven land use changes like clearing of forests, grasslands, or other ecosystems for growing crops or other commodities (Environmental and Energy Study Institute 2020).

With favorable government policies and efficient implementation, these fuels can become an effective alternative in future. Demand for sustainable fuels today is driven by rising fuel prices, need for energy security, and higher pollution levels. Fuels such as bioethanol and biodiesel have already been commercialized in many countries. Bioethanol is mainly produced from corn, sugarcane, and sweet sorghum, while biodiesel is produced from rapeseed and palm oil (first-generation feedstock). However, the cultivation of feedstock results in the depletion of grasslands and rainforests, negatively impacting the ecosystem. Utilization of food crops for fuel also creates food versus fuel concerns due to the increased strain on the food supply chain. Furthermore, while these fuels are considered carbon-neutral, as the carbon dioxide (CO_2) produced will be reutilized by plants, the fuel consumed for biomass transportation as well as the energy and water required in the production process adversely affects the environment. Researchers are working on developing solutions that will make these fuels more sustainable. The biofuel industry is still in nascent stages owing to quite a few challenges that it faces in upscaling processes. Latest researches in biofuel production are exploring ways to reduce the costs along with deploying artificial intelligence (AI) to bring in efficiency in process development and maintenance.

2.4 Technologies for Biomass Conversion

There are a number of technologies which can be used for producing bioenergy depending on the type of biomass used, type of bioenergy intended to be produced, environmental regulations, economic factors, etc. There are three primary conversion technologies for biomass, namely biochemical, thermochemical, and physiochemical. The three conversion technologies further have different processes as follows (Adams et al. 2018; Balat 2006; Mokraoui 2015; Dornburg and Faaij 2001; Kar et al. 2018; Nanda et al. 2014; Sharma et al. 2014; Srirangan et al. 2012; Tursi 2019):

- Biochemical conversion: anaerobic digestion and fermentation;
- Thermochemical conversion: pyrolysis, gasification, combustion, and hydrothermal processing; and

- Physiochemical conversion: consists principally of extraction (with esterification).

Let us discuss the conversion technologies in detail.

2.4.1 Biochemical Conversion

As the name suggests, biochemical conversion of biomass uses microorganisms and enzymes for conversion of the biomass into fuels—gaseous such as biogas or liquid such as bioethanol. Anaerobic digestion and fermentation are the two most commonly used biochemical conversion technologies, as illustrated in Fig. 2.1 (Chen and Wang 2016; Zafar 2020a, b).

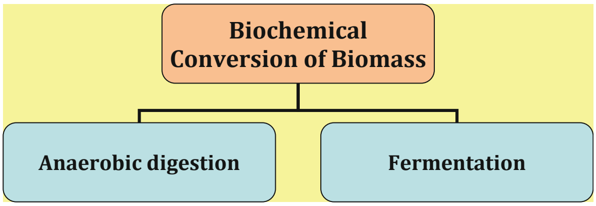
2.4.1.1 Anaerobic Digestion

Anaerobic digestion is carried out in anaerobic environment, to convert the organic waste into biofertilizer and biogas. The technology is most commonly used for conversion of biodegradable industrial, domestic wastes, or sewage sludge or special-grown crops for production of fuel. Moist organic waste is biochemically broken down in highly controlled, anaerobic environment, producing biogas. The biogas thus produced can be further used for electricity and heat generation (Arif et al. 2018; Batstone and Virdis 2014; Braber 1995; Náthia-Neves et al. 2018; Zafar 2020a, b). The process of anaerobic digestion has been illustrated in Fig. 2.2.

Acetic-acid-forming bacteria and methane-forming archaea are some of the microorganisms effecting anaerobic digestion. They act as catalysts in the production of biogas through a number of chemical reactions (Evans et al. 2009). The process is carried out in physical containment, excluding gaseous oxygen from the reactions (Beychok 1967). There are four phases in anaerobic digestion, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis. As part of the process, anaerobic microorganisms biochemically convert the organic material into carbon dioxide (CO_2) and methane (CH_4), as depicted in Eq. (2.1).

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \tag{2.1}$$

Fig. 2.1 Biochemical conversion of biomass



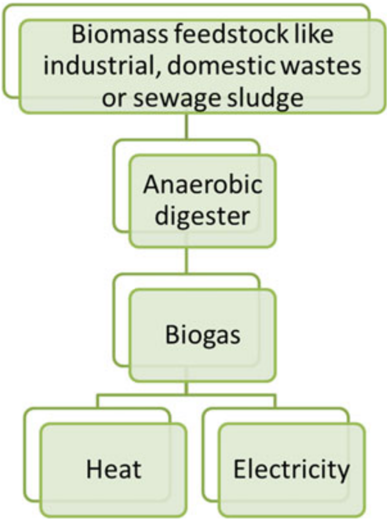


Fig. 2.2 Anaerobic digestion of Biomass

Hydrolysis

Biomass is composed of large polymers which are organic in nature. Anaerobic digestion process involves breaking down large polymers into monomers through bacterial action. Once decomposed, they become freely available to acidogenic bacteria. This process is termed as hydrolysis, wherein, smaller molecules are dissolved into solution (Sleat and Mah 1987). During this stage, simple sugars, fatty acids, and amino acids are generated. In the process, extracellular enzymes are involved, which are secreted by hydrolytic bacteria (Li et al. 2011). The process of hydrolysis takes place under the action of organisms like bacteria, fungi, and protists. It is further significant to understand that certain substrates, like lignin and cellulose have complex structures which make it difficult to break them down, and hence, enzymes are often used to augment their hydrolysis process (Lin et al. 2010).

Acidogenesis

The second stage is acidogenesis which further leads to breakdown of the monomeric products by acidogenic (fermentative) bacteria, leading to the production of Volatile Fatty Acids (VFAs). Additionally, ammonia, carbon dioxide, and hydrogen sulfide are also produced in the process (Alexiou and Panter 2004; Bergman 1990). The concentration of VFAs thus produced varies in terms of the class of organic acids (Bergman 1990). This stage is the fastest among all the other stages of anaerobic digestion (Deublein and Steinhauser 2008).

Acetogenesis

Acetate produced in the previous stage renders a part of the original substrate into the one suitable for acetoclastic methanogenesis (Fournier and Gogarten 2008). In this stage, acetate is formed, and hydrogen and carbon dioxide are also released (Hansen and Cheong 2013). This stage is closely interrelated with the subsequent stage namely methanogenesis in terms of providing substrates for methanogens (Hedderich and Whitman 2006; Liu and Whitman 2008).

Methanogenesis

Methanogenesis is the final stage of anaerobic digestion. In this stage accessible intermediary products from the preceding stages are changed to methane, carbon dioxide, and water by methanogens, also called as methanogenic microorganisms (Ferry 2010). These methanogenic microorganisms are sensitive to oxygen and need a higher pH level as compared to earlier stages (Wolfe 2011). According to researches, Methanosarcina spp., unlike other sensitive microbes, tend to be comparatively vigorous and can tolerate ammonia, sodium, and acetate concentrations. They can also withstand pH levels which are otherwise damaging to other methanogenic microbes (De Vrieze et al. 2012). The culmination of this stage is determined by the end of biogas production (Verma 2002).

Anaerobic digestion is thus a four-stage process, including continuous breakdown of wastes by anaerobic microorganisms and converting it into methane, carbon dioxide, and trace gases, known as biogas (Zhang et al. 2016). Each stage has its own set of microorganisms with their distinct features and environmental requirements (Deublein and Steinhauser 2008). Environmental concerns and waste menace have catalyzed anaerobic digestion as a promising technology for biomass conversion having a wide range of applications (Meegoda et al. 2018). Table 2.1 summarizes the different phases of anaerobic digestion.

2.4.1.2 Fermentation

Fermentation is an anaerobic technology which decomposes the glucose component of the biomass. The process is composed of biochemical reactions wherein simple sugars are converted into ethanol, CO_2, glycerol, and carboxylic acids. The process is carried out under anaerobic conditions by microorganisms mainly yeasts (Lin and Tanaka 2006; Strezov 2014). Microalgae species like Chlamydomonas, Scenedesmus, Chlorella, Spirulina, and Dunaliella have been found to gather large amounts of glycogen, cellulose, and starch (Günerken et al. 2015; Holtzapple 1993a, b, c). The process of fermentation is depicted in Eq. (2.2) (Strezov 2014).

Table 2.1 Phases of anaerobic digestion

Phase	Type of microorganism	Output
Hydrolysis	Acidogenic bacteria	Simple sugars, amino acids, and fatty acids
Acidogenesis	Acidogenic (fermentative) bacteria	Volatile fatty acids (VFAs), ammonia, carbon dioxide, and hydrogen sulfide
Acetogenesis	Methanogenic microorganisms	Acetate, hydrogen and carbon dioxide
Methanogenesis	Methanogens or methanogenic microorganisms	Methane, carbon dioxide, and water

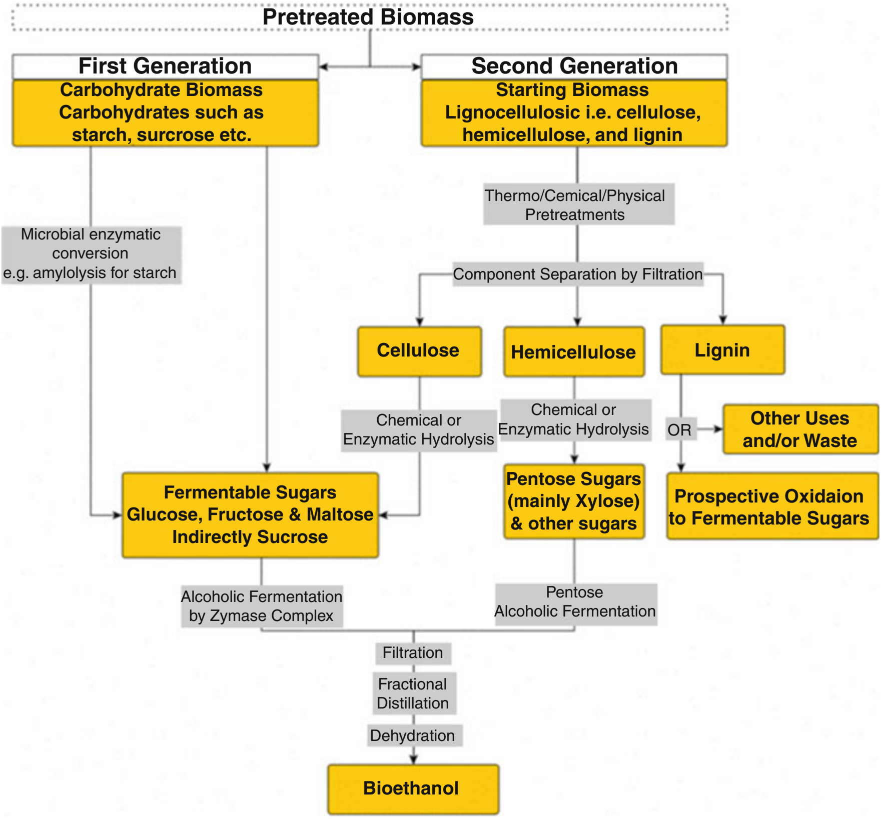


Fig. 2.3 Fermentation of biomass for ethanol production (Zammit 2013)

$$\text{Sugars} \rightarrow \text{Ethanol} + \text{CO}_2 + \text{byproducts} \tag{2.2}$$

Bioethanol production requires complex polysaccharides as raw materials. However, microbes are not able to metabolize the polysaccharides and therefore, hydrolysis is required to break them down to simple sugars before they can be used (Günerken et al. 2015). Crude alcohol generated ought to go through a concentration phase by distillation (Bibi et al. 2017). The remaining solid matter can further undergo processes such as gasification and liquefaction (John et al. 2011). Figure 2.3 depicts the process of fermentation of biomass for ethanol production.

2.4.2 Thermochemical Conversion

The second type of biomass conversion technology is thermochemical biomass conversion which includes controlled heating or oxidation of biomass (Demirbas 2004; Goyal et al. 2008). This technology of biomass conversion is centuries-old and

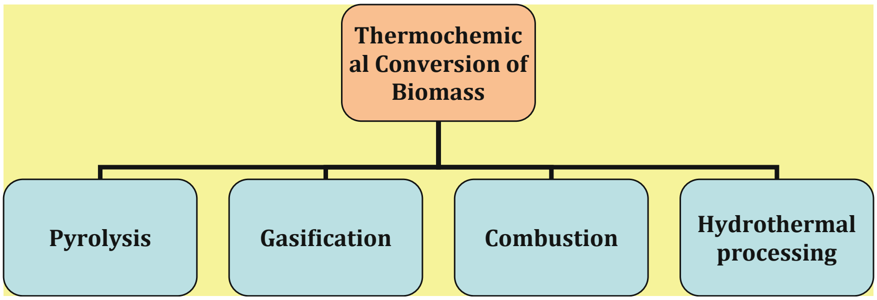


Fig. 2.4 Thermochemical conversion of biomass

has been used in different forms and settings (Park et al. 2018). Thermochemical conversion further constitutes different methods to produce biofuels using biomass, namely pyrolysis, gasification, combustion, and hydrothermal processing, as illustrated in Fig. 2.4 (Demirbas 2009; Ong et al. 2019).

2.4.2.1 Pyrolysis

Pyrolysis is an advanced thermochemical technology to produce synthetic gas from biomass in anaerobic conditions, at temperatures around 1000 °C. It is usually the prime step in combustion and gasification routes (Bridgwater 2003; Yang et al. 2001). Pyrolysis involves thermal breakdown of the biological matter to get solid, liquid, and gaseous produce (Yaman 2004). Due to anaerobic conditions, the volume of gas released through pyrolysis is much lower than gasification; however, it has comparatively higher calorific value (Lupa et al. 2012; Mohan et al. 2006a, b; Neves et al. 2011).

Pyrolysis has a number of advantages which are both economic and environmental in nature. Some of the advantages are listed below (Dutton 2020):

1. It provides a carbon-neutral route for utilization of renewable resources.
2. Waste products like agricultural residues can be fruitfully utilized.
3. The process is helpful in producing liquid fuels having high energy density.

Temperature is an important factor to be considered in pyrolysis. As the temperature goes up, the production of charcoal goes down. To capitalize on the generation from pyrolysis, following factors need to be considered (Abella et al. 2007; Balat et al. 2009; Mohan et al. 2006a, b; Uddin et al. 2018):

1. Production of charcoal requires low temperature and low heating rate process.
2. Further, low temperature, higher rate of heating, and short gas residence time, are good for liquid fuels.
3. Lastly, a high temperature, low heating rate, and a long gas residence time favor the production of gaseous fuel.

Fig. 2.5 Types of pyrolysis

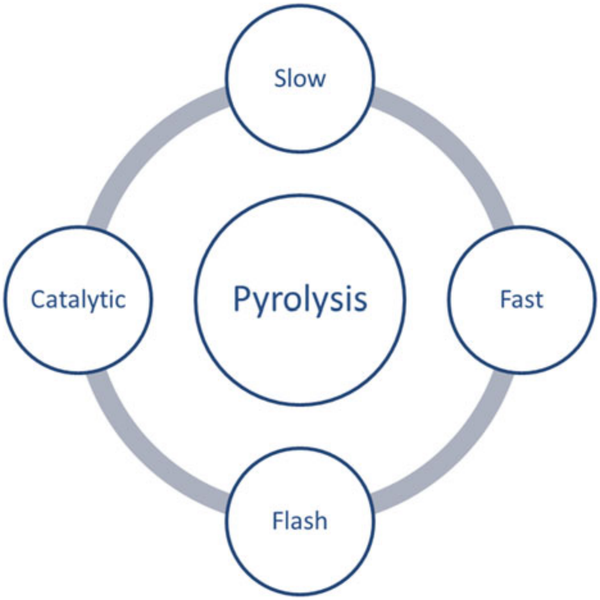


Table 2.2 Pyrolysis methods and their operating conditions

Type of pyrolysis	Temperature (°C)	Residence time	Heating rate (°C/s)	Major output
Slow	400–500	Long (5–30 min)	Low (10)	Gases, char, bio-oil
Fast	400–650	Short (0.5–2 s)	High (100)	Bio-oil, gases, char
Flash	700–1000	Very short (<0.5 s)	Very high (>500)	Gases, bio-oil

Source: Boyt (2003)

Pyrolysis process has different types namely into slow, fast, flash, and catalytic (Fig. 2.5).

The differentiating factors are the process environments including residence times, rate of heating, particle size, and temperature (Bakis 2008; Balat et al. 2009; Zhang et al. 2007). Table 2.2 depicts the classification of pyrolysis methods with differences in operating conditions.

Slow Pyrolysis

In this process, slow rates of heating the biomass (5–7 K/min) are used for pyrolysis, which produces more of char and less of liquid and gases (Antal and Grönli 2003; Goyal et al. 2008). In this process, good quality charcoal can be produced using slow pyrolysis at low temperature and heating rates, with gas residence time of about 5–30 min (Bridgwater et al. 2001). Slow pyrolysis produces low quality bio-oil which is further reduced by longer residence time (Demirbas 2005; Tippayawong et al. 2008).

Fast Pyrolysis

Fast pyrolysis is a direct thermochemical technique used to produce liquid bio-oil from solid biomass (Demirbas 2006; Huber and Brown 2016; Pattiya 2018). In this process, feedstock is quickly heated to higher temperatures in anaerobic conditions. The primary produce of fast pyrolysis process is high-grade bio-oil (Goyal et al. 2008). It is a speedy thermal disintegration of carbonaceous matter in anaerobic environment. Usually, fast pyrolysis is carried out in moderate temperatures, rapid rates of heating, and short times of residence of the biomass and pyrolysis vapors (Demirbas 2004, as cited in Mašek 2016). To reach the required high heating rate, biomass content requires intensive heat transfer and thus, small particle sizes prove to be a better choice, owing to poor thermal conductivity of biomas (Mašek 2016). Fast pyrolysis has been used to thermally deconstruct biomass feedstock such as algae and a variety of mixed wastes, manure, and organic byproducts from manufacturing (Bridgwater 2003; Manara and Zabaniotou 2012; Mohan et al. 2006a, b).

Flash Pyrolysis

Flash pyrolysis constitutes a reaction time of only a few seconds or less. This technology is marked by very high thermal rate, biomass residence time of only several seconds and fairly small size biomass particles (as rapid heating is needed). Major glitch in the contemporary reactors for this process is the quality of the produced oil. Flash pyrolysis is further divided into (Gercel 2002; Funino et al. 1999; Lede and Bouton 1999):

1. Flash hydropyrolysis, done in the presence of hydrogen, at a pressure up to 20 Mpa.
2. Solar flash pyrolysis uses concentrated solar radiation.
3. Vacuum flash pyrolysis is conducted in vacuum to enable the elimination of condensable matter from the hot reaction zone.

Flash pyrolysis is a method which involves rapidly heating the organic materials in anaerobic environment, leading to the production of organic vapors, gases and char. The vapors are further condensed to bio-oil. As high as 65–70% of the dry feed can be transformed into bio-oil through flash pyrolysis.

Catalytic Pyrolysis

It has been observed that the liquids obtained from above pyrolysis technologies cannot be used directly and needs upgradation. This is because of high oxygen and moisture content present in them (French and Czernik 2010; Wang et al. 2010). Catalytic pyrolysis is a process to improve the quality of the oil thus produced (Balat et al. 2009; Pattiya et al. 2006, 2008). Catalysts can be incorporated into a fast pyrolysis system as in situ (mixed with biomass feedstock or as heat-transfer medium) or ex situ (close-coupled in the reactor above the bed or as a secondary reactor) (Pattiya 2018). Catalytic cracking is used to improve the quality of bio-oil through a catalytic medium. In the process, oxygen is removed from bio-oil compounds in the form of water and carbon dioxide, involving the chemical reactions of rupturing the C–C bonds via dehydration, decarboxylation, and decarbonylation (French and Czernik 2010; Thangalazhy-Gopakumar et al. 2011, 2012; Wang et al. 2010).

Thus, pyrolysis is a thermochemical treatment, which is suitable for any organic (carbon-based) product. During this process, the material goes through chemical and physical separation on exposure to high temperature, in anaerobic conditions.

2.4.2.2 Gasification

Gasification treatment includes heating the material at temperatures ranging between 800 °C and 1000 °C in a gasifier, with restricted oxygen. In such an environment, a significant portion of the material is converted to "syngas" which constitutes methane, hydrogen, carbon monoxide, carbon dioxide, and nitrogen. It also leads to the production of some amounts of char, as a byproduct of gasification (Molino et al. 2016; Sansaniwal et al. 2017; Victoria State Government 2020).

Direct combustion of biomass, the most commonly used conventional process, results in emission of toxic gases, smoke, and dust (Cormier et al. 2006). On the other hand, gasification, as a method of treating biomass can reduce the harmful emissions and provide environmental benefits. The process of producing syngas, involving chemical reactions, is catalyzed by gasification agents (Faaij 2006; Prins and Wagenaar 1997; Santos and Alencar 2020; Sikarwar et al. 2016; Williams and Larson 1996). Syngas can be purified before being combusted, and it has higher efficiency than that of solid biomass used for its production (Farzad et al. 2016). Gasification, as a technology, is more efficient than combustion for generation of electricity. Nonetheless, its requirements for biomass are more stringent like moisture level and size of particle (Hlina et al. 2014; Rutberg et al. 2011).

2.4.2.3 Combustion

Conventionally, combustion has been one of the most commonly used technologies for biomass conversion, constituting 97% of total bioenergy production globally. It comprises of a number of chemical reactions including oxidation of carbon and hydrogen to carbon dioxide and water respectively. The most common uses of biomass fired domestic stoves include heating and cooking in different regions. Nowadays, biomass residues are extensively used for production of electricity wherein biomass undergoes direct combustion leading to the production of steam and in turn, driving a generator to produce electricity (Demirbas 2007; Nussbaumer 2003). Combustion constitutes complex exothermic reactions between oxygen and hydrocarbon present in the biomass (Jenkins et al. 1998; Babu 2008). Incomplete combustion can lead to production of air pollutants like CH4 and CO (Robbins et al. 2012). There are a number of applications of biomass treated through combustion process like cooking, heating, generation of steam in boilers, electricity generation through steam turbine, and so on. Biomass is used either separately or as a supplement to fossil fuels (Basu 2018).

2.4.2.4 Hydrothermal Processing

Hydrothermal processing is a significant process in converting biomass into biofuel. As the name suggests, the process involves water, where the biomass is degraded into smaller fractions. The settings in terms of pressure, time, and temperature during the process depend on the kind of end-product being targeted, i.e., bio-oil, bio-gas, or bio-carbon. The advantage of this technique is that it works with all kinds of biomass, especially because these materials have high moisture contents which do not require pre-drying for this treatment (Kumar et al. 2018; Tekin et al. 2014).

There are two types of hydrothermal process, namely liquefaction and gasification. Hydrothermal carbonization is another method which is comparatively novel (Erlach et al. 2012; Sevilla and Fuertes 2009; Xiao et al. 2012). Hydrothermal treatment is given at temperatures of about 250–374 °C and a pressure of 4–22 MPa (Elliott 2011; Yokoyama and Matsumura 2008). Hydrothermal process might be carried out under either subcritical or supercritical water conditions (Elliott 2011; Karagöz et al. 2005). Most biomass components are soluble in high temperature, also called supercritical water. In supercritical environment, gas is produced by breaking down the macromolecules present in biomass. On the other hand, at lower temperature or subcritical conditions, viscous bio-oil product is produced (Savage et al. 2010).

Using hydrothermal technique, bio-char, oil and gas can be produced from biomass by regulating the variables under which the process is carried out (Yokoyama and Matsumura 2008). Bio-oil can be used in place of petroleum oil and also as a fuel for co-firing with coal. Additionally, the oil can also be transformed into high-quality distillate fuels, such as diesel and gasoline (Savage et al. 2010).

2.4.3 Physiochemical Conversion

The physicochemical technology is aimed at improving the properties of biomass, both chemical and physical. The ignitable constituent of biomass is converted to high-density bio-fuel pellets, having possible applications for steam generation (Zafar 2020a, b).

2.4.3.1 Esterification

A variety of oils and animal fats can be changed to first generation biodiesel using the processes of esterification and/or transesterification, as physiochemical treatments to biomass (Fukuda et al. 2001). Similarly, for second- and third-generation biodiesel, waste oils and microbial oils could be respectively used. It is significant to note that oils primarily comprise of triglycerides, which cannot be used as fuels. Thus, they often lead to issues like incomplete combustion and therefore, crude oils need to be converted through processing. This processing primarily is called transesterification which breaks down the triglyceride molecules into fatty acids and glycerol. Further, through the process of transesterification, the triglycerides are converted into methyl or ethyl esters (biodiesel) using methyl or ethyl alcohol, respectively, as depicted in Eq. (2.3). The process is carried out at temperatures of around 50–70 °C (Leung et al. 2010).

$$\text{Oil} + \text{Short chain alcohol} \rightarrow \text{Biodiesel} + \text{Glycerol} \tag{2.3}$$

The glycerol is subsequently separated from biodiesel, and the excess alcohol is removed. Later, biodiesel is usually purified by water-washing to eliminate any residues before it is finally dried and stored (Canakci and Van Gerpen 1999).

2.5 Examples of Biofuels

2.5.1 Bioethanol

Bioethanol is produced from agricultural wastes such as lignocellulosic biomass which is a second-generation feedstock that is abundantly available. If not disposed of properly this feedstock is often a cause of pollution. Efficient technologies that use microorganisms have been developed to produce bioethanol. Certain microorganisms can utilize second-generation feedstock as they have higher resistance to alcohol during fermentation. Biorefinery is also a feasible option to enhance the sustainability of fuel production. Moreover, revenue can be generated from other valuable products obtained from biomass. Lignin, for instance, is a polymer found abundantly in biomass but hard to extract and thus can be explored for generating other materials. Researchers are now able to treat biomass effectively, and recover lignin and fermentable sugars using enzymes, microorganisms, and different chemical processes.

2.5.2 Biodiesel

Biodiesel is largely produced from a variety of oils like rapeseed, palm, soybean, and waste cooking oil. Even though it is an ideal solution the availability of feedstock is a major hindrance. An alternative is to use nonedible oils from plants such as camelina and rubber along with animal fats like beef tallow, and chicken fat. Further genetically modified species of these nonedible oil seed plants like Camelina sativa which have higher oil content have been created. A process for producing synthetic oil using microorganisms has also been developed which significantly reduces dependence on edible oil seed plants. Ecofriendly enzymatic and chemical catalysts with higher oil conversion efficiency are used by industries to simplify separation, thereby speeding up the biodiesel purification process. Using genetically modified microorganisms in biodiesel production reduces the consumption of chemicals. Biodiesel production from microalgae, which is a third-generation feedstock, is another option explored by many companies; however, due to lower yield and complexities associated with the process, very few companies have succeeded in commercializing it. The processes or alternatives mentioned above help in enhancing the sustainability of biodiesel production.

2.5.3 Biogas

Biogas is used to generate electricity or as an alternative to CNG, a fossil fuel used mostly for transportation. Sustainability of biogas production has been enhanced with development of microorganisms producing biogas with higher methane content. CO_2 is a byproduct of the biogas production process. Researchers opine that the CO_2 thus produced can be utilized in the cultivation of microalgae. Moreover, the process to convert this CO_2 into methane has been developed which could help in increasing the methane content in biogas.

2.5.4 Other Sustainable Fuels

Fuel production from carbon emissions using different processes has recently been explored. CO_2 can be converted into liquid fuels like alcohols using the electrochemical and gas fermentation process. Many companies are either developed or developing a commercial process for the production of fuel. Upgraded reactors in terms of design, use of a better catalyst which increased the efficacy of the thermochemical process (gasification); production of different alcohols from renewable feedstock are being researched actively to increase the sustainability of different fuels.

While sustainable fuels cannot replace fossil fuels immediately, they can help in achieving energy security, reducing pollution levels and making the ecosystem healthier when blended with fossil fuels. With favorable government policies and efficient implementation, these fuels can become an effective alternative in future. Overall, continued development in sustainable fuels can lead us to a viable solution for curbing global warming (Joshi 2020).

2.6 Benefits of Biofuels

Biofuels offer a range of social and environmental benefits including energy security, reduced greenhouse gas (GHG) emissions, employment generation and so on. Some of the benefits have been listed below.

2.6.1 Reducing Greenhouse Gas Emissions

One of the primary advantages or benefits of using biofuels is reduction in the GHG emissions. This however, varies depending on factors like the type of biomass used, method of production and procurement, and efficiency of the technology used to produce bioenergy. Usually, GHG emissions reduction from bioenergy systems is maximum when waste feedstock is converted to heat or combined heat and power near the place of waste generation. Bioenergy's GHG reduction potential is higher than those of other renewable sources of energy. For example, stubble, an agricultural waste left after crops are harvested is often burnt in the fields. This stubble can be fruitfully be harvested and combusted in a controlled bioenergy plant. Hence, GHG emissions are reduced at two levels—first by preventing stubble burning in the fields and second by decreasing the use of fossil fuels by producing biofuels.

2.6.2 Generating Heat and Electricity

Biomass can generate both heat and electricity in a combined heat power (CHP) plant unlike most other renewable energy sources. These can then be used for a variety of thermal applications in industry, townships, or neighborhoods.

2.6.3 Better Air Quality

The biomass residues in the form of stubble, other agricultural waste that would otherwise have been openly combusted in the field, are fruitfully combusted under controlled conditions to make bioenergy. This greatly reduces the emissions of GHGs and hence helps in mitigation of climate change.

2.6.4 Biofuels Are Biodegradable

Biofuels such as ethanol and biodiesel are biodegradable unlike fossil fuels which are detrimental to the environment and are one of the major pollutants of surface and ground water.

2.6.5 Local Economic Development

Bioenergy production creates new revenue generation opportunities for the local communities and encourages regional economic development and employment. More market options open up for agronomists for their conventional harvests and for the use of agricultural waste. Requirement of biomass also presents novel openings to farmers to indulge in growing new varieties, especially areas with poor rainfall. Subsidiary activities like growing and harvesting biomass, transportation, construction, operation, and maintenance of bioenergy plants all provide new opportunities for employment.

2.6.6 Providing Support to Agricultural and Food-Processing Industries

Biomass utilization helps building resilience in supporting industries like agriculture and food-processing industries. All the wastes generated through these industries find fruitful outlet in bioenergy production. Such a practice reduces their energy costs as well as supplements their income as they are able to sell the energy derived from biomass to the grid.

2.6.7 Cost Savings

Bioenergy is very useful for remote and difficult terrain areas which are not connected to the grid, or where grid supply is not feasible, or where electricity transmission losses are high. Bioenergy is off-grid energy and can be supplied to local communities and can cut down on their fuel costs. At the same time it will replace use of fossil fuels which are GHG emitters.

2.6.8 Less Landfills

As bioenergy production relies on organic waste from agriculture, forests, food processing industries, municipal waste, etc. it prevents all these wastes from entering the landfills. Landfills, apart from using a big land parcel, cause stench, breeding of insects and germs, and lead to pollution of soil and ground water.

2.6.9 Energy Security

Bioenergy acts as a domestic and local source of energy which can run uninterrupted, thus, enhancing the regional energy reliability and security. During times of peak electricity demands, bioenergy can also supplement the large thermal power plants to fulfill the energy needs.

2.6.10 New Technologies and Applications

With the advent of research in this area, there are reliable technologies in place for generating fuels, heat, and electricity from biomass. Production of bioenergy and biofuels also leads to generation of additional bioproducts. For instance, organic digestates is an excellent fertilizer, produced as a byproduct of anaerobic digestion of biomass.

2.6.11 Alternatives to Prescribed Forest Burning

To deal with the problem of prescribed burning of forests, bioenergy production serves as an excellent alternative wherein, biomass removal for bioenergy is done to reduce toxic fuels. This is especially beneficial in areas where risks associated with prescribed burning are severe. Thus fuel reduction combustion is replaced with biomass harvesting. Thus, biomass harvesting is a practice widely encouraged and used in forests and woodlands in different countries.

2.6.12 Environmental Benefits from Bioenergy Crops

Special crops called bioenergy crops can also be produced for supplementary vegetation cover in different areas. For instance, farms can be used to grow trees which can be harvested for their wood (acting as biomass), in addition to providing aesthetics, shelter, salinity control and acting as carbon sinks. Some species even have an ability to reshoot and hence can be harvested continually.

2.7 Uses of Biofuels as Sustainable Renewable Energy

As biofuel is considered to be a safe alternative fuel, there are various uses of biofuel that help in reinforcing its replacement with diesel or other fossil fuels. Biofuel can be used in various sectors like transportation and power generation and can help in making our net negative impact on the environment negligible, if not zero. Some of the possible uses of biofuel have been listed below (French 2004; Huang et al. 2012; Marquard and Bahls 2020; Nunez 2019; Miller and Mudge 1997; Rodionova et al. 2017; Tirado 2018).

2.7.1 Transportation

The transportation sector is highly dependent on fossil fuels and thus is accountable for global warming. Worldwide, transport takes accounts for 24% of energy consumption and more than 60% of absorbed oil. This suggests that over one-third of the oil is used to operate vehicles. This not only accounts for greenhouse emissions but also puts pressure on limited resources to meet the demands of the globe. Nowadays, various factors like oil price hikes and awareness generation have influenced consumers to switch to biofuels to save money and reduce their dependence on oil. Biofuels such as ethanol, biodiesel, methanol, methane, can be used as fuels for transportation. For instance, ethanol, one of the most widely used biofuel worldwide, is found being used in various ways, either separately or along with other fuels. Biodiesel is a renewable substitute for diesel. In diesel engines, it is used as a fuel additive in the ratio of 20% blends (B20) with petroleum diesel. The cost of the fuel and the desired benefits are considered while creating other blend levels to suit the purpose (Shell n.d.).

As a result of intensive researches conducted, biofuel is not only used for road transportation, but also in aviation and railway industries. For example, United Airlines, in 2011, became the first airlines in the world to fly aviation flight on a microbially derived biofuel. Not only that, various railway trains are run on biodiesel. For instance, in 2007, Disneyland started the park trains on B98 which is 98% biodiesel. Also, in 2004, the then Indian Railway Minister announced to use 5% bio-diesel in Indian Railways' Diesel Engines (Business Standard 2014).

2.7.2 Power Generation

Apart from vehicular fuel, biofuel has a power generating application that is available for electricity. Biofuel can act as a stable and renewable source of energy that not only is cost-effective but also can replace coal-based thermal power plants. For effective production of power through biomass, the feedstock should be of high calorific value with low moisture content. One such application can be observed in the operations of waste to energy plants that recover the energy from calorie-rich organic waste. Biomethanation is a technology used in to convert waste to energy in plants that digest the organic mass anaerobically and thereby producing biogas. Electricity can be produced feeding this biogas in the gas engine. The electricity then produced can be used in facilities like schools, hospitals, and residential apartments.

2.7.3 Heat Generation

Biomass has been used since ancient times to produce heat, known as bioheat. Materials like wood, cow dung, dried leaves have been used extensively in rural and urban regions to generate heat. The key component of bioheat is vegetable oil and animal fats. The primary advantage of bioheat is that it is nontoxic, renewable, and biodegradable. Also, it is considered to be less polluting than the petroleum-based alternative.

Biofuel such as biodiesel can be utilized in burning stoves to produce heat. This will replace the otherwise used gas or electricity and would also reduce the emission of nitrogen and sulfur dioxide. This application of biofuels to provide heat can be used in homes and replace the electric heaters that produce carbon monoxide and are considered harmful to humans.

2.7.4 Remediation of Oil Spills

Since many decades, crude oil has been polluting the water bodies. Biofuels can be used as a cleaning agent (faster and more effective than other cleaning agents) to prevent this pollution from further deteriorating the environment and marine life. It lives up to its ecofriendly reputation, when it comes to cleaning oil spills and grease. It has a significant capacity to dissolve crude oil and lowers the viscosity of crude oil because of its methyl ester component.

2.7.5 Cooking Fuel

Although the most common ingredient to be used for stoves and nonwick lanterns is kerosene, biodiesel works equally well. Methanol, which is another type of biofuel, is considered to be very versatile and can also be utilized as cooking fuel. However, the use of solid biofuels like fuel wood and cow dung in rural households for cooking purposes poses a lot of health risks and causes indoor pollution.

2.7.6 Other Uses

In addition to its application in the above sectors, biofuel has other noteworthy uses. Biofuels can also be used as lubricants in the automation industry because of high viscosity and can be used in diesel engines. Like biodiesel, it has better flammability and can be transported easily when compared to petrol or diesel. It has high flash point which identifies it to be a safe good. Due to all these properties, biofuel also helps in extending the life span of vehicle engines. Another notable use is that it can be used in removing paints and adhesives. Commonly used paint removing agents are toxic in nature, and biofuels provide a complete ecofriendly solution to remove paints and adhesives even though they are a bit pricey. Also, due to its less toxic nature, biofuel can be used as an industrial solvent and is suitable for cleaning industrial metals.

2.8 Conclusion

While the energy demands are increasing globally, the finite resources are on the verge of depletion, in addition to causing irreparable environmental damage. Combustion and use of fossil fuels leads to emission of GHGs and adds carbon dioxide to the atmosphere. Thus, there is a shift of attention toward clean, sustainable, and renewable sources of energy. These sustainable sources of energy are critical to solve the arising energy crisis in the world. Bioenergy is an excellent resource for meeting our energy demand. It is derived from living organic materials called biomass, and can be converted to fuels, heat, electricity, and other useful products. Biofuels being derived from organic mass are sustainable and are less toxic to the environment. These fuels have possible applications in various industries and can reduce our dependence on diesel or petrochemicals. Such resources are way forward and would help us operate in an ecofriendly manner in our day-to-day lives. Based on current progress and application of biofuel, it is believed that the large-scale production of biofuels is urgent and achievable. With the advent of innovative and contemporary high efficiency bioenergy technologies, it has become possible to improve energy security and access in a sustainable manner. Furthermore, government policies, programs, research, and development would supplement the adoption and utilization of biofuels on a larger scale. Bioenergy is significant for enhancing regional energy independence by decreasing dependence on fossil fuels. Further, it is important in meeting GHG reduction targets for climate change mitigation and achieving other sustainable development goals and objectives.

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Biofuel from Microalgae

3

Aparna Agarwal, Ruchi Sharma, Abhishek Dutt Tripathi, and Rizwana

Abstract

The rapid rise in emissions of greenhouse gases due to utilization of fossil fuels led to the increase in pollution level and climate change along with depletion of the resources. Thus, biofuels produced from microalgae provide an alternative approach toward replacing fossil fuels. Microalgae are the photosynthetic microorganisms which grow in marine and fresh water. The biofuels obtained from microalgae are more sustainable, economical, renewable, and prevent elevation of greenhouse gas emissions. The microalgal biofuels are considered under third generation of biofuels. Also, microalgae used for biofuels possess the advantage of providing nutrients such as lipid, carbohydrate along with requiring less land and water for cultivation. However, biofuels produced commercially are not sustainable due to low production and costly operating procedures. The main purpose of this chapter is to enlighten the concepts as well as technologies which are involved in evolution of biofuels such as biodiesel, biomethane, bioethanol, and biohydrogen. Also, it highlights the generations, benefits, drawbacks, global production of biofuels along with the other applications of microalgae in different

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A. Agarwal (✉)
Department of Food & Nutrition and Food Technology, Lady Irwin College, New Delhi, India

R. Sharma
Department of Agriculture and Environmental Sciences, National Institute of Food Technology Entrepreneurship and Management (NIFTEM), Sonepat, Haryana, India

A. D. Tripathi
Department of Dairy Technology and Food Technology, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi, Uttar Pradesh, India

Rizwana
Department of Food Technology, Bhaskaracharya College of Applied Sciences, Dwarka, New Delhi, India

M. Srivastava et al. (eds.), *Bioenergy Research: Biomass Waste to Energy*, Clean Energy Production Technologies, https://doi.org/10.1007/978-981-16-1862-8_3

areas. The usage of microalgae in the production of biofuels proves to be a novel and scientific outlook in reducing environmental degradation as well as increasing the awareness toward sustainable approach.

Keywords

Biofuel · Microalgae · Fossil fuels · Energy · Environment

3.1 Introduction

With the advancement in technology, increasing urbanization and industrialization, the energy utilization and its requirement is increasing at a faster pace and is predicted to be increased by 50% by the year 2030, which pose a threat toward the environment leading to rise in pollution level and climate change due to the release of harmful and toxic gases (Shuba and Kifle 2018; Kumar et al. 2016). The reason is the utilization of fossil fuels to produce energy in order to cope with the energy demand globally, due to the combustion of fossil fuels which led to rise in greenhouse gas emissions resulting in global warming that ultimately affects the environment (Chandrasekhar et al. 2015). After going into the atmosphere, greenhouse gases combines with the sunlight and other atmospheric components and leads to the formation of more potent secondary pollutants including aerosols, ozone, and acids. Acids are also formed in clouds by precipitation of sulfur and nitrogen oxides to form sulfuric and nitric acids in the form of acid rain. Accumulation of these acids in the soil and water deteriorates the vegetation and living habitat of animals as well as humans (Barbir et al. 1990). Although production of energy through fossil fuels helps in developing the industrial sector, but, by eliminating the existing natural resources and making them extinct, it has led to environmental degradation, which is not acceptable. This results in the need for evolution of biomass-based, sustainable, ecofriendly, and renewable energy alternatives for the utilization of fossil fuels in order to protect environment as well as mankind for a better and sustainable world (Chandrasekhar et al. 2015). There can be many alternatives for the fossil fuels including biofuels, geothermal, solar, hydroelectric, and wind energy. Among all these alternatives, biofuels are more efficient which can be used to replace fossil fuels. Biofuels are termed as those types of fuels which derive their energy from living organisms through carbon fixation. These can be obtained through various environment-friendly renewable sources of energy including vegetable oils, biomass waste, starch, microalgae, and animal fats (Shuba and Kifle 2018). Microalgae promised to be an efficient and renewable method for the production of biofuels including biodiesel, biomethane, bioethanol, and biohydrogen which can help in reducing pollution as well as harmful and toxic greenhouse gas emissions, for example, methane, carbon dioxide (CO_2), hydro fluorocarbons, per fluorocarbons, and hexafluoride in the environment. It also blends up to 20% with other fuels such as diesel without making any alterations in the production equipment (Baral et al. 2015). Biofuels are the type of fuels usually produced from bio-based microalgae including methane, firewood, and petroleum. Biofuels are found in three different forms as solid, liquid, and gaseous fuels. These fuels are renewable and are used to produce heat, energy, light, and power (Ruan et al. 2019). In the formation of biofuels, energy is utilized for the growth of crops and is converted into biofuels. A variety of biomass is available which is used for the production of biofuels such as agricultural waste, crops, and forest residues. With the increase in the demand for the biofuels, biomass resources are also getting valued (Shahare et al. 2017). Production of biofuels leads to various advantages such as reducing the carbon dioxide emissions, ease of storage, and transportable energy source and provides economic viability (Callegari et al. 2020).

This chapter enlightens the novel approach toward biofuel obtained from microalgae. It focuses on the characteristics and production of microalgae along with the various forms of biofuel obtained from microalgae including bioethanol, biodiesel, biomethane, and biohydrogen. Also, it sheds light on the generations, benefits, drawbacks of biofuel, and applications of microalgae in other relevant areas.

3.2 Characteristics of Microalgae

Algae are considered as photosynthetic microorganisms which grow in ponds, lakes, rivers, oceans, and wastewater. Algae, on the basis of size, are categorized into microalgae and macroalgae. Macroalgae are known to be large and multicellular algae which also termed as seaweed and visible with the naked eye (Khan et al. 2018). Microalgae are referred as photosynthetic microorganisms as they utilize photosynthesis process to convert from solar energy to the chemical energy. They include prokaryotic microorganisms including cyanobacteria and eukaryotic microorganisms, for example, algae. Microalgae are usually found in single-celled form with few exceptions in multicellular form (Duygu et al. 2017). They can be grown in multiple environmental conditions which are not feasible for other raw materials, for example, soybean, rapeseed, and palm seed oil in the evolution of biodiesel. The microalgae growth as well as productivity is very high in comparison with the traditional ones, and they also demand very less area of agricultural land for production. During their period of growth, they become double in every 24 h. During their peak growth period, they become double in every 3.5 h (Patel et al. 2016). They have various advantages such as quick growth, large amount of oil content, greater productivity, shorter rotation, greater bio-chemical activity, and greater photosynthetic efficiency (Chen et al. 2012). Also, microalgae results in the formation of various bioactive compounds as described in Table 3.1. Due to the growth of microalgae in a very small area under the water surface, in order to maintain the algal growth, it is important that mixing of microalgae culture should be properly performed. Strong mixing of culture increases the productivity, enhances the carbon dioxide supply, and remove the excess oxygen, while inferior mixing leads to the formation of clumps in the cells. Various methods can be employed to improve the mixing characteristics such as using internal static mixers and increasing the fluid

Table 3.1 Bioactive compounds and characteristics of microalgae (Khan et al. 2018)

S. no.	Bioactive compounds	Examples	Characteristics
1.	Carotenoids	Phycocyanin, Phycobiliproteins, Phycoerythrin, lutein, β-carotene, astaxanthin	Role in food, cosmetics, biopharmaceuticals, fluorescent agents, antioxidant property, anti-inflammatory effects, anticancer activity
2.	Proteins and enzymes	Cyanovirin, Microcolin-A, superoxide dismutase (SOD) enzyme	Enzymatic properties, immunosuppressive effects, antiviral properties
3.	Polyunsaturated fatty acids	Docosahexanoic acid (DHA), Eicosapentaenoic acid (EPA), gamma-linolenic acid (GLA), linoleic acid (LA), arachidonic acid	Anti-inflammatory properties, prevent cardiovascular diseases, heart diseases, asthma, headache, arthritis
4.	Sterols	Sitosterol, stigmasterol, campesterol	Anticancer activity, hypo-cholesterolemia effects, anti-inflammatory properties, neurological properties
5.	Vitamins	Vitamin E (tocopherol), Vitamin A (β-carotene), Vitamin C (ascorbic acid)	Enhance immune system, strong bones, energy
6.	Toxic metabolites	Cyanotoxins, microcystins	Antibacterial effects, antifungal properties

velocity (Zhang et al. 2013). The microalgae have also a property known as pyrolytic property which is the degradation of the microalgae in the heat only without the presence of oxygen. Due to this property, microalgae can be utilized to produce fuels and can replace petroleum or natural gas in the power stations and heating supplies. Example of such microalgae include green algae *Chlorella protothecoides*. Also, to determine the pyrolytic properties of microalgae thermogravimetric analysis is a widely accepted technique (Peng et al. 2001). Microalgae also provide food for zooplankton and constitute the lower portion of the food chain. They are present everywhere in ecosystems including aquatic and terrestrial, and environment as a variety of species; around 200,000–800,000 species of microalgae are in existence (Odjadjare et al. 2017).

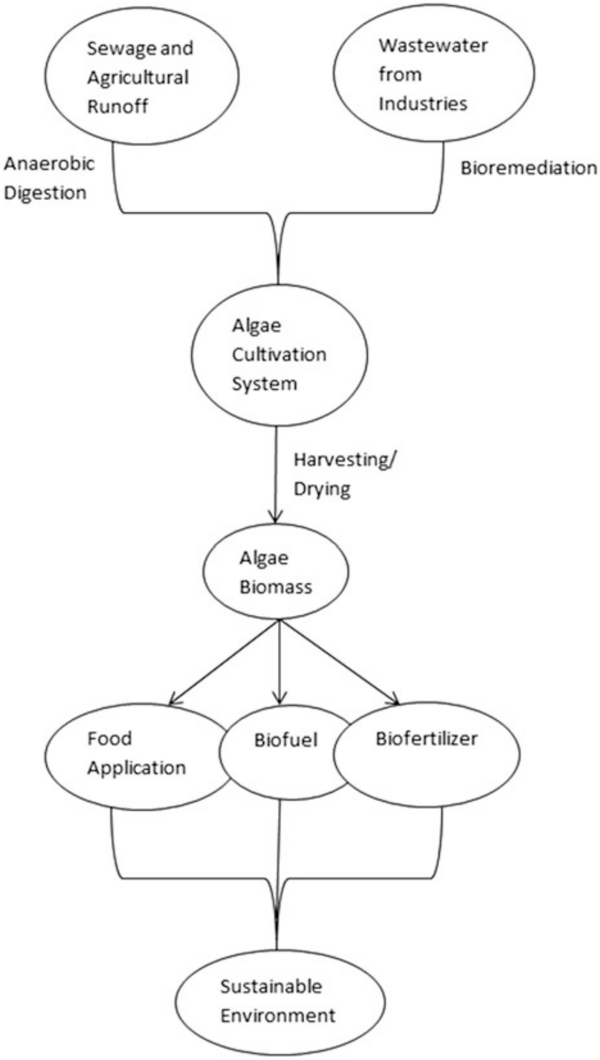
Microalgae are also utilized as a supplement for both humans and animals such as spirulina, which is a high-protein microalgae. In addition to this, spirulina can also be employed for development of energy-production system which is helpful in reducing global warming. This energy-production system functions by recovering the energy from spirulina using thermochemical liquefaction process which converts the wet algal biomass into bio-oil (Huang et al. 2011). Liquefaction is generally a thermochemical technique which operates on higher pressure and lower temperature in order to disintegrate biomass such as microalgae into smaller fragments of molecules in a solvent which repolymerizes to form oily compounds with varying molecular weights (Huang et al. 2013). One more essential feature of microalgae is the drying technology. Drying characteristics play a crucial part in production of the higher quality biofuels from microalgae. Drying methods help in increasing the functionality of the solvent-based extraction of bio-based oil along with the prevention of the production of water and oil emulsion. There are many drying methods employed for the production of biofuels such as solar drying, rotary drying, spray drying, convective drying, vacuum shelf drying, flashing drying microwave drying, and cross-flow drying. According to one study the technique of microwave drying with its rapid and evenly distribution of heat flow into sample is employed in microalgae *Chlorella vulgaris* at 20 W/g which help in providing larger amount of fat(lipid) and carbohydrate to yield good quality biofuel (Villagracia et al. 2016). Kinetic characteristics are one of the other important characteristics of microalgae as it helps in improving its lipid content, enhancing microalgae biomass, and reducing the operational cost. Kinetic characteristic of microalgae varies in different phases of microalgae cultivation, i.e., adaption, growth, stationary, and decline phase. By keeping this in mind, a study was done on the kinetic functionalities of microalgae *Chlorella vulgaris* in several physiological stages by regulating light, carbon, and nutrients. The results revealed that lipid productivity in microalgae enhanced with the value 130.11 to 163.42 mg/L/d which shows that biofuels can be effectively produced with the help of microalgae at a larger scale (Liao et al. 2018).

Extraction of biofuels and other resources are widely utilized and can be obtained through various methods such as gasification, combustion, liquefaction, pyrolysis, fermentation, and thermochemical conversion. However, extraction of microalgae results in large amounts of residue which need to be treated effectively as it can harm water, soil, and crops due to leaching of heavy metals in agricultural fertilizer. Combustion technology is the safest and acceptable technology for treatment of microalgae extraction residue as it directly converts the fuel into heat. Combustion of microalgae extraction residue takes place in three major steps including free water volatilization, decomposition of various nutrients including proteins, fats (lipids), carbohydrates and finally results in minerals decomposition (Fang et al. 2019).

3.3 Production of Microalgae

Bio-based microalgae are considered as the innovative producers of plant biomass with high production capacity due to availability of nutrients, water, and carbon dioxide (CO_2) for the cells, enhanced and efficient absorption of sunlight for the growth of cells, and their simplicity (Terry and Raymond 1985). The first microalgae were produced in Japan in early 1960s with the help of Nihon Chlorella containing the culture of Chlorella. Then onwards need for the bio-based microalgae started due to the crisis in conventional oils in 1970s (Mata et al. 2010). In the present era, microalgae is produced for multiple purposes such as in human nutrition, wastewater treatment, animal products, health supplements, industrial commodities, and production of biofuel which ultimately help in production of sustainable environment (Fig. 3.1). For the production of all these components, various factors play a vital role such as culture characteristics, heat transfer medium, and availability of light

Fig. 3.1 Production and Significance of Bioalgae (Akubude et al. 2019)



source (Fernandez et al. 2013). Drug research recently claimed that microbial groups possessing microalgae and cyanobacteria provide antiviral, antimicrobial, and anticancer properties. These microalgae and cyanobacteria are usually produced from natural habitats or ponds or photobioreactors (Zittelli et al. 2013).

The production of algae takes place in a very distinct environment in which the algae grows in the open environment without being contaminated by the presence of other species of algae and protozoa. For example, *Chlorella* algae grow in media containing essential nutrients, *Dunaliella salina* originate in higher saline environment, whereas *Spirulina* grows at greater pH conditions and high bicarbonate concentration. Other marine algae such as *Chaetoceros*, *Skeletonema*, *Thalassiosira*,

Table 3.2 Lipid content (%) of various microalgae species (Hossain et al. 2019; Schlagermann et al. 2012)

Microalgae species	Lipid content (%)
Chlorella sp.	19
Spirulina platensis	8
Rhodomonas sp.	15
Chlamydomonas reinhardtii	21
Porphyridium cruentum	11
Scenedesmus sp.	12
Bellerochea sp.	15
Spirogyra sp.	16
Dunaliella salina	6
Botryococcus braunii	25–75
Nitzschia sp.	45–47

Tetraselmis, *Isochrysis* and dinoflagellate *C. cohnii* grow in closed environment (Borowitzka 1999). This is due to the reason of being an open environment where the microalgae are not able to grow due to the risk of contamination from other bacteria, fungi, protozoa, and microalgae. Thus, in such cases photobioreactors are widely accepted which provide closed controlled culture atmosphere in order to prevent the microalgae from the invasion of other microorganisms. In photobioreactors the intensity of light (usually >90%) did not come in contact with the surface of culture; however it passes from the walls of bioreactor to reach the cultivated cells (Tredici 2004). Further, there is a barrier for the liquids, gases, and particles between the culture and the atmosphere. Photobioreactors are mainly categorized based upon their design and mode of operation (Zittelli et al. 2013). There are varieties of closed photobioreactors which can be employed in the production of microalgae such as horizontal tubular reactors, helical tubular reactors, cascade reactors, alveolar flat panels reactors, vertical flat panel reactors, and bubble columns reactors. Out of these, horizontal or helical tubular reactors and vertical flat panels in combination with bubble column reactors are most widely used scalable bioreactor designs. Vertical flat panel bioreactors possess greater advantages than other bioreactors as they can be utilized for the microalgae species production in huge volume (Sierra et al. 2008). Apart from open systems as well as bioreactors, an immobilized culture system is another technique for the evolution of bio-based microalgae. In this method, unialgal cultures are inactivated inside a polymeric matrix and originate in artificial streams or over the surface of rotating biological contactors. This method is broadly classified into two categories, namely enclosure and non-enclosure method. In enclosure methods, algae cells grow inside a polymeric matrix or encapsulated in a particular space whereas in non-enclosure methods, algae cells grow over the surface of a solid matrix without the presence of any enclosure. Since in this immobilized culture system, cells are attached to the carriers despite being immersed in the culture media, it has several advantages such as increased productivity and ease of harvesting of algal biomass (Shen et al. 2009).

Microalgae cultivation also provides a vital opportunity in enhancing its fat/lipid content. Lipid content of various microalgae species are summarized in Table 3.2.

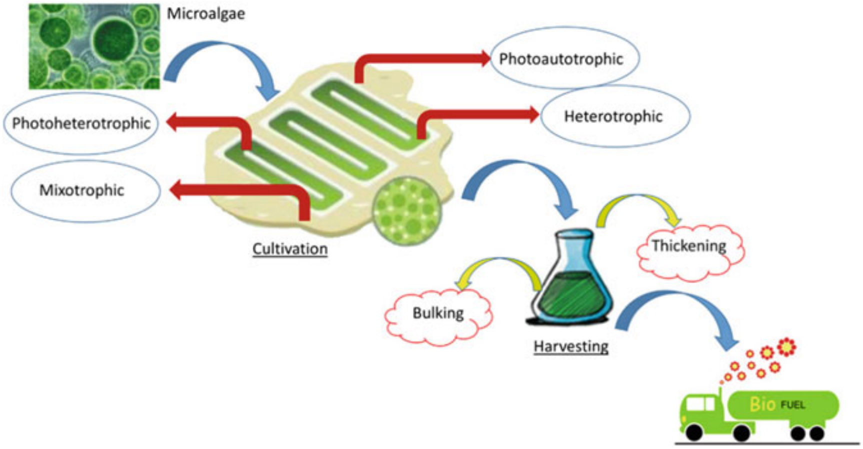


Fig. 3.2 Cultivation of microalgae by different methods (Javed et al. 2019)

Usually, photoautotrophic culture is utilized for cultivating microalgae. In this method, light energy is consumed by the cells, and then releases a carbon source, i.e., carbon dioxide (CO_2) but this procedure results in higher harvesting cost of biomass due to low biomass concentration obtained. So, to replace this method, heterotrophic culture is widely accepted which consumes different carbon source, i.e., sugars and organic acids without the presence of light. However, some studies stated that heterotrophic culture results in higher biomass production which leads to the accumulation of lipids. To overcome this limitation, mixotrophic culture can be used in which organic carbon and carbon dioxide are assimilated simultaneously. Fig. 3.2 represents the cultivation of microalgae by different methods (Cheirsilp and Torpee 2012).

3.4 Harvesting of Microalgae

Harvesting plays an important role in removing water from the microalgae which is essential for converting into biofuels (Pragya et al. 2013). It is mainly a method used to separate the microalgal biomass cells from their media utilized for cultivation in order to convert microalgal cells into effective and efficient acceptable product (Patil et al. 2020). It involves two main mechanisms: first is the cultivation and the other involves the separation of microalgae. Separation of microalgae can be carried out through biological, chemical, mechanical, and electrical methods (Rakesh et al. 2020). There are various methods employed for harvesting of microalgae which include sedimentation, centrifugation, flocculation, membrane filtration, and a combination of these (Rawat et al. 2011).

Centrifugation is the technique which involves centripetal force and thus separates the microalgae based upon their density difference. Sometimes, centrifugation is also employed following sedimentation in order to separate the supernatant

(Pragya et al. 2013). Some studies claimed that centrifugation is an effective method; however, other studies claimed that centrifugation method used in the harvesting of large amount of culture results in higher cost with more time consumption (Chen et al. 2011). Sedimentation is a gravitational method of harvesting which utilizes gravity to collect the microalgae. However, it is greatly affected by the algae density (Xu et al. 2020). Flocculation is another method of algal harvesting in which individual dispersed solutes gathered together and results in the formation of bigger units or also called as flocs which are settled down with the help of certain flocculants or coagulants. These flocculants are produced by three ways: patching, charge neutralization, sweeping and adsorption bridging (Yin et al. 2020; Uduman et al. 2010). Membrane filtration is a technique which is employed for the separation of the microalgal cells and is usually classified into two types, namely microfiltration and ultrafiltration. The former involves the pore diameter of 100–10,000 nm and the latter include the pore diameter of 1–100 nm. Different shapes are formed under different applications using different materials including tubular, hollow, compressed, spiral, and multichannelled reactors (Suparmaniam et al. 2019).

One study has been conducted on the harvesting of *Chlorella* species by utilizing magnetic iron oxide nanoparticles. Magnetic particle sticks to the surface of microalgal species and makes their harvesting easier when placed under strong magnetic field. This helps to reduce the energy and time required in the overall production costs.

Floatation is another harvesting method which is also termed as inverted sedimentation technique in which gas bubbles are dispersed in the broth for the transportation and separation of the particles. It is a more effective method compared to sedimentation. However, the drawback is the usage of flocculants when floatation technique is employed for large-scale processing. This method is usually employed for wastewater treatment (Kucmanová and Gerulová 2019; Barros et al. 2015).

3.5 Generations of Biofuels

The demand of oil in the transportation sector is elevating globally, although it is responsible for the one-fifth of the total carbon dioxide (CO_2) emissions. Along with this, the growth of lighter vehicles is estimated to reach by two billion in 2050 which ultimately causes rise in the demand of fossil fuels. However, fossil fuels are decreasing with an alarming rate and demand is increasing side-by-side which leads to increase in the fuel price. Thus, biofuels need to be introduced in order to fulfill the demand by protecting the environment through reducing the carbon dioxide emissions which cause global warming (Villagracia et al. 2016). Biofuels are referred to those types of fuels which are majorly produced from biomass including wood, agricultural crops, and forest waste. They can be found in liquid, solid, or in gaseous form: solid biofuels include wood, charcoal, and bagasse; plant oils, vegetable oils, and bioethanol are liquid biofuels; and methane gas obtained from animal waste, domestic waste, and wastewater treatment sludge are gaseous biofuels (Jamwal et al. 2020).

Biofuels are broadly categorized into four different generations (Fig. 3.3). Biofuels from first generation are usually obtained from consumable bio-based materials such as sugarcane and sugar beet, corn, wheat, and potato starch. The examples include biodiesel, biogas, and bioethanol (Alalwan et al. 2019). These fuels are cheap and commercially viable. The other feedstock required for the production of first-generation fuels include agriculture waste, sweet sorghum, food by-products, and domestic and municipal wastes (Shahare et al. 2017). The utmost drawback for first-generation biofuels includes their unsustainability in production. Also, it is produced from edible resources which negatively affect the food supply chain and increases the greenhouse gas emissions. This limitation has been overcome by the production of biofuels of second generation (Rajee et al. 2014). The second-generation bio-based fuels are majorly obtained from inedible sections of the crops after harvesting such as leaves, stems, husk, from other inedible crops including jatropha, switchgrass, miscanthus, and through industrial waste components including skin and pulp of fruits, as well as wood chips (Janda et al. 2012). These fuels are not cheaper and commercially feasible. The process of conversion of these fuels involves two major steps, i.e., hydrolysis of cellulose in sugar units and then sugar fermentation to obtain alcohol through yeast (Shahare et al. 2017).

Biofuels from third and fourth generations are derived from photosynthetic microorganisms. The major difference between both is that third-generation biofuels are obtained by processing of algal biomass whereas fourth-generation biofuels are produced through algae-based metabolic engineering using oxygenic photosynthetic microorganisms (Lü et al. 2011). Fourth-generation biofuels are more sustainable and versatile because they are obtained through the technique of genetic engineering or nanotechnology (Ziolkowska 2020). Some feedstock can be referred as both first and second generation; for instance, vegetable oil is a first-generation fuel feedstock, but when it is not suitable for cooking or eating, it is regarded as waste and comes under second-generation fuel feedstock (Callegari et al. 2020).

3.6 Types of Biofuels from Microalgae

There are several forms of biofuels which can be originated from microalgal biomass such as biodiesel, bioethanol, biohydrogen, and biomethane. Some of the biofuels produced from microalgae are shown in Table 3.3. Production of biofuels from microalgae requires various steps such as adequate strain selection, cultivation method, harvesting, and finally conversion into biofuels. There are more than three million microalgal strains present in nature. But, the microalgal strains should be selected on the basis of economic feasibility and kind of end product required. After the strain selection, it is important to select the cultivation strategy. There are various cultivation methods such as open ponds, closed photobioreactors, and tubular photobioreactors, but based upon the microalgal strain and its properties cultivation strategy should be selected. The microalgae after cultivation is removed from water and dried to produce biomass. For harvesting, different methods can be employed such as mechanical (centrifugation), chemical, biological, and electrical system.

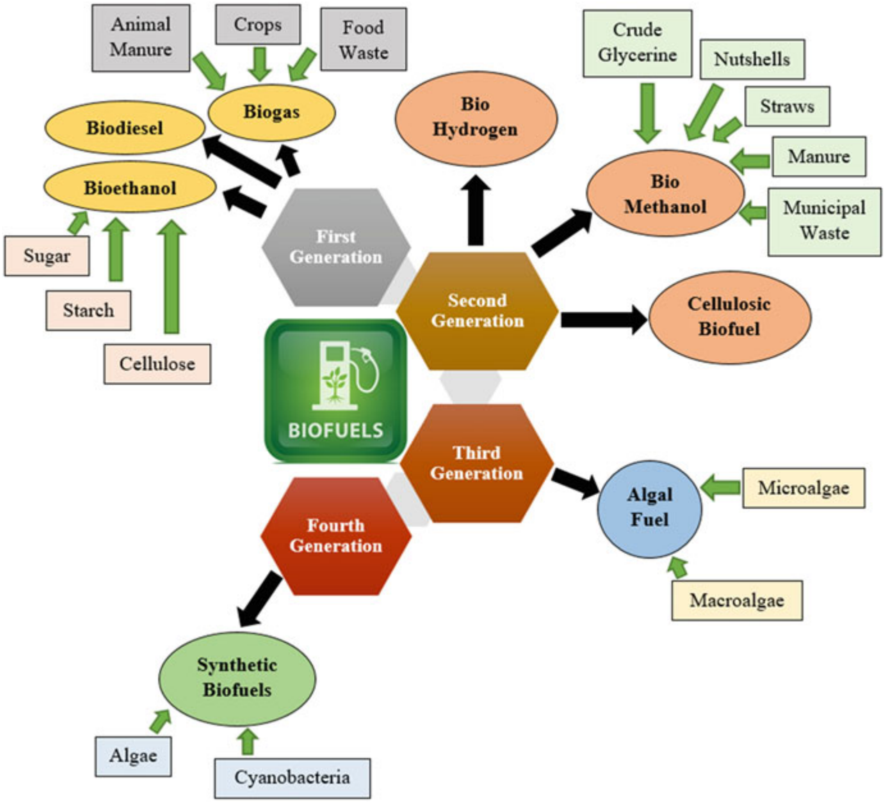


Fig. 3.3 Generations of biofuels (Javed et al. 2019)

Table 3.3 Evolution of biofuels from microalgae (Oncel 2013)

S. no.	Treatments	Biofuels
1.	Oil extraction and transesterification	Biodiesel
2.	Oil extraction and hydrotreatment	Green diesel
3.	Anaerobic digestion	Methane
4.	Fermentation	Ethanol, hydrogen
5.	Biophotolysis	Hydrogen
6.	Pyrolysis	Bio-oil, syngas, charcoal
7.	Gasification	Syngas

After harvesting, biomass is converted into various biofuels such as hydrogen, syngas, methane, ethanol, and diesel by fractionation or extraction method (Chowdhury and Loganathan 2019). The types of biofuels produced from different microalgal species are discussed in Table 3.4.

3.6.1 Biodiesel

Due to the increased demand of energy in the periods 1930s and 1940s, vegetable oils have been utilized as diesel fuels. But,with the advancement in the industry, the increasing need for energy demanded an alternative approach that led to the development of biodiesel. Biodiesel is usually obtained from biomass-based oils such as vegetable oils (Huang et al. 2010). It is usually colorless with sometimes yellow in color, constitutes of alkyl fatty acid esters of short-chain alcohols. The structure of biodiesel comprises of 12–22 carbon atoms, around 12–22 in numbers and double bonds, around 0–2 in number (Ruan et al. 2019). It is an ecofriendly and nontoxic liquid fuel which consists of mono alkyl esters of long-chain fatty acids produced from any vegetable oil, micro and macroalgae oil (Akubude et al. 2019). The prime challenge in the production of biodiesel involves feedstock selection as feedstock selection affects 75% to the production cost of biodiesel (Callegari et al. 2020). Conventional fuels can be easily replaced by biodiesel as summarized in Table 3.5. Microalgae are gaining a wide acceptability as an effective biomass for the evolution of biofuels including biodiesel and other fuels. Biodiesel production is a stepwise process that involves cultivation, harvest, oil extraction, and conversion of algal lipids. Extraction of oil in production of biodiesel takes place by utilizing various methods such as homogenization, autoclave, ultrasound, freezing, osmotic shock, and bead milling (Kim et al. 2013). The schematic diagram showing the production of biodiesel from microalgae is shown in Fig. 3.4.

Biodiesel is widely acceptable around the world due to many reasons such as reduced carbon dioxide emissions in the environment, less amount of sulfur content, not comprising of any aromatic compounds and chemical agents which can degrade the environment, and possess renewable and economic viability (Huang et al. 2010). Microalgae which are having high concentration of oil are employed for the formation of biodiesel. To obtain biodiesel, the oil which is utilized must comprise of

Table 3.4 Biofuels produced from different microalgal species

Types of biofuels	Conditions	Microalgal species	Properties affected	Researchers
Biodiesel	Biodiesel production from microalgal strain	*Scenedesmus obliquus*	Lipid content, saponification value, acid value	Mandal and Mallick (2009)
Biohydrogen	Fermentative hydrogen production by *Clostridium butyricum* CGS5	*Chlorella vulgaris ESP6*	Glucose concentration, xylose concentration	Liu et al. (2012)
Bioethanol	Bioethanol production from coastal waters microalgal strains	*Scenedesmus abundans, Mychonastes afer*	Carbohydrate content, protein content, FTIR spectroscopy, algae Saccharification	Guo et al. (2013)
Biodiesel	Volumetric lipid productivity and fatty acid profiles of microalgae strains	*Ankistrodesmus falcatus, Chlamydocapsa bacillus, Ankistrodesmus fusiformis, Kirchneriella lunaris, Chlamydomonas sp., Coelastrum microporum, Desmodesmus brasiliensis, Scenedesmus obliquus, Pseudokirchneriella subcapitata, Chlorella vulgaris, Botryococcus braunii, Botryococcus terribilis*	Cetane number, iodine value, oxidation stability, cold filter plugging point	Nascimento et al. (2013)
Biodiesel	Fatty acids profiling for screening microalgae species	*Dunaliella sp., amphora sp., Chlorella vulgaris, Chlorella emersonii, Chlorella salina, D. salina Shariati, Ankistrodesmus sp., Chlamydomonas reinhardtii, Scenedesmus armatus, Chlorella protothecoides, D. salina*	Cetane number, iodine value, cloud point, cold filter plugging point	Talebi et al. (2013)

(continued)

Table 3.4 (continued)

Types of biofuels	Conditions	Microalgal species	Properties affected	Researchers
Biohydrogen	Effect of light intensity and illumination patterns	*Chlamydomonas reinhardtii*	Light intensity, pH, chlorophyll content, biohydrogen production, chlorophyll fluorescence, dry weight	Oncel et al. (2014)
Biogas	Co-digestion with sewage sludge of marine and freshwater microalgae under mesophilic and thermophilic conditions	*Selenastrum capricornutum, Isochrysis galbana*	Total solids, volatile solids, chemical oxygen demand (COD), protein content, Total sugar content, lipid content	Caporgno et al. (2015)
Biogas	Biogas purification through cultivation of green microalgae	*Chlorella vulgaris*	Cell count, optical density, pH, alkalinity, chemical oxygen demand (COD), fatty acid content, Total suspended solids, moisture content, lipid content, carbohydrate content, volatile suspended solids, Total nitrogen, Total phosphorus, fixed suspended solids, chlorophyll content	Ramaraj et al. (2016)
Bioethanol	Production of bioethanol from waste algal biomass	*Gracilaria corticata, G. crassa, G. verrucosa, G. cylindriaca*	Carbohydrate content, Saccharification percentage (%),	Shukla et al. (2016)
Bioethanol	Bioethanol production from marine microalgae	*Tetraselmis suecica, Nannochloropsis*	Carbohydrate content, specific growth rate, cell doubling time	Reyimu and Özçimen (2017)
Biohydrogen	Fermentative biohydrogen production	*Enterobacter aerogenes*	Initial gas-liquid volume ratio	Batista et al. (2018)
Biogas	Microalgae based anaerobic	*Chlorella vulgaris*	Volatile fatty acids, yeast	Llamas et al. (2020)

(continued)

Table 3.4 (continued)

Types of biofuels	Conditions	Microalgal species	Properties affected	Researchers
	fermentation for producing biogas		growth, Total cellular lipid content	

Table 3.5 Biodiesel as an alternative to conventional fuels (Mofijur et al. 2019)

Vehicles	Conventional fuels	Biofuels
Light vehicles (cars)	Diesel, LPG, gasoline	Biodiesel bioethanol, renewable gasoline, renewable diesel
Heavy vehicles (trucks)	Diesel	Biodiesel, renewable diesel
Marine (ships)	Diesel, fuel oil	Biodiesel, renewable diesel
Aviation (aeroplanes)	Aviation fuel	Renewable aviation fuel
Machinery (tractors)	Diesel	Biodiesel, renewable diesel

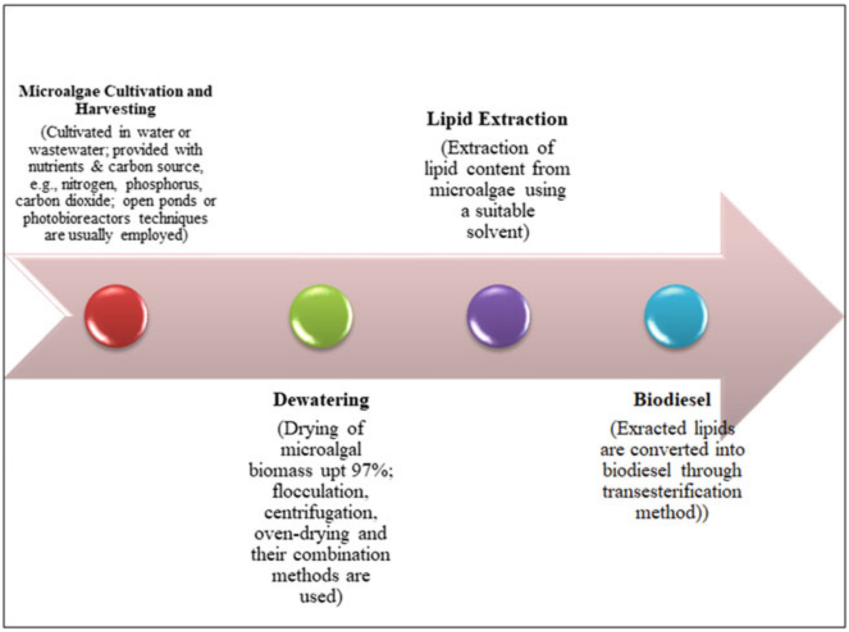


Fig. 3.4 Production of biodiesel from microalgae (Collotta et al. 2018)

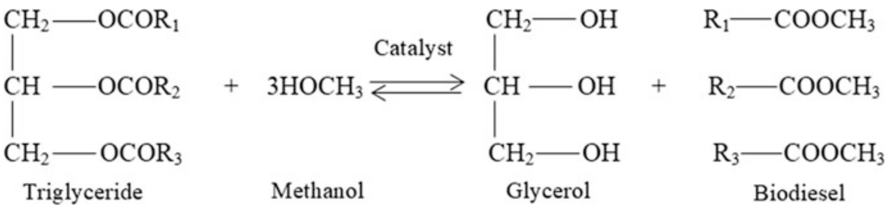


Fig. 3.5 Reaction involved in the production of biodiesel (Chisti 2007)

triglycerides which react with alcohol to obtain glycerol and biodiesel. The overall reaction is depicted in Fig. 3.5 (Chisti 2007).

Microalgae obtained through wastewater can also be used for the evolution of biofuels such as biodiesel as it helps in larger production of microalgal biomass for biodiesel production at a cheaper price. One study has been conducted on the growth of microalgae *Chlamydomonas polypyrenoideum* on wastewater obtained from dairy processing. The outcomes revealed that the microalgae produced on the wastewater from dairy processing help in reducing the pollution load of nitrate by 90%, nitrite by 74%, phosphate by 70%, chloride by 61%, ammonia by 90%, and fluoride by 58% on the tenth day of microalgae growth. The lipid content also increased after production of strain in dairy wastewater. Thus, by analysis through FTIR it was concluded that microalgae produced from dairy wastewater can be used for the evolution of biodiesel (Kothari et al. 2013). Green microalgae are more widely accepted for production of biodiesel as compared to blue-green algae. There are various microalgae which act as feedstock in the evolution of biodiesel including *Clorococcum* sp., *Chlorella* sp., and *Neochlorosis oleabundans* (Mondal et al. 2017).

Biodiesel produced form microalgae possess environmental advantages and its properties are somewhat similar to the petro-diesel including viscosity, density, heating value, and flash point. One exception is that the feedstock of biodiesel differ from the petro-diesel as biodiesel are very viscous in nature, and thus is not acceptable to be utilized directly in the diesel engines. Thus in such cases conversion of microalgal oil is necessary to meet the standard requirements which include pyrolysis, mixing with petro-diesel, transesterification, and micro-emulsions containing solvents. Among these, transesterification method is widely acceptable for the conversion but it also has disadvantages, such as it is used a high proportion of energy that increases its cost of production. To overcome this limitation, biocatalyzed/enzymatic catalyzed esterification method can be employed for the conversion (Rawat et al. 2013). One study was conducted which utilizes the coupling of supercritical carbon dioxide (CO_2) with transesterification to obtain biodiesel by using two microalgae strains, namely *Chlorella* sp. and *Chrysophyta* as feedstock. In the coupling method, first, the oil from microalgae is extracted and then it underwent downstream processing to obtain biodiesel. The remaining portion left following the process is reutilized in production of nutraceuticals and pharmaceuticals. The results of this study revealed that a 40 mesh alga was the optimum reaction condition along with 60 and 340 °C as the optimum extraction and reaction temperature, respectively. The yield of *Chlorella* sp. was higher, i.e., 63.78% as compared to *Chrysophyta* sp., i.e., 56.31% (Zhou et al. 2017).

3.6.2 Bioethanol

Bioethanol is one of the most efficient and major alcoholic biofuel utilized worldwide (Abomohra and Elshobary 2019). It is also called as ethylic alcohol or sometimes ethanol with CH_3-CH_2-OH molecular formula. It is widely employed in alcoholic beverages and liquid biofuels worldwide. The resultant bioethanol obtained through bio-based microalgae can be used to replace gasoline in engines (Ruan et al. 2019). Bioethanol can be produced from various sources including corn, sugarcane, sorghum, and microalgae. Out of these, microalgae possess various benefits over other sources such as it helps in preventing global warming by reducing the release of greenhouse gases, can grow nicely in the presence as well as absence of soil, and require very less harvesting time. Its production involves various stages such as pretreatment, saccharification, fermentation, and product recovery. In pretreatment, the fermentable sugars are released so that they can be available in the fermentation step (Harun et al. 2011). The first-generation biofuel, i.e., bioethanol can be obtained through utilizing sugarcane as a feedstock. However, the second-generation biofuels also include bioethanol which can be obtained after milling, pretreatment, hydrolysis, and detoxification by using lignocellulosic as feedstock before fed into biofermenters (Callegari et al. 2020). Pretreatment involves several techniques/methods including chemical methods such as acid hydrolysis, alkaline hydrolysis, supercritical carbon dioxide and ammonia fiber explosion, enzymatic methods, combined methods, and mechanical techniques including bead beating, ultra-sonication, high pressure homogenization, and autoclaving (Phwan et al. 2018). Biomass pretreatment is an essential and an expensive stage that reduces the crystal nature of biomass and enhances the substrate digestibility by increasing the surface area. Among the various methods of pretreatment, alkaline pretreatment is most widely acceptable due to its low temperature and pressure involved in the process which ultimately decreases the production cost. One study has been conducted to obtain bioethanol by utilizing alkaline pretreatment method on bio-based microalgae. Bioethanol concentration, cell size, and glucose concentration were determined to analyze the consequence of pretreatment method. The results revealed that bioethanol obtained resulted in maximum yield with 26.1% g ethanol/g at 0.75% (w/v) NaOH for 30 min at 120 °C. Thus, alkaline pretreatment proves to be an effective method for the evolution of bioethanol (Harun et al. 2011). To obtain bioethanol, microalgae *Chlorella vulgaris* is most widely acceptable as it can accumulate around 37% of starch. However, the microalgae *Chlorella vulgaris* can accumulate up to 70% of starch in the conditions prevailing toward protein synthesis suppression. The production of bioethanol from microalgae usually takes place in five major steps (Fig. 3.6). The first step includes the utilization of sunlight energy by the microalgae for its cultivation in open ponds or closed flat plate,

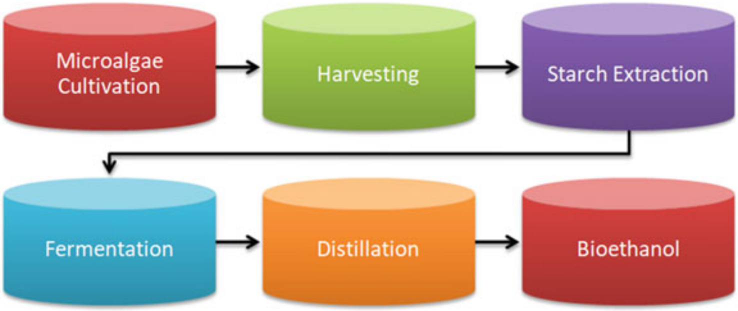


Fig. 3.6 Process of bioethanol production (Mussatto et al. 2010)

tubular, and other photobioreactors. The second step involves the concentration and low-cost harvesting of microalgal biomass. In the third step, biomass microalgae starch is usually obtained through the cells by the means of enzymes or some mechanical equipment. The fourth step involves the production of fermentable sugars with the help of amylolytic enzymes which lead to the alcoholic fermentation by addition of *S. cerevisiae*. The last step is to drain the fermented broth consisting of bioethanol and then feed it to a holding tank which later goes toward a distillation unit (Mussatto et al. 2010).

From 2000 to 2007, bioethanol global production increased from 17.25 billion liters to 46 billion liters, respectively, and it is projected to be increase till 160 billion liters by the end of 2020 (Phwan et al. 2018). Bioethanol obtained through bio-based microalgae is accomplished using three methods. The first method involves the traditional method in which microalgae passes through pretreatment, enzymatic hydrolysis, and then yeast fermentation. Then, the second method is the dark fermentation method in which hydrogen, acids, and alcohols are produced from photosynthesis pathway. The last method include photofermentation pathway or also called as genetic engineering but it is practically inefficient and thus is not recommended (Silva and Bertucco 2016). One study was conducted on the production of bioethanol by utilizing microalgae *Chlorococum* sp. through yeast (*Saccharomyces bayanus*) fermentation. Results revealed that the lipid-extracted microalgae produces high amount of ethanol concentration, i.e., 3.83 gL^{-1} as compared to dried microalgae at 30 °C fermentation temperature. This proves that microalgae can be utilized for obtaining bioethanol at commercial scale (Harun et al. 2010).

Apart from utilizing the single culture of microalgae, mixed culture of microalgae is gaining a wide acceptability as mixed culture helps in increasing the economic viability and large-scale production of bioethanol. A research was done based on the utilization of mixed microalgae culture to produce bioethanol by acidic and enzymatic hydrolysis. The study also determined the effect of sugar extraction in order to obtain bioethanol. Results revealed that the bioethanol yield was highest in the case of enzymatic hydrolysis pretreatment without drying and primary acid treatment in comparison with the acid hydrolysis (Shokrkar et al. 2017).

3.6.3 Biomethane

A lot of waste produced from different sources lead to the increase in pollution which degrades the environment. In order to prevent the waste from polluting the environment, biodigestion of waste can be done for the production of biomethane. However, factors including carbon/nitrogen ratio and pretreatments of substrates affect the biomethane production. External pretreatments help in enhancing the yield of biomethane production by eliminating the interfering components such as volatile fatty acids (Iyovo et al. 2010). One study has been conducted on the pretreatment of the microalgae *Chlorella* sp. at different temperatures for the production of bioethanol. Results revealed that yield of methane enhanced by 37% and 48% with temperatures 70 and 90 °C, respectively whereas the highest yield of methane occurred at 121 °C (Wang et al. 2017).

To obtain biomethane by using algal biomass, anaerobic digestion is employed. However, due to compact cell walls of microalgae, anaerobic digestion results in a poor production of biomethane. Thus, pretreatment of microalgae indicates a vital role in enhancing the biomethane production. Several pretreatment methods of microalgae are employed such as enzymatic, hydrothermal, ultrasonic, and thermochemical methods. Out of these methods, hydrothermal method is a stable and efficient method for the evolution of biomethane. One study has been conducted on the solar-driven hydrothermal pretreatment for the production of biomethane. Solar-driven hydrothermal pretreatment is used because conventional hydrothermal treatment utilizes a large amount of energy which declines the commercialization of biomethane. In this study, anaerobic digestion is carried out for the pretreatment and consequences of different factors on the yield of organic matter were determined. The results revealed that the evolution of methane through solar-driven hydrothermal pretreatment increased by 57% and thus proves solar-driven hydrothermal pretreatment as an alternative approach toward saving energy and enhancing quality of biomethane (Xiao et al. 2019). Another study has been conducted on the production of biomethane from lipid removed microalgal residues of *Ettlia* sp. by anaerobic digestion. The physico-biochemical parameters were observed for the evolution of biomethane as well as volatile fatty acids. Results showed that the production of biomethane was increased in alkali-autoclaved samples by 40% and its heating value was enhanced, i.e., 6.6 MJ kg^{-1} VS and production of volatile fatty acids were increased by 30% in alkali-sonicated samples. Also, the pretreatment method enhance the solubilization of lipid removed microalgal residues and led to the enhanced formation of biomethane as well as volatile fatty acids (Suresh et al. 2013).

3.6.4 Biohydrogen

Hydrogen is a pure, odorless, colorless, simplest, and lightest combustible gas found in nature. This gas is known as the carrier of energy for the upcoming time due to its environment friendly behavior (Ruan et al. 2019). Hydrogen is the most required option in the replacement of non-renewable and carbon containing fuels. It has the higher energy value, i.e., 122 KJ/g (per unit weight basis) compared to other fuels. Upon combustion, it releases only water vapor (Dubini and Gonzalez-Ballester 2016). Hydrogen gas is considered as one of the most cleanest and sustainable carriers for the formation of biofuels as replacement for fossil fuels. Hydrogen containing fuels are sustainable fuels that are utilized in various fuel cells because it does not produce any harmful or toxic emissions which can pollute the environment. Green algae and cyanobacteria are the most widely utilized for the evolution of biofuels, for example, biohydrogen. The production of biohydrogen from microalgae requires the capacity of strain to synthesize the enzymes required for hydrogen metabolism (Khetkorn et al. 2017). Several techniques/methods are present toward the production of biohydrogen; however, conventional methods such as gasification, water splitting, and reforming process are more likely used until now. Among the conventional method, biomass gasification is widely employed, but it has limitation of providing low thermal efficiency. In order to overcome this limitation, biological pathways involving algae and bacteria are utilized for biohydrogen production which utilize less energy and can be employed at ambient conditions (Singh and Das 2018). Biohydrogen produced from microalgae is widely accepted due to its high energy density, i.e., 2.75 more, when compared with other biofuels (Rashid et al. 2013). After extracting oil and pigments the residual microalgae is utilized for obtaining biohydrogen. This provides an advantage of producing renewable energy as well as enhancing the sustainability of microalgal industry. One study has been conducted on the evolution of biohydrogen from the algal biomass left after extraction of oils and pigments from them, with microalgae *Nannochloropsis* sp. as the feedstock. Oil and pigments can also be extracted from microalgal biomass using the supercritical carbon dioxide extraction method. After extraction, remaining microalgal biomass was used to obtain biohydrogen by dark fermentation method using *Enterobacter aerogenes* (Nobre et al. 2013).

Three enzymes inherit vital added benefits for the production of biohydrogen from microalgae, namely hydrogenase, nitrogenase, and uptake hydrogenase. Enzymes, particularly hydrogenase, are mainly utilized for the occurrence and oxidation of hydrogen. Hydrogenases are classified into three categories based upon the metal cofactor, namely [Ni-Fe]-hydrogenase, [Fe-Fe]-hydrogenase, and [Fe]-hydrogenase. On the other hand, heterocysts of cyanobacteria constitutes nitrogenous enzyme and help in fixing atmospheric nitrogen into ammonia and results in the evolution of a by-product, i.e., hydrogen. The third enzyme, i.e., uptake hydrogenase is an oxygen tolerant enzyme contrary to hydrogenase enzyme (Jimenez-Llanos et al. 2020). The beginning of formation of biohydrogen takes place through the microalgae cultivation which is to be done under optimum parameters including pH, light, temperature, and nutrients. Based on the environmental conditions, culture system is divided into two methods, namely open systems and closed systems (Oncel 2015). Biohydrogen production occurs in two major steps. The first step is the aerobic stage in which cells undergo photosynthesis to store the organic compounds along with the release of oxygen. The second step involves the anaerobic stage where cells deteriorate the organic compounds and release hydrogen. Stage two can be considered as photofermentation if it occurs under light condition, and is called dark fermentation if the process occurs in the absence of light (Rashid et al. 2013). Dark fermentation converts the carbonaceous matter into organic acids and releases several gases including hydrogen (H_2), carbon dioxide (CO_2), and methane (CH_4). However, higher feedstock cost and low hydrogen yield are the two limitations of using dark fermentation as method for biohydrogen production (Nagarajan et al. 2020). Microalgal biomass based biohydrogen is usually produced by the process of biophotolysis and catabolism of endogenous substrate. In biophotolysis, the water disintegrates into hydrogen and oxygen. Light-based biophotolysis involves two major methods, namely direct photolysis and indirect photolysis (Show and Lee 2014). Several microalgal biomass species have the capacity to produce biohydrogen including *Tetraspora* sp., *Anabaena* sp., *Chlorella* sp., *Scenedesmus* sp., *Platymonas* sp., *Coelastrella* sp., *Monoraphidium* sp., *Chlamydomonas* sp., and *Micractinium* sp. (El-Dalatony et al. 2020). In order to increase the yield of the biohydrogen formation, genetic engineering is now widely employed. Genetic engineering helps in improving the utilization of substrates, carbon flow, and resistance of enzymes toward oxygen (Goswami et al. 2020).

3.7 Benefits and Drawbacks of Microalgae-Derived Biofuel

Microalgal-based biofuels provides a wide scope and diversification toward the sources of fuel and assist in mitigating the negative consequences of oil crisis and sustainable replacement of fossil fuels. These bio-based microalgal fuels have the capacity to enhance the social, environmental, and economic sustainability (Gouveia 2011). Microalgae-derived biofuels which contain high amount of lipid content promise to provide an absolute feedstock for the production of biodiesel which is considered as one of the energy-density transportation fuels (Pienkos and Darzins 2009). They provide many benefits in comparison with the conventional fuels such as being cheaper, ecofriendly, and helps in eliminating carbon-dioxide emissions (Oltra 2011). They have the advantage of being sustainable, cost effective, and utilize less energy in comparison with petroleum-derived fuels (Griffiths et al. 2011). The production of second-generation biofuels provides many benefits as compared to first-generation biofuels such as cleaner fuels, higher quality, and low carbon dioxide profile. Also, biofuels derived from microalgae provides greater annual growth rates, higher amount of lipid content, and helps in improving the air quality. The biodiesel produced from microalgae proves to be more attractive than other biofuels as it contributes to net zero amount of carbon dioxide, negligible amount of sulfur components produced during combustion, and possess no harmful, aromatic, and toxic compounds (Brennan and Owende 2013).

With the advantages of microalgal biofuel, there are few disadvantages such as large-scale development of such biofuels being still in progress and is very complex in nature. Also, development of large-scale production of biofuels leads to higher capital costs (Bahadar and Khan 2013).

3.8 Worldwide Production of Biofuel

With the increased advancement, urbanization, and industrialization, the need for energy is accelerating at a faster pace which affects the fossil fuels utilization. The fossil fuels utilization is not recommended as it leads to greenhouse gas emissions, acid rain, and pollution, which cause global warming. Thus, biofuels from microalgae provide a safe solution toward sustainable usage of fuels (Kiran et al. 2014). In 1970s and 1980s, the Aquatic Species Program in U.S., under the Department of Energy, discovered the production of fuels from algae (Sani et al. 2013).

In the current scenario, evolution of biofuels is less worldwide, although it is increasing day by day among different countries. Many countries have set goals to switch from fossil fuels to biofuels. In the European Union (EU), the usage of biofuels for transportation has occupied 5.75% in 2010 and reached 10% of energy for transportation in 2020. The overall production of biofuels globally was 62 billion liters in 2007, which is estimated to be around 1.8% of total global transport fuel. The greater amount of biofuels produced in 2007 in two countries, namely Brazil (20%) and USA (3%) (Ajanovic 2011). The year 2012 was the weakest year which involved the slowest growth of fossil fuels. Petroleum oil was the slowest growing fuel due to its rise in prices and decline in subsidies. Thus, biofuels from microalgae serve as an alternative and sustainable fuel against petroleum oil without affecting the supply chain (Sani et al. 2013). However, the projected worldwide usage of biofuels is approximately 30% by 2030. World requirement for biodiesel production has gained much attention as compared to other biofuels. In 2003, biodiesel production was approximately 1.8 billion liters worldwide. According to several studies, the usage of biodiesel helps in reducing the toxicity in the air by 90% along with the cancers by 95% in comparison with the conventional diesel (Huang et al. 2010). By 2019, the bioethanol and biodiesel production was estimated to be increased at 160 billion liters and 41 billion liters, respectively worldwide (Ziolkowska 2020).

3.9 Other Applications of Microalgae

Due to three major components, i.e., proteins, carbohydrates, and lipids, microalgae possess wide applications in food industry, pharmaceuticals, and phycoremediation. Currently, they are utilized in environmental sector in the form of nanocomposites and nanoparticles. Also, microalgae in raw or semi-decomposed condition are utilized as an organic bio-fertilizer in crops (Aishvarya et al. 2015). They are used in biofuel production and also in various other industrial applications which are summarized in Table 3.6. Microalgae are utilized in human nutrition such as in form of capsules, tablets, and liquids. They can be employed as food colorants and nutritional supplements. In addition to this, microalgae can be incorporated in food items such as candies, pasta, snacks, and beverages. Four major microalgae species including *Chlorella*, *D. salina*, *Arthrospirai,* and *Aphanizomenon flos-aquae* possess applications in human nutrition (Spolaore et al. 2006) These microalgae provide health benefits such as reducing hypertension, increasing hyperlipidemia, prevention

Table 3.6 Industrial applications of microalgae (Mobin and Alam 2017)

Microalgae species	Industrial applications
Spirulina	Antiviral agent, cholesterol reduction, enhance immune system, health tablets and capsules, coloring agents in foods, cosmetics
Chlorella	Antitumor, enhance immune system, free-radical scavenger, decrease blood sugar level, Hepatoprotective agent, health tablets and capsules, beverages, coloring agents in foods, cosmetics
Dunaliella	Anticancer agent, antihypertensive property, health tablets and capsules, bakery, coloring agents in foods, cosmetics
Haematococcus	Antioxidant activity, immunomodulatory action, anticancer agent, Colouring agents in foods, cosmetics

against renal failure, decreasing elevated serum glucose level, and increasing growth of intestinal *Lactobacillus* (Kim and Kang 2011). Microalgae helps in treating the wastewater discharged from various industries. The wastewater consists of carbon, nitrogen, phosphorus, and dissolved oxygen. When this wastewater is directly, without treatment, is dispersed into the environment, it causes eutrophication, algal blooms, fish deaths, and cyanotoxin production. Thus, microalgae grown in wastewater help in the effective elimination of phosphorus (P), nitrogen, carbon (C), and dissolved oxygen and ultimately preventing environmental degradation (Show et al. 2017). Apart from this, microalgae have wide applications in environmental biotechnology. They help in treating the wastewater from different sources that may cause severe health related diseases. To treat the wastewater, high rate algae pond system is employed which helps in stabilizing the algae growth. In this system, shallow ponds are mixed with the help of paddle wheels to increase the nutrients and photosynthetic efficiency. This system helps in reducing the pollutants such as chemical oxygen as well as provides applications as animal feed and biodiesel feedstock (Chu 2012).

Microalgae also provide functions in agricultural sector in the form of biofertilizers and soil conditioners. Cyanobacteria are used for fixing the nitrogen and producing biofertilizers. Also, for fixing the atmospheric nitrogen and enhancing the physicochemical characteristics of soil such as enhancing grain quality and soil nitrogen, blue green algae such as *Anabaena*, *Nostoc*, *Aulosira*, and *Tolypothrix* are widely used (Priyadarshani and Rath 2012). Marine microalgae also possess various applications such as *Porphyridium*, *Rhodella*, and *Arthrospira* acting as antiviral agents, ion-exchangers, therapeuticals, nutraceuticals, and possess anti-tumor effects (Raposo et al. 2013).

3.10 Conclusion

With the increase in environmental pollution due to rise in emissions of greenhouse gases and other pollutants, fossil fuels are diminishing at a faster rate with rise in the need for energy. In order to reduce environmental degradation and global warming, bio-based fuels act as a replacement toward the fossil fuels. Biofuels are usually obtained from biomass in solid, liquid, or gaseous form. Biofuels are majorly produced by environment-friendly and renewable source, i.e., microalgae. There are four generations of biofuels produced from edible biomass (first generation), non-food sections, comes under second generation and photosynthetic microbes (third and fourth generations). Microalgae upon cultivation as well as harvesting lead to the development of biofuels including biodiesel, biomethane, bioethanol, and biohydrogen. The microalgal biomass derived from biofuels possess many advantages over conventional fuels such as decrease carbon dioxide emissions, increase economic viability, and sustainability. Apart from producing biofuels, microalgae have also been employed in other applications such as in cosmetics, health supplementation, coloring agents, pharmaceuticals, bakery, and providing health benefits such as anticancer, antitumor, antioxidant capacity. However, further studies need to be addressed regarding the advanced technologies for converting the biomass into ecofriendly fuels in order to scale up biofuels needed for commercial production.

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Waste to Bioenergy: Recent Technologies

4

Loveleen Kaur Sarao, Sandeep Kaur, and Maninder Arora

Abstract

Currently, biomass is used as common source of renewable energy. Its benefits are being exploited owing to issues related to undesirable influence of consuming fossil fuels such as global warming, climate change, and their unfavorable impacts on human health. The possibility of generating a broad range of bioenergy using biomass residue and wastes has been backed scientifically. On comparison with fuels and different renewable energies, the cost is not competitive. In order to bring down the production costs, efforts are being targeted at improving the conversion technologies. The main aim of this chapter is to discuss the well-documented and upcoming energy transformation possibilities for converting biomass residue and wastes to obtain biofuels with cost effectiveness. The concept, available choices, and prospective for implementing these technologies have been highlighted. Discussion has been done of the advancements in two primary conversion routes. These are thermochemical (gasification, pyrolysis, and liquefaction) and biochemical (anaerobic digestion, alcoholic fermentation, and photobiological hydrogen production) transformation methods. Besides this, transesterification has been discussed that seems simple and cost effective method for generating biodiesel at large scale. Strategies to directly transform biomass residue and wastes into bioelectricity and combustion and microbial fuel cells have been discussed in this chapter. Designs discussed

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L. K. Sarao (✉)
Punjab Agricultural University, Ludhiana, Punjab, India

S. Kaur
Department of Agriculture, Maharishi Markandeshwar University, Ambala, Haryana, India

M. Arora
Department of Processing & Food Engineering, Punjab Agricultural University, Ludhiana, Punjab, India

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exhibit potential for future large-scale operations which are sustainable and environmentally benign.

Keywords

Waste conversion · Bioenergy · Biofuel · Biogas · Biomass · Thermochemical conversion · Gasification

4.1 Introduction

The issue of environmental pollution and energy source is ever prevailing. Owing to this, biomass and wastes have gained importance for fuel and energy production. The deleterious wastes generated as a result of pollution pose a threat to the environment. Hence, these wastes are now being channelized toward energy conversion (Ningbo et al. 2018). The energy drawn from a fuel that comes from biomass is referred to as "bioenergy." In present times, many countries are interested in developing biomass as a fuel. This is being done keeping the energy crisis of 1970 as a challenge. One of the important components of biowaste is municipal solid wastes (MSW) (Martin et al. 2020). Biowaste is a consortium of household wastes obtained from kitchen and garden. The EU's Waste Framework Directive (2008) gave the definition of biowaste as "biodegradable waste from parks and gardens." This also includes household wastes obtained from kitchen such as the food waste. The wastes from catering industry, eating joints, etc. also add on to this. The wastes obtained after processing of food are also included in this Directive 2008/98/EC (2008).

In the industrialized nations, the economic and political impact of bioenergy is highly taken into consideration. This is depicted by startups such as "Biomass Action Plan" and the "Multi-Year Plan." These are prepared by the European Commission and the US Department of Energy, respectively (Chum et al. 2011). As a matter of fact, biomass has an appreciable contribution as resource of renewable energy (Lauri et al. 2014). It has significant potential for the production of biofuels. Such biofuels could be used for transportation, electricity, and heat (Lebaka 2013).

The issue of environmental degradation caused by pollution is matter of worry. This can be curbed by employing the biomass and wastes as energy resource. The biomass is a completely renewable energy resource. The CO_2 let out on its combustion and use cause no increase in atmospheric carbon dioxide. This is because of its biogenic origin. To make it more clear, plants use CO_2, released into the environment for their growth and for their metabolic processes. This happens as a result of the degradation of other plants (Tkemaladze and Makhashvili 2016). Hence, exploitation of biomass results in faster transfer of CO_2 into the atmosphere. Further, this can be used again by plants for generating biomass (Fig. 4.1) (Kaltschmitt 2013). This lowers dependency on the fossil fuels. Biomass has been considered as a possible feedstock to generate sustainable energy. In times to come, it will be one of the important renewable sources of energy. The inclination toward biomass energy has reduced. This is owing to technological breakthrough which renders

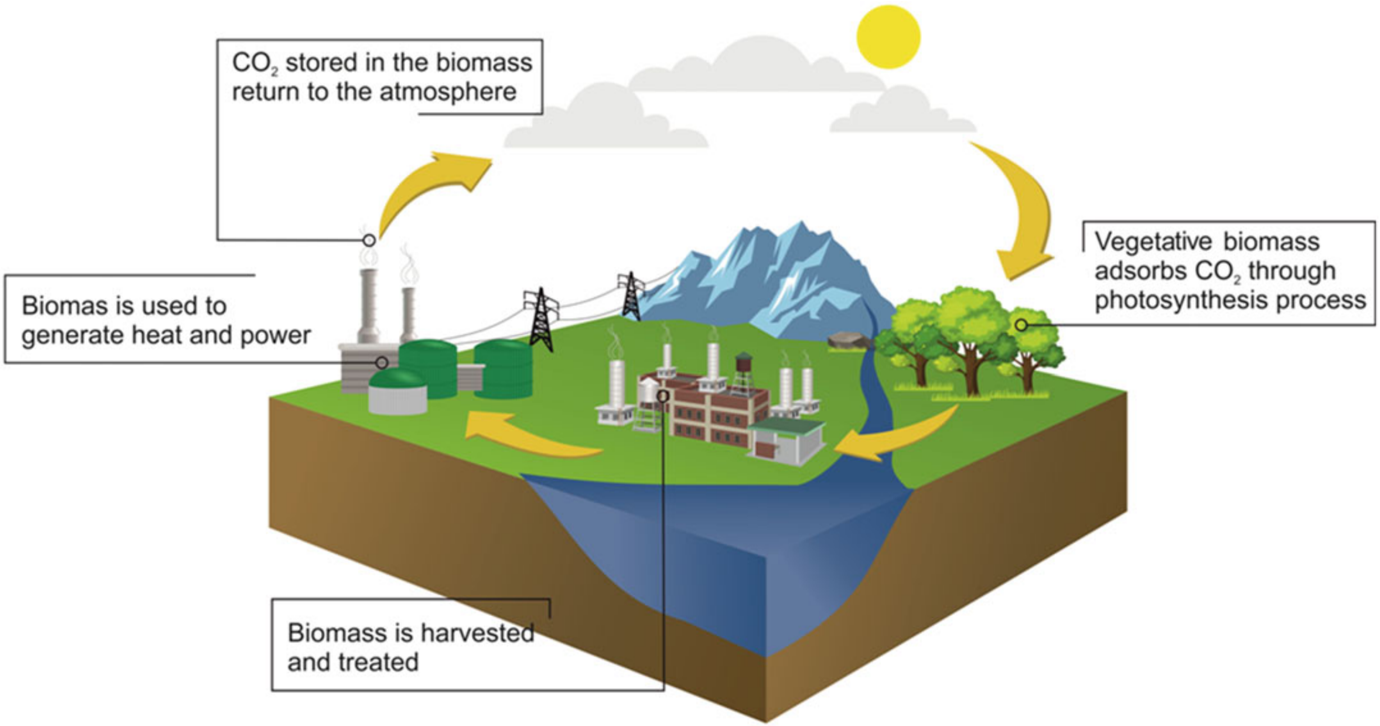

Fig. 4.1 The Carbon cycle as observed in the production and utilization of biomass (adapted from Antonio 2019)

fossil energy comparatively cheaper. Massive researches are being undertaken to generate bioenergy. This has been done owing to harmful air pollution and huge amounts of greenhouse gases. The rising and falling energy rates which are determined by the fossils and worldwide enhancement of transportation fuel requirement also contribute to this.

Since ancient times, biomass in the form of firewood via direct combustion has been put to use. This has been done for generating energy for humans. For generation of biofuel in industrialized countries, different feedstock are available. These include wastes of agriculture and forest. The MSW, industrial and construction waste are also included. Such biofuels are referred to as second-generation feedstock. The second-generation biofuels are drawn from lignocellulosic materials (e.g., jatropha, cassava, switchgrass, wood, and straw) and biomass residues. The biofuels that are generated from edible food crops are referred to as first-generation biofuels. The edible food crops commonly used are wheat, sugarcane, and corn. Barley, potato, sunflower, soybean, and coconut are also used. In order to curb environmental crisis linked to disposal of waste, use of biomass residues and waste as a primary source seems quite potent. The wastes are transformed to beneficial biofuels. This is better than just disposing them off as such.

For third-generation biofuels, algae, another biomass is being tried as feedstock. It shows good potential for producing massive amounts of lipids. These lipids are appropriate for generation of biodiesel. This rapidly growing biomass can be used for producing different biofuels. This chapter highlights technological details pertaining to methods used for conversion of biomass and wastes to biofuels and bioelectricity. An outline of waste to energy technological choices has been drawn. Gasification, liquefaction, anaerobic digestion, pyrolysis, alcoholic fermentation, transesterification, photobiological hydrogen production, combustion, supercritical fluid processing, and photosynthetic microbial fuel cells (MFC) are the conversion methods which have been discussed. Latest information pertaining to bioenergy generation from biomass residues and waste in quickly expanding bioenergy field has also been compiled.

4.2 Biomass Residues and Wastes

The generation of biomass residues and waste occurs as by-products. This happens on plantation, processing, and consumption of sought-after raw products. This is unlike the biomass that is specially cultivated with an aim of energy generation (Speight and Singh 2014). To explain it more easily, there are types of biomass residues, namely primary, secondary, and tertiary groups. The first category, i.e., the primary residues are obtained while planting in the field, the sought-after crops for food besides the products of the forest. These include the straw, stalks of corn, leaves, and stem. As crops for food are channelized into the ultimate products, secondary residues are generated. Few examples of wastes obtained from agriculture and processing of food are coffee husk, sugarcane bagasse, woodchips, and rice hull.

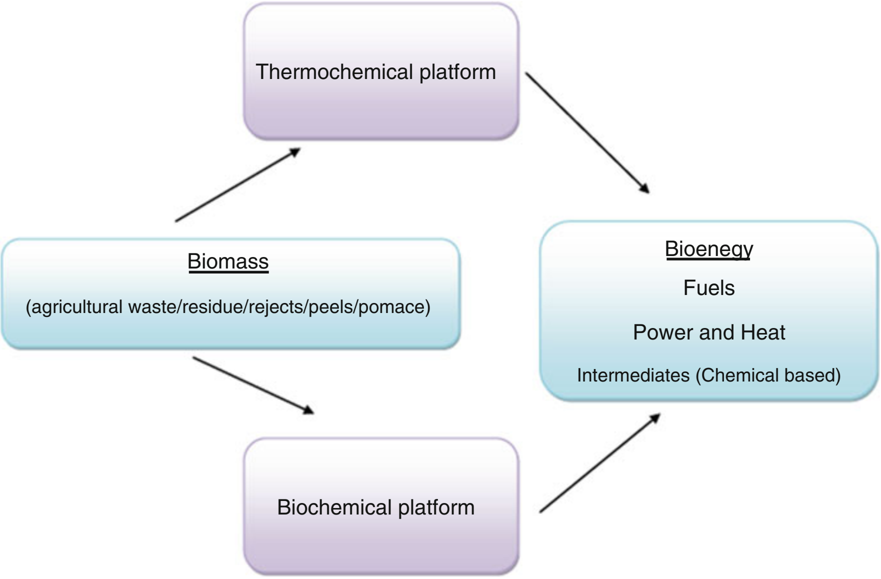

Fig. 4.2 A simple outline of conversion of waste to bioenergy (Keri et al. 2008)

Wastes such as bagasse obtained from sugarcane, the cake obtained from palm kernel are also included.

On biomass derived from product consumption by human and/or animals, the formation of tertiary residue is observed. This residue is seen in the form of MSW. MSW are next channelized to form sewage sludge and/or wastewater (Chen et al. 2018; Li et al. 2009). Figure 4.2 outlines biomass to bioenegry conversion. Figure 4.3 shows the generation of biofuels and its development and illustrates production of second-generation biofuels from waste and biomass residues. The pathways for the conversion for production of different kinds of bioenergy, including bioethanol, bio-oil, syngas, electricity, biochar, biogas, biodiesel, and biohydrogen have also been highlighted. Promising capabilities have been noticed in the residues of wood and agriculture. These also include the primary and secondary residue of biomass and oils used for cooking which are waste (these constitute the tertiary residue of biomass). The biomass of microalgae is also included.

4.3 Residue of Agriculture and Wood

Wood chips, sawdust, and the logs which are discarded are the "wastes obtained after processing of the wood in sawmill as well as in the lumber processing plants." These are the feedstock employed to generate biofuels (Ragauskas et al. 2006). The saw and paper mills industry generated wood residues and sawdust that are treated as fuels for boiler and feedstock for generation of ethanol. Straw constitutes for nearly

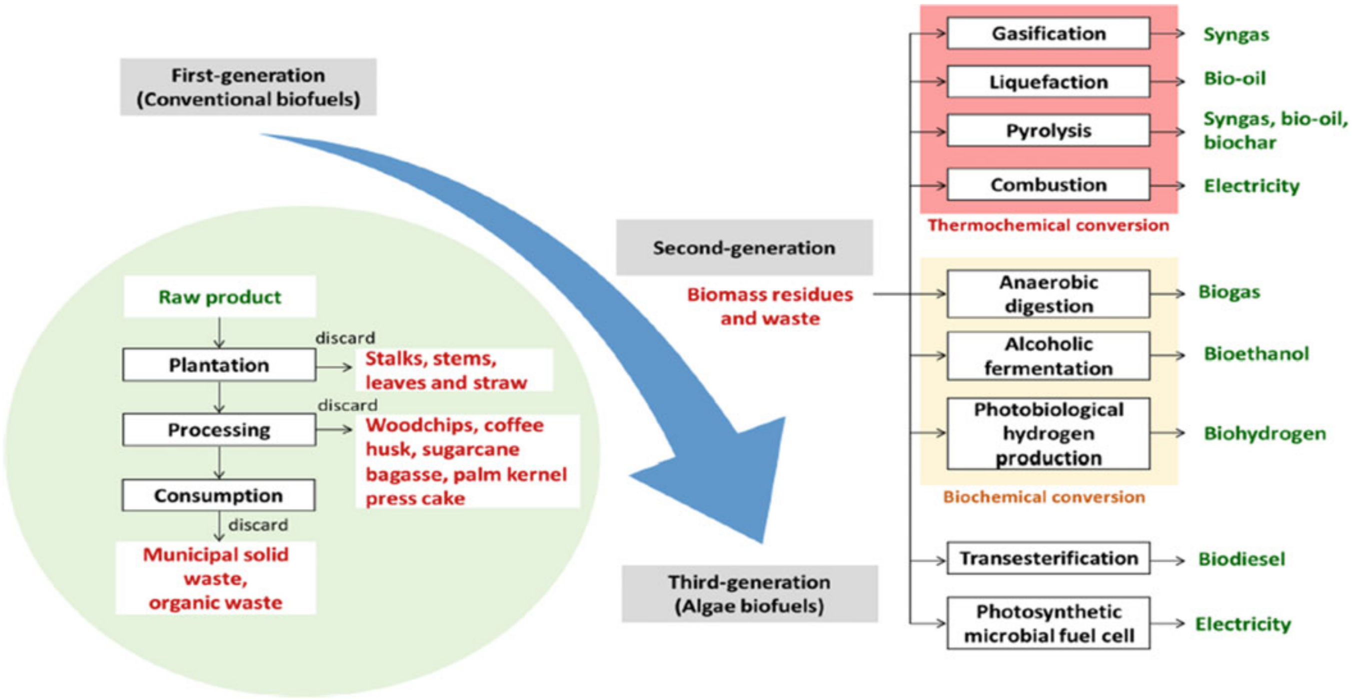

Fig. 4.3 Biofuel generation development. The figure highlights second-generation biofuels obtained from biomass residues and waste. The conversion pathways involved in producing different types of bioenergies have also been shown (adapted from Lee et al. 2019)

72.2% of biomass-based energy resources in the Chinese region. After harvesting the crops grown for food such as wheat, rice, sugar, corn, beans, and cotton, the residues obtained are referred to as straw.

Documentation is there that corncobs, stalks, and leaves can be transformed into sugars which are fermentable for generation of bio-butanol (Qureshi et al. 2010). Jørgensen et al. (2010) and Cerveró et al. (2010) documented that press cake obtained from palm kernel, obtained after palm oil extraction exhibits potential for generation of bioethanol through fermentation. Sugarcane residue of tropical nations, particularly sugarcane bagasse and leaves exhibit capacity for using the residue economically to generate bioethanol (Krishnan et al. 2010; Chandel et al. 2012) and biochar, a different kind of biofuel (Inyang et al. 2010).

4.4 Algal Biomass

Grouping of algae can be done into two main categories. First group is macroalgae also referred to as seaweeds while second one is microalgae. Macroalgae refer to huge multicellular algae. These are commonly seen growing in water bodies such as ponds. The other category, microalgae, are tiny, unicellular algae. These are often observed growing as a suspension within a water body. A number of compounds which are bioactive are recorded in a macroalgae. As compared to microalgae, macroalgae lead to lower amounts of biofuel generation (Bansemir et al. 2006).

Owing to high levels of lipid accumulation and quick proliferation rates, microalgae are a potential oil source. Besides this, microalgae do not compete solely for agricultural and huge freshwater resources. The biomass of microalgae which is spent is transformed to biofuels. This is done after extracting desired products such as oils and some other compounds having high value from biomass of microalgae just like the biomass residues and waste.

Several studies have reported different algae having the potential to use wastes obtained from animals as a medium for growth (Barlow et al. 1975; Chiu et al. 1980; Ayala and Bravo 1984; Olguín et al. 1994; Yang and Duerr 1987; Wilkie and Mulbry 2002). Employing an algal turf scrubber which colonized with filamentous algae in freshwater, for treating raw manure from swine has been documented by Kebede-Westhead et al. (2003).

4.5 Waste Oils (Used Cooking Oils)

Chosen feedstock are employed for obtaining high quality food grade virgin oil but used cooking oil which is s waste can be used to generate biodiesel which is cheap (Zhang et al. 2003a, b). Supple et al. (2002) reported that by using cooking oil which is useless rather than using as the feedstock, the virgin oil for biodiesel production seems an excellent way for lowering the cost of material for the generation of biodiesel. Talebian-Kiakalaieh et al. (2013) reported that biodiesel production cost is lowered (60–90%) by using oils which are otherwise waste. Meng et al. (2008)

documented that reutilizing waste oil helps in curbing issues related to disposal of enormous amounts of frying oil which are no more apt to consume owing to a very high content of free fatty acids. Biodiesel blend of 20% (vol) which we get from oils which are waste and 80% (vol) diesel (B20) can be employed in engines as such with no requirement of any huge modification (Phan and Phan 2008). On comparison to unused oils, the quality of edible oils which are used does not differ significantly. To remove water along with unwanted solid particles before the subsequent transesterification basic pretreatments like heating and filtration can be employed (Jacobson et al. 2008).

4.6 Bioenergy "Conversion Techniques"

As an outcome of present environmental and economic situations, there is an urgent requirement for recycling and energy saving. To use waste for production of bioenergy, various different technologies were exploited and developed. Transforming waste materials into various types of fuel which are employed for supply of energy constitutes the methodologies for converting wastes to obtain energy. In present times, an effective approach for developing renewable energy is the exploitation and transformation of ecofriendly biomass waste to obtain chemical fuel. For biomass energy conversion, numerous technologies and process choices are present. Thermochemical and biochemical conversion are the two common techniques which are employed for transforming waste biomass to energy besides the technique of transesterification. Thermochemical conversion involves decomposing organics present in the biomass. This is achieved by heating. On the contrary, the conversion which is biochemical employs microbes or uses enzymatic action to transform biomass and waste to obtain the energy which is beneficial. The thermochemical conversion involves the following steps in order: first step of pyrolysis, next gasification, then liquefaction, and finally combustion. On the contrary, biochemical conversion has three processes, namely anaerobic digestion (first), alcoholic fermentation (second), and photobiological reaction (third). In the subsequent parts of this chapter, researches linked to bioenergy transformation by employing different techniques have been depicted in Table 4.1.

4.7 Thermochemical Conversion

In the thermochemical conversion technology, a chemical reformation process at elevated temperature is carried out. This method involves splitting of bonds and reformation of organics resulting in biochar, which is a solid, a synthesis gas, and a bio-oil (liquid) that is highly oxygenated. This transformation involves physically converting biomass at elevated temperatures to split bonds of organics and reformation of such substances resulting in hydrocarbon fuels, synthesis gas, and charcoal residue (Cantrell et al. 2007; Bridgwater 2003).

Table 4.1 Bioenergy conversion using different methods (adapted from Lee et al. 2019)

S. no.	Method	Bioenergy type	Feedstock type	Composition/ yield/efficiency/ energy recovery	Operating conditions	Reference
1	Gasification	Fuel gas	Eucalyptus chips and coffee husk	Higher heating value ($MJ{\cdot}N^{-1}\ m^{-3}$): Eucalyptus chips: 6.81 Coffee husk: 7.76	Eucalyptus chip Temperature: 22.1 °C Air inputflow: 182.7$Nm^3{\cdot}s^{-1}$ Air consumption: 38.2 nm^{-3} Coffee husk Temperature: 26.3 °C Air input flow: 124$Nm^3{\cdot}s^{-1}$ Air consumption: 13.4 nm^{-3}	de Oliveira et al. (2018)
		Fuel gas	Pine woodchips	Syngas composition: H_2 gas: 26–42% CO gas: 25–37% CO_2 gas: 16–19% CH_4 gas: 8–11%	Dual circulating fluidized-bed gasifier Temperature: 700–900 °C Steam to fuel ratio: 0.3 $kg{\cdot}kg^{-1}$	Ngo et al. (2011)
		Fuel gas	Rice straw	Efficiency: 33.78% CO gas: 2.01% H2 gas: 5.48% CH_4 gas: 0.51%	Temperature: 600–800 °C Oxygen ratio: 33% Air flow: 0.6 $Nm^3{\cdot}h^{-1}$ Feed rate: 1.12 $kg{\cdot}h^{-1}$ Equivalence ratio: 0.2	Liu et al. (2018)
		Fuel gas	Acid hydrolysis residues and sewage sludge	Cold gas efficiency: 70.68%	Co-gasification using downdraft fixed gasifier at atmosphere pressure. Temperature: 800 °C Catalyst: CaO	Chen et al. (2018)

(continued)

Table 4.1 (continued)

S. no.	Method	Bioenergy type	Feedstock type	Composition/ yield/efficiency/ energy recovery	Operating conditions	Reference
					Sewage sludge composition: 50 wt% CaO/C (molar ratio):1.0 Equivalence ratio: 0.22	
		Bioelectricity	MSW and hazardous waste	Plant efficiency: 41.1% Power: 81 MW	Co-gasification using plasma gasifier. Composition of MSW: 90% wt Oxygen volume: 95%	Mazzoni et al. (2017)
2	Liquefaction	Bio-crude oil	*Jatropha curcas* cake	Energy recovery: 41.48–54.78%	Temperature: 250 °C Catalyst: ChCl–KOH DESs Reaction time: 40 min	Alhassan et al. (2016)
		Bio-crude oil	Microalgae	Yield: 60.0%	Temperature: 350 °C Reaction time: 15 min	López et al. (2015)
		Bio-crude oil	Human faeces	Yield: 34.44%	Temperature: 300 °C Reaction time: 30 min Total solid content: 25%	Lu et al. (2017)
		Crude biodiesel	Wet and dry microalgae (*Nannochloropsis* sp.)	Biodiesel yield Wet microalgae: 14.18% Dry microalgae: 12.48%	Fermentation and ethanol-assisted liquefaction Temperature: 265 °C Ethanol: 15% (v/v) Ethanol to algae ratio: 2:1	Rahman et al. (2018)
		Bio oil	Domestic sewage in high-rate ponds	Yield: 44.4%	Temperature: 300 °C Operation time: 15 min Biomass/water ratio: 1/10 ($kg \cdot kg^{-1}$)	Couto et al. (2018)

		Methane and energy	Microalgae Chlorella 1067	Methane: 32–117% Energy recovery: 70.5%	Integrating HTL and anaerobic Digestion with zeolite adsorption process HTL process: Temperature: 300 °C Reaction time: 30 min Air pressure: 20 bar	Li et al. (2019)
3	Pyrolysis	Bio-oil	Sugarcane residues, sugarcane leaves and tops	Yield: Sugarcane leaves: 52.5 wt% Sugarcane tops: 59.0 wt%	Fast pyrolysis Temperature: Sugarcane leaves: 429 °C Sugarcane tops: 403 °C Nitrogen gas flow rate: 7 L·min^{-1} Biomass feed rate: 300 g·h^{-1}	Pattiya and Suttibak (2017)
		Bio-oil	Pinyon-juniper wood Chips	Yield: 47.8 wt%	Temperature: 400 °C Catalyst: Red mud Feeding rate: 0.9 kg·h^{-1} HDO of oil produced: Temperature: 350 °C Catalyst Ni/red mud	Jahromi and Agblevor (2018)
		Bio-oil	Beech wood	Yield: 86.1%	Hydrotreatment Temperature: 250 °C Catalyst: NiCu/Al2O3	Boscagli et al. (2018)
		Biochar, bio-oil, and gas	Greenhouse vegetable, wastes, and coal	Biochar yield: 40.22, 54.65, 45.93%	Fast pyrolysis Temperature: 500 °C Catalyst:calcite, dolomite, and zeolite Nitrogen gas flow: 1450 mL·min^{-1}	Merdun and Sezgin (2018)

(continued)

Table 4.1 (continued)

S. no.	Method	Bioenergy type	Feedstock type	Composition/yield/efficiency/energy recovery	Operating conditions	Reference
		Syngas (H_2 and CO)	Spent coffee grounds loaded with cobalt	Yield concentration H_2: 1.6 Mol% CO: 4.7 Mol%	Generation of H2: CO2 As atmospheric pressure Reaction time: 110 min Generation of CO: Temperature 700 °C	Cho et al. (2018)
4	Anaerobic digestion	Methane	Sewage sludge	181 mL CH4/g volatile solids	Thermal pretreatment Temperature: 95 °C Reaction time: 10 h Anaerobic incubation Temperature: 35 °C	Passos et al. (2015)
		Methane	Biomass from co-culture of microalgae and bacteria	325 mL CH4/g volatile solids	CaO pretreatment Temperature: 72 °C Reaction time: 24 h Anaerobic incubation temperature: 35	Solé-Bundó et al. (2017)
		Methane	Biomass from mixed culture of three microalgae strains	146 mL CH4/g COD 171 mL CH4/g COD	Batch culture of biomass ammonia concentration: 250 mg NH4 +·L^{-1} Temperature: 23 °C Reaction time: 14 h Illumination 10 days Anaerobic incubation with sludge from wastewater plant Temperature: 35 °C	Molinuevo-Salces et al. (2016)

					Semi-continuous culture of biomass ammonia concentration: 300 mg NH4 +·L^{-1} Temperature: 23 °C Reaction time: 14 h Illumination 25 days Anaerobic incubation Temperature: 35 °C	
5	Alcoholic Fermentation	Bioethanol	Microalgae biomass (*Chlamydomonas mexicana*)	0.22 g ethanol·L^{-1} h^{-1}	Simultaneous enzyme hydrolysis of biomass and fermentation with immobilized yeast Anaerobic incubation Temperature: 30 °C RPM: 120	El-Dalatony et al. (2016)
		Bioethanol	Biomass of 2 microalgae strains	0.18 kg·kg^{-1} biomass	Combined sonication, heat, and enzyme pretreatment of biomass Anaerobic incubation Temperature: 37 C pH 5.5 Hydraulic retention time: 2.5 days	Hwang et al. (2016)
		Mixture of acetone, butanol, and ethanol	Microalgae biomass (*Chlorella vulgaris*)	0.32 g·L^{-1} h^{-1}	Lipidextraction of biomass: Ionic liquid, acid hydrolysis (2% H_2SO_4) and detoxification (resin L-493) of biomass residue, then fed	Gao et al. (2016)

(continued)

Table 4.1 (continued)

S. no.	Method	Bioenergy type	Feedstock type	Composition/ yield/efficiency/ energy recovery	Operating conditions	Reference
					to yeast under anaerobic condition	
6	Hydrogen production Photobiological	Hydrogen	Microalgae biomass (*Chlamydomonas reinhardtii* CC124)	0.60 mL L^{-1} h^{-1}	Medium:sulfur-free TAP40 mg·L^{-1} nanoparticle Anaerobic condition Reaction time:72 h	Giannelli and Torzillo (2012)
		Hydrogen	Microalgae biomass (*Chlorella* sp.)	11.65 mL L	Medium: modified TAP Glycerol concentration: 16 g·L^{-1} Anaerobic condition pH: 6.8 Light intensity: 48μmol·m^{-2} s^{-1} Temperature: 30 °C Reaction time: 24 h	Sengmee et al. (2017)
		Hydrogen	Microalgae biomass (*Chlamydomonas reinhardtii* CC124)	1.05 mL L^{-1} h^{-1} 1.3 mL L^{-1} h − 1	Medium:sulfur-free TAP Light intensity: 50 μE·m^{-2} s^{-1} Anaerobic condition Reaction time: 120 h Medium: Sulfur-free TAP Lightintensity: 50μE m^{-2} s^{-1} Anaerobic condition Reaction time: 120 h	Oncel and Kose (2014)
7	Transesterification (acid/base enzyme catalyst)	Biodiesel	Crude oil of *Pongamia pinnata, Jatropha curcas,*	90%	Esterification: Temperature: 60 °C Reaction time: 3 h	

			and *Calophyllum innophylum*		Transesterification: Mixture of oil with methanol Temperature: 60 °C Reaction time: 2 h	
		Biodiesel	Triacylglycerols	–	Catalyzed by acid or base	Muller et al. (2014)
		Biodiesel	Recycled cooking oil	MgO + CaO: 98.95%	Mixture heated to 55 °C for 20 min, added with methanol and warmed to 75 °C, moved to decanter after 4–6 h	Tahvildari et al. (2015)
		Biodiesel	Refined sunflower oil	Yield: 94%	Optimized conditions: Methanol-to-oil molar ratio: 9:1 Catalyst: 0.3 wt% Temperature: 67 °C Reaction time: 3 h	Bet-Moushoule et al. (2016)
		Biodiesel	*Mangifera indica* oil	MgO: 79.26% ZnO: 77.14% SiO2: 94.9%	Optimized conditions: Methanol-to-oil molar ratio: 15:1 Catalyst: 0.5 wt% Temperature: 64 °C Reaction time: 1.5 h	Jadhav and Tandale (2018)
8	Supercritical fluid	Biodiesel	Fame	100%	Optimized conditions: Methanol-to-oil molar ratio: 40:1 Pressure: 200 bar Temperature: 350 °C Reaction time: 10 min	Farobie and Matsumura (2015)
		Lipid	Corn	99%	Optimized conditions: Temperature: 60 °C Pressure: 300 bar CO_2 flow: 3 mL/min	Toribio et al. (2011)

(continued)

Table 4.1 (continued)

S. no.	Method	Bioenergy type	Feedstock type	Composition/ yield/efficiency/ energy recovery	Operating conditions	Reference
					10 min static extraction 150 min dynamic extraction	
		Lipid	Spent coffee grounds	Yield: 98.14	Optimized conditions: Temperature: 40 °C ethanol (18 mL/100 g) As modifier Pressure: 250	Deshpande et al. (2017)
9	MFC	Bioelectricity	MSW	Power density: 1817.88 mW m^{-2}	Two chamber MSW MFCs with alkali hydrolysis pretreatment	Chiu et al. (2016)
		Bioelectricity	Wastewater	Power density: 642 $mW \cdot m^{-2}$	MFC equipped with Pt electrode	Akman et al. (2013)
		Bioelectricity	Fermentable household waste	Power density: 29.6 $mW \cdot m^{-2}$	Dual-chamber MFCs	Chatzikonstantinou et al. (2018)

There are three main process processes available within thermochemical conversion. These are gasification, pyrolysis, and liquefaction (He et al. 2000; Priyadarsan et al. 2004). The type and amount of biomass feedstock and the choice of energy type affect the selection of conversion type. The end-use parameters, environment-related guidelines, process economics, and research requirements are taken into account (Goyal et al. 2008). Multiple research studies have revealed that the thermal conversion technologies have gained notice because of the availability of industrial infrastructure for supplying highly developed thermochemical transformation equipment, reduced process duration, lowered H_2O use, and additional benefits to generate energy using plastics waste that cannot undergo digestion through action of microbes (Uzoejinwa et al. 2018). In addition to this, for production purposes, thermochemical transformation is not dependent on environment factors. Hence, it becomes important to know the various thermochemical process options for determining their potential in future.

4.7.1 Gasification

The process of gasification involves a chemical reaction in an oxygen-deprived environment. The heating of biomass at extremely high temperature (500–1400 °C) and atmospheric pressures up to 33 bar and in either low or absent oxygen content is done for producing a mixture of combustible gases. Carbonaceous constituents are transformed into syngas. This comprises of hydrogen, carbon dioxide, carbon monoxide, nitrogen, higher hydrocarbons, and methane. This occurs in the presence of a gasification agent along with a catalyst in the technique of gasification. Different kinds of energy or energy carriers are supplied by putting to use this syngas. These are biofuel, biomethane gas, and hydrogen gas. Heat, power, and certain other chemicals are also generated.

The gasification process has been reported to be an excellent method to generate hydrogen gas by utilizing biomass (Ahmad et al. 2016). The technique of gasification is thought of as a self-dependent autothermic channel. This method finds its basis on the energy balance. This contrasts additional thermochemical conversion techniques. It has been reported that recovery of energy is higher by biomass gasification. Even the heat capacity is higher compared to combustion and pyrolysis. This finds basis on exploiting the currently available feedstock of biomass optimally. This is done to produce heat and power. Owing to complicated methodology, highly dependent on conditions of operation, the conversion of carbon monoxide and hydrogen via pyrolysis and liquefaction is not satisfactory (Sansaniwal et al. 2017). This is also accounted for by existence of secondary reaction which occurs as a result of solid substances (hot) and volatiles.

The general conversion via methanation (catalytic) of carbon monoxide and carbon dioxide from syngas leading to natural gas (synthetic) is other beneficial outcome of gasification process (Pandey et al. 2015). Hence, to convert various types of biomass comprising of wastes of agriculture and industry, gasification of biowaste is considered to be an appropriate channel. The wastes from farm, food, and kitchen are also included under this.

The composition of gas generated via gasification process differs based on various factors. These are variants of gasifier, agent for gasification, kind of catalysts, and size of particle. Enormous quantities of carbon dioxide and carbon monoxide are obtained commonly via gasification containing huge amounts of carbon and oxygen.

Among all the waste feedstock, it has been found that the MSW and wastes of agriculture have greater carbon monoxide and carbon dioxide content (Watson et al. 2017). Sulfur is released as H_2S during gasification process, which leads to gas separation and treatment. This leads to a need for gas treatment method for feedstock having huge quantity of sulfur. On a general note, biowaste feedstock constitute <1.5 (percent weight) of sulfur. The sewage (1 wt%) and animal waste (0.5 wt%) comprise the maximum amount of sulfur (Watson et al. 2017).

Four types of gasifiers are employed in the gasification of the wastes. These are fixed bed gasifier, fluidized bed gasifier, entrained flow gasifier, and plasma gasifiers. There are two distinct forms for the fixed bed gasifier, namely downdraft gasifier and updraft gasifier. As a result of its capacity for producing good quality gas at a fast pace and in huge amount and to use up available moisture of biomass, the downdraft gasifier is more popular (Sansaniwal et al. 2017). The gasifiers set up at a small scale are put to use for production of electric power generation. Cogeneration of power and heat is also being done (Ogi et al. 2013). The various kinds of gasification carried out recently have been depicted in Table 4.2.

A study related to generation of energy from waste of canola stalks have also been carried out. The use of new bimetallic catalysts which found support on activated carbon and graphene nano sheets was found out. This was reported in hydrothermal gasification method (Salimi et al. 2018). The incorporation of catalysts having basis of metal such as nickle, rubidium, copper, and cobalt sped up the reaction. This led to enhanced production of hydrogen and methane. High production of hydrogen, carbondioxide, and carbonmonoxide, enhanced catalytic activity and overall stable reaction was noticed with 20% nickel activated carbon, and 20% nickel and 2% copper activated carbon as catalyst.

The feasible nature and behavior of fuel gas obtained via gasification of wastes obtained from coffee was studied (de Oliveira et al. 2018). In a gasifier, feedstock were exposed to gasification, the gasifying agent being air. The gasifier is cheap, downdraft, and is an open source. The gas obtained from eucalyptus chips reported higher heating value. There was a predominance of CO.

Another latest thermochemical technique that can be employed for deleterious wastes is plasma gasification. This is an allothermal process. This employs power from external source to raise the temperature and keeping up with it. Syngas, slug, and ash are the main products produced by this process. Plasma gasification process breaks down almost all the materials including bandages, infusion kits, and antibiotic. The biomedical waste containing cytotoxic drugs, biomolecules, and organisms are also broken down. These are deleterious if let out in the environment. This is owed to the high temperature usage in the process (Messerle et al. 2018).

Table 4.2 Common types of gasifiers used for gasification of biowaste (adapted from Lee et al. 2019)

S. no.	Gasifier type	Benefits	Feedstock	Temperature (°C)	References
1	Fluidized bed gasifier	(a) Moderate requirements of gasification medium (b) High heat transfer rate (c) Thorough mixing of feedstock and bed material	Beech wood	750–850	Pecate et al. (2018)
			Rice straw	600–800	Liu et al. (2018)
			Wood and bark waste	300–400	Wilk and Hofbauer (2013)
			Pine woodchips	700–900	Ngo et al. (2011)
2	Fixed bed gasifier	(a) Able to withstand high moisture content feedstock (b) Low tar accumulation (c) Minimum sensitivity toward feedstock size and quantity (d) High tolerance of ash content	Wood	800–900	Olwa et al. (2013)
			Sawdust	650–960	Hosseinpour and Najafi (2018)
			Sewage sludge	800	Chen et al. (2013)
			Palm shell	750	Pranolo et al. (2018)
3	Plasma gasifier	(a) Nontoxic method to destroy hazardous waste (b) Easy removal of ash as slag (c) Capable to treat both hazardous and nonhazardous wastes	Biomedical waste	1326	Messerle et al. (2018)
			MSW and plastic solid waste	1250–1315	Mazzoni and Janajreh (2017)
			Hazardous waste from oil and gas	1500	Mazzoni et al. (2017)
4	Entrained flow gasifier	(a) Short processing time (b) Uniformity of temperature throughout reactor (c) Flexibility in types of feedstock (d) Low tar production in gas	Empty fruits bunch	900	Ogi et al. (2013)
			Straw biomass	900	Yang et al. (2018)
			Jatropha curcas shell	1000	Pambudi et al. (2017)
			Bituminous coal and wheat straw	1300	Wu et al. (2017a, b)

A study was carried out on plasma co-gasification. This was done for evaluating plasma gasification in recovering energy from MSW. The plastic solid wastes were also analyzed (Mazzoni et al. 2017). It was reported that the process takes up air having high quantity of oxygen for formation of plasma. This leads to enhanced plant efficiency beyond 26%. For the conventional grounded combustion, this performance is considered to be a vital point of reference.

4.7.2 Liquefaction

Two techniques that result in the production of bio oil are liquefaction and pyrolysis. The generation of bio-oil at reduced temperature and raised pressure is done in the presence of hydrogen in thermochemical liquefaction process. This is done in the presence or absence of a catalyst while hydrogen is present.

Another liquefaction method is an established one. It puts to use subcritical H_2O at intermediate temperatures. The temperature range is 250–374 °C. While the working pressure is 40–220 bar for the conversion of biomass to obtain bio-oil. It is referred to as hydrothermal liquefaction (HTL). It is known as hydrous pyrolysis as well. In this technique there occurs decomposition and repolymerization. The reactions are to convert bio-oil and dissolved chemicals (aqueous). These also stand for solid deposition and gas.

The water is maintained in liquid state. This happens owing to high pressure in HTL method. There occurs a blend of raised pressure and temperature. This leads to lowering of the dielectric constant and density. The resulting hydrocarbons are water soluble (Dimitriadis and Bezergianni 2017). It has been seen that the HTL method employs biomass. This biomass contains high amount of moisture. This leads to reduction in the drying cost or the phase of dewatering. Hence, for the generation of bio-oil, feedstock which has different amounts of moisture are more suitable. The wood-based biomass and algal biomass are the few desirable ones.

It has been reported that nearly 700 million tons of dry waste generation occur in United States per year. This biomass feedstock may be used to produce biofuel. This report is based on research conducted by the US Energy and Agriculture Department. Almost 350 million dry tons could be contributed by the forestry and agriculture resources (Messerle et al. 2018). This type of waste seems potent to obtain bio-oil as they are available in huge amounts. For HTL, a potential feedstock is wood-based biomass. This is attributed to its components. It is composed of cellulose (30–50%). The hemicellulose content is 15–35%. Lignin constitutes 20–35%.

At room temperature, cellulose has nonpolar existence. As the temperature rises, it exhibits the property of being soluble. It also has the benefit of high degree of polymerization. Cellulose has appreciable intramolecular and intermolecular interactions in the hydrogen bonding.

For hemicelluloses, there is a weak arrangement. The hydrogen bonding is less resilient. This results in quick splitting of molecules. The production of bio-oil from wood-based biomass is influenced by various factors. These include the operation parameters, presence/absence of catalyzing agent, and kind of solvent. The percentage of bio-oil generated varies (17–68 wt %). This has been revealed by research carried on wood-based biomass via the HTL (Dimitriadis and Bezergianni 2017). Several researches are being carried out using varied HTL methods to convert biomass.

Deep eutectic solvents were tested as catalysts. This was done in HTL of Jatropha cake which was de-oiled (Alhassan et al. 2016). This is due to its direct preparation, less toxic nature, stability at reduced temperature, and cost effectiveness. With the HTL technique involving de-oiled Jatropha, biocrude was obtained. The biocrude obtained was of high energy (41.48–54.78%). A 2-stage HTL experiment was carried out by Costanzo et al. (2016). This involved an initial reduced temperature. Then it was followed by HTL at elevated temperature. This was coupled with hydrodenitrogenation and hydrodeoxygenation catalyzing agent. This was done to obtain biocrude from algae. They reported biocrude obtained finds similarity with conventional gasoline.

A derivative of wastewater treatment is sewage sludge comprising of proteins, lipids, and fiber. It also contains carbohydrates (nonfibrous) and ash. For HTL process, sewage sludge serves as good resource owing to its easy availability in huge quantity. Besides this, it has been documented that there is a decrease in the consumption of energy by 30% with wet sludge as compared to dry sludge (Li et al. 2009).

Bio-oil was produced using dewatered sewage sludge. The moisture content above 85% is the biggest challenge (Qian et al. 2017). Many studies have targeted at the reduction of moisture content of sludge. This include utilization of dry straw (Li et al. 2015), n-hexane for isolation of bound water (Wu et al. 2017a, b), and co-liquefaction (Biller et al. 2018). Methanol can be used to extract extracellular polymeric substances (Sun et al. 2018). SCW pretreatment can be carried out for disintegrating the sludge cells. This leads to release of surface water both free and bound (Tran Nguyen et al. 2013).

The HTL of sludge to produce bio-oil have been carried out by Yang et al. (2018a, b). The effects of simultaneous pretreatment of cationic surfactant and nonionic surfactant SCW were studied. A high quantity of bound H_2O is released from the sludge. This leads to bio-oil production of nearly 47.6%. By employing the co-pretreatment of cationic surfactant fatty alcohol polyoxyethylene ether AEO9 SCW, there was an improvement in the results. The hydrocarbons in bio-oil were enhanced. There was an upgradation in the calorific value by 15.5%. In the HTL process, the entire organic matter is not transformed into bio-oil. In the liquid, there are left out organics. This includes the wastewater obtained after hydrothermal liquefaction. These have several important nutrients. Nearly 20% carbon is transformed into post-hydrothermal liquefaction waste water. The carbon is transferred into various forms. These range from monosaccharides to oligosaccharides. Organic acids such as acetic acids are also included (Lu et al. 2017; López et al. 2015). Hence, it is important to develop a methodology by which one can recover the rest of the organic carbon from post-hydrothermal liquefaction waste water, and thus, obtaining high valued end products. This will result in an economic and viable HTL process.

An integrated method was introduced by Li et al. (2019) involving post-hydrothermal liquefaction waste (PHWW) water from *Chlorella*. The method involved HTL and anaerobic digestion. Methane and energy was generated via this method. Zeolite adsorption anaerobically was used for the energy recovery from PHWW. They documented that the energy recovered was nearly 70.5%. This value was achieved by adding zeolite in an integrated method. Enormous work is being done related to HTL using wet microalgae. This is being carried out owing to its advantages. The drying step is eliminated in the bio oil generation. This could be done either in the presence or absence of a catalyzing agent (Chiaramonti et al. 2015).

A green biorefinery concept has been developed recently involving marine microalgae *Nannochloropsis* sp. (Rahman et al. 2018a, b). This involved the fermentation and ethanol-assisted liquefaction clubbed for ethanol generation. Enhanced lipid generation was reported. The biodiesel production increased three times by integrating algae to liquid process. This is in contrast to microalgal liquefaction.

4.7.3 Pyrolysis

There are two processes for thermochemical biomass conversion. These are pyrolysis and gasification. Pyrolysis involves decomposition done in absence of oxygen. The biomass is decomposed thermally. The operating temperature range is 350–550 °C. This could rise to 700 °C. Decomposition of organic materials takes place in pyrolysis. A mix of solids, liquids, and gasses is obtained. Gasification produces fuel gas. It is combusted for obtaining heat. Pyrolysis generates pyrolysis oil. It is also known as bio oil and is a liquid fuel. This is how gasification and pyrolysis differ. For static heating and electricity generation, bio-oil can be used. This oil can be easily stored and its transportation is feasible. This liquid fuel has benefits over the gaseous one (Dhyani and Bhaskar 2018). Three types of pyrolysis processes are present (Fig. 4.4). These processes differ based on their operating conditions. The three processes are slow, fast, and flash pyrolysis. The operating conditions influence the constitution of the products. In slow pyrolysis, charring is done at reduced temperature. The rate of heating and extended vapor resident time is recorded in decomposition process.

The primary output of fast pyrolysis is bio-oil. This occurs at temperature of 500 °C. The residence time is less than 2 s. Heating rate is above 200 $^{\circ}C{\cdot}s^{-1}$. The reaction time is quite short. The heating rate is more in flash pyrolysis. Presently, liquid generation via fast pyrolysis is the most sought after method. This is attributed to the high production of py-oil (nearly75 wt.%), with the technology being economical, potent, and environment safe (Bridgwater 2012; Jahirul et al. 2012). Py-oil has dark brown color. It is highly viscous and has low calorific value. It has acids, alcohols, aldehydes, phenols, and oligomers having their origin from lignin (Rahman et al. 2018a, b). The major concern currently is upgradation of py-oil properties. This finds importance for its utilization as a crude oil substitute. Several ways are used for upgradation of py-oil. These are physical, chemical, and catalytical methods.

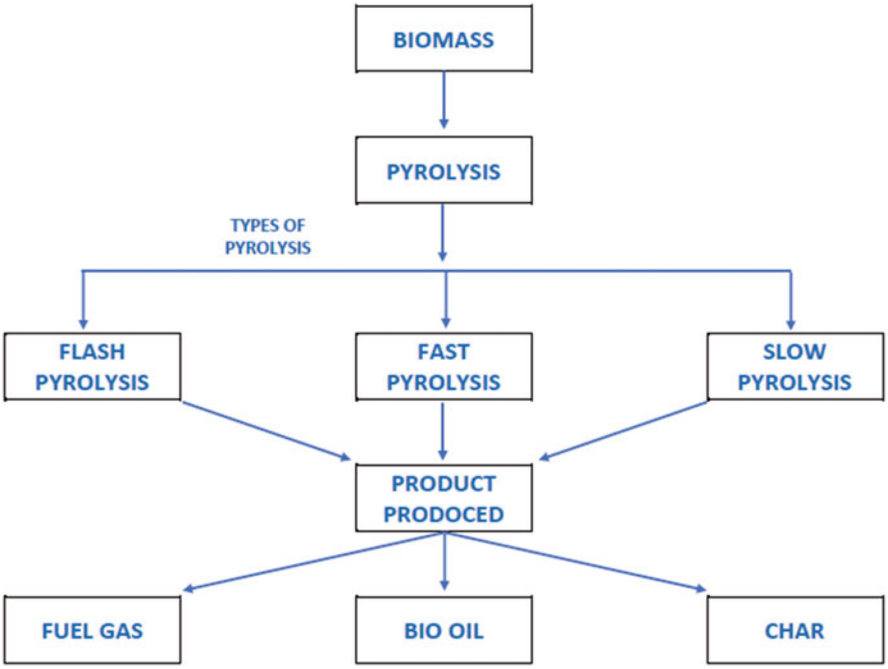

Fig. 4.4 Different types of gasifiers. These are based on recent researches related to biowaste gasification

4.8 Physical Upgradation

The most common technique used to get good quality bio-oil is hot vapor filtration while employing the method of physical upgradation. The initial molecular weight of the oil is lowered. The rate at which bio-oil ages is slowed. The bio-oil of pine sawdust pyrolysis was studied by Case et al. (2014). The chemical and physical variations were studied. They use different hot gas filtration parameters. The oil obtained was quite stable. Char and inorganic substances are eliminated from oil by the application of hot gas filtration. This happens because of exclusion of highly unstable compounds. This includes the ring conjugated olefinic substitutes. The guaiacol like components are transformed into catechol and phenol like components.

Hot filter was used by Pattiya and Suttibak (2017) on pyrolysis of sugarcane. Leaves and tops of sugarcane were used. Fluidized bed reactor was used. They reported a decrease in bio-oil output. The reduction observed was 7–8 wt%, but an improved viscosity and stability was recorded in the filtered bio-oils. Hot gas filtration (HGF) unit was carried out for hot gas filtration by Ruiz et al. (2017). Typical pyrolysis was carried out in situ. The bio-oil output and chemical constitution was studied by them. They observed that secondary reactions affected the output. This was controlled by various HGF factors. The factors being temperature, char cake thickness, and alkali and alkaline earth metallic content of the raw feedstock.

4.9 Hydrodeoxygenation Upgradation

Hydrodeoxygenation upgradation (HDO) leads to enhanced output of oil (Bridgwater 2012). It is also known as hydrotreatment. The carbon recovery and oil quality is better via this method. In this method, oxygen is removed from oxygenated hydrocarbon. This is done via catalytic reaction. The operating pressure is nearly 200 bar. The temperature is nearly 400 °C. The HDO process has been reported to have enhanced the py-oil quality. This is owed to refining oil stabilization and enhanced energy density (Zhang et al. 2013). Py-oil HDO is influenced by four main reactions: (1) hydrogenation of C−O, C=O and C=C bonds; (2) dehydration of C−OH group; (3) condensation and decarbonylation of C-C bond cleavage using retro-aldol; and (3) hydrogenolysis of C−O–C bonds (Li et al. 2010; Furimsky 2000; Huber et al. 2006). Deactivation of catalyst is the biggest problem in py-oil HDO. There is a requirement for effective synthesis of catalyst for HDO technique.

Several catalysts were analyzed with an aim to upgrade pyrolytic oils. The catalysts were non-noble and noble metals. A new multifunctional catalyst was obtained by Jahromi and Agblevor (2018). It was red mud-supported nickel catalyst. They documented that the use of this new synthesized nickel resulted in liquid hydrocarbon, because of cross-reaction of HDO intermediate on Ni/red mud. No such product was obtained by commercial catalyst. Bio-oil with better quality was obtained as shown by a research on py-oil HDO. The intermediatory pyrolysis and hot gas filtration of beech wood were integrated. The kind of catalyst has an influence on the transformation, conversion, and products. The HDO temperature also influences this (Boscagli et al. 2018). Employing Pd/C as a catalyzing agent is an appreciable way to obtain high oil yield. This has been documented by various studies (Elkasabi et al. 2014; Huang et al. 2016). Two types of researches were carried out by Wang and Lee (2019) for using Pd/C catalyst. The first was fluidized bed fast pyrolysis of *Miscanthus*. The second was HDO of bio-oil. Based on the observed results, there was successful upgradation of the oil as an alternative for transport fuel.

4.10 Catalytic "Upgradation"

Employing catalysts is a substitute way to upgrade py-oil. For enhancing pyrolysis oil quality, two procedures are used. First method comprises a downstream process. First, metallic or bifunctional (hydrogenating and acidic) catalysts' are involved. Then, in-situ upgradation is done via integration of catalytic pyrolysis (Jahirul et al. 2012). In catalytic procedure, the vapor undergoes extra cracking. This happens inside the catalyst pore. Components having low molecular weight are formed.

Carboxylic and carbonyl groups are the unwanted products which result in increased oil acidity and viscosity in the py oil.

In pyrolysis, catalysts bearing capacity to alter the organic acid to alcohol are vastly employed for refining oil. One such example is zeolitic catalyst. They have the ability for breaking long chains. They encourage aromatic hydrocarbon production. Size of micropore/mesopore should be considered in most zeolite catalytic studies. This is done to ensure entry of big biomass chain in zeolite pores' for enhancing the production of hydrocarbons (Rahman et al. 2018a, b).

The C-O and C-C bonds between guaiacyl, syringyl, and p-hydroxylphenyl get split by the transformation of pyrolysis vapors through acid-catalyzed reaction. This results in generating intermediates for the coke production. This happens on zeolite surface (Rahman et al. 2018a, b). The mesoporosity of the zeolite was noted. It rose by employing ZSM5 which resulted via desilication (Hoff et al. 2017). The increased mesoporosity improved the aromatic yields. This was noted in red oak pyrolysis. For py-oil, in-situ method is sought after as its temperature of operation can be varied. Even loading ratio of the catalyzing agent can be adjusted (Rahman et al. 2018a, 2018b).

4.11 Biochemical Conversion

Yeast and special bacterial organisms are used either together or individually in biochemical conversion. Through these, wastes are converted to energy. Anaerobic digestion, alcoholic fermentation, and photobiological methods constitute the classical process options which end with the production of different biofuels.

4.11.1 Anaerobic Digestion

Full use of the biomass will add to the cost effective, sustainable, and green attributes of microalgae biorefineries. This is credited to the microalgal biomass rich in nutrients. It has carbohydrate, protein, and lipid (Sialve et al. 2009). Digestion of biomass obtained from biodiesel production waste occurs anaerobically. This helps in extraction of nutritional compounds completely. In anaerobic digestion, the spent microalgae biomass is transformed to biogas by microorganisms. The biogas contains CH_4 and CO_2 with small amount of H_2S. Moist biomass having moisture of nearly 90% can be accommodated by digestion carried out anaerobically (Brennan and Owende 2010). In anaerobic digestion, there are three prime phases. The first one is hydrolysis, the second one is fermentation, and the third one being methanogenesis. Complicated components of biomass are transformed to simpler ones in hydrolysis. The simple biomolecules are used up by fermentation. Alcohols, acetic acids, fatty acid (volatile), and gaseous mix of H_2 and CO_2 are produced.

Biogas having methane (nearly 60–70%) and carbon dioxide (nearly 30–40%) is let out by methanogens metabolizing this gas mixture (Cantrell et al. 2008). Besides the key nutrients found in microalgae biomass (carbon, nitrogen, and phosphorus), trace elements (such as iron, zinc, and cobalt) present in the biomass have also been noted to boost up methanogenesis (Grobbelaar 2004). Having information about the amount of organic compound in microalgal biomass, the theoretical CH_4 and NH_3 generation from anaerobic digestion can be determined. Higher yields of methane are obtained with high lipid content. The rate of hydrolysis is slower in lipids. It is faster in carbohydrate and proteins. For adequate hydrolysis of biocompounds for anaerobic digestion the minimum duration was calculated to be 0.18, 0.43, and 3.2 days for carbohydrates, proteins, and lipids respectively (Pavlostathis and Giraldo-Gomez 1991).

The nutrients in biomass, working temperature, working pH, biomass loading rate, and hydraulic and solid retention time influence the yield and energy content of biogas. In order that the hydrolysis method is not limited by slow loading rates and the methanogenesis process is not bounded by rapid loading rates, the hydraulic and solid retention time must be standardized (Sialve et al. 2009). The 'rate limiting' step is hydrolysis as there is difficulty in hydrolyzing microalgal cell walls. Hence, selected microalgae species greatly influence loading rate. The retention time is also affected by it. The operating pH boosts the ratio of methane in the biogas in the methanogenesis phase. With the progress of fermentation, pH rises. This happens owing to increase in NH_3. The CO_2 in the fermentation broth dissolute owing to high pH. This leads to increase in CH_4 in biogas. High content of CH4 is preferable, as it leads to enhanced energy of biogas. Besides the pH, microbial activity and CH_4 production are supported by higher operating temperature. It has been recorded that the increase in temperature from 15 °C to 52 °C employing *Spirulina maxima* biomass enhanced the CH_4 productivity. The volatile solids were reduced by 35% (Samson and Leduyt 1986). The prime challenge being the reduced biomass in feed stream in anaerobic digestion. It has been stated that a concentrating step for microalgal biomass is required for optimum operation of the anaerobic digester. Microbial communities got drained out due to lack of digestible nutrients when biomass feed stream was highly diluted. Another problem that arises is recalcitrant nature of microalgal cell walls. This leads to delaying of the hydrolysis process. For combating it, cell disintegration should be done on microalgal biomass for breakdown of cell wall. Consequent to this, the nutritional components in microalgal cells can be used for hydrolysis. Subsequently they can be taken up by microbial communities.

Improved CH_4 yields are noted in the biogas with the higher availability of short-chain nutrients. There are three prime categories of the cell disruption methods. These are physical (microwave, ultrasonication, and bead milling), chemical (acid/alkali treatment), and enzymatic methods (Günerken et al. 2015). Another issue for anaerobic digestion is low carbon to nitrogen (C/N) ratio of microalgal biomass. Nutrient imbalance is observed in anaerobic microbial community. This occurs when C/N ratio is below 20, resulting in the release of NH_3 as nitrogenous wastes. Methanogens are suppressed by the high concentrations of $NH_{3.}$ This leads to accumulation of volatile fatty acids in digester (Sialve et al. 2009). Co-digesting microalgal biomass using wastes like pig manure (González-Fernández et al. 2011) cow manure (Saxena et al. 1984), and paper waste (Yen and Brune 2007) can head toward tackling of low C/N ratio.

4.11.2 Fermentation-Alcoholic

Alcoholic fermentation of biomass residue comprising of fermentable sugars can lead to bioethanol formation. The sugars are transformed from cellulose and hemicellulose component of biomass. This happens in the presence of yeasts or bacteria. Huge amount of starches, glycogens, and celluloses seem to get collected by microalgae species such as *Chlorella, Scenedesmus, Chlamydomonas, Spirulina,* and *Dunaliella*. These are complex polysaccharides. These serve as raw material for bioethanol generation. The microorganisms seem to find it difficult to metabolize the polysaccharides. Therefore, the hydrolysis is done for splitting polysaccharides to simpler sugar.

Acid/alkali and enzymes are used in general hydrolysis processes. The treatment involving acid is cost effective and quick, but acidic environment transforms the sugars into components which are not preferable. Contrary to this, the treatment with enzymes is useful and does not end with any by-products which are unfavorable. The shortcoming of this method is that the enzymes are high in cost and are slow acting. Prior to hydrolysis, cell disintegration methods should be followed for improving efficiency to lower the time span of hydrolyzing (González-Fernández et al. 2011). The crude alcohol produced having 10–15% ethanol should be concentrated by distillation (Bibi et al. 2017). Using liquefaction, gasification, or microwave-assisted pyrolysis the remaining solid residue can still be processed into valuable products to enhance yields of valuable metabolites or switch to the production of a different metabolite. Genetic engineering of microalgae strains has been researched. Conversion of CO_2 to biofuels via photosynthesis is one of the target of genetic engineering. This pathway would not spend energy toward the assembling and break down of biomolecules needed for energy storage and cell structures. Via the Calvin cycle, during photosynthesis, glucose and other metabolites are generated. Here, ribulose-1,5-bisphosphate reacts with CO_2 yielding two 3-phosphoglyceric acid. These serve as the precursors to the assembly of glucose (John et al. 2011). Several studies have targeted at the redirection of phosphoglyceric acid molecules to accumulate ethanol instead by inserting genes involved in ethanol synthesis (pyruvate decarboxylase and alcohol dehydrogenase). A proteobacteria *Rhodobacter* sp. was successfully engineered into an ethanogenic recombinant strain in one such study. The recombinant strain was an anaerobe, generating ethanol in the company of light and without oxygen.

4.11.3 Hydrogen Production: Photobiological

Naturally, there is the ability to generate H_2 gas in the presence of light by biomass such as microalgae. Microalgae transform water molecules into O_2 and H^+ in the photosynthesis. Next, the H^+ is reduced into H_2 gas by hydrogenase enzyme under anaerobic conditions. During the photosynthesis, O_2 released inhibits hydrogenase enzyme and interrupt releasing of H_2 gas. This indicates that anaerobic condition is necessary for culturing of microalgae for H_2 gas production (Cantrell et al. 2008). For extracting photosynthetic H_2 using microalgae, there are two main methods. In the first method, there is co-production of O_2 and H_2 in the presence of light. Via oxidation of water molecules, electrons generated are used by hydrogenase enzymes to yield H_2. In this method, higher production is recorded theoretically as compared to the other method. The drawback being that H_2 production is rapidly inhibited by the O_2 production (Ghirardi 2000). The other method employs two-phase system. The first phase is to culture microalgae normally. The second phase is promotion generating H_2 continuously under anaerobic and sulfur deficient environment.

Sulfur deficit puts the microalgae in a condition where the energy requirement of cells is fulfilled by releasing of H_2. This H_2 production goes down after 60 h in two-phase system. The theoretical maximum H_2 yield could reach 198 kg H_2 ha^{-1} day^{-1} (Melis and Happe 2001). In sulfur-constrained cultures, duration of H_2 generation could be made longer by adding small quantity of sulfur. Microalgae cells' conditions were enhanced. On sulfur addition, the PSII systems of these were activated temporarily without the presence of an aerobic environmental condition (Kosourov et al. 2005). Over a period of 1 month, the regular sulfur addition over five intervals allowed cells' reconstitution. This also improved the total H_2 yield by 3–4 times compared to the control culture with no sulfur addition (Kim et al. 2010). For H_2 generation, nonstop systems have been tried by employing a two-stage chemostat bioreactor. The microalgae culture in chemostat was continuously fed with new cells and small quantities of sulfur, and H_2 production persisted for a period of five and a half months. Immobilizing cells on a solid surface during culturing is another method to prolong microalgae H_2 production to enable H_2 generation for 90 days; when immobilization on glass has been carried out (Laurinavichene et al. 2006), the alginate matrix immobilization has increased the specific H_2 productivity and O_2 resistance of the cells compared to the control (non-immobilized) culture.

4.12 Transesterification

For biofuel production, using biomass which is cellulose based is more complicated. This is attributed to the properties and performance of the extracted oil that needs to be tuned to suit the properties of hydrocarbon-based fuels. The conversion of the oil and fats obtained from these biomasses into suitable biofuels is the biggest challenge, so that these can be effectively used as a conventional fuel substitute. There is also an issue of viscosity, low vitality, and polyunsaturated characteristic with biofuel obtained from biomass such as lignocellulosic materials. Many pretreatment methods are there which can help tackle these issues. Transesterification is one such method. This involves the conversion of fat and oil to ester and glycerol in the presence of catalyzing agent. Fatty acid methyl ester (FAME) produced has the physical characteristics comparable with the commercially available petroleum fuel. The glycerol produced as by-product is commercially valuable.

4.13 Acid/Base and Enzyme Catalysis

To generate biodiesel, three groups of catalyst are exploited. These are acid, base, and enzymes. For commercial production, base-catalyzed transesterification is generally in trend. This is done as it yields higher FAME rapidly with mild reaction conditions. This is contrary to the transesterification, which is acid catalyzed. The enzyme catalysts are more safe for the environment. Though their reaction rate is slow paced, they yield high quality products. In order to make these more feasible, the costs need to be worked on. A two-step esterification-transesterification method is employed for obtaining biodiesel. The lipid granule contents need to be transformed to a less viscous form. This is required to generate biodiesel appropriate for common internal combustion engines. In general, this is achieved via transesterification of triacylglycerols. This leads to the production of fatty acid alkyl esters. Lipase/chemical, such as an acid or base, may serve as a transesterification catalyst. Owing to the high energy consumption, huge volumes of salt and water are required. There is a need for conventional transesterification process. For this there is a high recommendation for developing an enzymatic transesterification, catalyzed by intracellular or extracellular lipase (Muller et al. 2014).

For improving enzyme catalyst performance, several methods such as protein engineering, enzyme immobilization and whole cell catalyst can be used. With a low-energy consumption, enzyme catalyst works in gentle environments. These also lessen the requirement of separation step after transesterification. Saponification is prevented by enzyme catalysts. Only simple purification steps are required, they have slow reaction rate and are not cost effective. Enzymes are deactivated upon exposure to alcohol and temperature as they are susceptible leading to drop in the biodiesel yield. A single-step method transesterification to be done directly has been studied recently. It involves the successive usage of acid base catalysis for biodiesel production from the crude oil of *Pongamia pinnata* with the conservative two-step esterification-transesterification technique (Yunus Khan et al. 2018).

A combo of methanol and sodium methoxide as the base catalyst and boron trifluoride as the acid catalyst is employed in the direct transesterification. In direct transesterification, production time saw a decline by 1.5 times to get final biodiesel product. No significant difference was found between the quality of the fuel produced from both the esterification transesterification and direct transesterification methods. A way for free fatty acids esterification is the quick potential reaction among sodium methoxide in methanol and vegetable oil (Demirbas 2008). This lets the researchers conclude that transesterification is a potential process which lowers processing time, reduce solvent need, and be applied to other nonedible feedstock (Chew et al. 2018).

The implementation of advanced biofuel generation has been studied. This is based on rapid and risk-reducing industrialization of nano-catalytic processes. For reducing reaction time and cost as compared to utilizing available catalysts, new green biocatalysts are being worked on. An environmentally friendly and recyclable option is heterogeneous catalyst. High yield of biodiesel is produced by them. It possesses a long life span and can be easily split from the liquid (Islam et al. 2013). CaO and MgO heterogenic nano-catalyst coupling was employed for the transesterification reaction. This was done to generate biodiesel using recycled cooking oils (Tahvildari et al. 2015). The transesterification was not catalyzed by nano-MgO. When used in combination with nano-CaO, a significant enhancement in the yield was observed. A high contact area was possessed by the combined catalyst. Its repeatability was much better compared to using nano-CaO alone. Enhanced biodiesel was produced by the higher proportion of nano-CaO to nano-MgO. To produce biodiesel from *Mangifera indica* oil nano-MgO, nano-ZnO, and nano-SiO_2 was studied (Jadhav and Tandale 2018). Nano-SiO_2 reported maximum yield. This was owing to the super-acidity characteristics having positive impact on the catalytic reactivity. Maximum yield can be obtained by using nano-SiO_2. This is so as it serves as robust activator and stimulates the reactions.

For the production of biodiesel, obtaining Ag/bauxite nanocomposites has also been researched (Bet-Moushoul et al. 2016). Increased catalytic activity was noted through large porous structure of the nanocomposite. This was achieved by having more surface area and contact between alcohol and oil. This resulted in higher efficiency of transesterification reaction. For the biodiesel production, the heterogeneous catalysts can provide an efficient and effective conversion of feedstock to biodiesel. This is so with a beneficial attribute of recyclability (Sharma et al. 2018). In the commercialization of biodiesel production, fabrication of nanocomposites, having acid and base sites, higher surface to volume ratio, and larger pore distribution also play a role.

4.13.1 Supercritical Fluid Extraction (SFE) Method

The technique of supercritical fluid extraction (SFE) is an extraction route which puts to use supercritical carbon dioxide (SC-CO_2) as solvent. An important option for enhancing yield and selectivity profile while extracting organics of plants is the SC-CO_2 extraction technique (Azevedo et al. 2008). Compared to conventional extraction methods, SFE has few benefits. These include higher selectivity, shorter processing time, and usage of non-toxic solvents. This technique has no requirement of consequent processing steps for separating solvent. This is opposite to conventional extraction methods which need solvent separation that causes the degradation of the desirable compounds. Methanol, propanol, acetone, methyl acetate, and dimethyl carbonate are the other supercritical solvents that can be used. The hydrogen bonds in solvents will be greatly reduced. This happens when the solvents reach supercritical state. This leads to a decline in the polarity and dielectric constant. This lets the molecules of the solvents to act as free monomers. Owing to this phenomenon, supercritical solvents can solvate nonpolar triglycerides into homogenous liquid phase. This leads to the production of FAME and diglycerides.

The critical pressure possessed by SC-CO_2 is 73.9 bar. This ends in a suitable costing of compression. Its critical temperature is low (31.1 °C). Hence, this solvent has the ability for extracting temperature sensitive lipid fraction with success. No degradation is observed in this method. The SC-CO_2 is not that flammable. It does not react with ease. Hence, this results in a safe extraction (Azevedo et al. 2008).

To obtain biodiesel, supercritical alcohols are known for producing good results. Methanol is one such supercritical alcohol. By adjusting temperature and pressure, the solvent polarity of such fluids having supercritical nature can be optimized. Hydrogen bond network in methanol is broken. This happens under supercritical environment. Such reduction in hydrogen bondings supports stronger direct nucleophile attack by methanol on carbonyl group. An elevation in reaction rate is seen as the dielectric constant of methanol lowers. This happens at the supercritical state (Hoang et al. 2013). For evaluation of the cost and performance, the selection of alcohol is important. Alcohols such as ethanol can be easily generated using wastes from agriculture. This is preferred over methanol. Ethanol has high power for dissolving oils. Therefore, it exhibits suitability to transestrify vegetable oil. Fuels having better properties are generated by alcohol having structural branching. Heat contents and cetane number goes up by the additional carbon supplied via ethanol.

Lipid from several varied biomass has been extracted by SFE. These include soybean using SC-CO_2 (Jokić et al. 2011) and spent coffee ground employing SC-CO_2 (Pattiya and Suttibak 2017). The residual corn using SC-CO_2 (Toribio et al. 2011), linseed using supercritical-ethanol (Abrahamsson et al. 2015), organosolv lignin using supercritical-ethanol (Kim et al. 2013), shrimp waste using SC-CO_2 (Sánchez-Camargo et al. 2011), and white pinewood (Wang et al. 2013) are also used. A lot of work has been done on SFE. Lipids haven been extracted from third-generation feedstock. Using a supercritical anti-solvent fractionation technology (SAFT), extraction of lipids was done from milk. This method consists of H_2O miscible organic solvent and H_2O. Using a supercritical solvent, the resultant solution goes through extraction involving dimethyl ether. By SAFT, good amount of lipid was obtained. Nearly 70% neutral lipids and 30% phospholipids are generated (Catchpole et al. 2012). One simple biofuel generation method is supercritical transesterification. No catalyst is required here. This method was developed to combat the shortcomings of catalyzed transestreification. Some of its disadvantages are extended reaction duration, regeneration of catalyst, poisoning by the catalyst, saponification, and biodiesel washing. This process is costly as well.

There is no requirement of catalysts in supercritical transesterification, as it occurs in supercritical operating environment. This reduces the complexity involved. The cost of catalyst employment is also lowered (Deshpande et al. 2017). To create the supercritical conditions, there is a necessity for increased temperature and pressure. This calls for expensive material to construct equipments which are operated at elevated parameters. Even then, the supercritical method exhibits advantages. A variety of feedstock can be tackled by it. Reaction process and biodiesel yield are affected by the design of the transesterification reactor. For generating biodiesel through non-catalytic transesterifications, a novel spiral reactor was made (Farobie and Matsumura 2015). This was done to curb the heat recovery issue in commercial production. The FAME output through spiral reactor was noted to rise. It was also recorded that the temperature and reaction time was high. At "the same reaction conditions, good output was recorded in comparison of batch reactor. In commercial production of biodiesel, supercritical fluid has been used. This reveals its possible scalability. It also exhibited its feasibility as a potential technology.

4.14 Bioelectricity Production from Biomass

It is possible to obtain bioelectricity from renewable feedstock. This form of bioenergy comprises the spectrum of energy technology. For developing potential bioenergy, there occurs transformation of wastes obtained from agriculture and forestry into the biomass feedstock. This is done to generate electricity directly and also for heating. Generally, the production of bioelectricity can be done by combustion of lignocellulose feedstock. This feedstock from biomass sources. The biomass sources being obtained from agriculture, residue, plantation forest, residues from saw mill, and native forest. Bioelectricity generation from biomass was carried out by Farine et al. (2012). This was done to bring down greenhouse gases emissions in Australia. They employed lignocellulosics from forest and agriculture biomass. By this they obtained electricity by direct combustion. Nearly 15% of Australia's electricity production was from forestry and agriculture production. It was observed that first-generation technology enhanced electricity generation by 9%. About 28% of electricity let out and 9% nationwide let out were mitigated by the energy production systems. This leaves a great influence on greenhouse gases emission.

A study combining the agricultural and forestry aspects in the United States showed another economic model used (White et al. 2013). This was done for enhancing generation of renewable bioelectricity by employing simulated standards. As per documented data of this model, the agricultural and forestry sector exhibit a potential for supplying nearly 10–20% of the electricity need. Here, a big part of biomass feedstock is expected to be procured via energy crops and other crop residue. In a 15-year period, lowering of greenhouse gases emission is chalked at nearly 27 million ton of carbon dioxide. In China, production prospect of crop residue for bioelectricity generations contribute toward worldwide bioenergy interest. By 2020, biomass electricity capacity was targeted at 30,000 in China. For electricity generation, more efficient consumption of China's resources based out of agriculture biomass will be done (Clare et al. 2016).

In Amsterdam, the Netherlands, research was done to access the potential of bioenergy supply (Clare et al. 2016). It was documented that supplying flexible bioenergy via urban waste streams can lead to production of renewable energy in urban sector (Jiang et al. 2017). Having a futuristic approach for electricity generation, development of urban electricity system model was done. They reported a requirement of nearly 1300–2800 t waste biomass/day in various conditions. About 1400 t being average per day wastes originating in Amsterdam. This will tend to change because wastes' production will go up proportionately as urban and economical situation develop further. The policy making to explore potential bioenergy generation from local biomass to contribute toward sustaining electricity set up is supported by such estimates. Bioelectricity generation could be achieved by means similar to other bioenergy production methods. One such method is thermochemical conversion. Combustion is also a means to obtain bioelectricity. There occurs combining of biomass and oxygen in combustion. This occurs at a high temperature resulting in CO_2, H_2O, and heat. Chemical energy is stored in the fuel in the combustion process. This energy is released as light, heat, radiations, and some other forms of energy. Biomass get changed to char and other volatile compounds. These volatile gases interact with oxygen releasing heat. In combustion, bioelectricity generation occurs via steam. This steam is obtained from heat generated via combustion. To produce electricity, this steam runs steam turbines. For enhancing power generation, different turbine blades or operation modes for steam turbine (reciprocating or screw-type turbines) are carried out (Brown 2011).

Biomass gasification is another technique for bioelectricity generation. Energy is extracted from the solid fuel through gaseous conversion in gasification. Syngas and some heating compounds are produced from biomass wastes through gasification. Certain contaminating products obtained along side are tar, char, sulfides, and chlorides. In terms of energy saving and ecological preservations, effective usage of syngas from gasification is considered way better than combustion (Brown 2011). Gasifiers have the pros of being able to be used in country side. Using biomass waste available locally, the issues of rural area electricity supply can be tackled. Electrical efficiency up to 35% increase was observed by integrating both combustion boilers with gasifiers.

Use of MFC is the recent potential technology for the transformation of biomass to electricity. Bioelectricity generation is done via conversion of organic substrate. To facilitate this, electrogenic bacteria are employed under anaerobic condition (Chatzikonstantinou et al. 2018). There are two chambers in the MFC. A proton exchange membrane separates the biotic anode and abiotic cathode. Different wastes (food wastes, household wastes and MSW) can be simultaneously treated and electricity be produced.

In an MFC, current and power density produced can be changed. This can be done controlling by operating parameters, such as temperature, pH, loading rate, concentration of substrate, microbes, static magnetic field, and hydraulic retention time (Akman et al. 2013). Besides this, several parameters have been studied for determining augmentation of electricity production of MFC (Chiu et al. 2016). The parameters are linked to material of electrode, architecture, process economics, and the characteristics of the membrane.

Utilization of Ti-TiO_2 electrode was done by Akman et al. (2013). They revealed nearly four time more power density when compared to Pt electrode. In addition to this, as the substrate in the MFC, the utilization of food residue biomass resulted in highest power density. This indicated that hydrolyzing food residues biomass can increase performance of MFC (Chatzikonstantinou et al. 2018). Being a green and sustainable process, the MFC shows great potential. A new insight for bioelectricity generation can be provided by its implementation.

4.15 Current Challenge and Future Prospects

This chapter highlighted several methods for the conversion waste to bioenergy technological means. These are available at our dispense for the generation of bioenergy from waste feedstock/substrates. For the renewable energy production, using wastes is cost effective. It also has the benefit of cleaning the environment. From varied parts of the world, biomass residue and wastes are obtained in huge quantity. Such waste products have a potential for generating bioenergy. For this we need cost effective and viable technological advancement.

Many shortcomings have been noticed in developing biomass residue as intermediate source of energy. The primary issue is the cost effectiveness. This is so because waste to bioenergy generation is not yet as cost-competitive as fossil-based fuels. This is concluded on the basis of current technologies developed. The utilization of MSW to generate bioenergy economically is not profit bearing. This is owed to high cost of incineration, gasification, and pyrolysis (Ng et al. 2014). An investigation related to waste to bioenergy for MSW was done. It was reported that gasification results in high cost of operation. It is nearly 250,400 USD/d. Incinerator, landfill gas recovery systems, and anaerobic digestion also add to cost (Tan et al. 2015).

There is a set-back when we commercialize the technology for converting waste to obtain bioenergy. This is because of the high energy requirement for pretreatment of waste. The step to purify the biofuels, equipments for setting-up the plant, the reactors and all the maintenance also adds to the cost. Improving environment should be the target while implementing the conversion waste to bioenergy aspect. This must facilitate reduction in landfilling of the waste. Letting off unwanted and deleterious end products into environment occurs owing to processing of waste to bioenergy. For instance, inappropriate design and improperly operated MSW combustion system to generate electricity results in releasing trace organics, some of these being furan, polychlorinated dioxin, lead, mercury, and cadmium (Ruth 1998). When combustion of MSW is done, volatiles like mercury might get vaporized. This interferes with its effective removal by using particulate removal equipment.

For curbing release of deleterious complexes and tackling the appropriate mix up and temperature of air/fuel and to avoid “quench” zones in furnace some precautions are mandatory. To curb the release of deleterious volatile compounds in conversion of wastes to bioenergy, an appreciable control technology should be continuously developed. While choosing conversion technology for wastes into bioenergy, deleterious gases released must be kept in view. Compared with anaerobic digestion, incinerator normally results in increased production of polluting agents. In order to transform MSW which has more moisture content, anaerobic digestion can be done. This is so when we require low heat energy and cleaner technology (Tan et al. 2015). In order to make sure we achieve high energy recovery efficiency while generating power and minimizing environment hazards, proper waste classification is quite inevitable (He and Lin 2019).

4.16 Conclusions

The fuel for transportation and bioelectricity can be generated by employing transesterification, thermochemical, and biochemical pathways. Biomass residue and wastes are transformed through these processes. The ultimate product desired and the feedstock determine the choice of technique to be employed.

The thermochemical technology which involves thermal heat is not sensitive to biomass waste composition. This is observed on comparison of biochemical strategies to generate biofuels. Still, we consider generating biofuels from biomass wastes as better in material handling, transportation, and conversion technology, when compared to traditional editable food crops based biofuels. Using biomass-derived energy carriers might help beneficially in several ways, i.e., economic, environmental, and health. The production of biomass derived energy could be attained under any geographical conditions because of the large availability of biomass globally while simultaneously contributing to efficient management of various waste streams. Filling up the voids and possibilities in the existing technologies and improving the efficiency and economics of the production technologies employed is the prime target of the current research.

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Bioenergy from Agricultural Wastes

5

Sandeep Kaur and Loveleen Sarao

Abstract

Unchecked increase in population has put the energy resources under a tremendous pressure, and the world is reaching the brink of energy crisis. Hence, the scientists are looking towards natural renewable resources to fulfill the energy demands and also an alternative to fossil fuels. Biomass, especially agricultural biomass, is a good alternative to the problem. It is not only present in abundance all over the world, but also holds the potential to be the next generation fuel. Bioethanol, biodiesel, and biogas are alternatives to petroleum, diesel, and natural gas respectively. Agriculture is the main occupation in majority of countries all over the world; in other words, agriculture holds a special place in world's economy. There is no dearth of raw material, as agricultural wastes are produced along with crops and require no extra land or efforts. So far, agricultural waste has been treated as waste, which was either ploughed in fields or burnt away. But conversion of this waste into fuel/energy is not only a step toward a greener and sustainable future but also economical. Rich in lignocellulosic material, agricultural waste needs to be pretreated, and each kind has its own pros and cons, but in final terms the process is not only environment friendly but also will be pocket friendly in the long run. Using the biomass for energy generation will also put use to waste dumps all over the world, as this waste can also be used for energy generation. Not only use of agricultural waste will solve energy crises, but it will also use up waste which was till now dumped up adding to nuisance, but being

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S. Kaur
Department of Agriculture, Maharishi Markandeshwar University, Ambala, Haryana, India
e-mail: kaursandeep@mmambala.org

L. Sarao (✉)
Punjab Agricultural University, Ludhiana, Punjab, India

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environmental friendly, it will also help control pollution and give us a cleaner environment.

Keywords

Energy · Renewable energy · Bioenergy · Agriculture waste · Environmental pollution

5.1 Introduction

With growing population, energy demands have been on constant rise and so is the pressure on energy resources. Humans have been constantly exploiting natural resources without any check, which has alarmed the world with energy crisis in near future. If the exploitation of natural resources continues with the same pace, very soon we will be left with nothing. Hence, alternative methods or resources to generate energy are the need of the hour. Bioenergy is the new concept put forward by scientists as an alternative means to meet energy requirements. As per Wikipedia definition, "Bioenergy is renewable energy made available from materials derived from biological resources." It is the energy derived from biomass. Biomass can be any living or dead organism or any byproduct of those organisms, plants, or animals (eesi.org 2020). When we talk of biomass, we exclude fossil fuels like coal and petroleum. Basically, it refers to immediate products from living organisms—dead or alive. Besides energy crisis, currently world is facing the major problem of pollution of land, water, and air. Cleaner and renewable energy resources can be a part of solution to the challenges put forward by injudicious use of fossil fuels on all fronts in terms of climate, economic, environmental, and security (UCS 2012). Bioenergy is not only an alternative fuel source but also a sustainable, low carbon alternative to fossil fuels. Many countries have adopted them as a part of comprehensive climate strategy, e.g., USA, which intends to cut its oil usage in half by 2030 by increasing use of bioenergy resources. Biomass ranks fourth in various energy source, first three being coal, petroleum, and natural gas. About 14–15% of energy requirement of world is fulfilled by biomass (Ertas and Alma 2010).

Agriculture is the main means of livelihood in majority of the countries of the world, especially the developing ones, and the quantity of waste generated from agricultural biomass every year is in considerable amount. The amount of waste produced from every ton of grain harvested is 1 ton (Virmond et al. 2013). Agricultural biomass can be an important energy resource, not only in developing countries but also in developed ones also. Maximum generation of biomass in United States is from crop residues (UCS 2012). Most of the waste generated ends up as landfill or left to degrade on its own (Mohammed et al. 2018). Waste dumped in landfills degrades to generate methane which can be trapped and used.

5.2 Biomass

As we discussed, biomass is produced from living organisms/beings. On the basis of source, biomass is classified as follows:

Agricultural Waste It includes biomass from crop residues like wheat straw, paddy straw, corncob, sugarcane bagasse, husks, and shells.

Forestry Waste Logs, trunks, leaves, tree branches, sawdust residues, and bark.

Energy Crops Starch producing species like root crops, cassava, and woody biomass such as bamboo and Leuceana.

Municipal Solid Waste It includes sewage sludge, kitchen wastes, office wastes, fabrics, cattle waste, and clothes (Gupta and Mondal 2020).

Livestock waste makes up an important part of waste generated in farmlands or rural areas. Animal waste can be used to produce biogas, and it can act as heat and power source for the farms (Mohammed et al. 2018). This will also solve the problem of water pollution caused by animal manure in many localities. Besides, giving biogas, the leftover can be used as manure which will enhance soil nutritional value. According to a Union of Concerned Scientists (2012) report, USA can use almost 60 million tons of manure for biogas production in 2030 (Table 5.1).

Table 5.1 Lignocellulosic composition of some crop residues

Crop	Residues	Residue	Composition	Dry weight basis
		Cellulose	Hemicellulose	Lignin
Rice	Straw, husk, stalk	0.36	0.24	0.16
Maize	Cob, husk, stalk, Stover	0.35	0.23	0.19
Soybean	Husk, stalk	0.40	0.16	0.16
Groundnut	Husk	0.30	0.30	0.40
Hazelnut	Husk shell	0.30	0.16	0.53
Tobacco	Stalk, leaf	0.36	0.34	0.12
Sunflower	Stalk, leaf	0.48	0.35	0.17
Almond	Shell	0.51	0.29	0.20
Wheat	Pods, stalk	0.38	0.27	0.18
Sugarcane	Bagasse, top and leaves	0.44	0.32	0.24
Cotton lint and cotton seed	Boll, shell, husks, stalks	0.80	0.20	–
Grasses	Straw	0.40	0.50	0.10
Barley	Straw	0.46	0.23	0.16

Source: Mohammed et al. (2018)

5.3 Biology of Biomass

Talking of agricultural biomass, we are talking about plants. Main building blocks of plant cell wall are cellulose, hemicellulose, lignin, pectin, and other compounds. These are rigid structured complex compounds, with good flexibility of structure and have a significant position in cycle of growth, development, and survival of plants (Kalluri and Keller 2010). Approximately 56 × 10^9 tonnes of CO_2 is fixed by land plants per year. Out of total biomass of 170–200 × 10^9 tonnes produced by land plants, 70% is contributed by plant cell walls (Kalluri and Keller 2010; Lieth 1975; Field et al. 1998) out of which only 2% is consumed/used by humans (Schubert 2006).

Major plant cell wall polysaccharides are cellulose, hemicellulose, and pectin. Cellulose is made of β (1→4) glycosidic linkage, which forms crystalline cellulose through H-bonding and Van der Waals forces. Hemicellulose has an amorphous structure made of branched mixed-sugar polysaccharides with β-linkages. The backbone of the structure contains acetyl and sugar groups making the compound non-crystalline (Gilbert 2010). Pectin is a water soluble carbohydrate which links cellulose and hemicellulose fibers, providing rigidity to cell wall. It contains α (1→4) linkages. Pectins play a role in maintaining porosity of cell wall and adhesion of adjoining cells (Caffall and Mohnen 2009). When utilizing agricultural biomass as energy source these compounds are the ones which need to be treated and deconstructed for generation of energy, which will be discussed later in this chapter (Table 5.2).

5.4 Agricultural Residues

Agricultural residue refers to the waste generated from agriculture. Produced as a byproduct during harvesting and processing of agricultural crops, agri-residue is mostly made up of carbon (Mohammed et al. 2018). The residues are of two types: primary and secondary. Primary residues are produced during harvesting, while secondary residues are produced along with product, hence also called process based residues. These are heterogeneous wastes which vary in bulk density, moisture content, particle size, and distribution. They are fibrous in nature, low in nitrogen

Table 5.2 Conversion processes for biomass and processed biomolecules

	Biomass		Components	
Conversion process	Fats and oils	Protein	Sugar and starch	Lignocellulosic
Direct combustion	✓			✓
Anaerobic digestion	✓	✓	✓	Cellulose only
Fermentation		✓	✓	Cellulose only
Pyrolysis	✓	✓	✓	✓
Gasification	✓	✓	✓	✓

Source: Mohammed et al. (2018)

content, and type of residue varies with geographical location and crop (Smith 1989). This residue is either used as animal feed or manure, but in majority of cases, which is almost 50%, it is burnt in field before sowing of next crop. Residue burning does more harm than good as it adds to air pollution and also effect the helpful organisms living in the field affecting soil fertility.

Major crop residue across the world is from corn, wheat and rice, which are sourced as food. These residues make almost 50% of the biomass. As discussed, until now it was either used as fodder or burnt in field. Recently, studies have been conducted for bioethanol production from crop residues and is being looked as an alternative to energy crises, by using it for generation of electricity and biofuel (UCS 2012). Another major advantage of crop residues is that, it is produced along with crop and neither you need additional land or resources nor any extra effort. It is a by-product of all major crops (USDA 2006). Legros et al. (2009) in their report for World Health Organization (WHO) and United Nations Development Program, stated that almost one-fourth of the world population have no access to electricity. It was also reported that almost 2 billion people use solid fuel in form of wood or dung cakes or any other form for cooking and heating. The burning of fuel leads to air pollution and health problems (Gustafsson et al. 2009).

According to Kumar et al. (2015) biomass production capacity of India is 500 Mt. which is capable of supplying 17,500 MW power. Similarly, USA can produce up to 680 Mt. of biomass resources annually, from which they can generate 10 billion gallons of ethanol or 166 billion KWH of electricity (Mohammed et al. 2018).

5.5 Types of Bioenergy

Biomass energy or bioenergy can be used in many forms. Few are listed below.

5.5.1 Bioalcohol

It is the most common biofuel obtained from wheat, wheat straw, corn, sugar beet, sugarcane molasses or any sugary or starchy material by simple fermentation of sugars. Basically any material, from which ethanol can be produced can act as substrate for bioethanol production (Cara et al. 2008). It is being promoted as an alternative for gasoline/petrol in motor vehicles. Scientists have worked and reported on conversion of lignocellulosic material into fermentable sugars and eventually into ethanol (Broder et al. 1992) (Table 5.3).

Another type of bioalcohol that is produced by fermentation of forestry and agricultural residues is biomethanol. The forestry waste can be both crop and forest residuals (Enguidamos et al. 2002).

Table 5.3 Biomass to bioenergy conversions for feedstocks

Feedstock/Biomass	Conversion	Energy product type
Starch (cereals)	Sugars → ethanol; Alcoholic fermentation	Ethanol
Sucrose (C-molasses and sugarcane sugar)	Sugars → ethanol Alcoholic fermentation	Ethanol
Oil (waste oil mixture, algae)	Transesterification	Biodiesel
Lignocellulose, products from forests and plantations, wood waste	Enzymatic fermentation	Ethanol
Lignocellulose, products from forests and plantations, wood waste	Combustion	Electricity

Source: Marina et al. (2011).

5.5.2 Biodiesel

It is a form of liquid biofuel, which is similar to diesel in nature and is manufactured from vegetable oils, animal fats, etc. It is considered safe causing lesser air pollution in comparison to petroleum-based diesel. It is used in both pure and blended forms with petroleum diesel (Mekala et al. 2014). Depending upon the biofuel share, biodiesel mixtures are B100 (pure, 100% biodiesel), B5 (5% biodiesel and 95% fossil fuel), and B20 (20% biodiesel and 80% fossil diesel) (Enguidamos et al. 2002).

The classification of biodiesel on the basis of source and manufacturing process is as follows (Enguidamos et al. 2002).

1. Esterificated oils: Methanol or ethanol undergoes a catalytic reaction producing a methyl or ethyl ester, as per initial alcohol used. This is the most widespread kind of biodiesel. Used in both pure and blended forms with fossil diesel, it can be used in diesel engines instead of fossil fuel.
2. Non-esterificated oils: These oils are unfit for human consumption and have high degree of acidity. These are suitable only for use in modified engines with special characteristics.
3. Waste vegetable oils: This is basically recycled cooking oil which is used as biodiesel. These oils are pre-processed, cleaned, and refined before transesterification process as oil components have degraded because of the high temperature reached during their original use.

The physicochemical properties of biodiesel like viscosity and boiling temperature are same as fossil diesel, and hence, it can be used in regular diesel engines. The biofuel differs to some extent in its solvent characteristics from fossil fuel, and hence, there are some changes required which include retardation of injection timing by two to three degrees and using synthetic seals in place of rubber seals (Enguidamos et al. 2002). Although biodiesel (weighing 860–900 kg/1000 L) is heavier than fossil diesel (820–860 kg/1000 L), still it mixes well with fossil diesel and works efficiently.

5.5.3 Biogas

It is obtained by anaerobic digestion of organic materials inside a bioreactor (Mekala et al. 2014). It mainly consists of methane (CH_4), carbon dioxide (CO_2), and hydrogen sulphide (H_2S). It is prepared from cow dung waste and domestic waste.

5.6 Bioenergy Production

As discussed in the previous section biofuel, biodiesel, and biogas are the three main forms of bioenergy. The production of biofuel and biogas involves treatment of lignocellulosic material. There are many methods of treatment and conversion of lignocellulosic material into bioenergy forms. Catalyzed chemical reactions, fermentation, and enzyme catalysis are few methods of degradation of plant cell wall (Kalluri and Keller 2010). Although a natural process, industrially it is a costly procedure and we need to develop a cost effective industrial process to make it more beneficial.

5.7 Raw Material

Raw material for bioethanol production is divided into three categories: simple sugars, starch, and lignocelluloses (Mustafa and Havva 2009). Current focus is to produce bioethanol from renewable energy crops like sugarcane, corn, wheat, and soybean. As mentioned, there are three groups of feedstock for bioethanol: (1) sugar-based feedstock (sugarcane, beetroot, sorghum), (2) starchy feedstock (corn, sweet potato, rice, cassava, wheat, etc.) and (3) lignocellulosic feedstock (wood straw, grasses and corn cob) (Mekala et al. 2014). Although sugary and starchy materials are the preferred substrate for bioethanol production, they are costly, and simultaneously, their demand in other processes puts a negative to their use as substrate (Enguidamos et al. 2002). Hence lignocellulosic biomass which is otherwise used as animal fodder or burnt as stubble seems to be a potentially favorable candidate for fuel production. Main concern in case of lignocellulosic/agricultural biomass is its pretreatment to convert it into fermentable form, i.e., glucose. Wheat straw, sugarcane bagasse, and straw are the most abundant forms of agricultural biomass available on earth.

Although a strong contender to petroleum-based diesel, biodiesel production is too costly for commercialization (Mekala et al. 2014). Oil rich feedstocks like microalgae and nonedible oils can be explored for biodiesel production. Substrate for biodiesel production can be any oil/lipid source. Most of these sources contain triacylglycerol molecules as main component. Again we can categorize the sources into three groups: pure vegetables, animal fats, and waste cooking oil (Mekala et al. 2014). Pure oils can be derived from various crops and plants such as soybean, canola, corn, cottonseed, flax, sunflower, peanut and palm, which are commonly used feedstocks by commercial biodiesel producers. Use of commercial crops for biodiesel production will lead to an increase in prices of food and commodities all over the world, which is a disadvantage to keep in mind and hence alternatives are to be found. Few alternative resources/substrates are jatorpha (Kumartiwari et al. 2007), *Pongamia pinnata* (Karanja) (Mohibbeazam et al. 2005), *Madhuka indica* (Kumari et al. 2007), and *Nicotiana tobacum* (Usta 2005).

Jatrohpha curcas is a perennial shrub in Euphorbiaceae family. Its seed contains up to 30% oil by weight. It is commonly found in Africa, India, and Central America. Jatropha contains higher percentage of saturated fatty acids, and its corresponding methyl esters represent relatively poor low temperature operability (Kumartiwari et al. 2007). Karanja (*P. pinnata*) is a medium-sized deciduous plant growing in damp and subtropical environments (Mohibbeazam et al. 2005). Primary fatty acid present in Karanja oil is oleic acid (45–70%) followed by palmitic, linoleic, and stearic acids (Karmee and Chadha 2005; Mekala et al. 2014). Parallel methyl esters from karanja are better in operability at low temperature as compared to jatropha oil methyl esters (Srivastava and Verma 2008). *Madhuca indica* (mahua) belongs to the family Sapotaceae and is found in central and northern plains and forests of India (Kumari et al. 2007). Its fruit is nonedible and dried mahua seeds contain 50% oil by weight. The oil is characterized by free fatty acids and a higher percentage of saturated fatty acids (Ghadge and Raheman 2006). It also contains unsaturated fatty such as linoleic (17.9%) and oleic acid (46.3%) (Singh and Singh 1991). As major percentage of mahua consists of saturated fatty acids, it possesses poor low temperature properties of parallel methyl esters (Mekala et al. 2014). *Nicotiana tobacum* (tobacco) is a commercial shrub growing in many countries all over the world, and cigarettes and other products with tobacco are prepared from its foliage. Seeds contain oil between 36% and 41% by weight (Usta 2005). Seeds contain 17% by weight free fatty acids and linoleic (69.5%), oleic (14.5%), and palmitic (11.0%) acids.

Since feedstock amounts to 75% of total cost of production of biodiesel, it is a critical aspect of biodiesel production. Lately, lipid residues from waste frying oil and nonedible human fat have been explored as an alternative substrates for biodiesel production. Proposal is to reuse oil residues to decrease costs (Mekala et al. 2014). Animal fats are wastes collected from chicken, cow, pork lard, etc. and are less expensive than vegetable oil. Oleic acid, palmitic acid, and stearic acid are the main fatty acids present, and corresponding methyl esters also have good oxidative stability (Wyatt et al. 2005). Chicken fat contains oleic (40.9%), palmitic (20.9%), and linoleic (20.5%) acid by weight. Because of high unsaturated fatty acid content chicken fat has poor oxidative stability but beef tallow is better in this regard. Pork contains stearic (121%), linoleic (127%), oleic (44.7%), and palmitic (26.4%) acid by weight (Jeong et al. 2009). Saturated fatty acid content is high, because of which oxidative stability of parallel methyl esters is good. Restaurant and other cooking waste oils have relatively high free fatty acids and water contents (Moser 2009). They also contains solid material which is removed by filtration before conversion to biodiesel. On the basis of source and availability, the waste cooking oil is 50% less expensive than vegetable oils (Predojevic 2008).

Another important feedstock source for biodiesel is algae. Carbohydrates, proteins, and lipids/natural oils make up algal biomass (Dunahay et al. 1996; Mekala et al. 2014). Algal oil is a triglyceride molecule which is an appropriate raw material for biodiesel production. Out of all resources which can be used as substrate for biodiesel production microalgae is the most beneficial and productive source. They grow rapidly and are rich in oil content as compared to other resources. Oil content of dry microalgae can be more than 70% by weight (Spolaore et al. 2006).

Animal manure and slurry, agricultural residues and by-products, digestible organic wastes from food and agro industries, organic fraction of municipal waste and sewage sludge are common raw materials for biogas production. Dedicated energy crops both herbaceous (grass, maize, and raps) and woody (willow, poplar, and oak) have also been tested for biogas production, although the problem of delignification remains with woody resources (Mekala et al. 2014).

5.8 Production of Bioenergy

Brazil and United States are the largest producers of biofuels, producing up to 89% of world's production (Lichts 2010) and European Union is the world's largest producer of biodiesel (OECD-FAO 2009). Primary substrate used for production of bioethanol in United States is corn grain or maize, whereas sugarcane bagasse is main substrate used in Brazil (Gupta et al. 2014). As mentioned, bioethanol can be produced from any sugary or starchy material, but in lignocellulosic crops like corn, wheat, maize, cassava, grass and other agricultural crop residues, we need to pretreat them to convert lignin and cellulose into glucose. This makes the process of ethanol production from lignocellulosic biomass a complicated one. Pretreatment is tedious, expensive and toxic process and hence adds an additional detoxification step to the process (Agbor et al. 2011). But use of proper technologies in harvesting, pretreatment, and processing can make bioenergy from biomass an advantageous process (Gupta et al. 2014). In a true biorefinery approach, if all components of biomass are converted into fuel, chemicals, or other value-added components (Fitzpatrik et al. 2010; Cherubini 2010).

Besides the objective of breaking the complex molecular structure into simple monomers, pretreatment enhances surface area, provides an easy access to enzymes, modifies and solubilizes the lignin (Gupta and Mondal 2020). Pretreatment consists of physical, thermal, biological, and chemical processes. Physical process including washing, grinding, extrusion; steam explosion, torrefaction, and ultrasound/irradiation are part of thermal process; fungal and enzymatic treatments constitute biological treatment; and acid, alkali, and ionic liquids are used in chemical treatment and thermochemical technologies. Each process has its own advantages. Physical treatment disintegrates biomass into smaller pieces, providing a uniform particle size and increased surface area, which allows bacteria and enzymes to easily access the substrate, while in thermal processes, it allows better heat and mass transfer (Kan et al. 2016). Sonification and gamma rays are also used. Sonification enhanced biogas yield when it was used to pretreat biomass before anaerobic fermentation (Carrere et al. 2010). The particle size remains unchanged with the use of gamma rays, but they break glycosidic bonds, hence reducing the crystallinity of cellulose and increases surface area. The biomass is converted to pellet form by high pressure treatment which decreases the moisture content and increases volumetric energy density (Erlinch et al. 2006). Although it is an odorless and power-saving process, it clogs the equipment.

Thermal treatment is one of the preferred treatments at both lab and industrial scale as it not only breaks the bonds but also dewaters, reduces viscosity, and removes pathogens (Edlemann et al. 2005). The two important processes in thermal pretreatment method are drying and torrefaction. Whereas drying removes moisture from biomass and thereby, increasing the process' efficiency, the biomass is treated thermally in an inert atmosphere and temperature range is between 200 °C and 300 °C, removing both oxygen and water from biomass (Gupta and Mondal 2020; Ren et al. 2013). According to Biswas et al. (2011), the digestibility of biomass in increased and pathogens are removed at a temperature of 50–250 °C in biological treatment. Steam explosion, hydrothermal treatment, liquid hot water, microwave heating, and ultrasound irradiation are some of the methods adopted in thermal treatment. In this temperature is maintained between 150 °C and 240 °C, and hot fluid at high pressure is used to treat biomass, which is depressurized after few minutes leading to explosion in biomass, breaking bonds. In liquid hot water treatment, temperature range is 180–190 °C, and it is used for substrate having low dry matter content (Wyman et al. 2005).

Different types of enzymes and fungi are used in biological treatment. Biological treatment is advantageous in terms that it consumes lesser energy because of mild working conditions and is also economical (Bundhoo et al. 2013). This method has an upper edge over thermal treatment in terms that long-term exposure to high temperature can cause unexpected reactions leading to formation of inhibitory substances and hence decreased process efficiency, whereas no such reactions or inhibitory products are formed in biological treatment. Biological treatment involves inoculation of biomass with fungal spores or enzymes. Biological process although slow and takes several days is a green technique and is economical, without any energy input for lignin degradation (Gupta and Mondal 2020).

In chemical pretreatment chemicals like H_2SO_4, HCl, HNO_3, and H_3PO_4 are used. Dilute acids are used, and treatment in both batch and continuous mode can be used (Lloyd and Wyman 2005). Although this is an efficient treatment, excessive use of chemicals leads to either loss of fermentable sugars or increase in pH which needs to be neutralized later on. Chemical pretreatment is preferred in biological conversion processes. In dilute alkali treatment, alkali like NaOH, $Ca(OH)_2$, and KOH are used. Both acid and alkali degrade lignin and carbohydrate link (Table 5.4).

Table 5.4 Pretreatment methods of lignocellulosic feedstock

Pretreatment	Source	Means	Effect
Biological pretreatment	Microorganisms	*Actinomycetes*, fungi	Removes lignin and reduces degree of polymerization (DP) of celluloses
Physical pretreatment	Comminution	Ball milling, compression milling, colloidal milling	Decrease the particle size, crystallinity, and DP of cellulose
	Steam explosion	High pressure steam	Partially hydrolyze cellulose and hemicellulose
	Ultrasonic radiation	Electron beam, gamma rays, microwave	Increases surface area and softens the lignin
Chemical pretreatment	Acid	Hydrochloric acid, hydroflouric acid, nitric acid, sulfuric acid, peracetic acid	Decreases the crystallinity and DP of cellulose, partial or complete degradation of hemicellulose, delignification
	Alkali	Sodium hydroxide, sodium carbonate, ammonium sulphate, lime	
	Gasses	Chlorine dioxide, nitrogen dioxide	
	Cellulose solvents	DMSO, Codaxen, CMCS	

Source: Farine et al. (2011)

5.9 Conversion to Biofuels

After pretreatment the raw material which has transformed into simple sugars is converted to biofuels or bioenergy forms. There are two type of conversions: biochemical and thermochemical. The technology used depends on type, extent and properties of biomass. Biochemical conversion requires microbes for biomass degradation, hence lignin content in substrate should be low, whereas in thermochemical process, lesser amount of moisture is preferred, which otherwise will add to extra energy and cost of drying (Gupta and Mondal 2020) (Table 5.5).

Table 5.5 Biofuel production share of different countries (percent)

Year	China	India	Brazil	United States	European Union	Rest of the world
2005	2	1	37	2	1	0
2010	4	5	47	3	4	2
2015	6	8	49	3	7	2
2020	8	11	58	4	10	2

Source: Rosegrant et al. (2006)

[a] Calculations were based by authors projections based on actual data available in 2005

1. Biochemical conversion: It is an environment-friendly and sustainable technique, as it uses microorganisms for conversion, Which metabolize the biomass to energy.
   (a) Anaerobic digestion and fermentation are two types of biochemical conversions followed.Anaerobic digestion: As the name suggests, it occurs without or in absence of oxygen. Biogas is a mixture of carbon dioxide and methane along with traces of other gases such as H_2S (Bala et al. 2019; Gupta and Mondal 2020). The type of digester used and the composition of waste influence the quality of biogas produced. The whole digestion process consists of four steps involving different microorganisms at each step. These microorganisms prepare the substrate for being further treated in next step. Steps are hydrolysis, acetogenesis, and methanogenesis (Gupta and Mondal 2020). Complex polysaccharides, proteins, and fats are converted to sugars, amino acids, and fatty acids respectively by hydrolytic bacteria (*Streptococcus, Bacillus, Enterobacteria*) through enzymatic reactions (Divya et al. 2015; Gupta and Mondal 2020) in hydrolysis. The products of step 1 are acted upon by enzymes such as acetate kinase, formate, hydrogen lysate, and acetaldehyde dehydrogenase produced by facultative and obligatory anaerobes (*Micrococcus, Syntrophomonas, Pseudomonas,* etc.) and are converted into fatty acids and organic acids in step 2. In the next step called acetogenesis, the acetogenic bacteria (*Syntrophomonas, Clostridium, Syntrophobacter*) converts the organic acids produced into acetic acid. In the last step, methanogenic bacteria (*Methanosarcina, Methanococcus, Methanobacteria,* etc.), convert acetic acid into CH_4, CO_2, and traces of H_2S, N_2, H_2, etc., and the process is called methanogenesis. The mixture of gases generated is known as biogas and microbes secrete enzymes like formylmethanofuran dehydrogenase, methyl coenzyme, and *m*-methyl transferase to bring out conversion (Divya et al. 2015). Anaerobic digestion is effective to carry out conversion of high moisture (80–90%) content waste. Substrate and inoculum used influence the composition of biogas produced. Biogas can be used in spark engines or turbines, or it can be upgraded to natural gas with removal of CO_2. The leftover waste is used as soil conditioner (Gupta and Mondal 2020).
   (b) Fermentation: Simple sugars are converted to alcohol and CO_2 by microorganisms during fermentation. Different types of biomass starch, cellulose, hemicellulose, and lignin are complex sugar polymers. They are converted to monomer glucose during pretreatment, which is acted upon by microorganisms to produce alcohol. Two gases produced by fermentation process are butanol and ethanol. For butanol production *Clostridium* spp. is used (Li et al. 2019). The process is commonly called acetone, butanol, and ethanol (ABE) fermentation. It is a two-step process, i.e., acedogenesis and solventogenesis (Ibrahim et al. 2018; Gupta and Mondal 2020). Heating value of biobutanol is higher whereas it has lower volatility and lesser ignition problems and lower viscosity than bioethanol. Bioethanol production is carried out by yeast such as *Saccharomyces cerevisae, Candida*

   albicans, Pichia stipitis, and *Kluveromyces*. The methods used for bioethanol production are separate hydrolysis and fermentation, simultaneous saccharification and fermentation and simultaneous saccharification and co-fermentation. The optimum conditions of fermentation are pH (4–5), temperature (20–35 °C) and 150–200 rpm for *S. cerevisiae* (Azhar et al. 2017).

2. Thermochemical conversion: Agricultural waste is treated with processes like pyrolysis, gasification, and combustion at high temperature. The end products are biooil, syngas, and biochar.
   (a) Pyrolysis: Biomass is depolymerized in an inert atmosphere with continuous supply of heat (Gupta and Mondal 2020). The process is endothermic in nature requiring temperature in range of 400–700 °C. Vapor mixtures of various hydrocarbons are produced due to rapid heating of biomass, which condense to give biooil on cooling (Gupta and Mondal 2019). Biooil is a brown colored viscous oil. It is a complex mixture of large number of organic compounds with some percentage of water present. The heating value is in range of 20–30 MJ/kg (Gupta and Mondal 2020). Besides condensable gases that form biooil, noncondensable gases like CO, CO_2, H_2, and CH_4 are produced, which can be used as a gaseous fuel because of their good combustion properties. The leftover is biochar, which can be used as solid fuel, absorbent, sensor, fertilizer, etc. Again, the end products depend on the type and composition of biomass and processing conditions.
   (b) It is a partial oxidative process carried out at a high temperature range of 800–1000 °C. The main end products are CO and H_2, together called as syngas. Besides CO and H_2, which are present in equal amount and make up 85% content, syngas contains 5% tar and 10% biochar (Ram and Mondal 2018). Besides CO and H_2, methane and other hydrocarbons are also produced. They can be used as fuel for engines and turbines as they have high calorific value. The process parameter for syngas production are temperature, heating rate, particle size, biomass feed rate, and equivalence ratio.
   (c) Combustion: It is a completely oxidative process using high temperature thermal degradation, producing heat and power along with carbon dioxide and water by converting chemical energy of biomass to products. The energy produced is utilized in steam turbines, boilers, furnaces, etc. (Gupta and Mondal 2020). The moisture content of the substrate should be below 50% and net conversion of biomass into bioenergy is 40%.

5.10 Advantages of Biofuels

Biofules are our alternative to fossil fuels. These are renewable resources and are produced from the second most abundant material present on earth's surface after water. There is no shortage of supply of agricultural residues, which is produced not only in fields in abundance every day, but also in houses, markets, and processing industry. This waste is just dumped off without any treatment into dumping grounds where it rots off producing methane gas, adding to greenhouse effect. If this gas which is naturally generated in those dumping grounds is captured and utilized, it will help to solve the energy crises. Also, utilizing this waste for energy generation will solve the problem of ever growing garbage on earth, which is already converting earth into a dumping ground instead of a place filled with green and blue gems.

There has been a threefold increase in global demand for liquid biofuels in the last decade, which shows the preference and also increasing trend toward fuels from feed stack (Ferreira-Leitao et al. 2010). The major advantage of utilization of natural resources as fuel resource is that the produced bioenergy provides independence and security of energy supply (Nigam and Singh 2011). The fossil fuels are unevenly distributed across the world, whereas agricultural residues or residues of similar type are produced all over the world as agriculture is an indispensible means of livelihood, practiced by notable percentage of population all over the world, and in most of the developing countries, it is still the major means of livelihood for majority of population. Hence, there is no shortage of agricultural residues, and every country has its own supply of raw material and hence can generate its own fuel and be energy independent and improve its economy, protect its environment, give its people a new means of livelihood and be financially stronger. The production of agri-residues is not effected by requirement of land for food and feed production. As mentioned, it is produced in abundance in forests, fishery industry, municipal wastes, food industry, and food services besides fields. With increasing population of the world, the everyday generation of waste is also beyond control. It is not only filling up the land, but also polluting water bodies and underground water (Ferreira-Leitao et al. 2010).

The use of lignocellulosic biomass for energy generation is the answer to significant expansion required in production of ethanol. The processes used for production of biofuels are also environment friendly as fermentation stands out where microbial metabolism is used to convert simple raw material into products of high energy and value. Experts believe that biorefineries are likely to be a key industry of the twenty-first century, and will lead to new industrial revolution because of the technologies they employ and their effect on actual industrial model (Santos et al. 2010; Visoili et al. 2014).

5.11 Effect on Environment and Economy

As already mentioned, biofuels are green fuels. They reduce greenhouse gas emissions. Scientists have reported that greenhouse gas emission could be lower than 20–90% than those from fossil fuels in some cases (Visoili et al. 2014). Biodiesel is known to provide significant reductions in CO_2 emissions, along with reduction in emission of sulfur oxides, particulate matter, and carbon monoxide (Enguidamos et al. 2002).

Biofuel production has been modeled by scientists for design optimization, for maximum ethanol yield, and power generation with minimum finances (Piccolo and

Bezzo 2009). Economics is critical to any process. According to some reports, about 18–20% of total estimated cost for biological production of bioethanol is for pretreatment. Hence to reduce the production cost of biofuels, we need to find an economical pretreatment method and also accelerate their commercial applications (Banerjee et al. 2010). Current preferred method of pretreatment is dilute acid pretreatment, which are followed by enzymatic hydrolysis and fermentation. According to Aden and Foust (2009) in commercial scale in some models of ethanol production from corn stover conversion process cost was USD 0.35 per liter. The estimated ethanol production cost ranges between USD 0.13 and USD 0.81 per liter ethanol (Galbe et al. 2002).

According to Kazi et al. (2010) dilute acid treatment has lowest product value compared to hot water and AFEX pretreatment for three downstream process variation.

5.12 Challenges and Advances

Biofules are being projected as future and have given hope to mankind that finally they might have found an environment-friendly, sustainable fuel which can be an ever-available source of energy. As mentioned in earlier sections, a certain percentage of population in developing countries do not have access to electricity and clean fuel, and they are dependent on solid fuel for energy and power. This is obviously leading to environmental pollution and health hazards as well. Tyagi et al. (2019) reported that there are almost 4.3 million deaths per year all over the world because of health issues due to use of solid fuels by underprivileged people. Out of these, almost a million deaths occur in India alone. Although promising, there are many challenges to pass before biofuels are a common thing. As discussed in previous sections pretreatment of raw material still makes up the major cost input of biofuel production. Although enzymatic treatment is a preferred method over thermal/acid treatment (Lugani et al. 2020), it is affected by factors like available surface area for enzymatic action, degree of crystallinity and polymerization, polysaccharide content especially lignin, enzyme synergy and effectiveness (Myat and Ryu 2016; Lugani and Sooch 2018). Besides the pretreatment methods, the effective fermenting strains is another major challenge faced in biofuel production. Since, a variety of substrates along with sugars are produced after pretreatment, a strain needs to have the potential to metabolize a variety of substrates (Lugani et al. 2020). Besides, it should be resistant to inhibitory metabolites produced during pretreatment or fermentation along with tolerance to high concentrations of sugar and ethanol (Hans et al. 2019). Since wild strains lack the above-said characteristics, developing genetically modified strains is the only solution to the problem.

We have already discussed conventional pretreatment methods, in our earlier sections. Each method has its own limitations, which include low yield, high cost, and environmental hazards, and hence, scientists have recently started exploring greener vistas in this arena (Capolupo and Faraco 2016). Green solvent pretreatment is either ionic liquid pretreatment or deep eutectic solvent pretreatment (Lugani et al. 2020).

Ionic liquids are made of ions, which are held together by strong electrostatic bonds, hence are less volatile and electrochemically stable (Socha et al. 2014). These liquids are also called green solvents because of better thermal and chemical stability, low vapor pressure, and non-flammable nature (Wu et al. 2014). Scientists have reported increase in surface area, decrease in lignin content, and reduced cellulose crystallinity with use of ionic liquids for pretreatment (Li et al. 2010; Kassaye et al. 2017; Xia et al. 2014; Financie et al. 2016). Although environmental friendly, it is still not pocket friendly, and thus, the issue of high cost of pretreatment persists.

Deep eutectic solvents (DES) are basically organic in nature and consist of hydrogen-bond acceptor and donor and a quaternary ammonium halide salt. The hydrogen bond donor can be amino acid, urea, amines, carboxylic acids, or carbohydrates (Zhang et al. 2016; Lugani et al. 2020). These are cheaper, nontoxic and biodegradable compounds (García et al. 2016). DES are a good option for substrate having higher concentration of lignin (Kim et al. 2018).

Another approach is strain improvement for lignocellulosic microorganisms. Basically, it is the enzymes produced by microbial strains which hydrolyze lignocellulosic material, such as glycosyl hydrolases (Sathya and Khan 2014), carbohydrate esterases (Nakamura et al. 2017), and auxiliary activity proteins (Ezeilo et al. 2017). The lignocellulosic strains are available in a variety of habitats. In fact, wherever lignocellulosic biomass is available, such as forests, rumens, processing plants both wood and sewage, composting soils, and so on (Patel et al. 2019) lignocellulosic microorganisms can be found. Two main lignocellulolytic systems are (Lugani et al. 2020):

1. Extracellular enzymes in filamentous fungi and aerobic bacteria, e.g., *Cellvibrio, Cellulomonas, Microspora, Thermobispora, Thermomonospora, Pseudomonas, Bacillus, Nocardia.*
2. Enzyme complexes called cellulosomes in anaerobic bacterial and fungal strains, e.g., *Acetovibrio, Clostridium, Ruminococcus, Orpinomyces.*

Although these strains are being used commercially for degradation of lignocellulosic material, the cost of enzyme production and overall yields of enzymes with limited productivity are still the limiting factors and hence, scientists are working on developing strains which are hyper-producing deregulated lignocellulolytic in nature. Scientists have adopted random mutagenesis, cyclic mutagenesis, site-directed mutagenesis, and protoplast fusion techniques to attain this objective (Lugani et al. 2020).

Besides improved strains for enzyme production, strain improvement is also being sought for improved fermentation abilities and co-fermentation of substrates. Genetic engineering, recombinant DNA technology, metabolic engineering, protein engineering etc. are some of the techniques adopted by scientists (Zhang et al. 2011). As xylose is one of the by-products of hydrolysis of lignocellulosic compounds, scientists are working on strains that are capable of fermenting both sugars simultaneously.

5.13 Conclusion

Bioenergy is our answer to fossil fuels and countering energy crises. Ever growing energy demand has made us look for alternative fuel which is efficient and sustainable. Agricultural wastes are present in abundance, and hence provide us with an option of exploiting them as fuels. Agricultural wastes are produced all over the world, thus giving equal opportunity to both developed and developing countries to explore their potential in the field. A transformation from fossil fuels to bioenergy is also going to effect a country financially making it power stable and financially independent. Agricultural wastes have tremendous potential of providing us energy in any form required and fulfill the uncontrollable energy demand of the world.

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Bio-Processing: Biomass to Commercial Alcohol

6

Amit Kumar Tiwari and Dan Bahadur Pal

Abstract

This chapter emphasizes on the conversion of agro-waste-based biomass into commercial alcohol/ethanol—almost all suitable process and possibilities are covered. A huge amount of agricultural waste is generated during harvesting, post-harvest handling, and processing that can be converted into various valuable products according to their compositional properties. Agro-waste may be from fresh fruits and vegetable residues like stems, leaves, outer skin, and rind, different parts of cereal and pulses crops like broken and damaged grains, husk and so on. Current trends and possibilities of research on ethanol or alcohol production from agro-waste-based biomass is discussed in this chapter; the most important factors and different types of pretreatments and methods that are required to achieve the best yield of ethanol/alcohol are also presented. The significance of the process, the incorporation of various parameters to make biomass conversion and fermentation processes easier to get improved ethanol production and the strategies for the selection of suitable microbes and culture are also highlighted. Other processes such as saccharification, co-fermentation, and bio-processing steps are mentioned. The challenges associated with the conversion of agro-waste-based biomass into alcohol are highlighted. Due to the adverse effects of these waste materials and their disposal mechanisms on environment and health, it is realized that it can be utilized as a potential alternative and renewable source of green energy. Production of bioethanol for biofuel is currently a widely used and most important process. Commercial production of alcohol for industrial, pharmaceutical and food beverages purposes is also a good opportunity; this may be the best way to utilize sugar- and starch-containing

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A. K. Tiwari · D. B. Pal (✉)
Department of Chemical Engineering, Birla Institute of Technology, Mesra, Ranchi, Jharkhand, India

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agro-waste which is generally discarded from the fresh fruit and vegetable markets and processing industries. Lot of research work has been done and processes are developed by using biological cultures; these techniques are economic and easier to conduct. The food processing industries like sugar industry, fruit, and vegetable industry have a large amount of waste which generates a large amount of biomass residues with fermentable sugars and starch. Agro-waste like fruit peel, stems, leaves, pulp, seed, and fruit rinds are rich sources of polysaccharides, disaccharides, monosaccharides, and starch, which can be commercially used as a raw material for alcohol production. In this chapter, emphasis is given on the selection of biomass, use of microbial strains and steps involved in the production of alcohol from agro-waste biomass.

Keywords

Ethanol · Biomass · Saccharification · Bio-processing · Bioethanol · Microorganisms · Biofuels

6.1 Introduction

Agro-waste based biomass is considered as organic material that is available all time from different sources. Due to its chemical composition (presence of fermentable sugar and starch), these biomass is a good storage of energy. The availability of simple or fermentable sugar is a result of photosynthesis; in this process, plants utilize sunlight to convert CO_2 and H_2O into simplest form of sugars and O_2. Production of biofuels (alcohol/ethanol) from sugars available in plant materials may be a sustainable option to solve the problems associated with the extensive exploitation of fossil fuels, and it can protect environmental pollution by reducing the CO_2 emission (Tilman et al. 2009). Sugars are found in the tissues of plant in the form of soluble free sugars, like disaccharides and monosaccharides, polysaccharides (starch) is also found as reserve source of sugars. Another important form of polysaccharides is structural polysaccharides such as cellulose and hemicelluloses are also considered as reserve source of sugars because they can be converted into fermentable sugars. These structural polysaccharides are known as lignocellulosic biomass material. According to the properties of raw material for ethanol production, these raw materials can be categorized into three main categories: (1) sugary, (2) starchy, and (3) lignocellulosic materials. Different types of crops are good sources of these materials (Fischer et al. 2010). Sugarcane is a main sugar crop of tropical regions, whereas in temperate region sugar beet, sweet corn, sweet sorghum, etc. are considered as main crops. Along with the rice and corn, many other cereals are good sources of starch for ethanol production; the yield of these cereals and grain is higher than the other crops, and they accumulate higher amount of starch (Mabee et al. 2011). Any plant material can be utilized to get ethanol because the vegetative portion is lignocellulosic material which is a lignocellulosic biomass. Alcohol/ethanol production can be achieved by direct fermentation of sugars found in the above-mentioned three main sugar crops, whereas for the production of alcohol/ethanol from starchy and lignocellulosic biomass, saccharification process (hydrolysis) is also required. Apart from the agro-waste-based biomass, forest-waste like fresh and old roots, bark, stems/wood, and leaves of living and dead plants such as shrubs and tree can be used for the production of ethanol after undergoing different types of pretreatments.

Residues from the post-harvest activities of different crops like fruit and vegetables crops, cereal and pulse crops, etc. are leaving a lot of biomass; harvesting and post-harvest operations related with forests also providing considerable amount of biomass which include fresh and old stumps, leaves, tops, and branches. Other noncommercial tree and plant species are left as it is in the forest areas for longer period; during the period of deforestation and rejuvenation these species are cut and removed or left behind at the same site. According to U.S. DOE and USDA (2005), the forest residues and other removals are accounting around 67 million tons (on dry basis) per annum. The possible use of this biomass for the production of energy and other valuable products has huge potential to convert these residues into marketable materials which will also generate money for the local people. In the past, these materials were considered as unsellable (unmarketable) items; therefore, most of the residues were left in the same site. In general processing residues from the forest produces like bark, sawdust, and black liquor are commercially utilized for energy generation (heat, power, etc.). Fresh bark, green sawdust, leaves, stems, and branches contains lignocellulosic materials, which could be utilized for the manufacturing of alcohol/ethanol. Generally the bark of the tree is industrially used for the production of resins, extraction of flavoring agents and tannins, preparation of dyes and pharmaceutical products; whereas, fruit and vegetable residues are used for preparation of commercial pectin, natural food colors, antioxidants and natural food flavors. After extraction of these elements from F&V produce, the residual portion which contains good amount of carbohydrate is generally dumped. After reviewing of research literature it is found that cereal and grain residues are fed to animals or used to convert it into low-priced products. These residues are also good sources of sugar and starch which could be converted into high-quality ethanol by using microbial strains at low-cost investment.

Agro-waste-based biomass is having a wide range of biomass that includes: the food crops such as sugarcane, corn, rice, soybeans, beets, potato, sweet potato, fruits and several other vegetable crops); non-food crops like corn leaves, corn stalks, corn cobs, trimmings, seed husks, and several types of grasses. Usually, these residues are rich sources of different commercially important materials like starch, sugars, and lignocellulosic components. But unfortunately, due to high cost of collection and transportation of these residues, they have not yet been commercially used as source of energy production. If economically feasible techniques and facilities could be developed to collect, transport and process biomass into alcohol/ethanol, it could help and encourage the utilization of this type of biomass. It is essential to note that these agro-waste and horticultural residues could be consumed for the above-mentioned purpose. During the time of harvesting, a considerable amount (around

Table 6.1 Categorization of agro-waste biomass

Starchy biomass	Maize, wheat, barley, rye, potatoes, cassava, beans (kidney, navy, pinto, black, cannellini), butternut squash, chickpeas, corn, lentils, parsnips, peas, potatoes, taro, yams, arrow root, sago palm, etc.
Sugary biomass	Sugar cane, beetroot, sweet corn, sorghum, sweet potato, black maple, black sugar maple, hard maple, rock maple, sorgo, flax, linseed, etc
Cellulosic biomass Lignocellulosic biomass	Switchgrass, miscanthus, willow, poplar, crop stover, bagasse, straw, bran, meal, etc
Mixed biomass	Sugarcane straw, sugarcane bagasse, rice straw, wheat bran, saccharified wheat meal, saccharified corn kernel, etc

50%) is commonly left on the field to maintain the nutritional quality and fertility of soil; these agro-wastes are sometimes also left to protect soils from the erosion. This category of biomass is generally a food-based part of the crops, which may be any part of the crop that contains significant amount of simple sugars, starch or lignocellulosic. Vegetable crops like potato, sweet potato, beetroot, and few leafy vegetable crops; cereal crops such as barley, corn (maize), wheat, rice; an important crop of Gramineae (Poaceae) is sugarcane; and fruit crops like apple, banana, mango, grapes, pineapple, and plums are very important and widely grown crops that contain good amount of fermentable sugars, starch, and lignocellulosic matter and are used for the production of various food products including fermented or alcoholic products like wine and beers. The non-food part of these crops is generally discarded at the time of processing which also contains complex carbohydrates; non-food part category includes several materials like corn stover, wheat bran, barley husk, rice bran, and oat straw. After pretreatment of stover and straw, these materials are converted into alcohol/ethanol. Perennial grasses are comparatively low in nutrient content but are sources of cellulosic and lignocellulosic materials; therefore, there is an advantage that they can be utilized as raw material for the production of alcohol on commercial scale. A large geographical area is covered by these types of grasses growing range, which are used to produce energy (Downing et al. 1995). Presently, around 64% of total ethanol is manufactured from corn (maize), 26% is contributed by sugarcane, 3% by molasses, approximately 3% from wheat and the rest amount from other cereals/grains or by beetroots. Due to compositional difference, variety/species, and quantity of agro-waste biomass, there is no single way to classify this biomass, so they could be grouped into different categories, depending upon their composition and applications. Agro-waste-based biomass can be categorized into various groups like starchy biomass, sugary biomass, cellulosic biomass, lignocellulosic biomass, and mixed biomass (Table 6.1).

Alcohol is a chemical, which is sometimes naturally occur in ripe fruits due to the activity of wild species of yeasts or bacteria through fermentation. Alcohol, also known as ethanol or ethyl alcohol, is a colorless, highly flammable and volatile component having a peculiar taste with a characteristic flavor. The molecular formula of alcohol/ethanol is C_2H_5OH. Alcohol/ethanol can be produced from any

Table 6.2 Country wise status of alcohol/ethanol production (Source: OECD/FAO 2020)

Country	Contribution in the world production (%)	Status		Country	Contribution in the world production (%)	Status
Argentina	0.9	9		India	2.1	6
Brazil	26.2	2		Indonesia	0.2	21
Canada	1.4	7		Paraguay	0.4	14
China	8.1	3		Thailand	1.4	8
Colombia	0.4	13		US	48.2	1

suitable biomass which contains a considerable quantity of sugars or other materials that can be modified into fermentable sugars. Fermentation by using microorganisms is a predominant pathway for alcohol production. Different types of biomass can also be fermented into alcohol through biotechnological or by various other pathways. In the time of old civilization, alcohol was continuously produced from the sugar-containing raw materials by fermentation process. Production of pure ethanol was started between twelfth and fourteenth century, by using distillation process. Distilled ethanol was especially used for the preparation of drugs and painting colors. According to Roehr (2000), starch-containing raw materials were first utilized for the ethanol production in Ireland during twelfth century, and the industrial production of bioethanol was started for the first time in nineteenth century by using distillation process. In 1860, ethanol was first used as a fuel by a German deviser Mr. Nicholas Otto in an internal combustion engine. After a long gap, Henry Ford constructed his first automobile engine that was based on ethanol (Solomon et al. 2007). The first time, ethanol was declared as “the future fuel” by Ford. In around 1925, Ford told that this fuel could be manufactured from various feedstocks like sawdust, fruits, vegetables, and weeds also (Turner et al. 2011). In the beginning of twentieth century, ethanol was widely used in different combustion engines, especially for the automobiles. For the ethanol production, various sugar cane and beet molasses based fermentation processes were also developed in this century Roehr (2000). Various countries are producing ethanol in different amount, and they are contributing to global ethanol production differently (Table 6.2). The global bioethanol production in 2011 was around 84.6 billion liters. It is projected that the global ethanol production will increase up to 140 billion liters by 2029 (OECD/FAO 2020).

For the production of alcohol/ethanol on a commercial scale, raw material like sugar-containing media is required; another main work is the selection of microorganism which will convert sugar into alcohol and other allied products at a suitable temperature. According to Garver et al. (2014), *Saccharomyces cerevisiae* is a yeast strain which is able to convert 90% sugar into alcohol yield, and it is tolerant against chemical inhibitors and can survive up to 10% v/v ethanol concentration. *Zymomonas mobilis* is a facultative anaerobic and gram-negative bacterium which has capabilities to produce 97% ethanol from sugars, and it is tolerant against 14% v/v ethanol (Garver et al. 2014). Saccharomyces produce ethanol from the sugars at a particular temperature of 30 °C in the absence of oxygen. During this fermentation process, some other by-products are also produced like CO_2 and nitrogen-based components. *Saccharomyces cerevisiae* is a prevalent microorganism that can produce 12.0–17.0% w/v alcohol with 90% theoretical yield (Claassen et al. 1999; Kumar et al. 2009). Actually, several studies have been conducted by several researchers to identify and find out a singular technical option to reduce production costs. Production of bioethanol is totally depended on three important steps like pretreatment of raw materials, saccharification (hydrolysis), and finally fermentation. After reviewing of available literature on ethanol production and as suggested by Wyman (1999), it is found that reduced selling price of ethanol could be achieved effectively by devoting more research efforts on the followings:

(a) Identification and introduction of new, low-cost, and abundant raw materials.
(b) Development of more efficient technologies for pretreatment.
(c) Creating more capable and genetically modified microbes for saccharification and alcohol production.
(d) Implementing process integration.

India is an economically growing and developing country, and therefore, the crisis of traditional fuel security will not end until the development of alternative fuels. Presently, molasses is widely used to produce ethanol in India. Indian policy has proposed a goal to reduce the scarcity of fuel by blending of bioethanol (20%) or biodiesel (20%) in gasoline. Since October 2008, it has become mandatory to add bioethanol in gasoline. To produce the maximum quantity of bioethanol, sugar industries were permitted to produce ethanol from sugarcane juice directly to overcome the scarcity of bioethanol (Ministry of New and Renewable Energy (MNRE) 2009). As per the MNRE, India (2009), the sugar industries have also pushed to increase bioethanol production to meet the demand of bioethanol for the purpose of mixing in gasoline that is recommended by the Government of India. It was also promised that this will not create any problem in the supply of sugar and alcohol for other requirements (MNRE, India 2009). Biomass can be utilized as feedstock for the manufacturing of several valuable products and alcohol through different technologies.

6.1 Composition of Biomass

The agro-waste-based biomass is available in diverse composition. Therefore, it is categorized into different categories (Table 6.1) like plant residues (straw, stover, bran, etc.) are chiefly composed of cellulosic, hemicellulosic, and lignocellulosic materials; whereas, other parts like fruits, grans, and tubers are composed of sugar, starch, etc. According to Yokoyama (2008), each chemical structure is responsible for a particular chemical property of the material. The percentage of these components may vary with the type of materials.

6.1.1 Cellulose

Linear polymer cellulose is a polysaccharide (complex carbohydrate) which has a high molecular weight with 10,000 monomeric units of dextrorotatory glucose (D-glucose). The molecular formula of cellulose is $(C_6H_{12}O_6)_n$ (where, n = degree of polymerization), and cellobiose is its structural base. It is a naturally occurring organic compound which plays a crucial role in the structural function in cell walls of the plant (Bonechi et al. 2017). The morphology and reactivity of cellulose is actually affected by the intermolecular H bond and the O bond. Due to the formation of these bonds, molecules are more rigid and stable in nature (Chen 2014). Any changes in cellulose, especially alteration in the crystalline and amorphous regions, can affect the approachability of its reactive functional groups. The reaction capacity of cellulose depends on the ability of its primary and secondary hydroxyl groups. The primary hydroxyl groups have higher reactivity than the secondary ones (Chen et al. 2017). After complete hydrolysis of cellulose, a monosaccharide (D-glucose) is generated; whereas, after partial hydrolysis, cellobiose (a disaccharide), and smaller polysaccharides are produced (n values may vary from 3 to 10) (Bonechi et al. 2017). The crystalline part of cellulose is hydrophobic in nature and not able to absorb water; therefore, to obtain hydrophilic cellulose a treatment which is called as mercerization is required. Due to prominent properties and applications of cellulose, it is considered as an important raw material for the pulp and paper and fiber industries. Apart from these, presently it plays an important role in different areas of environmental protection, for instance, remediation of water to remove pollutants (heavy metals and hydrocarbons) (Arias et al. 2017; Tursi et al. 2018a, b; Tursi et al. 2019). Due to the conversion ability of cellulose into mono sugars, there is a huge scope to utilize this component for the production of alcohol.

6.1.1 Hemicellulose

Hemicellulose is another main and important component of the cell wall of plants, and it consists of heterogeneously branched polysaccharides. Hemicellulose is sternly attached to the stratum of cellulose microfibrils. The elements and structure of hemicellulose may vary with the type of plant (Bala et al. 2016). The different sugar units in different proportions are arranged with different substituents. Hemicellulose can be decomposed thermally by using high temperature (180–350 °C), therefore various non-condensable products like gas, coal, and different types of aldehydes, ketones, furans and acids are produced (Carpenter et al. 2014). Hemicellulose is an amorphous material in nature and has adhesive properties. If it is dehydrated, it will convert into a highly tough material. Hemicellulose entirely consists of sugars with five carbon atoms like arabinose, xylose, etc. and six carbon atoms such as rhamnose, galactose, mannose, and glucose, with a molecular weight of $<30,000$ (McKendry 2002; Jindal and Jha 2016; Bonechi et al. 2017). Xylans, galactans, arabinogalactans, and mannans are the various important groups of molecules that are responsible for the making of hemicellulose. This material can be utilized for the production of alcohol by converting it into sugars.

6.1.1 Lignin

Plant cell walls also contain lignin; it is necessarily required for the function of binding. Thus, we can say that it is a cement-like material which puts fibers together. Lignin provides improved compactness and resistance to the plant structure. Lignin is also acknowledged for its encrusting effect because it provides a strong cover to the fibers. If we want to extract cellulosic fibrous material from the plant residues, then the degradation of lignin is an essential process. The lignin content may vary with the species and age of plants (25–30% in hardwood plants and up to 50% in very hardwood plants). Annual plants contain around 10–12% lignin. Lignin consists of carbon 61–65%, hydrogen 5–6%, and 34–29% oxygen (Fromm et al. 2003). The lignin is a complex, amorphous and aromatic polymer with a 3D network, in which numerous phenylpropane units are linked together. The monomeric units are generally bonded together in different ways: through the oxygen bridge between 2 propyl and phenyl groups, between 1 phenyl and 1 propyl group, or by C-C bonds between the same groups. Particularly, this macromolecule is made by the primal oxidative polymerization of 3 hydroxycinnamyl alcohols that represent the basic structural monomers like type H, type G and type S. Due to the different degrees of methoxylation, these compounds are different from each other (Xu et al. 2005).

6.1.1 Starch

Starch is the main component of vegetables, fruits, tubers and crop seeds and works as the main storehouse of carbohydrates. It is found in the cells as a granular component; in many plant species, it is present in different morphological state. Starch contains many millions of molecules of amylopectin and a huge number of amylose molecules. In nature, starch is generally found in two forms: (1) as amylose (25–27%), it is water-soluble (hot water) and (2) in the form of water-insoluble amylopectin (73–75%). Both forms of starch can be isolated from the material by using different methods, Amylopectin can be isolated without amylose from the starch prepared from "waxy corn"; whereas, without amylopectin, amylose can be separated by the process of hydrolysis of amylopectin by using enzyme pullulanase (Vorwerg et al. 2002). The experimental formula of starch is $(C_6H_{10}O_5)_n$ where n is a variable (Edwards et al. 2003). This is also considered as ready material for alcoholic fermentation after a few treatments.

6.1.1 Minor Organic Components

In many studies, it is given that various biomass substrates contain a varying amount of different organic and minor elements, which can affect the processes of treatment and fermentation (Vassilev et al. 2012). These minor components are almost found in all type of biomass, e.g., Algae contain lipids 2–40%, proteins 6–71%, and nucleic acid up to 6% (Demirbas 2010). Straws and flax contain acetyls approximately 2–4% (Tamaki and Mazza 2010). According to Huber et al. (2006) and Tamaki and Mazza (2010) in the biomass of pine, eucalyptus, and sorghum grass around 1–4% uronic acids is found; in the biomass of pine, reeds, spruce, birch, and maize, approximately 10% protein is found.

6.1.1 Inorganic Matter

Generally, inorganic components are also found in small quantity in different biomass; the quantity of these components may vary with the type of biomass (Alaswada et al. 2015). Magnesium, calcium, potassium, phosphorus, and sodium are the common inorganic components, but some other inorganic elements like aluminum, silicon, and iron are also found in biomass (Werkelin et al. 2005). Few major solid residues that are very common are also found in biomass; they are water-soluble residues like sulphates, oxalates, carbonates, chlorides, nitrates and are amorphous organic or inorganic materials. During the pretreatment of biomass at 105 °C and 750 °C, components like C, H, O, N, and S are evaporated as gas due to their chemical nature, while the residual matter (ash) remains as a product which contains oxide forms of mineral components (Chen 2014).

6.1.1 Other Elements in Biomass

In case of lignocellulosic biomass and plants biomass, other than C, H, O, N, and other basic elements, some other components are found in small quantities; these elements are alkaloids, pigments, terpenes, and waxes.

6.1.1 Fluid Matter

Some fluid materials are found in biomass in the form of an aqueous solution. These fluid materials contain different anionic and cationic variants. Biomass normally having a moisture percentage between 10% and 60%; when the biomass is fresh or raw, the moisture content may range between 80% and 90%. The amount of fluid matter depends on the proximate composition of biomass and can be determined as % values relative to high water % in the living cells. For example, fast-growing crops contain high moisture % and high quantities of typical elemental components like sodium, calcium, potassium, magnesium, nitrogen, phosphorus, chloride, and sulphur that are important for physiological activity and health (Vassilev et al. 2012).

6.1 Factors Affecting Ethanol Production

Several factors are important during fermentation, which can influence the rate of ethanol production, quantity, and quality of end product. These factors may include the composition of raw material or feedstock, especially the available sugar in the raw material, temperature of the substrate, fermentation time, microbial strain used for fermentation, pH of the substrate, and the parameters followed during the distillation process. Out of these factors, pH and temperature of the substrate and fermentation time are the most important factors. On the basis of the available literature and research findings, it can be revealed that the high amount of alcohol can be got by fermenting uncooked corn and wheat biomass. In the case of cooked biomass, the good amount of alcohol only can be produced within the first 46 h of the fermentation process; therefore it is recommended that a short duration fermentation process will be better for cooked biomass, whereas uncooked biomass requires longer time (around 72 h) for the production of good quality alcohol with maximum yield (Gutt and Gutt 2009). Due to continuous production of ethanol, during the entire process, it is noticed that the fermenting yeasts are suffered from osmotic stress due to high alcohol content, and they suffer from death. But the chance of contamination by microorganisms like wild yeast and Lactobacillus is more associated with uncooked biomass than with the cooked biomass. Production of ethanol by microbial fermentation using *Saccharomyces cerevisiae* is not only affected by process conditions like sugar concentration, temperature, and pH; but, it may also be affected by internal factors like microbial culture, medium, DO, immobilization of microbial and other micronutrients. Some of these factors are as discussed below.

6.1.1 Temperature

Temperature is very much important for the microbial growth and activity; a wide range of temperature is required for the growth and activity of individual microbial strain. Other than Saccharomyces species, many microbes show enhanced tolerance against alcohol at 10–15 °C, and therefore, they have good ability to contribute to the alcoholic fermentation process even at elevated temperatures with reduced fermentation time. High temperature is responsible for the inhibition of growth and multiplication of microbes, but a significant decline in the fermentation can be noticed (Lin et al. 2012). High temperature also affects the transportation activity of soluble compounds and the saturation level of solvents in the microbial cells, which may lead to accumulation of toxins and ethanol in the microbial cells (Lin et al. 2012). Moreover, high temperature can denaturate the ribosomes and enzymes indirectly and also creates issues like fluidity of membranes. Though at low temperature, the microbial cells show reduced growth and multiplication rates which is responsible for the lower rate of fermentation. In general, it is recommended that the optimum temperature range for the fermentation is 20–35 °C, and high temperature can be problematic for all types of fermentation (Macfarlane and Macfarlane 1993).

6.1.1 Composition of substrate

Composition of substrate is an important factor for alcoholic fermentation, because the presence of sugar in the substrate is mandatory for fermentation. The production or yield of alcohol is totally dependent on the quantity and type of sugar available in substrate, Sugars found in raw materials used for the production of ethanol are generally divided into two main categories: (1) simple sugars—(mono and disaccharides) like glucose, fructose and sucrose and (2) polysaccharides—like starch and glycogen. The mono sugars and disaccharides undergo direct fermentation in the presence of some alcohol-producing bacteria and yeast, while the polysaccharides require a specific treatment which is known as saccharification (hydrolysis)—in this specific treatment polysaccharide is converted into fermentable sugars like mono and disaccharides. Simple sugars are commonly found in most of the sugarcane, fruits, vegetables, molasses and other wastes of food industries. Polysaccharides are available in good amount in potatoes, tapioca, corn, rice, chicory, wheat and barley and lignin-cellulose waste (Bai et al. 2008). Cereals and potatoes are good sources of starch; this starch is the backup material for their energy. This polysaccharide consists of glucose residues. Starch is being utilized for centuries in the preparation of mixture for ethyl alcohol production. Enzymatic hydrolysis of starch is a traditional craft of distilleries; the natural source of starch hydrolyzing enzymes in this craft is malt (germinated barley grains). In the process of malting (germination), two enzymes: (1) a-amylase and (2) ß-amylase are produced that disintegrates the starches. Now, this craft is limited up to certain applications; malt is being replaced by microbial enzymes that are derived from microbes like *Bacillus subtilis* or fungi *Aspergillus niger* (Hector et al. 2011). Another useful industrial waste is molasses, which is a by-product of the sugar industry, and it is considered as q feedstock for ethanol production because it contains a high quantity of carbohydrates for direct fermentation (Parkash 2015).

6.1.1 Influence of pH

Fermentation activity and ethanol production can be increased by the control and optimization of process parameters like concentration of substrate, process temperature, and gas concentration. Apart from the concentration of substrate and process temperature, pH is also a vital factor that affects the fermentation. As we know that every microorganism requires a particular range of pH for their growth and multiplication, they require a specific pH environment for fermentation. According to Lin et al. (2012), the incubation time will be longer if the pH of the substrate is less than

4.0, but the production of ethanol will not be much affected in terms of concentration; but, if the pH is more than 5.0, the quantity of ethanol will be decreased substantially. Therefore, it is recommended that the optimum pH range for ethanol production or ethanolic fermentation is 4.0–5.0, this range is considered as the best operational limit for the anaerobic fermentation process (Lin et al. 2012).

6.1 Agricultural Waste for Production of Alcohol

6.1.1 Plant Crops

6.2.2.2 Sugarcane

Sugarcane (*Saccharum spp.*) is the main sugar-containing crop commercially grown in tropical and subtropical regions of India and almost in all parts of the world. It is a worldwide crop which is not only grown for the production of sugar, but also known as 'bioenergy crop' because of its capacity to produce huge amount of dry matter (bagasses). Much of the total quantity of ethanol is produced from sugarcane worldwide and the rest is produced from other crops like beetroot (sugar beet), sorghum, rice, corn, and wheat (Dufey 2006). The largest producer of sugarcane is Brazil which contributes around 27% of total global production, and thus, it serves as a major source of bioethanol production in this country. The starchy materials or crops like wheat, corn, and barley are mainly utilized by other countries such as Europe and United State (Linde et al. 2008).

6.2.2.2 Sorghum

Sweet varieties of sorghum are considered as perennial plant that belongs from the grass family; this family is now termed as 'Poaceae' (Ratnavathi et al. 2010). The plant of sweet sorghum is able to reduce carbon emissions. This crop is grown in all the three climates (temperate, subtropical, and tropical). All the components of this plant have good economic values; grains are utilized as food and feed material, green leaves and stems are fed to animals as forage, and the dry stalk (along with the grain) use the purpose of fuel. The cellulosic material (fibre) is used for the purpose of mulching also. Approximately 15–23% carbohydrates are found in the stalk of different cultivars of sweet sorghum. Sweet sorghum contains three main sugars, namely sucrose, glucose, and fructose that contribute 70%, 20%, and 10% respectively to the total amount of fermentable carbohydrates (Prasad et al. 2007).

6.2.2.2 Beetroot (Sugar Beet)

Beetroot is another sugar-containing crop which is commercially used for the production of sugar in many countries. The molasses of sugar beet is the most important sucrose containing feedstock for the production of bioethanol in European countries. It has the capacity to yield high amount of bioethanol than the other crops like wheat and sweet sorghum. The main advantage of this crop is it is a short duration crop with high yield capacity and high tolerance against climatic changes (drought, flood, etc.). It is a well-known fact that this crop requires low amount of water and fertilizer.

6.1.1 Other Sugar- and Starch-Containing Plant Produces

Among biomass, wheat, barley, and corn are the suitable examples of starch-containing raw materials (Balat et al. 2008). Some other crops like potato, sweet potato, and tapioca are also good in starch content and are the best materials for ethanol production. These starchy materials are pretreated using acid or enzyme to convert starch into high sugar material for the production of ethanol. As previously discussed, starch is a polymer which is a made up of D-glucose units, and therefore it can easily breakdown into fermentable sugars through the process of hydrolysis. Corn is a very common starch-containing crop used as a feedstock for bioethanol production followed by wheat (Cardona and Sanchez 2007). Apart from these agro-wastes, other plant produces like fruits and vegetables are also good sources of fermentable sugar, starch, and lignocellulosic materials. These wastes can also be utilized to produce ethanol in large amount.

6.1.1 Other Sources of Biomass

Presently, food waste is a big problem worldwide, it has been noticed that this category of waste has a big contribution in economic, social and environmental losses. According to the available data in an official publication of Eurostat (2017), more than 240,000 ton of food waste is generated in EU every year alone. Other bio-wastes like organic matters from municipal waste, solid waste from kitchen and gardens and food waste creating one-third of the total generated waste that could be utilized as feedstock for the production of valuable products including alcohol. The use of these bio-wastes, food wastes and other discards can open new ways for research, innovations and can also generate money. It is targeted that to help retailers and consumers, the wastage food will be reduced up to 50% by 2030 (European Commission 2018). The direct uses of by-products of food material and the use of food waste for conversion into other value-added products are still very limited. This situation is only because of the problems associated with quantification, transportation and supply system, unavailability of data related to its quality and non-homogeneity of food waste, etc. (European Commission 2018). The composition and the quality of available food waste are not permanently stable; these properties are changeable, depends on the season and place, and the eating habits of the peoples. Despite this type of variability in the composition of food waste, it can be stated that they are rich sources of proteins, carbohydrates, minerals and fat and the presence of these components make it a best suitable feedstock for the production of biofuels like ethanol. It can be converted by microbial fermentation (Patel et al. 2019; Carmona-Cabello et al. 2020). The product obtained after fermentation of sugar-containing raw materials is designated, as “first-generation” bioethanol, while bioethanol from the fermentation of lignocellulosic materials is termed as “second-generation” produce. The “third-generation” bioethanol is at an early stage of investigation and may be the product of algal biomass. The cellulosic material of plant origin is still an untapped source of sugars that can be fermented for ethanol production. A special category of raw material is a non-food waste of agricultural produces which include straw of wheat and rice, sugarcane bagasse, and rice husk. The cellulose, hemicellulose, and polysaccharides of these waste products are tightly associated with the lignin content of plant cell wall. This lignin acts as a physical barrier, and it should be removed, so that we could free the carbohydrates and make it available for conversion processes (Koshy and Nambisan 2012; Patel et al. 2006; Kang et al. 2014).

6.1 Pretreatment of Biomass

All the fermentation processes require some pretreatments of raw material before entering into fermentation mode; these treatments may be pasteurization, sterilization, acidification, and hydrolysis (saccharification). But in case of starchy, cellulosic, or lignocellulosic biomass, hydrolysis (saccharification) process is an essential step to produce ethanol. For example, steaming before enzymatic hydrolysis of starchy biomass enhances the conversion of cellulose into glucose in corn stover (Harmsen et al. 2010). If the biomasses are not pretreated, they require more enzymes for the completion of saccharification of biomass which is not an unfeasible event (Amidon et al. 2008). These pretreatments can also be categorized into chemical, mechanical, and biological treatments.

6.1 Fermentation Process

Now a days, agricultural crops waste from wheat, rice, sugarcane, maize (corn), horticultural waste from fruits like jackfruit, mango, grapes, pineapple, banana, plum and vegetable waste from beetroot, potato, sweet potato, leafy vegetables are the main biomass sources used for production of ethanol. Yeast *Saccharomyces cerevisiae* is a best suitable and popular microorganism used for the production ethanol; the popularity of this yeast is due to its high yielding capacity and tolerance against high ethanol content. To achieve noteworthy economic benefit and to lower environmental hazards, bulk amount of agro-waste based biomass could be used to manufacture ethanol (Taouda et al. 2017). Use of cereal crop, fruits, and vegetables crop waste for production of ethanol may be the best option. One of the best examples of fermentable sugar-containing raw material is pineapple waste that can be converted into bioethanol by microbial fermentation (Hossain et al. 2008), as these wastes contain important and fermentable components like sucrose, fructose, glucose, and other nutrients (Sasaki et al. 2002). Lignocellulosic compounds are the key structural elements of hard wood plants, and these structural elements are also found in non-woody plants. The fermentable biomass that contain significant

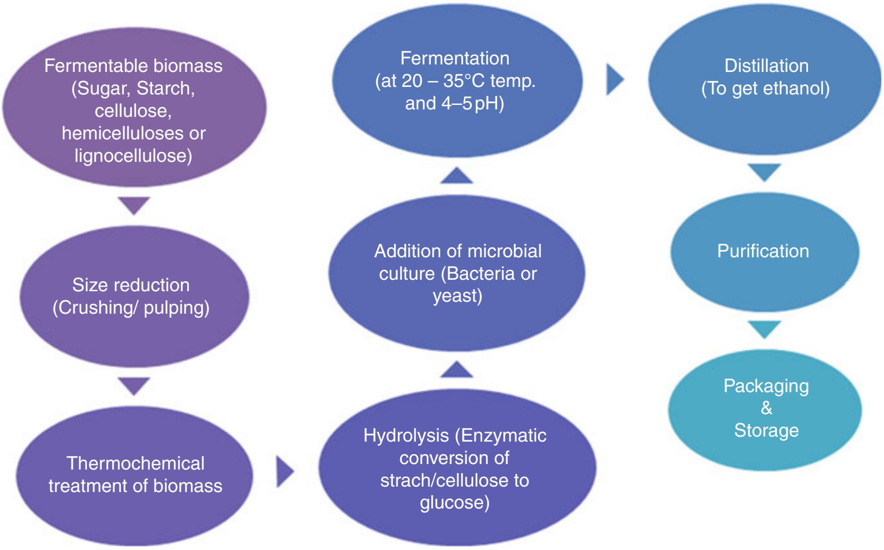

Fig. 6.1 Process flow of alcohol/ethanol production

amount of sugar, starch, cellulose, hemicelluloses or lignocelluloses are subjected to size reduction processes like crushing and pulping. After getting crush or pulp, biomass is thermochemically treated to avoid further contamination during the period of fermentation. In some cases, hydrolyzation of biomass is an essential process. Fermentation is carried out by the addition of microbial culture (Saccharomyces cerevisiae); the temperature of substrate should be maintained between 20 °C and 35 °C during the entire fermentation process. The obtained fermented must is filtered and a distillation process is required to remove alcohol/ethanol content from the must. After producing alcohol/ethanol, it can be purified, packed, and stored according to the need. The process flow of alcohol/ethanol production is shown in Fig. 6.1.

6.1 Case Studies

6.1.1 Production of Ethanol

Since last few decades, across the globe due to fast movement of population and goods from one place to another, transportation facilities have been drastically increasing which has increased the consumption of huge amount of traditional fuels exponentially. As a result of this advancement, our oil resources are continuously being depleted. Many developed countries are suffering from a fear of running out of oil fuels. The same problem is also a big issue for the rapid growing countries including India and China. Due to the increased demand for oil fuel and limited

Table 6.3 Ethanol production studies

Research studies	Researchers
Production of ethanol from sugarcane molasses	Singh and Jain (1995)
Production of ethanol from municipal solid waste	Green and Shelef (1989)
Production of ethanol from agricultural waste	Schugerl (1994)
Production of ethanol from the fruit wastes like papaya	Akin-Osanaiye et al. (2008)
Production of ethanol from mangoes	Reddy and Reddy (2007)
Production of ethanol from banana peels	Joshi et al. (2001)
Production of ethanol from pineapple	Muttara and Nirmala (1982)
Production of ethanol from grapes	Pramanik and Rao (2005), Asli (2010)
Production of ethanol from grape waste	Raikar (2012)

resources, the hike on oil prices and concern about environmental pollution, we are looking for the pollution free fuel and sustainable fuel resources as an alternative of oil fuel. In this context, biofuels which can be obtained from the different types of biomass are gaining more popularity at present. According to Saddler (1993), the production of bioethanol as a fuel by using different types of biomass may be the better solution of the problem. The biomass can be converted into fuel by using thermochemical and bio-chemical processes; it will also help in the remediation of environmental pollution. Various biofuels like ethanol, biodiesels, and methanol are produced from different types of agro-waste, municipal and food industry wastes by the process of microbial fermentation using Saccharomyces cerevisiae. Out of these biofuels products, ethanol is a more demanded biofuel as it is widely adopted because of its clean burning qualities and less pollution (Reddy and Reddy, 2007). In several countries, ethanol is used as an alternate fuel or it is mixed in particular ratio with other fuels as directed by the local governments. Many researchers conducted in-depth studies on the ethanol production from different raw materials (Pramanik and Rao 2005). Few examples of ethanol production from different raw materials are listed below (Table 6.3).

In all the above-mentioned studies, the fermenting microorganism used was *Saccharomyces cerevisiae*. The study conducted by Raikar in 2012 emphasized on the ethanol production from the waste of grapes; two microbes (*Saccharomyces cerevisiae* and *Benzyl penicillin*) were used in the fermentation study and the effect of *Benzyl penicillin* on the ethanol quantity was investigated. In the all case studies, it is found that these wastes were found suitable for commercial production of ethanol and the maximum production of alcohol can be obtained from *Saccharomyces cerevisiae*.

6.1 Conclusion

This chapter is based on the review of studies performed by various researchers on the production of alcohol/ethanol from different types of biomass from agro-waste. It is found that the composition of waste varies widely with the area and locality, due to which the standardization of ethanol production process has become a tedious job and almost impossible. Agro-wastes can be properly exploited in ethanol production, but the production of alcohols in higher quantities will require a more extensive research. Even though, a number of published studies in this field are available but promising results were obtained only from few researches in terms of increased yield of alcohol. During the review, it is shown that the quantities of agro- and food waste will continue to increase in the coming future and it could be electively utilized for commercial production of ethanol. A proper understanding about substrate composition, process temperature, substrate pH and other parameters that are important in fermentation will help to achieve the goals. The conversion of agro-wastes into bioethanol is a suitable way to encourage the use of underutilized resources and sustainability of environment. Due to abundant availability and low cost of cellulose, lignocellulose, starch- and sugar-containing wastes, they have great potential for ethanol production. As fermentation process does not require very specific environment, expertise, and hazards it can be adopted without any hesitation. Bio-conversion of agro-waste and vegetable/fruits waste into ethanol can be done commercially.

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Hydrogen Production by Utilizing Bio-Processing Techniques

7

Dan Bahadur Pal and Amit Kumar Tiwari

Abstract

Hydrogen is contemplated as one of the most reliable, hopeful option, and it is also considered that it would be the best option for next generation fuel. Hydrogen is also recognized as a carrier of green energy. In various countries, hydrogen is contemplated to be a prominent substitute vector of energy, which may be a causeway and a prospect to a sustainable energy resource. Hydrogen is not a freely accessible primary energy source in nature; it is a form of secondary energy source. There are good opportunities to convert this secondary energy source into other energy sourced like electricity. Hydrogen can also be produced from diversified energy sources using different manufacturing techniques and can be utilized in different areas. Bioprocesses provide opportunities to produce hydrogen from rechargeable, economical, and ecofriendly biological resources such as biomass and solar energy by different natural processes like photo fermentation, dark-fermentation, and direct or indirect photolysis. This chapter provides vast information on production of hydrogen using biological sources like microorganisms, different substrates concentrations, role of added chemicals, process variables, such as pH and temperature of substrates, agitation, and so on. Recent researches are giving more emphasis on sustainable and ecofriendly energy from electrolysis, biomass, biocatalysis, and photo-catalysis to replace traditional fossil fuels. These techniques may be the best choices with huge potential, which can meet the energy need and can ensure uninterrupted supply of fuel in the future. In this chapter complete attention is given on the different pathways of production of hydrogen and its practical application in different fields.

D. B. Pal (✉) · A. K. Tiwari
Department of Chemical Engineering, Birla Institute of Technology Mesra, Ranchi, Jharkhand, India

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Keywords

Hydrogen production · Utilization · Biomass · Water-gas shift reaction

7.1 Introduction

Industries that are involved in the production of petroleum and chemical are the large-scale users of hydrogen; these industries require massive quantities of hydrogen (Sema 2018). A petrochemical processing plant requires hydrogen for the purpose of hydro-cracking, hydro-dealkylation, hydro-desulfurization, and refining of crude oils. More than 40% of the total world's consumption of hydrogen is consumed by the industries, particularly those that are associated with synthesis of ammonia and methanol (Momirlana and Veziroglu 2005). Hydrogen is also used for the production of hydrochloric acid and is also used as a reducing agent in different metal ores. In food processing industries, hydrogen is commonly used for the production of hydrogenated fats and oils, which allows conversion of vegetable oils into margarine. Due to least density of hydrogen gas, it has vast applications in meteorological field; it is utilized as a gas in lift especially where other gases are more expensive or helium gas is not available (Abbas and Daud 2010). Pure and dry hydrogen is widely used in the balloons to carry radio-sound devices to monitor atmospheric conditions or to collect weather information. To record information about weather and condition of atmosphere, the big hydrogen balloons carrying a load of radio-sound devices levitates into the atmosphere. Hydrogen is really clean as the only by-product is water and it provides highest combustion energy per unit of weight, compared to energy released by any commonly occurring other fuel materials (Eq. 7.1).

$$H_{2(g)} + 0.5O_{2(g)} \rightarrow H_2O_{(l)}\ \Delta H^0 = 286\ \text{kJ/mol} \tag{7.1}$$

The amount of produced energy is 4, 2.8, or 2.4 times more than coal, gasoline, or methane, correspondingly (Abbas and Daud 2010). Due to this special feature of hydrogen, it is used as upper stages fuel in a multistage rocket. Hydrogen is also utilized as fuel in the space shuttles by NASA in its space program, and they also using hydrogen in fuel cells to generate electricity, heat, and drinking water for their astronauts.

Excluding these, due to its ecofriendly behavior hydrogen have been modified and upgraded as an optional fuel to substitute fossil fuels. Hydrogen has a potential to provide highly efficient processes like application in fuel cells. In future, hydrogen would be used commercially as fuel in aircraft and vehicles, and as source for power supply for houses and offices (Kalinci et al. 2009). Use of hydrogen can reduce great amount of greenhouse gases which is generally emitted from the power operated vehicles; this reduction may be achieved by the use of hydrogen fuel in the fuel cell of internal combustion engines. Furthermore, evolution and expansion of low-priced hydrogen fuel cells would help to reduce our dependency on expensive fuel (oil), and it will also increase the conventional energy conservation and energy security. Thus, many benefits are offered by hydrogen like unlimited source of renewable energy, which is an emission-free, cost-effective and cleanest fuel for today's and future energy demand. Hydrogen is an odorless and colorless gas, which is not freely available in the Earth; but in the nature it is found in large quantities as composite of oxygen (H_2O) and carbon (C_2H_5OH, $CnH_{2n} + 2$, $C_x(H_2O)_y$, etc.). For the production of hydrogen from water and carbon-containing materials, energy should be supplied properly. It is clear that hydrogen is not a self-source of energy, because energy is required to produce hydrogen (Eq. 7.2).

$$H_2O + \text{energy} \rightarrow H2 + 0.5O_2 \tag{7.2}$$

Due to useful and harmless properties of hydrogen, it is one of the best favorite rational choices to produce and utilize it as a carrier of energy by different ways (Abdalla et al. 2018). Marshall et al. (2007) also told that it is a pollution-free combustion product and due to abundance, it is considered as "energy carrier of the future." Presently, fossil fuel is used to supply around 98% of the total hydrogen requirement (Baykara 2004). Due to fast reduction rate and uncontrolled use of fossil fuels, it is becoming a severe problem for hydrogen production; therefore, researchers are searching for alternative and intensified sources of raw materials. It is estimated that yearly around 21.3 gigatonnes of CO_2 is produced due to burning of fossil fuels, but it is also estimated that about only half of that amount can be absorbed by natural processes, therefore around 10.65 billion tons of CO_2 is released into atmosphere per year. This process is responsible for the increase of atmospheric CO_2 level (Baykara 2004). CO_2 is considered as one of the greenhouse gases that is responsible for global warming and causing rise in the average surface temperature of the Earth and adverse effects on environment.

The biological production of H_2 involves a talented unconventional method for the making of fuel from cost effective, renewable, and ecofriendly resources (Srivastava et al. 2019). It can be done in normal conditions like ambient temperature and normal pressure (Silva et al. 2018). In nineteenth century, applications of biological processes for production of hydrogen were preliminarily described (Rittmann and Herwig 2012). In biological process microorganisms are used to convert organic substrates and water molecules into hydrogen; according to Silva et al. (2018), this process is catalyzed by two enzymes (nitrogenase and hydrogenase). Biological hydrogen may be produced by various processes like photo-fermentation, photolysis, and dark-fermentation.

7.1.1 Hydrogen Application

Hydrogen is used as a raw material in large amount in the chemical, food, and petroleum industry. In oil refining industries it required in very high amount; therefore, it is more demanded material in this industry and used for hydrogenation, production of chemicals, and desulfurization. Both chemical industries and refineries

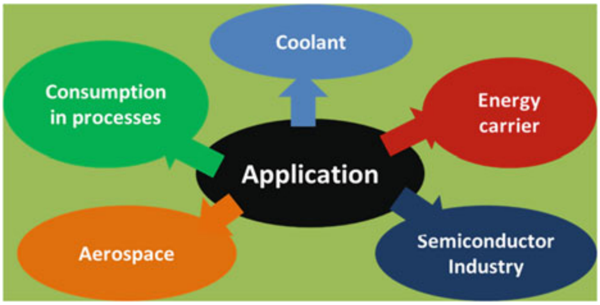

Fig. 7.1 Classification of hydrogen application in present days

use hydrogen for the production of various commodities, specialty chemicals like toluene, toluene-diamine, H_2O_2, NH_3, pharmaceuticals, specialty hydrogenations and also use it for the synthesis of gas. In 1988, due to the synthesis of methanol and production of other chemicals, a sale of H_2 was about 6.7%. Around 40% of the global utilization of hydrogen was consumed by the ammonia synthesis plants (Scholz 1993) and are involved in the production of huge quantity of hydrogen; H_2 is essential to lessen the nitrogen into ammonia.

Therefore, ammonia synthesizing units are really different form of H_2 production. Due to the excessive capacity of ammonia synthesis plants, conversion of ammonia synthesis plants into H_2 production units may be a good decision. In addition, for annealing of steels H_2 is also utilized in huge quantity by the steel industries. H_2 is used in large amount by electronics industries for the production of electronic devices. Food processing industries especially oil refineries use hydrogen in large amount for hydrogenation of fats and oils. Apart from these uses, large quantity of hydrogen is consumed as a fuel in different industries such as in space, aeronautical, chemical and fertilizer industries. The major applications of hydrogen are shown in Fig. 7.1.

It is actively considered that, there is another potential use of hydrogen associated with the environment and environmental conservation. Since the hydrogen combustion in the presence of oxygen is able to produce water without producing carbon dioxide as a co-product, hydrogen is considered as an ecofriendly and clean fuel for now and future also. The utilization of hydrogen as a source of energy depends on how it is formed and what types of raw material is used for hydrogen production; if fossil fuels are used to produce hydrogen, it is indirectly generating huge amount of carbon dioxide also which is not good for our environment. So the production of hydrogen from nonfossil fuel may be the best opportunity for the future with regard to environmental concern. Combustion of hydrogen with oxygen is considered as the ultimate clean fuel; because there is no production of carbon dioxide and NO_x is noticed during the entire process. As our Earth is a good source of infinite amount of water, if we can develop a new technology for the production of hydrogen from water, then we will be able to get it back into water during the generation of power, this might offer a much smart and ecofriendly expertise for energy production. In fact, refining industries are often able to manage their hydrogen requirements by balancing their industrial chemical reactions. Processes like hydro-desulfurization and hydro-denitrogenation are advented for the control of tougher emission in automobiles and controlling nitrogen oxide emissions in refineries. Refineries have responded by using these proven and acceptable techniques. The past production of large volumes of benzene as a refinery product often results in by-product hydrogen. Long back, refineries were considered as good producers of hydrogen, but presently it is noticed that the refining industries are big consumers of hydrogen. It is estimated and predicted that the supply and demand for hydrogen will be very difficult in coming century due to dramatic imbalance in supply and demand needs (Courty and Chauvel 1996; Simonsen et al. 1993). Cromarty and Tindall (1994), they also reported same predications, after completing a detailed study on a recent market review on hydrogen.

7.2 Hydrogen Production via Biological Processes

Biological manufacture of hydrogen can be achieved by using different processes; these biological processes may includes indirect biophotolysis or direct biophotolysis, photofermentation, dark fermentation, and mixed approach such as linking dark fermentation and photosynthetic processes (Das and Veziroglu 2008).

7.2.1 Biophotolysis

Biophotolysis is the photonic-driven mode of production of biohydrogen, which is found in green algae and cyanobacterium; it is due to principle of photosynthesis similar to undergrowth (Dincer and Acar 2015; Nagarajan et al. 2017). However, major difference is that biophotolysis is used for production of hydrogen, while it is accepted that photosynthesis is required to produce carbon hold biomass (Nikolaidis and Poullikkas 2017). Few well-known algal species are found suitable and utilized in biophotolysis process such as *Scenedesmus, Chlorella, Chlamydomonas reinhardtii*, and *Tetraselmis* (D'Adamo et al. 2014; Oey et al. 2016). Biophotolysis can be further classified in two categories, direct biophotolysis and indirect biophotolysis (Nikolaidis and Poullikkas 2017). Both microalgae and cyanobacteria (heterocystous and non-heterocystous strains) can be utilized to perform direct photolysis using enzymes such as bidirectional nitrogenase and hydrogenase. In the process of direct biophotolysis, water molecules are divided into H_2 ion and O_2 molecules by means of solar energy captivated by the photosystems found in the cyanobacterium and olive algae working as photo sensors (Dincer and Acar 2015).

7.2.2 Dark Fermentative Hydrogen Production

Manufacture of biohydrogen by means of the method of dark fermentation is considered as one of the best methods due its elevated rate of hydrogen production, possibility to use multifarious biomass (lingo-cellulosic), capacity to work at ambient situation, and low energy use (Sambusiti et al. 2015). While, dark fermentation is reported for deprived yield and little substrate utilization, it is due to the genesis of metabolites (acidic) by microbes during the process (Alvarado-Cuevas et al. 2013). Other than this, the stumpy realistic yield has been reported compared to speculative value. The reported maximum speculative yield of biohydrogen is 4 mol H_2 /mol $C_6H_{12}O_6$, whereas CH_3COOH was the chief end result of this process along with other metabolites such as $C_3H_6O_3$, C_2H_5OH (Chaganti et al. 2012). Multipurpose fermentative microorganisms can be used to produce biohydrogen using dark fermentation process; these microorganisms may include *Clostridium, Citrobacter, Lactobacillus, Rhodopseudomonas,* and *Enterobacter*. There are number of successful studies available as evidences of biohydrogen production after degradation of biotic waste (Corneli et al. 2016; Moura et al. 2018). Hydrogenase is accountable for the hydrogen producing reaction in microorganism during dark fermentation, and it is based on the ability of metal requisite, which can be grouped into various assemblies. Thus, through the augmentation in bioactivity, this enzyme can improve the total yield of biohydrogen.

7.2.2.1 Organisms

Some anaerobic fermentative microorganisms especially bacteria like *Bacillus* sp., *Enterobacter* sp. and *Clostridium* sp. are capable of generating hydrogen through dark-fermentation process (Kim and Kim 2011). Among these microorganisms, the most frequently used dark fermentative microbes are from the group of *Clostridium*; such as *C. thermolacticum, C. pasteurianum, C. buytricum,* and *C.bifermentants* (Bao et al. 2012). The genus *Clostridium* (gram positive) bacteria have abilities like high production rate of H_2, versatile metabolic pathway, and production of different by-products with hydrogen (Silva et al. 2018). The nature and quantity of volatile fatty acids and the produced H_2 may differ with the species of bacteria. According to Bao et al. (2012), production of hydrogen can be increased up to 2 times by using an assorted culture of *Brevumdimonas* sp. and *Bacillus* sp. in dark fermentation. It was reported that the amount of produced hydrogen was 1.04 mol from 1 mol glucose in bioreactor via starch (with no use of other steps for hydrolysis of starch) as substrate (Bao et al. 2012). Feel respect to state that, the use of a mix culture in a dark fermentation process faced hurdles such as existence of inauspicious microbes like sulfur-reducing bacteria, homoacetogenic bacteria, and methanogens that may possibly make changes in metabolic trail of H_2 synthesis or act as H_2 clients (Salem et al. 2018). By the alteration of conditions of bioreactor and use of pretreatments like chemical, physical, or biological treatments prior to starting the process of fermentation, the actions of microorganisms can be restricted (Salem et al. 2018). Normally, in comparison to genuine microbial culture, introduction of assorted microbial culture is the best option owing to its monetary advantage and possible potential of the use of a variety of substrates.

7.2.2.2 Consequences of Substrate

The type and concentration of substrate are crucial factors that can significantly manipulate the production of H_2 in dark fermentation (Srivastava et al. 2019).

Anaerobes are able to generate hydrogen from different carbon sources like mono sugars (e.g., lactose, glucose and sucrose), cellulosic wastes, and wastes from food industries, wastewater and starch containing wastes during dark fermentation (Kapdan and Kargi 2006). The consequences of different primary concentrations of substrate were also examined by Eker and Sarp (2017). Various studies are conducted by using waste paper (acid hydrolyzed paper), extracted glucose, and anaerobic mire (as a mother culture). Increased concentration of glucose (more than 18.9 g per liter) was responsible to reduce H_2 surrender due to the quantity of C_4H_3O–CHO produced during hydrolysis of paper waste using acid and generated volatile free fatty acids. To augment surrender of H_2 in fermentation (dark fermentation process) of sewage mire, three forest wastes (flower waste, sheared ryegrass, and fallen poplar leaves) in the batch fermentation system was added by Yang and Wang (2017). The results of fermentation of sewage mire combined with the biodegradable forest wastes revealed an increase in hydrogen surrender from volatile solids (11.2 ml/g) for individual sewage mire to 20.8, 32, and 51.7 ml/g volatiles when forest wastes like leafy waste of poplar, wasted flowers, and crushed ryegrass were applied respectively. These increments might be endorsed in the direction of the rise in the ratio of C and N in substrate and the higher amount of carbohydrates present in the substrate is resulted from combined-fermentation of sewage mire with the wastes of forest.

7.2.2.3 Effects of Trace Metals and Minerals

The hydrogen by dark fermentation is a method in which microbial involvement is required; this process is catalyzed by an enzyme (especially by hydrogenases) (Srivastava et al. 2019). Catalytic activities of such enzymes are the results of a series of electrochemical reactions during hydrogen production (Sun et al. 2019). Hydrogenases enzymes are metalloproteins that are based on atoms of metal such as [Fe], [Ni-Fe] and [Fe-Fe] in their active sites, and on the basis of these metals, hydrogenases can be classified into three groups (Bao et al. 2013). For improving the activity of these enzymes and to enhance hydrogen production, fermentation medium can be supplemented with metal ions (co-factor) that would be supportive in fermentation (Srivastava et al. 2019). The addition of Fe2þ ions have direct affects on catalytic activity of hydrogenase (Bao et al. 2013). The existence of Ni2þ in the nutrient culture media at best amount influences the vigorous side of hydrogenase [Ni-Fe] (Sekoai and Daramola 2018). The type and concentration of trace elements needed for dark fermentation may differ depending on bacterial strain and the environment of experiment (Argun and Kargi 2011).

7.2.2.4 Effects of pH

Fermentation processes are completely dependent on the pH of substrate processes like dark fermentation. It is found that, due to accumulation of byproducts like VFAs, the pH of dark fermentation is dropped during hydrogen produced by fermentation method (Ziara et al. 2019). Lower pH (below 5) could stop hydrogenase activity; as a result it can cause the termination of hydrogen production (Bao et al. 2013). In contrary, low pH values during dark fermentation is encouraging for

Clostridium sp. to generate organic solvents like butanol, acetone, and ethanol rather than hydrogen (Argun and Kargi 2011). Alkaline pH was reported to be effective to avoid formation of organic solvents (acid byproducts) during fermentation operations (Argun and Kargi 2011). Sustainable hydrogen production by controlling of pH at best is very vital during the entire process (Penniston and Kana 2018). On the basis of above-mentioned discussions, a wide set of most favorable pH for H_2 production through the dark fermentation are reported which can be illustrated by the applications of varieties of carbon sources and the particular microbial inoculums. Assessment of the best pH is vital in fermentation due to its noteworthy functions on metabolic conduit of the definite microorganism and secondary product creation as well as H_2 yield.

7.2.2.5 Effects of Temperature

Temperature/heat and dark-fermentation are much associated with each other; heat is a essential feature in production of hydrogen by fermentation. Conditions of gentle (25–40 °C), mild (40–65 °C), and comparatively high temperature (below 80 °C) can be utilized to conduct dark fermentation (Argun and Kargi 2011). The optimum temperature is important in the selection of microbial strains because it is specific to each and every microorganism and different types of carbon substrates (Ziara et al. 2019). Ziara et al. (2019) also scrutinized the consequences of temperature on dark fermentation H_2 production of anaerobic mire using lactate extracted from food processing industry; they found that compared to lower temperature (35 °C), cumulative hydrogen gas production was higher at higher temperature (45 °C). Higher temperature could be accountable for enhanced the metabolic reactions and hydrogen production. Furthermore, the constant biochemical response rate during the process of fermentation at elevated temperature would be enhanced. The control of process temperature is decisive in dark fermentation as it has an effect on the biochemical pathways and as a result hydrogen yield. It was reported that the butyrate is the principal metabolite which is formed under mesophilic environment; conversely, process under thermophilic environment affect the manufacture of acetate as an incidental product (Valdez et al. 2005). Generally, acetic pathway is found more suitable for dark fermentation. As the share of acetic and butyric acid was increased, the increased yield of H_2 production was also reported (Tomczak et al. 2018).

7.2.2.6 Effects of Hydraulic Retention Time (HRT)

HRT is a moderate habitation instance of medium for the microorganisms to exploit the substrate in the nonstop bioreactor (Karapinar et al. 2020). Fermentation under optimum hydraulic retention time is important to increase the hydrogen production and reduce the fruition of bad ethanol and other organic acids (Tomczak et al. 2018; Kumar et al. 2014). These are the hydrogen eating microorganisms and are generally deactivated by pretreatment procedure which is not helpful in the absolute inhibition (Karapinar et al. 2020). In dark fermentation (continuous process), shortening of hydraulic retention time has affirmative effects on increase of the population of H_2 generating microorganisms rather than H_2 overwhelming microorganisms

(Karapinar et al. 2020; Si et al. 2015). This shortening could be recognized to elevated expansion rate of H_2 producing microorganisms compared to H_2 consuming microorganisms (Karapinar et al. 2020). Therefore, low hydraulic retention time is useful in the reduction of concentration of unwanted metabolites and bacteria continuously in dark fermentation process; it leads to drop in conversion competence of a substrate due to little housing time of substrate in a bioreactor which requires organization of substrate at low concentration or applying elevated hydraulic retention time (Tomczak et al. 2018). Moreover, loss of biomass occurs at low hydraulic retention time that may cause decrease in production of hydrogen (Kumar et al. 2014). At low hydraulic retention time, the use of holding method (immobilization) leads to constant H_2 production along with lofty conversion ability with no removal of bacterial cell from the continuous process/system (Tomczak et al. 2018).

7.2.2.7 Effect of Partial Pressure

One more significant factor for biological synthesis of hydrogen is hydrogen partial pressure (HPP). Production of hydrogen by dark fermentation using bacteria (anaerobes) is generally affected by the metabolic conduit and final products (Junghare et al. 2012). When the concentration of hydrogen increases in the media, the metabolic conduit shifts toward the production of metabolites like lactate, butanol, acetone, and ethanol (Guo et al. 2010). HPP can be constrained by spraying of peripheral gasses like N_2 (Guo et al. 2010; Nguyen Tad et al. 2010), CO_2 (Guo et al. 2010) and argon or a mixture of recirculation gases (Lee et al. 2012). However, these gases might weaken the generated H_2 content which is required for hydrogen refinement in additional downstream processes (Lee et al. 2012).

7.2.3 Photo-Fermentative Hydrogen Production

Natural products like organic acids and VFAs formed in the reactions occurs during dark fermentation can work as substrate for photo fermentative microbes in the existence of enzyme (nitrogenase) for the production of biohydrogen through light energy in N_2 deficient conditions, and this method is recognized as “photo-fermentation” (Nikolaidis and Poullikkas 2017; Wang et al. 2017). *Anabaena* sp., *Chlorella*, *Dunaliellasalina*, *Rhodobacter* sp., *Rhodopseudomonas* sp., and *Rhodovulum* sp. are few common and important photo-fermentative bacteria (Corneli et al. 2016).

7.2.3.1 Organisms

Gram-negative prokaryotes (PNS) utilized in the procedure of photo-fermentation for the H_2 production (Sakurai et al. 2013). *Rhodobacter capsulatus, Rhodopseudomonas palustris, Rhodobacter sphaeroides, Rhodobacter sulfidophilus*, and *Rhodospirillum rubrum* are well-identified PNS bacteria that participate in the photofermentation process (Wua et al. 2012). These PNS having a versatile metabolism system, and they can grow photoautotrophically, chemoheterotrophically, and photoheterotrophically on the different environmental conditions like degree of anaerobiosis, light intensity, and carbon sources

(Parka et al. 2018). Photoheterotrophically form is favored by these bacteria for their own growth and evolution of hydrogen by them. Under photoheterotrophical situation, organic matters, and daylight are utilized as basis of power and carbon for the development of PNS and H_2 creation, correspondingly. Photofermentation performed by using two catalytic enzymes (nitrogenase and hydrogenase) via TCA cycle (citric acid cycle).

7.2.3.2 Effects of Substrate

Sustainable and reliable carbon sources are the vital factors in sustainable production of biofuels. The selection of an appropriate raw material will have various effects and benefits on a sustainable process like low environmental pollution, cost effectiveness, and high efficiency (Najafpour 2015). In photofermentation, growth rate of PNS, substrate conversion competence, and rate of H_2 production sturdily vary with the variety of carbon substrate chosen for experiment (Ghosh et al. 2017). PNS bacteria are able to adjust according to a broad range of carbon sources from large complex molecules like sucrose, fructose, and glucose to small crude organics (malic, lactic, acetic, butyric, etc.), flavored compounds (aromatics), and alcohol (Ghosh et al. 2017; Liu et al. 2015), although only a part of the reported substrates is appropriate for production of H_2 by PNS bacteria (Koku et al. 2002).

7.2.3.3 Effects of Trace Metals and Minerals

Nitrogenase is an important enzyme in the metabolism process of PNS bacteria. This enzyme is also acknowledged as a binary-enzyme because it contains two valuable proteins: (1) Mo-Fe containing protein and (2) Fe containing protein. Nitrogenase is fully active when both the proteins are present in it (Kim et al. 2006). Fe ion is also known as electron carriers of the ETC like ferredoxin and cytochromes (Zhu et al. 2007). According to Eroglu et al. (2011), increased production of hydrogen from olive mill effluent by *Rhodobacter sphaeroides* was 1.5 and 3 times more by using cultures enriched with Mo and Fe, respectively. In the meantime, the first bubble of H_2 was noticed after a long time in the culture in which Fe was added. Under Fe2þ limitation condition, 10% decrease in hydrogen production by *Rhodobacter sphaeroides* using a carbon source (sodium lactate) was also reported by Zhu et al. (2007). Malate as carbon source was used by Laocharoen and Reungsang (2014) in another research; they reported increase in H_2 production yield by *Rhodobacter sphaeroides* using enlarged amount of $FeSO_4$. There was no noteworthy increase in hydrogen production yield when $FeSO_4$ was added at n0.004 and 10^{-2} mg/cm^3, although, the application of $FeSO_4$ at higher composition, resulted setting and agglomeration of bacterial cells (Zhu et al. 2007). Yang et al. (2016) investigated the outcome of different heavy metal ions like Cd2þ, Cr6þ, Cu2þ, and Pb2þ on production of hydrogen by *Rhodobacter sphaeroides* HY01 from a mixed carbon source and a nitrogen source. They reported that the addition of Pb2þ, Cu2þ, Cr6 þ, and Cd2þ at the rate of 0.5, 0.05, 0.05, and 20 mg per liter has positive effect on H_2 yield and conversion rate was observed; these concentrations were also helpful in the removal of heavy metals simultaneously. The pH of photofermentation process and the activity of nitrogenase were significantly affected by high concentration of heavy metals. The pH between 7.1 and 7.3 is found suitable for the nitrogenase activity. Use of higher concentrations of metal ions will led to increase in final pH of the fermentation process; accordingly, catalytic activity of nitrogenase will deactivated (Yang et al. 2016) with the use of high concentration of metal ions (Yang et al. 2016).

7.2.3.4 Effect of Illumination

Light is the one of the most vital issue in the process of photofermentation; in fact, light sources, intensity of light, and its distribution is important for photofermentation. Skilled utilization of light is valuable, because the photosynthetic organisms require light for the synthesis of ATP. Higher amount of ATP is necessary to stimulate the transportation of electrons in the process of nitrogen fixation and hydrogen production (Akkerman et al. 2002). Sufficient dose of light intensity is required for generation of electrons; for example, by rising the strength from 2000 to 5000 m^2 cd of a tungsten bulb, the substrate conversion efficiency and rate of H_2 production can be increased by *Rhodobacter sphaeroides*. No drop in H_2 production was noticed even at more than 5000m^2 cd light intensity. This may be due to the saturation of light, the excess of adenosine triphosphate, and Fd in photosynthesis arrangement, which have pessimistic effects on the catalytic action of nitrogenase (Li et al. 2009). The reactors were operated in outdoor environment; but due to troubles related with infectivity and unbalanced luminosity, the photobioreactor's performance was poor (Chen et al. 2008a). In contrast, it is reported that the control of indoor operation was easier than the outdoor one (Akkerman et al. 2002). However, the application of an artificial illumination source in indoor photo bioreactors is a costly process due to high operational cost. To get the benefits of both operations, indoor reactor was illuminated by the use of combined source of energy (internal and external light) and solar power was utilized to excite optical fibers as a device for internal illumination (Chen et al. 2008b).

7.3 Biological Production of Hydrogen

Comparison to conventional fossil fuels, biohydrogen provides several environmental and technical benefits, which makes it a favorite choice for the transport sector. It has various benefits including reduction in greenhouse gases, e.g., reduced emission of CO_2, which will contribute to environmental health and ecosystem, the diversification in fuel sector, sustainability, biodegradability, and also supplementary marketplace for agro-products (Mustafa et al. 2009). Biophotolysis (direct and indirect), dark fermentation, photo fermentation, and bio-water-gas shift reaction (WGSR) are the five methods which are used for the production of hydrogen using biological processes. These processes are totally based on the natural sources of energy (solar energy), and special microorganisms are adapted to generate hydrogen during the process of photosynthesis (Jeffrey et al. 2010). In spite of different technical and biological challenges, photo-biological hydrogen production remains as number-one contender for renewable energy. The verification of exhibition of production of

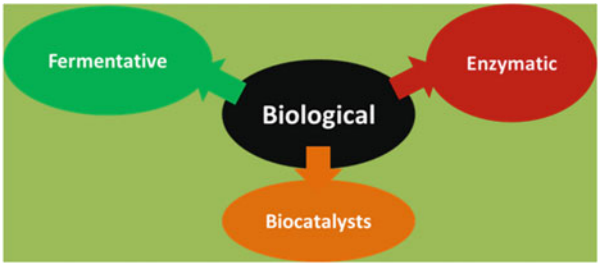

Fig. 7.2 Classification of hydrogen production by biological methods

hydrogen at admissible amount under open-air environment will be significant in this field. Even small-scale production of hydrogen by photo-biological processes may contribute in the future, not only in the production of renewable energy but also to save the surroundings by increasing production of BOD in wastewater which contains organic matters (Hidehiro et al. 2013). Sunlight, catalysts, a biological component, and an engineered system are required in the process of production of hydrogen. Few specific organisms, such as bacteria and algae, generates H_2 as a by-product during their metabolic process. These processes usually occurs in water, therefore water is biologically split into its different elements (Richa et al. 2004). Presently, this technique is still in the stage of R & D because the theoretical efficiency of conversion of sunlight is estimated only up to 24%. Biological processes of production of hydrogen are performed at ambient pressure and temperatures; therefore it is required a smaller amount of energy. These processes are ecofriendly and also open new doors for the utilization of indestructible resources of renewable energy (Richa et al. 2004). Biological hydrogen production by using microorganisms (Hallenbeck et al. 2012; Singh and Wahid 2015; Kadier et al. 2016) is a new area which involves photo and dark fermentation, biophotolysis (direct and indirect) of H_2O, and bioelectrolysis of organic stuff by bacteria. In biophotolysis, specific photosynthetic microbes like cyanobacteria and green algae generates H_2 by utilizing and splitting of water by their own natural metabolic system using sunlight (Hallenbeck et al. 2012; Martin and Frymier 2017; Khetkorn et al. 2017). The different types of biological hydrogen production processes shown in Fig. 7.2.

7.3.1 Fermentation

Organic matters store good amount of biochemical energy, which can be utilized by organisms to extract hydrogen with or without light; dark fermentation is a process of alteration of this stored biochemical energy into other energy forms without use of sunlight. Bioreactors which are utilized for dark fermentation are very simple and inexpensive than photo-fermentation because does not require solar contribution in the processing (Ibrahim and Canan 2015). Production of hydrogen by dark fermentation process has various benefits like skill to generate H_2 from organic wastes, ability to control contamination, and efficiency to stabilize biological wastes. Production of hydrogen from organic wastes has a potential to reduce the costs of hydrogen production as it is a cheap and easily available raw material. Koutrouli et al. (2009) conducted a study on hydrogen production from water diluted olive oil. The organic acids were further fermented by using photo-heterotrophic bacteria to generate hydrogen and carbon dioxide by a process which is known as light fermentation. A study was conducted by Argun et al. (2008) on mixed fermentation (dark and photo) they were reported that the improved H_2 formation yield was obtained from carbohydrates sources. A fermentation study by Marika et al. (2014) regarding H_2 production from hydrolyzates using dark fermentation was carried, and H_2 production was optimized. Currently, a large amount of the studies are being conducted on production of H_2 by fermentation especially from lignocellulosic hydrolyzates in batch mode. Based on the results obtained from these studies, the optimal pH (5.5–7) and hydrolyzates concentration (10–20 g per liter) is suitable for H_2 fermentation.

7.3.2 Enzymes and Biocatalyst

Enzymes that are either hydrogenase (H_2ase) or nitrogenase (N_2ase) are used as catalyzers for the hydrogen production by phototrophic organisms (Ghirardi et al. 2007).

7.3.2.1 Hydrogenases

The viability of photo-producing hydrogen was verified a longtime ago using an artificial system composed of hydrogenase from chloroplasts, *Clostridium*, and Fd from spinach (Benemann and Weare 1974). Different aspects of hydrogenase have been reviewed comprehensively (Ghirardi et al. 2007; Cammack et al. 2001; Vincent et al. 2007). Hydrogenase is the enzyme that catalyzes the following simple reaction:

$$2H^+ + 2e- \leftrightarrow H^2 \qquad (7.3)$$

Hydrogenases are basically metalloenzymes, which are categorized into two most important classes on the basis of their metallic co-factor as their vigorous centers: [Fe-Fe]-hydrogenase and [Ni-Fe]-hydrogenase. Due to their physiological functions, hydrogenases can be again divided into bidirectional hydrogenases and uptake hydrogenases. Bidirectional hydrogenases are found in the phototrophic organisms, and it also alienated into two groups: the first one is [Fe-Fe]-hydrogenase present in green algae and the second one is [Ni-Fe]-hydrogenase carried by cyanobacteria and photosynthetic microbes with NAD(P) H/NAD (P) + as a reaction partner. These two groups of bidirectional hydrogenases originate from different phylogenetic. The [Ni-Fe]-hydrogenase composes a large number of hydrogenases. Cyanobacteria may also contain [Ni-Fe]-hydrogenases in which both bidirectional and uptake hydrogenase enzymes may be present. It is recommended that both flavodoxins and ferredoxins could work as e-donors for the hydrogenase found in cyanobacteria (Gutekunst et al. 2014; Khanna and Lindblad 2015).

7.3.2.2 Nitrogenase

Nitrogenase is an enzyme required for the nitrogen fixation and is found only in few prokaryotes such as green sulfur bacteria, PNS bacteria, few strains of cyanobacteria; unidirectional production of hydrogen is catalyzed by nitrogenase enzyme during nitrogen fixation with the help of substantial energy (ATP) (Seefeldt et al. 2009). Therefore, nitrogenase is considered as a candidate enzyme for production of hydrogen by photo-biological process. Nitrogenase is capable of catalyzing the reactions during the nitrogen fixation process under optimal conditions for:

$$N_2 + 8e - +8H + +16ATP \rightarrow H_2 + 2NH_3 + 16(ADP + Pi) \tag{7.4}$$

Whereas, in the absence of N_2 (e.g., under Ar), all $e -$ s are allocated to hydrogen production:

$$2e - +2H^+ + 4ATP \rightarrow H2 + 4(ADP + Pi) \tag{7.5}$$

Production of hydrogen (unidirectional production) through photo-biological process is catalyzed by nitrogenase, and besides that the cells missing in hydrogenase activity can collect hydrogen for longer period even in the existence of oxygen. Molybdenum (Mo-nitrogenase) is found in the well-characterized, typical, and most widely distributed nitrogenase, under a condition of combined N_2 deprivation in the existence of Mo. The nitrogenase reaction is catalyzed by the interface of two separate proteins (e.g., nitrogenase). The homodimeric Fe protein, also known as dinitrogenase reductase, contains a single group per dimer that accepts e^- from Fdred or Fldred, and in turn donates the e^- to the Mo-Fe protein in an ATP-dependent manner requiring 2 ATPs. The Mo-Fe protein also known as "dinitrogenase" contains a P-cluster and the Fe-Mo co-factor that binds and reduces nitrogen and H+ (Lancaster et al. 2011; Einsle et al. 2002).

7.4 Biomass Production of Hydrogen

Biomass resources are categorized into four main groups, and all the groups have the possibility to be utilized as feed material for hydrogen manufacture. The first group is energy crops, which are especially grown because of energy substance, e.g., soybeans, maize, poplar and green algae. The second group consists of agricultural waste, in which animal and crop wastes are included. The third group is forestry waste, in which waste of harvested trees and clearing land is incorporated, whereas municipal and industrial waste comes under the fourth group (Ni et al. 2006). Nowadays, algal sp. (especially green algae) are highly considered as a favorable third generation raw material due to its carbohydrate content and high growth rate (Lin et al. 2017), which has gained more attention. Generally, raw biogas is a composed of 35–75% CH_4, and 25–55%CO_2. Siloxanes, H_2, N_2, O_2, H_2S, H_2O, CO, NH_3, some aromatics, and dust particles are also the other minor components of biogas (Lin et al. 2017). The process for the conversion of waste into energy has

Fig. 7.3 Process flow diagram of biomass hydrogen production (Lv et al. 2008)

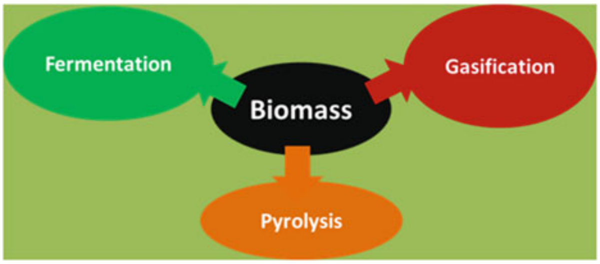

Fig. 7.4 Classification of hydrogen production by biomass methods

gained more attention due to its potential to become a main hydrogen source. It is predicted that around $1.08 * 10^8$ GJ of biomaterial (vegetable waste) is generated annually (Ni et al. 2006). This resource is from a totally waste stream, and use of this waste to convert into energy does not require extra space for processing it (Yuchen et al. 2018; Yildiz et al. 2009). Feedstock (biomass) is available from several sources like woody crops, civic solid wastes, residues from crop, short rotation crop waste, animal wastes, saw-dust, aquatic waste, short, waste from paper industry, maize, leaves of the plants, and much more (Levin et al. 2007; Asadullah et al. 2002; Bagchi et al. 2006). For the generation of hydrogen, by gasification, pyrolysis, conversion to liquid fuels by supercritical extraction, liquefaction, hydrolysis, etc. are the current biomass technologies which are followed in some cases like reformation and biohydrogen production (Demirbas 2006). The biomass hydrogen production process flow is shown in Fig. 7.3.

Biomass is a renewable and attractive alternative to fossil fuel raw materials because it has the potential to produce zero net CO_2 impact. Unfortunately, compared to natural gases which contain almost 25% hydrogen, only 6 ± 6.5% hydrogen content is available in biomass. Due to this fact, on the basis of cost, generation of H_2 by using biogasification or process of water-gas shift is not found suitable to emulate with the fully developed steam-based technologies for reforming of natural gas. However, a unified route by which a part of the biomass is used to manufacture costly items or chemicals and only remaining fractions are used to generate $H_{2,}$ may be an economically feasible choice (Richa et al. 2004). The different types of biomass hydrogen production processes shown in Fig. 7.4.

7.4.1 Pyrolysis

Pyrolysis (thermal decomposition) and gasification processes using biomass can be utilized to produce hydrogen. Methanol, coke, and other gases are yielded by the pyrolysis reactions. In the presence of air, gasification reaction generates a stream of 20% CO, 20% H_2, 5% CH_4, 45% N_2, and 10% carbon dioxide, which can be further processed to produce extra hydrogen from CO by treating it with steam (Richa et al. 2004).

In the first step, by using gasifying process biomass is transformed into a gas at high heat, which generates hydrogen rich vapor. In the second stage, gas is condensed in pyrolysis oils and then it is steamed to generate hydrogen. By this method 12 ± 17% of H_2 by Wt of the dry biomass is formed as a finishing product (Richa et al. 2004). Different types of raw materials like, plant material, wood chips, municipal wastes, saw dust, and agricultural wastes and leaves of plants can be utilized for this process. A wood fuel capitulate a typical mass with a typical composition of 45% O, 48% C, and 6% hydrogen along with the trail of S, N, and minerals. The chemical reaction is:

$$CH_{1.5}O_{0.7} + 0.3\ H_2O\ (g) = CO + 1.05\ H_2 \tag{7.6}$$

$$CO + H_2O = CO_2 + H_2 \tag{7.7}$$

Two stages method are described by Czernik et al. (2000) to produce hydrogen and carbon dioxide from bio-oil. The fast pyrolysis process is a thermal degradation in which a high heat transfer rate is required to produce the biomass and a short time for vapor residence in reaction zone. In 1990s, a number of fast pyrolysis techniques achieved their commercial status. Compared to conventional water-gas shift techniques, pyrolysis/steam reforming concept has various advantages. Fast pyrolysis technique is a thermo-catalytic conversion process, which can be described by its quick quenching, rapid heating rates, and O_2 exclusion capacity. Fast pyrolysis generates different precious chemical intermediates and gas from the biomass (Zhang 2012). Typical features and properties of crude bio-oil derived from woods are also examined. High moisture content in oil comes from the high moisture feed and reaction water, which cannot be separated easily. The values moisture/water may range between 15% and 35%. Bio-oil production is reported about 25% by weight with high heat value (18 MJ/kg) along with water content which cannot be separated (Bridgewater 2004). Pokorna et al. (2009) studied the production of pyrolysis oil produced from sewage sludge of three types. The flash pyrolysis was conducted at 500 °C, and the maximum oil production was reported to be 43.1%, and it was also reported that the water content in bio-oils was relatively low (10.3–17.0%), which was obtained from secondary sludge.

7.4.2 Biomass Gasification

Gasification technique is generally used with coal and biomass, and it is utilized in many commercial processes. It is a type of pyrolysis, which depends on partial oxidation of raw materials into a mixture of H_2, CO, CH_4, and nitrogen, nitrogen is known as a producer gas (Demirbas 2006). Various processes are suggested to reduce the percentage of tar produced in the reactor during gasification process. For instance, the application of an $Rh/CeO_2/M$ catalyst in the process of gasification is found suitable to minimize the formation of tar (Asadullah et al. 2002). From biomass, methane can be obtained as a natural gas. Actually, during fermentation or decay of organic matter, methane is produced naturally. Landfills with organic waste are the places, from where a good amount of methane can be collected. Methane is commercial used for heating/cooking and for electricity generation (Fayaz et al. 2012). Biomass gasification is also a fully developed technique for the production of syngas, but it is highly expensive due to requirement of high energy and inherent energy losses. In this process of gasification incomplete combustion of biomass is reported, which produce gases like CO, H_2, and CH_4 that are further combustible. Mixture of these combustible gases can be consumed to operate combustion engines (compression or spark ignition) and this mixture is also called as producer gas. The gasification used to produce producer gas occurs at 1000 °C in gasifier resulting in a partial combustion of biomass (Goswami 1986). According to Ahmed and Gupta (2009), the main features of biomass gasification is to produce gaseous products from steam gasification. The findings of steam gasification were compared with pyrolysis process. They conducted this study at a temperature ranges between 600 °C and 1000 °C. Florin and Harris (Florin and Harris 2008) conducted an investigation on biomass steam gasification as a promising, renewable and sustainable process for the production of H_2; they used CaO as a sorbent to capture CO_2. They reported that the maximum obtained H_2 concentrations without CO_2 capture was between 40% and 50% and when CaO was used to remove CO_2 from the gas produced, H_2 concentration was increased (40–80% on dry basis).

7.5 Water-Gas Shift Reaction (WGSR)

The WGSR is a vital industrial technique, which is used for the manufacturing of H_2 in which CO reacts with H_2O vapor as shown in the Eq. (7.4) From the reaction which is shown in the equation, it is clear that steam or H_2O can be considered as a raw material for the production of hydrogen. Italian Felice Fontana discovered this catalytic reaction in 1780. The high-temperature catalyst of oxides of Fe and Cr at 400–500 °C reduces CO concentration around 2–5%. The low-temperature catalyst such as oxide, Zn, alumina, and Cu is used at between 200 °C and 400 °C to reduce the 1% concentration of CO. Copper-ceria catalysts with copper loading in the range of 20–90% of Cu were prepared by the method of co-precipitation, and their performance was tested for WGSR in medium condition at 150–360 °C (Gunawardana et al. 2009). In the WGSR, catalysts were examined at 250 °C under atmospheric pressure and oxide systems was ranked as Cu–Cr > Cu–Fe> > Zn–Al > Cu–Co. After addition of small amounts of Cr_2O_3 in the surface of copper, a significant improvement in the activity of skeletal Cu catalysts for the WGSR were achieved. (Huang et al. 2004). Oxidation of the carbon monoxide to carbon dioxide was determined to follow the WGSR shown in Eq. (7.7) by using enzymes to catalyze the process. As it occurs at lower temperature and atmospheric pressure, thermodynamics favors an elevated conversion of CO to CO_2 and H_2 (Levin et al. 2004). This rate of conversion is relatively higher than the other biological processes, but it require dark condition and CO source (Levin et al. 2004).

7.6 Hydrogen in the Future and Economic Perspectives

Presently, around 22% of energy produced globally is utilized as electricity, rest 78% is used as fuel. In 2018, 81.4% of the global energy supply was totally depended on fossil fuels; apart from this situation 9.7%, 4.9%, 2.5%, and 1.5% energy supply was from biofuels, waste, nuclear energy, hydropower, and from other sources respectively (Taylor et al. 2017). While, shift towards the renewable energy is a better option, yet the contribution of renewable energy into global energy supply is very low (13.7%) (Taylor et al. 2017). At the starting of twentieth century, the justified consumption of energy will be the key in the sustainable development for both type developed and developing countries (Marechal et al. 2005). At present, fossil fuels are prominently used as primary energy sources, around 80% of global energy demand is fulfilled by using coal, crude oil, and natural gas (Evans 2007). Presently, approximately 40% of total global electricity need is fulfilled by using coal only, and it is predicted that it will remain as a main source for electricity generation for several decades because of its lower cost and huge availability. The largest part of this H_2 is produced by natural gas reforming with 70–75% efficiency or from coal gasification with 45–65% efficacy (Acar and Dincer 2014; Levin and Chahine 2010; Holladay et al. 2009) and has high CO_2 emissions. CO which is a major gas among the greenhouse gases and responsible for global warning; it is produced by combustion of fossil fuels and in other industrial activities like production of cement, refining of oils, and sweetening of natural gas (Keskin and Emiroglu 2010). Around 20% of global CO_2 emission is generated by the transport system only. Approximately 60% of total globally produced oil is utilized by transport sector (Balat and Balat 2009a, b). By reason of the increased mobilization of human beings and movement of goods from one place to another, this sector consumes more than 30% of energy used by Europeans (EU), and the demand is already increasing (Malca and Freire 2006). Energy requirement is increasing at a rapid rate and will grow continuously; especially in developing countries where more energy is required for economic growth to elevate the people from poverty, as petroleum fuels reservoirs are very limited and centered in certain regions of the world. Petroleum fuel sources are on the verge of reaching their peak production and due to the present rate of consumption, it is projected that they will be exhausted in the next 50 years (Sheehan et al. 1998). As supplies of fossil fuels dwindle and concerns about continued influences of additional carbon dioxide to the atmosphere support arise, there is an increasing need for new sources of energy from renewable carbon-neutral sources with minimal harmful environmental effect (Lovley 2006). These present technologies are expected to supply the near-term hydrogen market as well. Renewable energy is likely to play a major role in the global future energy establishment. Hydrogen and fuel cells are often considered as a key technology for future ecological energy supply. Renewable segments of 36% (2025) and 69% (2050) on the total energy demand will lead to hydrogen segments of 11% in 2025 and 34% in 2050 (Rohland et al. 1992).

7.7 Summary

There is a lot of scope for research and several developments in this field; many research studies and right step in this direction can be expected in the coming years. Presently, H_2 is mainly produced from natural gas using steam methane reforming process; although this process may be suitable to sustain economy of hydrogen for a short period, it also represents a minimum reduction in vehicle emissions. Hydrogen could be produced from biomass, but further development in this technique is urgently required. Production of hydrogen from economical and renewable resources like solar energy and biomass by using various methods like photo fermentation, direct and indirect photolysis, and dark-fermentation, will be more suitable. The production of biohydrogen from biological resources is already an economically and competitive way today. Use of traditional methods for production of H_2 is clearly not a sustainable way. Biohydrogen production using wind, biomass, and solar energy (renewable primary energy sources) is a good way for gradual replacement of fossil fuels. On the basis of available literature and readings, it can be concluded that the use of renewable biomass as a raw material for hydrogen production has received considerable regard in recent years as a future fuel.

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Bacterial Hydrogen Production: Prospects and Challenges

8

Ramchander Merugu, Ragini Gothalwal, S. Girisham, and S. M. Reddy

Abstract

Hydrogen is extensively thought of as the most hopeful fuel of the future. At present, most of it is generated from the nonrenewable fuels. Biological hydrogen production has several advantages over hydrogen production by other processes. Biological hydrogen production requires the use of a simple solar reactor such as a transparent closed box, with low energy requirements while electrochemical hydrogen production via solar-battery-based water splitting requires high energy. Microbial hydrogen production especially bacterial hydrogen production by mesophilic, thermophilic and phototrophic production has been described in this chapter.

Keywords

Hydrogen · Mesophilic · Thermophilic · Phototrophic bacteria · Bioreactors · Prospects

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R. Merugu (✉)
Department of Biochemistry, Mahatma Gandhi University, Nalgonda, India

Department of Biotechnology, Barkatullah University, Bhopal, Madhya Pradesh, India

R. Gothalwal
Department of Biotechnology, Barkatullah University, Bhopal, Madhya Pradesh, India

S. Girisham · S. M. Reddy
Department of Microbiology, Kakatiya University, Warangal, India

M. Srivastava et al. (eds.), *Bioenergy Research: Biomass Waste to Energy*, Clean Energy Production Technologies, https://doi.org/10.1007/978-981-16-1862-8_8

8.1 Introduction

Renewable energy sources have received great attention during the last few decades. These include solar power, wind power, hydroelectricity, and biomass which have one or other setbacks. Nowadays, hydrogen is thought as a great hope for future fuel as it is renewable, cheaper, transportable, and ecofriendly. It "has high energy content for per unit mass of any known fuel is easily convertible to electricity by fuel cells and on combustion it gives water as the only byproduct." Hydrogen is an important raw material used as feedstock in the chemical industries, metallurgical industries and assumes greater importance once cheap hydrogen is available. Hydrogen can be used in situation where transfer of energy as electricity is ineffective. At present, hydrogen is generated through steam reforming of methane (Sgobbi et al. 2016). In the midst of many methods of hydrogen generation, biohydrogen generation has garnered lot of interest (Trchounian et al. 2017). It does not create greenhouse gases upon burning. It has a greater probability use as an energy source for electrical storage and production of fuel cells.

Hydrogen is commercially produced by electrochemical and thermochemical processes. It may also be produced biologically. Biological hydrogen production has several advantages over hydrogen production by other processes. Biological hydrogen production requires the use of a simple solar reactor such as a transparent closed box, with low energy requirements while electrochemical hydrogen production via solar-battery-based water splitting requires high energy. Low conversion efficiencies of biological systems can be compensated by low energy requirements and reduced initial investment costs. Biological methods are known to be less energy intensive than chemical or electrochemical processes since they can be carried out at ambient temperature and pressure. Biological hydrogen production can be generated by the transfer of electrons from water to protons by a series of oxidoreduction reactions. Biological hydrogen production represents a potentially revolutionary technology to harvest solar energy (Ghirardi et al. 2005). The advancements in biological hydrogen production processes were excellently reviewed by Levin et al. (2004) and Das and Veziroglu (2008).

8.2 Microbial Hydrogen Production

Several microbes have enzymes, known as hydrogenases, that can oxidize H_2 to protons and electrons or reduce protons to liberate hydrogen (Vignais et al. 2001). Gorman (2002) has stated that a large amount of the biohydrogen is derived from microbes mediated fermentation processes. These microbes convert organic matter to carbon dioxide and hydrogen. Hydrogen producing bacteria can even grow autotrophically with hydrogen gas as the sole reducing power and energy substrate. In these bacteria, oxygen serves as a terminal electron acceptor leading to water as the end product (Belaich et al. 1990). Mark and Lynne (2006) investigated the process of hydrogen generation with electron donor as glucose. Bagai and Madamwar (1999) immobilized *Halobacterium halobium*, *Phormidium* *valderianum*, and *Escherichia coli* and studied them for their hydrogen generating abilities. Bagai and Madamwar (1998) studied the influence of nitrogen in these immobilized cells and concluded that it helped in enhancing hydrogen production. Hydrogen generation using *Halobacterium halobium* MMT22 and *Escherichia coli* was studied in a chemostat by Khan and Bhatt (1997). Bisaillon et al. (2006) studied the effect of limitation of phosphate and sulphate on hydrogen production by *Escherichia coli* with glucose. It was established that in *E. coli*, the enzymes [NiFe] hydrogenase-1 and [NiFe] hydrogenase-2 were involved in hydrogen oxidation (Dubini et al. 2002). Lee et al. (2002) found that phototrophic bacteria with anaerobic bacteria were the best for utilizing carbohydrate. *R. gelatinosus* CBS produced hydrogen when carbon monoxide gas was used as substrate. Maness and Weaver (2002) suggested that carbon monoxide dehydrogenase along with hydrogenase enzymes was involved in the carbon monoxide oxidation pathway. Kondo et al. (2002) reported hydrogen generation by *R. sphaeroides* RV and its mutant. The applying of blue cellophane film on *R. sphaeroides* RV growth did not show any difference in hydrogen generation when compared to its growth under normal conditions (Ko and Noike 2002). Akkerman et al. (2002) proposed that the main drawback of hydrogen generation in phototrophic bacteria was the susceptibility to oxygen. Immobilization of *H. halobium* and chloroplasts organelles in reverse micelles produced optimal amount of hydrogen (Singh et al. 1999). A review of occurrence of hydrogen metabolism in microorganisms discloses that the ability to evolve or utilize hydrogen is not a restricted metabolic pathway but rather found in large number of organisms of widely different physiological types. A number of chemotrophic, thermophilic and phototrophic organisms, as well as artificially reconstituted systems such as chloroplast, bacterial hydrogenase, and methyl viologen, can be used for hydrogen production. Chemotrophic bacteria such as *E. coli*, *Clostridium butyricum*, *Clostridium pasteurianum* (Aoyama et al. 1997), *Citrobacter freundii* (Zhang et al. 2005), *Enterobacter aerogenes* IIT 08 (Nath and Das 2004), *Enterobacter aerogenes* (Rachman et al. 1997), (*Clostridium butyricum* JM1 (Jo et al. 2008), *Bacillus coagulans* IIT BTS1 (Kotay and Das 2008), *Enterobactercloacae* (Ito et al. 2005), and *Clostridium paraputrificum* (Marimoto et al. 2005) were reported to produce hydrogen. High yield of hydrogen production has been reported by thermophilic bacteria such as *Thermotoga maritima*, *T. neapolitana*, *T.elfii* (Van Neil et al. 2002), *Thermoanaerobacter tengcongenesis* (Soboh et al. 2004), and *Caldicellulosiruptor saccharolyticus* (De Vrije et al. 2007). Green algae such as *Scenedesmus* (Florin et al. 2001), *Chlorella* (Chader 2008), and *Platymonas subcordiformis* (Guan et al. 2004) have the potential for hydrogen production from water. Light-dependent hydrogen production by the cyanobacteria such as *Synechococcus* sp. and *S. cedrorum* has been demonstrated by Ramana et al. (1990). Maximum hydrogen production by *Anacystis* was observed in dairy and sugarcane wastewater (Thangaraj and Kulandaivelu 1994). Photoassimilation of fructose to hydrogen and carbon dioxide by *Anabaena variabilis* was reported by Reddy et al. (1996). Ohta et al. (1981) reported that a salinity of 30% is optimum for hydrogen production by marine stains. Sangeeta Dawar et al. (1999) demonstrated the production of hydrogen by cyanobacteria such as *Nostoc* sp. ARM411. Anoxygenic phototrophic bacteria such as *C. vinosum* (Rajani 1992); *Rhodobacter*, *Rhodopseudomonas*, *Rps. feacalis* RLD53 (Ren et al. 2007); *Rc. tenius*, *Rsp. rubrum*, *Rps. plasutris*, *Rc. gelatinosus* (Das and Veziroglu 2008); *Rhodobactercapsulatus* B10 (Tatyana et al. 2008); *Rhodobacter* sp., *Rhodopseudomonas gelatinosus* and *Rhodospirillum rubrum* (Srinivas 2001) have been investigated for this purpose. Mixed cultures of many bacteria are also being used for the production of hydrogen (Wang and Wan 2008). Cultures which are employed along with phototrophic purple non-sulfur bacteria include *Clostridium butyricum* (Fang et al. 2006), *Lactobacillus* (Asada et al. 2006), and *Enterobactercloace* (Nath and Das 2009). *Methanogenic archaea* and homoacetogenic bacteria are H_2 consuming bacteria. Among the methanogenic bacteria *Methanosaeta* sp., *Methanosarcina* sp., and *Methanobacteria* sp. (Abbassi-Guendouz et al. 2013; De Vrieze et al. 2020) while homoacetogenic bacteria such as *Clostridium* sp. (Ryan et al. 2008), *Acetobacterium*, *Butyribacterium*, *Peptostreptococcus*, and *Sporomusa* are mostly found in bioreactors (Saady 2013) are mostly found in bioreactors. Santos et al. (2014) and Sivagurunathan et al. (2016) have reported that propionate producers consume hydrogen for their metabolism and were found to be prevailing in reactors operating at low HRT and high OLR. Bundhoo and Mohee (2016) stated that nitrate or sulfate reducers are the generally observed hydrogen consumers. Lactic acid bacteria present in bioreactors (Etchebehere et al. 2016) race with H_2 producers by transforming carbohydrates to lactate (Makarova et al. 2006). Fujita et al. (2010) reported the presence of spore-forming *Sporolactobacillus* sp. in dark fermentation, while Etchebehere et al. (2016) reported the presence of *Lactobacillus* sp. Sinbuathong and Sillapacharoenkul (2020) have studied dark fermentation for biohydrogen production using starch factory wastewater. Jayabalan et al. (2020a) used $NiCo_2O_4$-graphene nanocomposites in sugar industry wastewater fed microbial electrolysis cell for increasing biohydrogen generation. Biohydrogen production through the employment of succinate-rich fermentation wastewater was investigated by Hanipa et al. (2019). The effect of metal oxide/graphenenanocomposite catalysts in microbial electrolysis cell for promoting hydrogen production from sugar industry wastewater was studied by Jayabalan et al. (2020b). Enhancement of hydrogen production from brewery wastewater was studied by Arantes et al. (2019a). The strategies to improve the biohydrogen production from cassava wastewater in fixed-bed reactors were also developed (Corbari et al. 2019). Ilgi and Onur (2020) developed strategies for enhancing hydrogen production using acid hydrolyzed wastewater treatment sludge. Koroglu et al. (2019) developed an integrated system for biogas purification during acidogenic biohydrogen production from dairy wastewater. García and Cammarota (2019) studied biohydrogen production from pretreated sludge and biodiesel wastewater. The enhancement of hydrogen generation using pretreated brewery wastewater containing banana peels waste was studied by Hassan et al. (2018). Influence of temperature and pH on biohydrogen production using Lactate containing wastewater was studied by Ziara et al. (2019).

8.3 Mesophilic Bacterial Hydrogen Production

Dark fermentation is an acidogenic breakdown of carbohydrate containing substrates. Dark fermentation has garnered larger amounts of interest due to high hydrogen making rates and flexibility of possible substrates (Łukajtis et al. 2018). It is also observed that hydrogen production yield of 1–2 mol H_2/mol-hexose is obtained with mesophiles (Van Niel et al. 2002). Hydrogen yields can be improved by increasing hydrogen production through acetate end product reaction and by decreasing or preventing butyrate, ethanol, and propionate product reaction. Morimoto et al. (2004) and Atif et al. (2005) have used anaerobic microbes from palm oil mill wastewater treatment plant as inoculate for hydrogen production from glucose in batch cultivation. Vijayaraghavan and Ahmad (2006) have used mixed culture for hydrogen production from POME under mesophilic conditions with COD reduction. Bacteria that produce hydrogen by fermentation may be cultured as pure or mixed cultures. Hydrogen production starts with the anaerobic metabolism of pyruvate, either by pyruvate-formatelyase or pyruvate-ferredoxinoxidoreductase enzyme systems to produce acetyl CoA. ATP is produced from acetyl CoA, which are converted into either formate or reduced ferredoxin [Fd (red)], and this results in hydrogen formation. The enteric bacteria generate hydrogen from formate, while strict anaerobes generate hydrogen from Fd (red) (Hallenbeck and Benemann 2002). Lee and Zinder (1988) observed that hydrogen generation from carbohydrates was more complex than methane generation. Blamey et al. (1999) have reported hydrogen generation from *Thermococcus*, *Pyrococcus*, and *Eubacterium*. Fermentative hydrogen generation has also been studied for many fermentative bacteria (Kumar and Das 2000). Tanisho et al. (1987) found that the *Enterobacter aerogenes* E82005 bacterium produced hydrogen using glucose.

Dinesh et al. (2018) reported that the production of a theoretical maximum of 4 mol of H_2 per mol of hexose sugar. Production of hydrogen during continuous hydrogen fermentation in immobilized cell systems tested using *R. sphaeroides* (Zhu et al. 1999), *E. cloacae* (Kumar and Das 2001), and *E. aerogenes* (Rachman et al. 1998) was reported. Zhu et al. (1999) studied the hydrogen-making ability of phototrophic and heterotrophic anaerobic bacteria with tofu containing wastewater. Yu et al. (2002) investigated hydrogen generation from the anaerobic acidogenesis of a high-strength rice winery wastewater. Pushpa et al. (2005) reported hydrogen production from bagasse using *Bacillus licheniformis*, *Clostridium pasteurianum*, and *Enterobacter cloacae*. Jackfruit peel was treated with cow dung microflora for hydrogen generation (Vijayaraghavan et al. 2006). Gomez-Flores et al. (2017) reported significant amounts of hydrogen generation with cellulose as a substrate when *Clostridium termitidis* and *Clostridium beijerinckii* co-cultures were used. Zhang et al. (2016) reported hydrogen production from *C. sartagoforme* FZ11 using microcrystalline cellulose. The process of dark fermentation process can be done at thermophilic or mesophilic conditions. Mesophilic processes are less energy intensive as they are operated at lower temperatures. Ren et al. (2007) and Bao et al. (2016) have reported maximum hydrogen yield of 2.09 mol H_2/mol-hexose under batch conditions. A mesophilic bacterial consortium was investigated by Zagrodnik and Seifert (2020) for hydrogen generation using cellulose and starch by pretreatment of substrate at 100 °C (20 min). Carver et al. (2012) reported 0.35 mol H_2/mol-hexose by mixed microbial cultures under thermophilic fermentation using microcrystalline cellulose. Hydrogen production by dark fermentative method is seen in obligate or facultative anaerobic microorganisms. These organisms survive at different temperatures (from 15 °C to 65 °C) (Lee et al. 2011) and can be seen in landfill leachate (Wong et al. 2014), sewage sludge (Reilly et al. 2014), compost (Song et al. 2013), digested sludge (Bakonyi et al. 2014), and hot spring cultures (Koskinen et al. 2008). In dark fermentation, fermentative microorganisms generate hydrogen during the process of their metabolism (Li and Fang 2007). The most common metabolic pathway for generation of hydrogen by mesophilic and thermophilic bacteria is Glycolysis/Embden-Meyerhoff pathway (Lee et al. 2011; Vipotnik et al. 2016). The fermentation hydrogen process can be inhibited by accumulated hydrogen (Beckers et al. 2015). Nicotinamide adenine dinucleotide (NADH) is partially or totally utilized for the generation of volatile fatty acids or alcohols, and the remaining NADH and ferredoxin is used for hydrogen generation (Saady 2013). Hydrogen-producing bacteria are strict anaerobes belonging to the family of Clostridiaceae. *Clostridium* sp. are the most widely studied mesophilic fermentative bacteria which are found to be dominating in different cultural conditions (Baghchehsaraee et al. 2008; Mäkinen et al. 2012; Jeong et al. 2013; Si et al. 2015; Chatellard et al. 2016). *Clostridium butyricum* and *C. acetobutylicum* produce H_2 via acetate and butyrate pathway with optimum hydrogen production conditions such as around pH 5.0 (Masset et al. 2010). *Bacillus amyloliquefaciens* FS2011, a hydrogen-producing strain isolated from an effluent of biohydrogen production reactor, was found to utilize a variety of carbon and nitrogen sources to generate hydrogen at pH range between 5.29 and 7.38 (Song et al. 2013). Rambabu et al. (2019) investigated the production of hydrogen from *Clostridium thermocellum* ATCC 27405 from date seeds. Murugan et al. (2020) investigated biohydrogen production by *Acinetobacter junii* AH4 utilizing various industry wastewaters. Nano-ferrihydrite was used to enhance biohydrogen production by *Clostridium* (Zhang et al. 2020). Biohydrogen production from fruit waste by *Clostidium* strain BOH3 was reported by Mahato et al. (2020). Guerrero et al. (2020) have reported biohydrogen production by a degenerated strain of *Clostridium acetobutylicum* ATCC 824. Influence of silver nanoparticles (AgNPs) and henna on hydrogen produced by *Clostridium beijerinckii* (KTCC1737) was investigated by Khan et al. (2020). Ramu et al. (2020) used rice mill wastewater for studying dark fermentative hydrogen production.

8.4 Thermophilic Bacterial Hydrogen Production

High temperatures have many advantages such as lower pathogen survival rate (Hasyim et al. 2011). H_2 was produced from sugarcane vinasse at 55 °C which was inhibited by higher concentrations of volatile fatty acids (Santos et al. 2014). Claassen et al. (1999) reported hydrogen generation from carbohydrate using hyperthermophiles and anaerobic-trickling filter (Van Groenestijn et al. 2002). Teplyakov et al. (2002) studied the biohydrogen production from *Rhodobacter capsulatus* and *Thermohydrogenium kirishis* using glucose. *Thermotoga elfii*, when cultured at higher temperatures, generate hydrogen using glucose (Claassen et al. 1999). Van Niel et al. (2002) reported hydrogen generation using sugar as substrate for *C. saccharolyticus* and *T. elfii*. *Thermotogales* sp. produced hydrogen between 25% and 30% oxygen levels and was shown to withstand oxygen (Ooteghem 2001). Higher concentrations of hydrogen inhibited hydrogen production in lactose growing *Clostridium thermolacticum*. Claassen et al. (1999) investigated hydrogen production using agro-industrial wastes from thermophilic bacteria. In comparison to mesophiles, thermophiles are more promising for hydrogen generation, as they are more versatile in nature and can use variety of substrates. Thong et al. (2008) have observed higher hydrogen generation rates under thermophilic conditions when compared to mesophilic conditions. Hence thermophilic bacterial hydrogen production is more feasible and is economical when compared to mesophilic production. Thong et al. reported *Thermoanaerobacterium*, *Clostridium*, *Caldicellulosiruptor,* and *Thermoanaerobacter* as competent hydrogen gas generators under thermophilic conditions. Ottaviano et al. (2017) have stated that microorganisms belonging to the genus *Thermoanaerobacterium* are the widely investigated thermophilic hydrogen gas producers. Karadag and Puhakka (2010) observed that *Thermoanaerobacterium* sp. are the most prevalent bacteria in a dark fermentative bioreactor, when the temperature was increased from 37–45 °C to 50–60 °C. Many hyperthermophilic microorganisms, including *Caloramator* sp. (Ciranna et al. 2014), *Thermotoga* sp. (D'Ippolito et al. 2010; Nguyen et al. 2010), *Thermoanaerobacter* sp. (Vipotnik et al. 2016), *Caldicellulosiruptor* sp. (Zeidan and Van Niel 2010), and *Thermococcus* sp. (Kanai et al. 2005) are studied for hydrogen generation as pure cultures. Apart from this, use of mixed cultures would be advantageous due to lower cost. In a study with mixed cultures, Hasyim et al. (2011) and Gadow et al. (2013) have observed *Thermoanaerobacter* sp. and *Thermoanaerobacterium* sp. as dominant microorganisms when the temperature range was above 70 °C with glucose and cellulose as substrates with sewage sludge as inoculum. Qiu et al. (2011) reported the presence of *Coprothermobacter* sp., *Caldicellulosiruptor* sp., *Caldanaerobacter* sp., *Thermotoga* sp., and *Thermobrachium* sp., from cow manure digestate during dark fermentative H_2 generation from ethanol distillery wastewater at a temperature between 65 °C and 80 °C. Anaerobic bacteria from anaerobic sludge of palm oil mill effluent (POME) treatment plant were used for generation of hydrogen (Sompong et al. 2011**).** Temperature of 60 °C and pH of 5.5 were found to be optimal by response surface methodology which gave a maximum hydrogen production. Phylogenetic analysis has shown that the bacteria were related to *Thermoanaerobacterium thermosaccharolyticum* (Sompong et al. 2011). The major disadvantage of these types of hydrogen generation process is the requirement of energy for operation of the bioreactor (Perera et al. 2010). Metabolic aspects of thermophilic biohydrogen production at low pH from sugarcane molasses was studied by Oliveira et al. (2019).

8.5 Phototrophic Bacterial Hydrogen Production

In contrast to cyanobacteria, green algae, and higher plants, the photosynthetic bacteria contain a single photosystem and do not evolve O_2. Advantages which phototrophic bacteria hold over cyanobacteria and green algae include not only an ability to consume organic substrates but also to produce hydrogen at higher temperatures. In case of cyanobacteria and green algae, there is simultaneous production of oxygen with production of hydrogen which inhibits the hydrogen evolving system. However, in the anoxygenic phototrophic bacteria, such a problem does not arise, and also pure hydrogen can be obtained with much difficulty since carbon dioxide is the only contaminant. The nitrogenase mediated hydrogen evolution by photosynthetic bacteria is more efficient than hydrogenase mediated hydrogen evolution by green algae. The other advantage which phototrophic bacteria hold over cyanobacteria and green algae include not only an ability to consume organic substrates but also to produce hydrogen at higher rates (Zabut et al. 2006). Compared to non-phototrophic bacteria, phototrophic bacteria produce threefold amount of hydrogen per mole of substrate utilized. When the conversion efficiency of substrate into hydrogen by chemotrophs is restricted to 33.3%, phototrophs can reach upto 100%. A major route for hydrogen production is biological nitrogen fixation (Prince and Kseghi 2005). In the absence of nitrogen or any other substrate of nitrogenase, the enzyme reduces protons to hydrogen. Hydrogen production in photosynthetic, non-sulfur bacteria involves two main enzymes, namely hydrogenase and nitrogenase. Vignais et al. (2001), had clearly shown that hydrogen production depends more on nitrogenase activity but not on hydrogenase activity. Purple non-sulfur photosynthetic bacteria produce H_2 from a variety of organic substrates and industrial and agricultural effluents (Lazaro et al. 2012; Keskin and Hallenbeck 2012; Hallenbeck and Beneman 2002). Bacteria used include *Rhodobacter sphaeroides* (Han et al. 2013), *R. rubrum* (Zürrer and Bachofen 1979), *R. palustris* (Oh et al. 2004), and *R. capsulatus* (Zhang et al. 2016).

8.6 Structure and Functions of Nitrogenase and Hydrogenase

Nitrogenase enzyme is responsible for photo heterotrophic hydrogen generation. Koku et al. (2002) have studied the effect of oxygen on nitrogenase and reported that it is irreversible. Matsunaga et al. (2000) reported that trace amounts of oxygen may induce hydrogen generation in *Rhodovulum* sp., while oxygen at higher concentrations hinder hydrogen production. The three different types of nitrogen system seen are nif, vnf, and anf. Molybdenum containing nitrogenase is most studied of all diazotrophs. All three nitrogenase systems consist of two dissociable component metalloproteinase, competent 1 (dinitrogenase, Mo Fe, V Fe protein, and FeFe protein) and component 2 (dinitrogenase reductase (Fe protein)). Mo nitrogenase is encoded by Nif HDK genes. This enzyme consists of two oxygen sensitive metalloproteins, an Fe protein, and Mo Fe protein. Fe protein has two or possibly three functions. First, this is required for the initial biosynthesis of Mo Fe cofactor, essential for the incorporation of Mo Fe cofactor into Mo Fe cofactor deficient Mo Fe protein, and it may play a role in regulation of alternative systems (Burgess and Lowe 1996). Nitrogenase synthesis is regulated by several factors such as presence of light, oxygen, nitrogen, and metal found in the structure of nitrogenase. Since molecular nitrogen is the main substrate for the nitrogenase, the presence of it suppresses hydrogen production (Koku et al. 2002). Three major groups of hydrogenase are distinguished according to their metal content: metal free, Fe, and the NiFe hydrogenase (Vignais et al. 2001). Though nitrogenase is largely responsible for hydrogen evolution in phototrophic bacteria, hydrogenase also contributes to hydrogen production at lower rates. One of the possible physiological functions of hydrogenase is to recycle hydrogen thus recovering some of the energy. Hydrogen recycling has already been demonstrated in resting cells of *Rb. capsulatus* adapted of endogenous substrates. In addition, hydrogenase plays a major role in autotrophic growth. *Rb. capsulatus* was shown to use hydrogen as electron donor under anaerobic conditions as electron and energy source for aerobic autotrophic growth. Under the later conditions, hydrogen serves to reduce carbon dioxide and oxygen. The process of nitrogen fixation thus involves an inherent release of hydrogen that corresponds to maximum of 25% (possible 40–60%) of electron flow through nitrogenase.

8.7 Factors Influencing Hydrogen Production

The broad substrate utilization and high conversion efficiencies make them suitable for use in photoproduction of hydrogen from wastewaters. Hydrogen production by purple non-sulfur bacteria using solid wastes (Mizuno et al. 2000), cellulose wastewater (Lay and Noike 1999), sugary wastewater (Ueno et al. 1996), kitchen waste (Shi et al. 2008), and organic cane molasses waste (Sasikala et al. 1992) has been reported. Optimum hydrogen production was observed in mid log phase culture (Sasikala et al. 1991).

8.7.1 Pretreatment

The result of innoculum pretreatments on mesophilic and thermophilic fermentation have been reported (Dessì et al. 2018). Possible substrate for hydrogen making via dark fermentation is the redundant lignocellulosic biomass from plant and other sources which is very widely available in nature (Kumar et al. 2015). In addition, it is renewable. Since it is not easy to use lignocellulosic biomass as substrate for biofuel production (Kumar et al. 2015; Łukajtis et al. 2018), it may require pretreatment with physical, chemical, or biological methods. But many are not feasible due to furfural and phenolic compounds which act as inhibitors for hydrogen generation (Cai et al. 2016). Most effective pretreatment was acidic pretreatment (Mockaitis et al. 2019). Yang et al. (2019) showed that alkaline treatment of antibiotic fermentation residue gave the highest hydrogen yield. This approach is not economically advantageous, because an additional stage of biomass hydrolysis is required. Nagarajan et al. (2019) have suggested consolidated bioprocessing in which cellulase production, substrate hydrolysis, and fermentation are carried out in a single step by mixed bacteria cultures. Deng et al. (2019) reported that acid-treated grass silage led to a threefold higher hydrogen yield. Lay et al. (1999) investigated the biohydrogen generation using from municipal solid waste with heat-pretreated digested sludge. The results obtained found that the Gompertz model was the best for predicting the hydrogen yields (Lay et al. 1999). Although innoculum pretreatments are done, they have some drawbacks, such as elimination of non-sporulating hydrogen producers, while sporulating hydrogen consumers and competitive bacteria may continue to exist (Bundhoo and Mohee 2016). Saady (2013) opined that pretreatment is not a sustainable approach as it cannot be maintained for a long time when wastewater is used as feedstock. Numerous pretreatment processes are based on the fact that hydrogen producers, like *Bacillus* sp., *Clostridium* sp., and *Thermoanaerobacterium* sp., produce spores under unfavorable conditions and germinate under favorable conditions again (Galperin 2013). But in the case of hydrogen consumers which are non-spore forming, they do not withstand unfavorable conditions and thus perish. Wang and Yin (2017) have reported other pretreatment processes using 2-bromoethansulphonate acid (BESA) or chloroform and physical conditions like aeration, microwaves, ionizing irradiation, ultrasonication, and electric shock.

8.7.2 Light Intensity

Effect of illumination intensity on hydrogen generation was different with different kinds of bacteria (Sasikala et al. 1991 and Ooshima et al. 1998). Hydrogen production begins at very low light intensities of 4000–5000 lux (Hilmer and Gest 1977). The light source optimum for hydrogen production was of longer wavelength (above 590 nm) or xenon lamp (Nogi et al. 1985; Miyake and Kawamura 1987). Kinetics of light limited growth and biological hydrogen production from carbon monoxide and water by *R. rubrum* was investigated by Klasson et al. (1993). Light penetration onto cell suspension of phototrophic bacteria in relation to hydrogen production was studied by Nakada et al. (1995). Prevention of high uptake hydrogenase activity by complete removal of hydrogen from culture device under continuous illumination caused prolonged hydrogen production (Vincenzini et al. 1986). Akkerman et al. (2002) has used a light intensity within a range of 400–950 nm for hydrogen generation. Different sources of light such as simulated sunlight (Wakayama et al. 1998), tungsten lamp (Nakada et al. 1995; Fascetti et al. 1998; Zhu et al. 1999), halogen lamp (Barbosa et al. 2001; Kim et al. 2004), filters (Takabatake et al. 2004), and fluorescent lamp (Matsunaga et al. 2000) have been used for hydrogen production. The optimum light intensity was found in the range of 5000–8000 lux. The reported optimum light intensities were 5000 lux for *Rb. sphaeroides* O.U.001 (Sasikala et al. 1991), 3000 lux for *Rb. Capsulatus* ST410 (Ooshima et al. 1998) and 6000–8000 lux for *R. palustris* (Yang and Yang 2002). The inhibitory intensity was reported to be 9000 lux for *R. palustris* (Yang et al. 2019). In some organisms, *Rb. Sphaeroides* O.U.001 (Sasikala et al. 1991) 10000 lux was not inhibitory.

8.7.3 Temperature

Karadag and Puhakka (2010) stated that temperature is an important factor in dark fermentation. At higher temperatures acetate production pathway in dark fermentation process leads to the highest H_2 yield (Verhaart et al., 2010). Fermentation at higher temperatures generally increases hydrogen generation when compared to mesophilic temperatures (Zheng et al. 2014). Singh and Srivastava (1991) and Sasikala et al. (1991) have studied the effect of temperature on hydrogen production by the bacteria studied by them. Optimum hydrogen production rates are generally observed between 30 °C and 34 °C (Oh et al. 2004; Zürrer and Bachofen 1982). Temperature and pH are commonly used pretreatments to choose spore-forming microbes (Wang and Yin 2017). Higher temperatures result in lysis of cells and protein denaturation (Appels et al. 2008), while pH may inactivate regulatory enzymes and change the internal pH of the cells (Rafieenia et al. 2018).

8.7.4 pH

A number of factors including cultural conditions have been shown to affect the photoevolution of hydrogen by phototrophic bacteria. Hydrogen production is reported to be influenced by pH which varies with the organism (Sasikala et al. 1991; Vasavi et al. 2004). Glucose as a model for understanding the effects of pH on hydrogen production was studied by Fang et al. (2006). Srinivas (2001) has reported a pH of 6.5 for *Rc. tenius* for optimum production of hydrogen. Similarly, Vasavi et al. (2004) reported maximum production of hydrogen at a pH of 7.0 by *Rps. rutila,* isolated from sewage water. Maintaining pH is a decisive step toward hydrogen generation, as it influences activity of hydrogenase (Dabrock et al. 1992) as well as metabolic pathways (Kumar and Das 2001). The pH optima value for hydrogen generation using batch mode was 9.0 while pH of 4.0–4.5 was needed for continuous hydrogen generation using sucrose (Lee et al. 1999; Ren et al. 2007). *Clostridum acetobutyricum* produced solvents at pH 5.5 under the limitation of phosphate and iron. When these were added, it produced H_2 above pH 5.0 (Dabrock et al. 1992).

8.7.5 Carbon Sources

The most preferred organic carbon sources are carbohydrates for hydrogen-generation. Glucose was used as carbon source for hydrogen generation by Chen et al. (2001). Sugar factory wastewater was anaerobically treated with microflora for generation of hydrogen (Ueno et al. 1996). Oh et al. (2002) reported hydrogen production by *Rhodopseudomonas palustris* P4, using carbon dioxide along with other carbohydrates. A wide variety of organic substrates such as carbohydrates (Vasavi et al. 2004; Singh et al. 1994), lactate, malate, benzoate (Sasikala and Ramana 1995 and Srinivas 2001), acetate (Barbosa et al. 2001), butyrate (Lee et al. 2007), lipids and fatty acids (Tatyana et al. 2008), alcohols (Vasavi et al. 2004; Koku et al. 2002), and some inorganic sulfur compounds like thiosulphate and sulfide are utilized by different species of phototrophic bacteria as electron donors for hydrogen production. However, the substrate specificity for hydrogen production varied with the species (Najafpour et al. 2004). Koku et al. (2002) have reported the use of organic acids and carbohydrates for hydrogen production. Hydrogen production by *Clostridium thermolacticum* during continuous fermentation of lactose was reported by Christopher et al. (2003). Srinivas (2000) has investigated the effects of various carbon sources on hydrogen production from *Rc. tenius*. (Silk cotton whose major constituent is cellulose was utilized as a substrate for growth, and hydrogen production was observed in marine photosynthetic bacterium *Rb. marinus* (Burgess et al. 1994). Najafpour et al. (2004) also surveyed the various carbon substrates for hydrogen production using *Rh. rubrum*. Similarly, Vasavi et al. (2004) has reported the effect of various carbon sources on hydrogen production from *Rps. rutila*. Mizuno et al. (2000) reported hydrogen from solid waste while cellulose wastewater was used by Lay et al. (1999) for hydrogen generation. Hydrogen generation was seen in the pH range of 5.5–5.7 with sucrose and starch (Khanal et al. 2004). *Enterobacter* and *Bacillus* have been reported to produce hydrogen using carbohydrates (Fabiano and Perego 2002; Kalia et al. 1994).

8.7.6 Nitrogen Sources

Photoevolution of hydrogen by phototrophic bacteria is reported to be influenced by a number of factors including cultural conditions (Najafpour et al. 2004). Lakshmi and Polasa (1993) also emphasized the importance of nitrogen source on the growth medium for photoproduction of hydrogen. Utilization of aromatic acid by *Rb. sphaerodies* and *Rps. palustris* for hydrogen production was demonstrated by Harwood and Gibson (1988) and Fissler et al. (1995) respectively. Glutamic acid was effective as nitrogen source with no inhibition on nitrogenase activity, but may be expensive for industrial use. Ethanolamine as nitrogen source with sugars D-glucose, D-xylose, and D-cellobiose which induced a large amount of hydrogen by *Rb. capsulatus* (Katsuda et al. 2000). *Rc. tenius* produced more amounts of hydrogen under the presence of a nitrogen source (Srinivas 2001). Vasavi et al. (2004) reported influence of a nitrogen source on hydrogen production in *Rps. rutila*. Mizuno et al. (2000) reported the stimulation of hydrogen production in the presence of glucose by nitrogen gas sparging. Ammonia inhibits hydrogen generation as it represses nitrogenase activity through glutamine synthesis (Sweet and Burris 1981). Hydrogen production in entrapped *Rhodobacter sphaeroides* was not affected by ammonia while it was shown to influence entrapped cultures of *Clostridium butyricum* by Zhu et al. (2001).

8.7.7 Immobilization

Enhancement and stabilization of hydrogen production could be achieved by immobilization as it protects the cells from inhibitory effect of oxygen, nitrogen, osmotic stress, and pH. There are many advantages of immobilized cells such as protection against adverse environmental conditions, accelerated reaction rates, no washout of cells, better control over the photocatalytic process and the presence of cofactors and continued biosynthesis within the cell contributes to longevity of enzymatic activity. Immobilized cells can be extensively used for the production of useful products (Chang and Chou 2002). Immobilization not only simplifies separation and recovery of the immobilized bacteria but also makes the application reusable which reduces the overall cost. Since most of the biological systems studied are of limited stability, immobilization of the cells improves the yield as well as the duration of hydrogen production. Hydrogen production capabilities can be increased for longer periods by immobilizing the cells in a suitable matrix. Various immobilization techniques are being used to enhance and stabilize photoproduction of hydrogen by photosynthetic bacteria. Von Feiten et al. (1985) used agar, agarose, alginate, pectin, and k-carrageenan for hydrogen production by *Rhodospirillum rubrum*. Of all these tested agents, agar proved to be the best agent for hydrogen production. Cationic polyelectrolyte was used to entrap anoxygenic phototrophic bacteria for enhanced hydrogen production (Zhu et al. 1999). Hydrogen production could be increased by photoreactive nonporous latex coating of *Rhodopseudomonas palustris* CGA 009 (Gosse et al., 2007). Sunita and Mitra (1993) reported increased hydrogen production from sewage and wastewater by immobilized cells of *Rhodopseudomonas* and *R. rubrum* respectively. Singh et al. (1994) and Vasavi et al. (2004) have also recorded that immobilized cells produced more hydrogen than free cells. Lozinsky et al. (2003) have successfully used cryogel polyvinyl alcohol (PVA) as an immobolizing agent for hydrogen production.

8.7.8 Metal Ions and Co-Cultures

A cell density of 1.6–1.8 mg dry weight per ml was optimum for hydrogen production (Sasikala et al. 1991). Trace elements also enhance hydrogen production (Macler et al. 1979). Metal factors such as cobalt, copper, molybdenum, zinc, nickel, and iron plays significant role on growth, hydrogen photoproduction, and nitrogenase activity of photosynthetic microorganisms (Rajani 1992; Kars et al. 2005). Some co-cultures of Phototrophic bacteria with *Cellulomonas* (Odom and Wall 1983), *Vibrio fluvialis* (Ike et al. 1999), *Lactobacillus amylovorus* (Kawaguchi et al. 2001), *Clostridium butyricum* (Zhu et al. 1999), and *Halobacterium salinarum* (Zabut et al. 2006) have been used for the production of hydrogen. *Vibrio fluvialis* T-522 was able to induce hydrogen production in *R. marinum* A-501 from acetic acid and ethanol (Ike et al. 1999). Light conversion efficiency was enhanced for certain co-cultures from individual cultures (Kondo et al. 2002). Genetic studies on photosynthetic microorganisms have focused on enhancing the hydrogen-producing capabilities of photosynthetic bacteria and cyanobacteria. Genetic modification of bacteria for hydrogen production can be achieved by several ways such as over expression of cellulase, hemicellulase, and ligninase that can maximize substrate availability, elimination of uptake hydrogenase, and also reelimination of metabolic pathways that compete for reduction required for hydrogen synthesis. Strategies for improving hydrogen production efficiency also include the reduction in size of light harvesting complexes to increase light capture efficiency (Kondo et al. 2002). Genes for uptake hydrogenase were knocked out to study their effect on hydrogen production (Franchi et al. 2004).

8.7.9 Inhibitors

Ooshima et al. (1998) compared hydrogen production by *Rb. Capsulatus* from malate under various gases in the headspace and found that hydrogen yield was severely affected by O_2 and N_2. Hydrogen production by *Rhodopseudomonas* sp. from acetate was stimulated by small amounts of ammonia but was inhibited by large concentrations of the same (Hoekema et al. 2002). The inhibition was found to be reversible. Similar study conducted in *Rb. Sphaeroides* RV using lactate as substrate by Zhu et al. (1999) also showed that ammonia inhibition of hydrogen production was reversible. Krahn et al. (1996) reported that oxygen reduced hydrogen production by 50% for two strains of *Rb. capsulatus*. Ormerod et al. (1961) established that the hydrogen producing activity of *R. rubrum* from malate was completely inhibited with 99% N_2, but it became reversible when N_2 was replaced with helium.

8.7.10 Bioreactors

Bioreactors for dark fermentative H_2 production are continuous stirred tank reactors (CSTRs) (Li and Fang 2007), packed bed reactors (PBRs), fluidized bed reactors (FBRs), membrane bioreactors (MBRs), and upflow anaerobic sludge blanket reactors (UASBs) (Show et al. 2011). Show et al. (2011) have showed that in membrane bioreactors, the binding of microbes together produce biofouling and increases the operating costs. Oh et al. (2004) suggested the use of trickling bed reactors (TBRs) for dark fermentative H_2 production. FBRs are mainly capable of H_2 production because the mass transfer improves between the biomass and substrate (Barca et al. 2015). High H_2 partial pressure inhibition of hydrogen also does not take place in these kinds of bioreactors (Barca et al. 2015). Lay (2001) have observed alcohol production after the peak hydrogen and VFA production in batch studies using heat-treated sludge as innoculum and microcrystalline cellulose as substrate. Vavilin et al. (1995) found butyrate and propionate were the main fermentation products for *C. butyricum* and *C. propionicum*. The effect of interruption of feed supply for *Selenomonas* sp. for 6 h a day showed a change in butyrate H_2 producing spore-formers population compared to propionate producing non-spore formers

(Cohen et al. 1985). Yokoi et al. (2001) reported the 0.1% polypeptone requirement for breaking sporulation of *Clostridium butyricum*. Low HRT was reported to yield higher H_2 yields as it causes the washout of hydrogen consuming methanogens and homoacetogens. Dos Reis and Silva (2011) obtained a maximum yield of H_2 at an HRT of 2 h. Gas sparging with nitrogen or carbon dioxide gases decreases partial pressure of hydrogen within bioreactors (Kim et al. 2006) but may dilute the yield. Two gas separation membranes were attached to a dark fermentative reactor to overcome this problem so as to separate H_2 from CO_2 (Bakonyi et al. 2017). This resulted in 30% increase in hydrogen yield (Bakonyi et al. 2017). Lay (2000) reported that an agitation speed 100–700 rpm enhanced hydrogen production rate when starch was used as substrate. Anaerobic hydrogen generation sewage sludge bacteria in fixed-bed bioreactors consisting of loofah sponge, activated carbon, and expanded clay was investigated, and it was found that the hydrogen gas was found to be 25–35% with major soluble metabolite as butyric acid, propionic acid, acetic acid and ethanol (Shu et al. 2002). Homoacetogenesis was inhibited by temperature of 55 °C and pH 5.5 (Luo et al. 2011). Chang and Lin (2004) reported hydrogen generation from sucrose using upflow anaerobic sludge blanket reactor. Mesophilic acidogenic reactor was reported to generate hydrogen-producing ability with a solids retention time of 0.25 days and pH of 5.7 (Lin and Chang 1999). Yetis et al. (2000) reported that the highest hydrogen-producing capability of *Rb. sphaeroides* OU 001 in a photobioreactor. Cellulose was used for hydrogen generation in a hyperthermophilic CSTR reactor, by inoculating with digested sewage sludge (Gadow et al. 2013). Similarly, Qiu et al. (2011) have reported hydrogen generation from bioethanol distillery wastewater from CSTR.

8.8 Prospects and Challenges

Hydrogen is strategically significant as it has no emission and is environmentally benign, and represents a sustainable energy system. With regard to environmental issues, biological hydrogen processing is the most difficult field of biotechnology (http://www.fao.org/3/w7241e/w7241e0g.htm). The future of biological hydrogen production depends not only on scientific developments, i.e., improving performance by genetically modified microorganisms and/or the development of bioreactors, but also on economic considerations (fossil fuel costs), societal acceptance, and the development of hydrogen energy systems. Anaerobic bacteria that produce hydrogen during fermentation are classified as either strict or optional anaerobic: *Clostridium*, *Ethanoligenens*, and *Desulfovibrio* are strict anaerobic agents, while *Enterobacter, Citrobacter, Klebsiella, Escherichiacoli*, and *Bacillus* are optional anaerobic agents (Yoshida et al. 2006; Ren et al. 2007). Strict anaerobes obtain electrons from pyruvate oxidation, which are then transferred to ferrodoxin (Fd) and subsequently to hydrogen. Other producers of hydrogen mainly use formatoxidation, which is catalyzed by format-hydrogen lyase (Shin et al. 2007). Fermentative mixed culture produces the highest hydrogen yield based on the dominant organic products, that are divided into acetate/butyrate and acetate/ethanol forms. In acetate/butyrate fermentation, *Clostridium* species are typically the dominant hydrogen producers (Li and Fang 2007; Chang et al. 2006), while *Ethanoligenens* species are abundant producers of hydrogen in acetate/ethanol fermentation (Xing et al. 2006).

Pyruvate/Fd pathway for hydrogenformation relies on both approaches. The type of fermentation that is dominant tends to regulate reaction pH. A pH of 5–6 was found to result in the formation of acetate/butyrate, and pH 4.5 results in acetate/ethanol (Lee et al. 2008). A realistic aim of fermentative biohydrogen will be to optimize hydrogen production, meaning that in terms of electron distribution, organic products must be minimized (Lee and Rittmann 2009). Compared to other choices, the advantage of dark fermentation is that the hydrogen production rate can be enhanced by several orders (Tartakovsky et al. 2009). Hydrogen can be formed from carbon-free resources or from fossil fuels. Maddy et al. (2003) have opined that hydrogen could contribute considerably to the decrease of greenhouse gas emissions. In the year 1977, work on hydrogen as an energy carrier was initiated with the help of International Energy Agency. But it was delayed due to the availability of inexpensive oil and nuclear energy. In this circumstance, hydrogen fuels are the key elements for a new era in the field of energy (Orecchini 2006). While regulating the structure and abundance of hydrogen generating bacterial population is of great importance for optimizing the production of fermentative hydrogen, better knowledge of the physiology of putative H_2 consumers will also help to find optimal reactor conditions in order to prevent their growth and thus improve the overall production of hydrogen (Castelló et al. 2009). A high rate of production but low conversion efficiency from the organic substrate to hydrogen is provided by fermentative hydrogen. The microbial electrolysis cell is an emerging technology that can achieve high conversion efficiency (Lee et al. 2010). Biohydrogen involve any H_2 production technique that involves biological material (Mohan and Pandey 2013). The raw material could be carbon substrates or solar. Although algal biohydrogen production can be tried, but algal oxygenic photosynthesis inhibits the hydrogenase that makes H_2. To overcome this, Kubas et al. (2017) has suggested developing O_2-resistant hydrogenase. Tiwari and Pandey (2012) proposed a technology which uses cyanobacteria for hydrogen production through hydrogenase and nitrogenase. Phylogenetic diversity of the microbial community involved in the process of hydrogen production needs to be evaluated for understanding the diverse mechanisms in which hydrogen generation takes place. Cabrol et al. (2017) felt that the gap of knowledge between microbial ecology features and ecosystem functionality has to be filled for enhancing hydrogen generation. Syntrophy is seen in different microbial ecosystems where some microorganisms use fatty acids and produce hydrogen from NADH (Cabrol et al. 2017). Another approach suggested by Cabrol et al. (2017) is based on the process of natural selection and competition between microorganisms. Johnson et al. (2009) opined that a suitable environment should be created for enriching the growth of microbes in a bioreactor which could enhance the production of hydrogen. This was observed when suitable operating conditions were imposed on microbes with regard to the amount of substrate (Tapia-Venegas et al. 2015), pH (Boboescu et al. 2014), and salt concentration (Pierra et al. 2014). In addition to "natural" adaptation and selection of the microbial population to particular operating conditions, bioaugmentation strategies have been proposed to artificially increase the percentage of high-performance main hydrogen-generating species in real substrates that already contain a high endogenous microbial diversity (Cabrol et al. 2017). Metabolically well-adaptive bacterial consortiums could be produced by enriching a complex waste with particular hydrogen-producing bacteria previously isolated from it. This may be more productive than inoculating with a pure generic H_2-producing culture that may be poorly suited for this particular waste (Cabrol et al. 2017). Moreover, when the augmented strain does not function alone but with the help of the substrate endogenous microflora, the production of hydrogen is typically improved. The production of hydrogen was favored when the applied HRT enabled the coexistence of the bioaugmented (strict anaerobe) *Clostridium* strain with the indigenous *Klebsiella pneumoniae* in CSTR treating sugarcane juice at various HRT (Pattra and Sittijunda 2017). Bacteria can produce hydrogen by using protons as an electron sink during dark fermentation of organic substrates. Fermentative hydrogen production utilizes pyruvate-ferrodoxinhydrogenase or pyruvate-formatelyase, and the ultimate electron donor is an organic compound such as a sugar. As the source of the organic compound is biomass, fermentative hydrogen can be considered renewable, since the biomass itself originated from photosynthesis (Lee et al. 2009). The most commonly cited problems for fermentative hydrogen production are: (q) poor yield, typically less than 20% and at maximum 30% (De Vrije et al. 2007); (w) sensitivity to end product accumulation (Van Neil et al. 2002); and (3) economic sustainability (Hallenback and Benemann 2002). The biggest problem is that the hydrogen yield is poor for fermentative hydrogen. The 100% conversion to hydrogen will yield 12 mol hydrogen/mol glucose for glucose as a substrate. The theoretical maximum H_2 yield is only 4 mol hydrogen/mol glucose based on known fermentation reactions, and this can only be accomplished when the only electron sinks are H2 and acetate (Lee and Rittmann 2009). The potential optimum yield thus reflects just 25% of the substrate's conversion into biological hydrogen. In actuality, butyrate, propionate, ethanol, lactate, and other organic sinks, including biomass, are also generated in significant amounts. These additional electron sinks further lower the real hydrogen yield (Lee and Rittmann 2009), decreasing the overall yields observed under mesophilic, acidic conditions to approximately 2 mol H_2/mol glucose (Lee and Rittmann 2009). In addition to causing low biohydrogen conversion, which is about 17%, the organic products generated in a fermentative hydrogen system may also trigger problems due to their high demand for biochemical oxygen (BOD); thus, the high-BOD effluent needs to be handled. In addition, some of these organic products also have offensive odors or can reduce sulfates into highly odorous hydrogen sulfide. Thus, efficient means to capture the equivalents and the energy content of the soluble organic products are essential for successful hydrogen generation by fermentation. One possible option is to use microbial electrolysis cells (MECs) for enhancing hydrogen production. In this the hydrogen yield can be enhanced upto 81% (Lee et al. 2010). Another possibility is methanogenesis that can be coupled with fermentative biohydrogen for the production of methane from acetate (Ueno et al. 2007; Venetsaneas et al. 2009). Anoxygenic photosynthesis using purple non-sulfur bacteria, which can use soluble organic fermentation products as their electron donors for the development of photosynthetic hydrogen, is a more forward-looking choice. Another significant problem associated with fermentative hydrogen is that until it is harvested, the generated H_2 may be transformed into undesired items. With hydrogenoxidizing methanogens and homoacetogens, which oxidize hydrogen and reduce carbon, the risk of this occurring is greatest with H_2-oxidizing methanogens and homoacetogens which oxidize hydrogen and reduce carbon dioxide to produce methane gas and acetate, respectively (Lee et al. 2010). Operation at a low pH is one technique to reduce methanogenesis and homoacetogenesis, which is generally considered inhibitory to their development (McCarty and Smith 1986). Hydrogen oxidizing methanogens, however, are considered to be acid-tolerant and are present in acidic conditions (Hales et al. 1996), while homoacetogens that are acid-tolerant have also been found (Go´ßner et al. (2008). These species can reduce the development of hydrogen at a pH of approximately 55 (Calli et al. 2008).

Thermal pretreatment of the innoculum will be another approach to suppressing hydrogen consumers in order to selectively select hydrogen producers that are spore-formers like *Clostridium* that can survive these conditions (Li and Fang 2007). Pretreatment of the innoculum, however, is ineffective if the input organic substrate is rich in microorganisms that absorb hydrogen (Lee et al. 2010). Therefore, the most common means of preventing hydrogen oxidation is rapid and effective harvesting, as soon as the hydrogen has been produced, for which effective technologies are to be developed. The promise of high rate of hydrogen production from complex organic feedstocks is provided by dark fermentation, but the yield is around 17%. The main move for fermentative hydrogen performance is to increase the bioenergy yield from 17% to 80 by combining it with a microbiological system that transforms soluble organic products into usable energy production while also removing significant environmental pollution (Lee et al. 2010). MEC, methanogenesis, and anoxygenic phototrophy are options for posttreatment need to be integrated with dark fermentation. Improved technology for rapid and successful hydrogen gas harvesting as soon as it is generated is the second critical step (Lee et al. 2010).

8.9 Conclusions

Bacterial biohydrogen is based on the concept of using bacterial biomass for the generation of hydrogen. The hydrogen generation with removal of CO_2 that would make it an ideal source of energy generation coupled with the removal of greenhouse gas emission would be in agreement of Kyoto protocol. All our energy demands can be satisfied by using sources such as sunlight and wind power. But in some areas, sunlight and flow of wind are inadequate. In such areas, there is a search for the best renewable energy source. Hence, hydrogen especially biohydrogen makes a perfect source of energy as it can be stored and utilized as well as transported when required. The advantages of using biohydrogen make it a perfect component of a renewable and sustainable source of energy. Although hydrogen generation is possible by other methods, using bacteria for hydrogen generation has to be investigated further to make the process economical and sustainable.

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Bioethanol Production from Biodiesel-Derived Glycerol: A Case Study

9

Atia Al-Shuhoomi, Saif Al-Bahry, Yahya Al-Wahaibi, and Sanket J. Joshi

Abstract

Waste frying oil is gaining traction as a useful commodity, rather than a waste, especially for the production of biofuels, such as biodiesel. Transesterification of waste frying oil to biodiesel using alkali as a catalyst with addition of different solvents (such as methanol) also yields glycerol as a byproduct. Glycerol bioconversion into several valuable products is favored because it is relatively inexpensive, easily available, and also due to the possible utilization of different microorganisms. Bioethanol, glycerin soap, several organic acids, and chemical compounds are some of the examples of converted products using glycerol as substrate. In this chapter, bioethanol production by locally isolated bacterial strains and the comparison of the ethanol fermentation profile using glycerol as a sole carbon source are reported. Besides ethanol, production of several chemical compounds and organic acids are also possible. In total, nine isolated bacterial strains were tested for their ability to utilize glycerol and produce bioethanol. These isolates include *Escherichia coli, Serratia marcescens, Aeromonas veronii, Shewanella putrefaciens, Acinetobacter johnsonii, Pseudomonas putida,*

A. Al-Shuhoomi
Department of Biology, College of Science, Sultan Qaboos University, Muscat, Oman

S. Al-Bahry
Department of Biology, College of Science, Sultan Qaboos University, Muscat, Oman

Oil & Gas Research Centre, Sultan Qaboos University, Muscat, Oman

Y. Al-Wahaibi
Petroleum and Chemical Engineering Department, College of Engineering, Sultan Qaboos University, Muscat, Oman

S. J. Joshi (✉)
Oil & Gas Research Centre, Sultan Qaboos University, Muscat, Oman
e-mail: sanket@squ.edu.om

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Enterobacter kobei, Klebsiella pneumoniae, and *Chryseobacterium gleum.* Different parameters were evaluated and optimized for each strain, to screen the most potent strain that has the ability to utilize glycerol to produce ethanol. We observed that bacterial isolates produced ~0.12–0.25% ethanol, using biodiesel glycerol, within 24 hours. Although the yield was comparatively lower as compared to other reports, it is still encouraging, and could possibly be employed in bioethanol production using better-suited microorganisms.

Keywords

Waste frying oil · Biofuel · Biodiesel · Bioethanol · Glycerol

9.1 Biofuels

Different types of gaseous biofuels (biosyngas, biogas, methane, green hydrogen) and liquid biofuels (green methanol, bioethanol and biodiesel) are considered as an alternative to petro-based fuels in the near future, and are expected to play a pivotal role in reducing toxic-harmful emissions, as well as to provide a steady-secured energy supply (Nigam and Singh 2011; Datta et al. 2019; Geetha et al. 2020). Biofuels can be classified into older generation and newer generation or secondary biofuels. The older generation biofuels such as wood, charcoal, animal dung mixed with agriculture residues, etc., are still used for heating, cooking in many underdeveloped countries, and also in rural areas of some developed countries for electricity production. Those biofuels are neither energy efficient nor environmentally friendly. Whereas, the new generation or secondary biofuels have better energy efficiency, are less polluting, and are generally produced by extensive processing of such wastes and biomass (Demirbas 2011; Nigam and Singh 2011; Datta et al. 2019; Geetha et al. 2020). Those secondary biofuels are further divided into first, second, third, and fourth generation biofuels, depending on the type of raw materials used for their production. In brief, first generation biofuels: substrates used are food based crops, grains, seed, vegetable oils, animal fats, or sugar, to produce bioalcohols (such as ethanol, butanol), biodiesel, biosyngas, biogas; second-generation biofuels: substrates used are non-food based crops and residues, lignocellulosic biomass, municipal solid waste, to produce bioalcohols (such as ethanol, butanol), bio-oil, bio-dimethylether, biohydrogen, bio-Fischer–Tropsch gasoline/diesel, bio-methane; third generation biofuels: substrates used are algae and sea weeds, to produce biodiesel, bioethanol, and hydrogen; and fourth generation biofuels: substrates used are vegetable oils, biodiesel, to produce biogasoline (Demirbas 2011; Nigam and Singh 2011; Datta et al. 2019).

Several studies reported the likelihood and prospective of gaseous and liquid biofuel production and electricity generation from agro-industrial wastes, animal and biomass waste, etc. (Granda et al. 2007; Markevičius et al. 2010; Demirbas 2011; Nigam and Singh 2011; Stamatelatou et al. 2011; Xia et al. 2016; Kucharska et al. 2018; Fivga et al. 2019; Padilla-Rivera et al. 2019; Ardebili Khademalrasoul 2020;

Peres et al. 2020). More specifically, for gaseous biofuels, recent studies highlight recent advances in production, efficiency enhancements, and different applications, such as for biogas (Abraham et al. 2020; Elangovan et al. 2020; Fu et al. 2020; Kapoor et al. 2020; Rasapoor et al. 2020; Tabatabaei et al. 2020a, b; Zabed et al. 2020), syngas (Göransson et al. 2011; Daniell et al. 2012; Pala et al. 2017; Al Nouss et al. 2020; Li et al. 2020; Liuzzi et al. 2020; Radenahmad et al. 2020), and green hydrogen (Melis and Happe 2001; Bion et al. 2012; Dincer 2012; Nikolaidis and Poullikkas 2017; d'Amore-Domenech et al. 2020; Martinez-Burgos et al. 2020). However, gaseous biofuels are the mainly preferred source of energy to provide heating, cooking, and electricity generation, at source, or transported, with few exceptions (such as hydrogen) to be used in transportation sector. Storage is one of the major issues in gaseous biofuels applications. Liquid biofuels are preferred for all sort of applications, as storage is easier, and it also provides more energy per density/volume, as compared to gaseous biofuels. Several researches highlighted the economics and versatility of production and applications for liquid biofuels, mainly bioethanol (Ingale et al. 2014, 2019; Esmaeili et al. 2020; Kumar et al. 2020; Ramachandra and Hebbale 2020; Rezania et al. 2020; Sophanodorn et al. 2020; Susmozas et al. 2020), green methanol (Araya et al. 2020; Chakrabortty et al. 2020; Devlia et al. 2020; Ishaq and Dincer 2020; Ravikumar et al. 2020; Yadav et al. 2020) and biodiesel (Abomohra et al. 2020; Geetha et al. 2020; Goh et al. 2020; Jacob et al. 2020; Mahlia et al. 2020; Mofijur et al. 2020; Singh et al. 2020; Hoang et al. 2021; Muhammad et al. 2021). However, earlier generation liquid biofuels suffered from 'food versus fuel' conflicts, apart from technological advances. As most of those substrates were originating from edible feedstocks, the competition for land-water resources, and the production costs were also high that pushed back widespread biofuel applications. However, recent updates in production processes and possibilities of using cheaper waste resources, oleaginous microbes, and nonedible feedstocks gave much needed push to advocate worldwide applications of liquid biofuels (Singh et al. 2020; Muhammad et al. 2021). Another advantage in liquid biofuel production, especially in case of biodiesel, is byproduct glycerol, which can also be used for several applications, which brings down the economic balance of overall production cost, making it a more lucrative process. In this chapter, we will highlight this biodiesel production process using waste frying oil, and using its byproduct glycerol to produce bioethanol and soaps.

9.2 Glycerol: A Byproduct of Biodiesel Industry

Glycerol (1, 2, 3-propanetriol) is a colorless, odorless, and viscous liquid, derived from both natural and petrochemical feedstocks. The Greek word for "sweet" is "glykys" is the origin that the glycerol term derived from, and the term "glycerin" also tends to be used more often to describe the same (Pagliaro and Rossi 2008). Briefly, it is an alcohol with different uses in cosmetics, food, pharmaceutical, and biofuels, or it can be used in chemicals production as a feedstock. Glycerol can be produced from petrochemical feedstock by chemical pathways or by microbial fermentation (Wang et al. 2001). In recent years, focus on sustainable and renewable energy is highlighted considerably, leading to increased biodiesel production from different sources such as rapeseed oil, cooking oil and animal fats. With compaction to traditional feedstocks for biodiesel production (edible vegetable oils), waste cooking oil (WCO) has the advantage to reduce the overall cost by 60% (Xiu et al. 2019; Crosse et al. 2020; Geetha et al. 2020). Biodiesel production generates glycerol as a byproduct and its proportion during biodiesel synthesis dramatically increased. According to the glycerol reaction volumes, which constitutes around 10%, glycerol has been considered as waste by many biodiesel industries because of glycerol market saturation (Johnson and Taconi 2007). Glycerol conversion into liquid biofuels and bioenergy by fermentation processes can provide effective solution to manage glycerol, which can improve biodiesel industries economically. There are different types of biofuels that could replace fossil fuels. Currently, bioethanol is the most attractive one, which is being used, and already being produced in large-scale fermentation processes (Lynd et al. 2005; Ingale et al. 2019). Biotechnology industries use glycerol as an inexpensive feedstock which success in coproduction of valuable and attractive products (Liu et al. 2012; Clomburg and Gonzalez 2013). Glycerol-based refineries are the microbial fermentation pathways that use inexpensive crude glycerol to be the main feedstock for fuels and chemicals production (Clomburg and Gonzalez 2013; Nwachukwu et al. 2013; Crosse et al. 2020). In this context, glycerol is used as an alternative for sugars, which are considered as a traditional feedstock for such fermentations. In comparison to sugars, glycerol represents a greater degree of reduction. A sign of glycerol increasing in reducible state is the exclusive synthesis of reduced products during fermentation. Glycerol is converted to phosphoenolpyruvate or pyruvate that generates other reducing products. An important pathway of glycerol fermentation is the one that produces ethanol and organic acids as byproducts (Suhaimi et al. 2012). In this study we hypothesized coproduction from crude glycerol fermentation as it has wider applications. First is the evaluation of ethanol production from crude glycerol obtained from biodiesel synthesis using waste frying oil. Aerobic fermentation was carried out using bacterial strains isolated from Sultan Qaboos University botanical garden area near the pond.

9.3 Microbial Fermentation of Glycerol to Bioethanol and Other Alcohols

The conversion of crude glycerol to produce value-added products can be either by biological or chemical pathways. For example, the concept in the chemical pathway is the etherification of glycerol with either alcohols or alkenes that produce valuable fuels or solvents, as well as the production of methanol and hydrogen achieved by steam reforming of glycerol (Trinh and Srienc 2009). A variety of biomass feedstocks and many conversion technologies are applied to produce bioethanol. Bioethanol (also known as ethyl alcohol, grain alcohol, $CH_3–CH_2–OH$) is a liquid fuel that is considered as a valuable alternative fuel as long as it is produced from a renewable bio-based resource. Also, it is oxygenated, thereby provides the potential to decrease particulate emissions in compression–ignition engines (Balat et al. 2008). Nowadays, the major feedstocks of bioethanol production are accomplished by food crops such as corn, sugarcane, wheat, and soy. This has led to unwanted effects by putting pressure on production of food. To eliminate such effects on food production, biomass or glycerol-containing waste is considered to be an effective substitute in bioethanol production (Adnan et al. 2014). In addition, the estimated cost to produce bioethanol from glycerol is approximately 40% lower than when corn is used, as the price of glycerol is much cheaper than corn (Nwachukwu et al. 2013).

Because of biodiesel industries' development, the abundance of glycerol production is increased which is the main cause for low cost of glycerol. As long as glycerol is a byproduct of biodiesel production, if this byproduct is not handled and disposed of in a proper way then excess glycerol may increase the cost of biodiesel production. Therefore, this byproduct can be utilized in an economical manner by using a variety of microorganisms that consider glycerol as a source of energy and also as a sole carbon source. Valuable and useful chemicals can be produced by microbial fermentation of glycerol; such chemicals are 1, 3-propanediol, dihydroxyacetone, ethanol, and succinate. In this context, many traditional feedstocks are used as an alternative for glycerol in industrial fermentation, for instance, sucrose, glucose, and starch. In comparison with glucose fermentation, glycerol as previously mentioned is much cheaper, available in abundant quantities and the main feature is that it has high reduction degree than sugars does. Also, the state of being more reducible during glycerol fermentation shows an acceptable production of reduced products. Glycerol fermentation converts glycerol to pyruvate that produces twice the reducing equivalents amount than the amount of pyruvate generated from sugars. Further, in fermentation, half of the sugars have been lost during bioconversion as carbon dioxide; consequently, glycerol fermentation has a yield of twice that of glucose by producing ethanol and formic acid (or ethanol and hydrogen). Bioconversion of glycerol into beneficial chemicals and products has added a great value to the biodiesel industry (Suhaimi et al. 2012).

Glycerol is considered as a carbon source with a high degree of reduction, which can be used as a platform to produce chemicals anaerobically of reduced nature (Dobson et al. 2012). Various types of bacteria can utilize glycerol as a source of sole carbon to produce highly valuable metabolites. Metabolites that can be derived from glycerol are: 1, 3-propanediol (1, 3-PD), hydrogen, and ethanol. In the glycerol fermentation, the pH will decrease gradually as organic acids as byproducts are accumulated. Moreover, biodiesel waste has limited bioethanol productivity compare to the pure glycerol that applied to several ethanol producers which show high production of ethanol. Currently, studies of biodiesel waste reported that the family Enterobacteriaceae and its mutant strains have the ability to utilize biodiesel glycerol to produce much higher amounts of bioethanol than pure glycerol does (Suzuki et al. 2014). Enterobacteriaceae family species such as *Klebsiella pneumoniae*, *Citrobacter freundii*, *Clostridium butyricum*, and *Pantoea agglomerans* are used during fermentation of glycerol to produce 1, 3-propanediol (Wang et al. 2001). For bioconversion pathway to be acceptable and produce valuable bioproducts, the selected microorganisms must have the ability to tolerate and represent a little sensitivity towards biodiesel glycerol impurities (Dobson et al. 2012).

9.4 Other Applications of Glycerol

Glycerol has different applications in other industries as well, such as food industry, paint, pharmaceutical, cosmetic, soap, and toothpaste. The abundance and cheaper price of glycerol makes it a source to derive value-added commercial compounds. Nowadays, high-value chemicals, polymers, and fuels, including citric acid, lactic acid, 1,3-PD, hydrogen, ethanol, and additives are also produced from glycerol that is considered as great versatile feedstock. This will add an advantage to biodiesel production cost and benefit the biodiesel industry (Fan et al. 2010; Crosse et al. 2020). In addition to bioenergy field, cosmetic products can be produced, specifically glycerin soap, which can be improved to desirable scent, colors and can be produced as either bar or liquid soap.

9.5 Laboratory Scale Case Study

9.5.1 Biodiesel and Crude Glycerol from Waste Cooking Oil

The feedstocks for biodiesel are largely triglyceride oils which can be edible/non-edible vegetable oils. For example, in Europe, the main feedstock is canola oil, and in the United States, the soybean is dominantly used for the production of biodiesel. However, in China and with its huge population, a considerable quantity of edible oil is imported just for direct consumption and to cover the food processing industry. In addition, the challenge in China has been to find out an alternative from low-cost feedstock to produce biodiesel. The WCO is touted as a better substitute to edible or vegetable oils, as it is considered as an economical source and could also solve issue of environmental pollution if discarded as such (Wang et al. 2012; Geetha et al. 2020). Generally, the cost of biodiesel production from WCO is much lower than that was produced by a variety of types of edible vegetable oils. The main reason for the cost reduction is the feedstock price; WCO price is 30–60% cheaper than the edible vegetable oil used. In addition, the equal quality of biodiesel produced by WCO and either partially or fully of refined vegetable oils can be succeeded by optimized processing conditions. Therefore, the increased worldwide food consumption led to higher volumes of WCO/fat. The elimination of the negative environmental effect of the waste oils disposal into drainage systems can be successfully achieved by generating fuel from WCO (Wang et al. 2012).

In our biodiesel production process we collected 200 ml of WCO in a glass container, filtered it to remove any food particles and other impurities, warmed at 50 °C with continuous stirring at 100 rpm. In another container, we prepared a catalyst by adding 4 g alkali (KOH) and 40 ml of solvent (methanol) and dissolved

Fig. 9.1 The components used for biodiesel production ((**a**) WCO, (**b**) methanol, (**c**) Alkali) and finished products ((**d**) mixed product after the reaction, (**e**) biodiesel, and (**f**) glycerol)

completely on a magnetic stirrer. The catalyst mixture then was added to the hot oil and was stirred for 30–45 min and was let to separate into two distinct layers overnight; the top layer was the biodiesel while the bottom layer was the desired product consisting of crude glycerol (Harabi et al. 2019; Geetha et al. 2020). Biodiesel was collected and washed repeatedly with water to remove any impurities and glycerol was separated in another container to be used further. Figure 9.1 shows all the components used for biodiesel production and finished products. In this method of transesterification, WCO reacted with methanol with base (KOH) as a catalyst. Crude glycerol is produced, and it mainly contains variety percentage of glycerol, free fatty acids, catalyst, methanol, and soaps. The crude glycerol may have different types of impurities, which mainly depend on the type of catalyst, solvent used and oil molar ratio and feedstock oil quality and composition (Chen et al. 2018).

Glycerol is an essential commercial byproduct of the biodiesel production pathway based on transesterification of triglycerides that are originated from edible/non-edible oil or waste oil with alcohols, such as methanol and/or ethanol, with the presence of a homogeneous base catalyst like NaOH or KOH or an acid catalyst. In general, for every 10 kg production of biodiesel can yield around 1 kg of crude glycerol (~10%). Currently, the capacity of world biodiesel production is increasing dramatically, and any further increase in production ratio of biodiesel will significantly boost the quantity of crude glycerol (Cai et al. 2015; Geetha et al. 2020).

9.5.2 Isolation, Screening, and Characterization of Glycerol-Utilizing Bacteria

We collected 50 ml water samples from Sultan Qaboos University botanical garden pond, in sterile sampling bags and transferred to the lab (Fig. 9.2), to isolate environmental bacteria. To get single colonies from samples for identification, serial dilution was performed. About 1 ml of stock sample was removed by sterile pipette and transferred to 10 ml bottle containing 9 ml sterile water. The bottle was covered and mixed well, and 1:10 dilution was produced. Previous step was repeated to

Fig. 9.2 Sample collection site, Sultan Qaboos University botanical garden pond, Oman

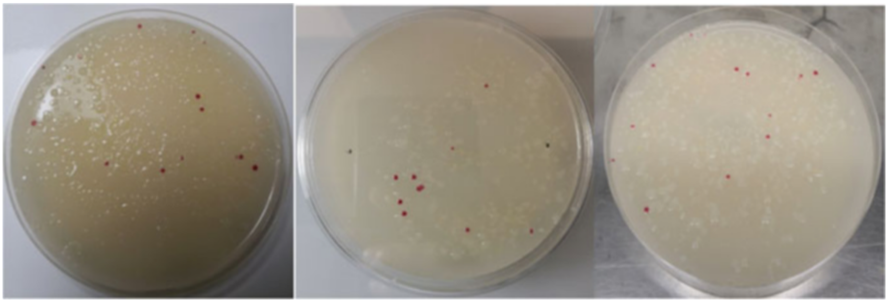

Fig. 9.3 Bacterial colonies grown on the agar containing glycerol as only carbon source

produce as many dilutions as required. Second dilution is 1:100, prepared by transferring 1 ml from first dilution into 9 ml sterile water. With each dilution bacterial concentration was decreased by a factor of 10. Both dilutions with stock sample were then spread on glycerol-based agar medium. The media was prepared using the following composition (g/l): 1, KH_2PO_4; 1, $(NH_4)_2SO_4$; 1, yeast extract; 15, NaCl; 1.5% (w/v) agar and with addition of 2% glycerol as the sole carbon source to favor the growth of glycerol-utilizing bacteria. The plates were incubated for 24 hours at 29 ± 2 °C mimicking the pond conditions. After 24 h, subculturing was carried out to obtain single colonies (Suhaimi et al. 2012).

Bacterial colonies grown on the glycerol-based agar medium indicated that those isolates were able to utilize glycerol as carbon source. Nine well-isolated bacterial colonies were isolated to screen for aerobic fermentation (Fig. 9.3). Classification

Table 9.1 Identification of the strains that have the ability to grow in glycerol media

Isolate No.	Bacterial strain as identified by MALDI-BioTyper
1	*Serratia marcescens*
2	*Aeromonas veronii*
3	*Shewanella putrefaciens*
4	*Acinetobacter johnsonii*
5	*Pseudomonas putida*
6	*Enterobacter kobei*
7	*Klebsiella pneumoniae*
8	*Chryseobacterium gleum*
9	*Escherichia coli*

and identification of the isolated single colonies was carried out by MALDI-Biotyper (Bruker, Germany), at Central Analytical and Applied Research Unit (CAARU), SQU, Oman. It provides high-speed, high-confidence identification and taxonomical classification of microbes (Zurer 1997). Table 9.1 shows identification of the bacterial isolates by MALDI-BioTyper.

9.5.3 Screening for Ethanol Production

Each strain was tested independently for ethanol production. A colony of specific identified strain was inoculated in 250 ml flask that contained 200 ml glycerol-based broth medium and incubated in a shaker at 29 ± 2 °C, 120 rpm of agitation for aerobic fermentation. After 24, 48 and 72 h, 30 ml of samples were collected from fermented broth. The supernatant was collected by centrifuging to obtain separate cells from the broth (Zurer 1997), then subjected for ethanol analyses using a Gas Chromatography-Flame Ionization Detector (GC-FID) in CAARU. Figures 9.4 and 9.5 show the ethanol production and growth profile for each strains, where produced ethanol concentrations were in the range of 0.12–0.25%; an example for GC-FID analysis of one sample is shown in Fig. 9.6. Nine strains isolated from botanical garden were identified and tested for their ability to ferment glycerol to ethanol. These are *Escherichia coli, Serratia marcescens, Aeromonas veronii, Shewanella putrefaciens, Acinetobacter johnsonii, Pseudomonas putida, Enterobacter kobei, Klebsiella pneumoniae, Chryseobacterium gleum*. The strains showed their ability to grow in glycerol-based medium and produced ethanol. Different natural microorganisms such as, *Klebsiella, Clostridium, Enterobacter, Citrobacter*, *Lactobacillus,* possess the ability to utilize glycerol and generate a valuable product that can be used in different fields (Maru et al. 2016; Xiu et al. 2019).

The strains *E. coli*, *S. marcescens*, *A. veronii*, *S. putrefaciens*, *A. johnsonii*, *P. putida*, *E. kobei*, *K. pneumoniae and C. gleum* were used for the optimization studies, tested with different factors including pH, incubation temperature, agitation speed, and medium composition. The production of bioethanol was highly affected by media composition and the nutrients component depending on the microorganism

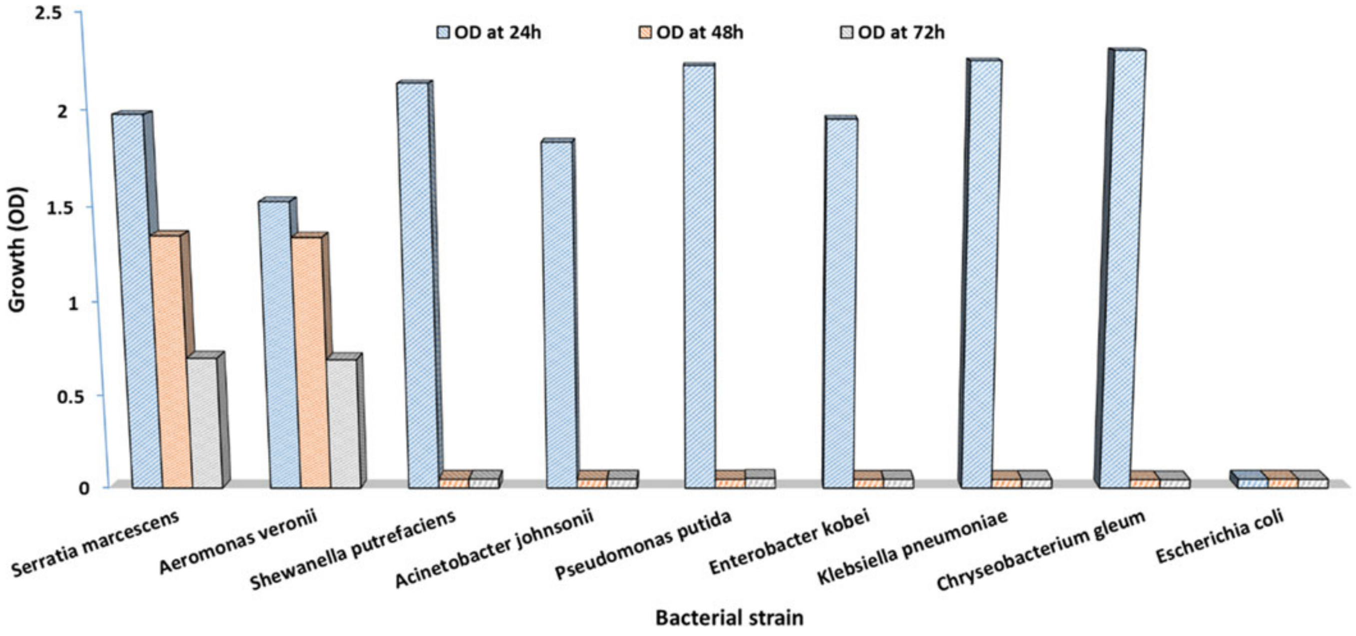

Fig. 9.4 The growth profile of selected bacterial isolates, using biodiesel-derived glycerol as a carbon source

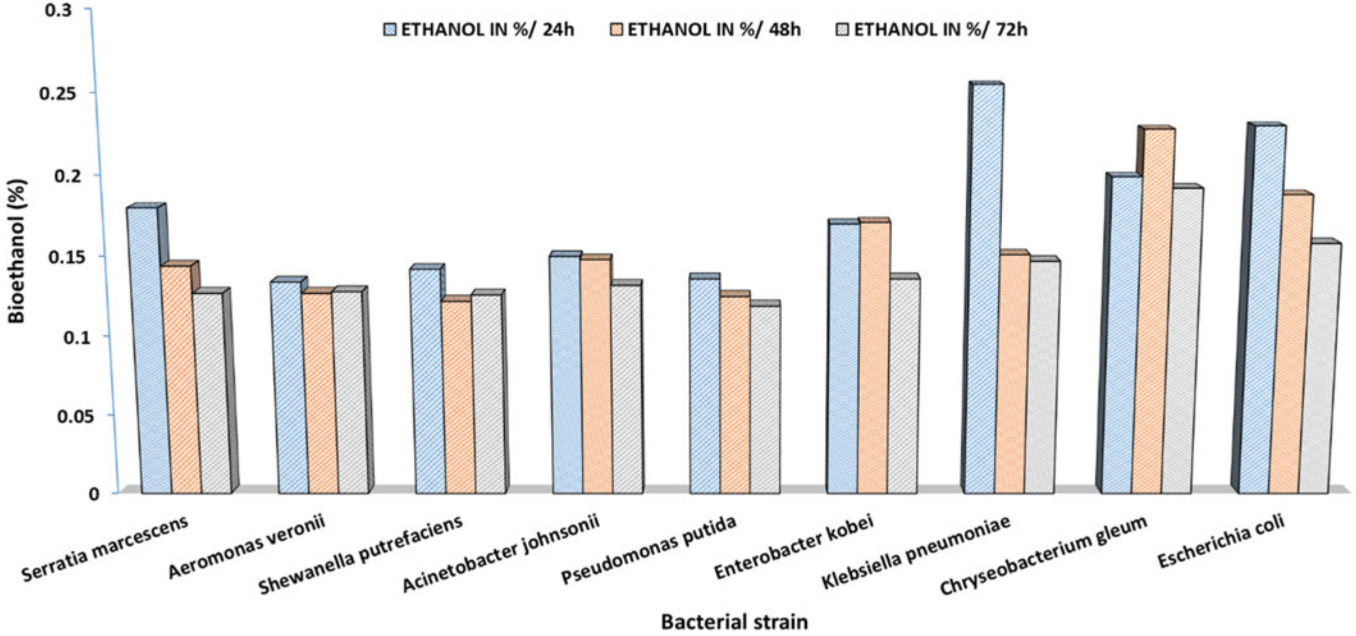

Fig. 9.5 The ethanol production profile of selected bacterial isolates, using biodiesel-derived glycerol as a carbon source

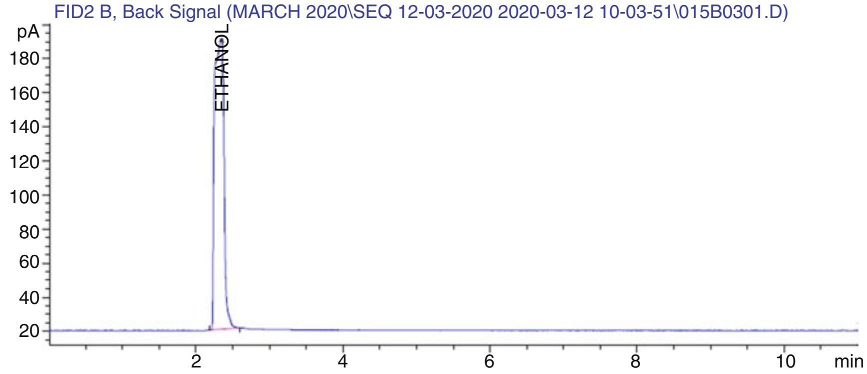

Fig. 9.6 GC-FID chromatograph of bioethanol produced from biodiesel-derived glycerol

types. In this study, low-nutrient medium was used which contained only glycerol as carbon source rather than glucose or other sugars. As described by Suhaimi et al. (2012) *E. coli* SS1 strain produced 6.53 g/l ethanol. A packed-bed bioreactor showed that under optimal operating environmental conditions *E. aerogenes* produced ethanol at 1.0 mol/mol glycerol. During fermentation, the biomass growth achieved stationary phase during incubation after 12 h, high optical density. The study by Dharmadi et al. (2006) reported that the strain of *E. coli* demonstrated faster growth using glycerol as substrate, where >70% glycerol was consumed during the initial 24 h. Despite different types of microorganisms having the ability to produce ethanol by glycerol fermentation, the optimization process to select the best isolates must be considered for rapid growth as well as its ability to maintain metabolic activity under aerobic conditions. Furthermore, ethanol fermentation profile using glycerol can be compared with glucose as substitute for glycerol. During glycerol bioconversion, the products yields were increased as opposed to glucose and different sugars, due to the higher degrees of reduction per carbon in glycerol than in sugars (Yazdani and Gonzalez 2007). For example, wild-type *E. coli* has the ability to produce high yield of ethanol with other byproducts involving hydrogen and several organic acids at minor amounts from glycerol. The yield of ethanol during glycerol fermentation was approximately three-fold higher than that of glucose fermentation (Adnan et al. 2014). Several researchers also highlighted using biodiesel byproduct glycerol for bioethanol production (Choi et al. 2011; Metsoviti et al. 2012; Clomburg and Gonzalez 2013; Thapa et al. 2013; Varrone et al. 2013; Jitrwung and Yargeau 2015; Chanthoom et al. 2016; Vikromvarasiri et al. 2016; Sunarno et al. 2019; Wang et al. 2019; Crosse et al. 2020).

9.5.4 Glycerin Soap from Biodiesel Byproduct

To make soap out of biodiesel glycerol, we collected 100 ml of glycerol, and heated up to 65 °C to remove any excess methanol. Lye solution was prepared by measuring

25 ml of water and mixed with 3.85 g of lye (NaOH); the mixture was heated to 37 °C until all lye was dissolved completely in water. The lye solution is poured into the glycerin, the heating was continued for another 10 min to get homogenize mixture. The pH of the soap was measured to determine whether it is acid or base. Finally, the soap was poured into a container and allowed to cool. Once it is solidified, it is cut into bars. The lye solution determines the physical phase whether it is liquid or solid. Commonly sodium hydroxide was used to make solid soap as bars. But NaOH is used exclusively in liquid soap production. Glycerin soap contains just the raw materials, lye solution and glycerin, which produce completely pure glycerin soap. For the soap to be advanced, other ingredients along with glycerin can be added. This may include different types of oil as desired, dyes and synthetic materials. Commonly the ideal soap that prefers to match and perfectly balance human skin should have a pH balance of 5.5–6.5 (Nyquist et al. 1983).

9.6 Concluding Remarks and Future Prospects

Humans' hunger for energy is never-ending, and it keeps on increasing with increase in population, urbanization, and industrialization. However, the challenge is to provide energy security, at economical rates to all 'poor-and-rich', in an environmental-friendly manner. In the beginning, early biofuels showed a probable future of cleaner, and renewable energy for all, but it posed a challenge and moral dilemma of 'food versus fuel', as there are millions of people starving around the world. Next generation biofuels showed potential in using wastes and biomass, as an alternative to food based substrates. However, still tremendous amount of research is needed to reduce the manufacturing costs, to make it an economically viable alternative.

An improved collection and storage of waste substrate, proper storage, and distribution and blending of finished product in the distribution network are some of the main challenges for commercial biofuel plants. Some possible mechanisms for better implementation of biofuel usage are: a stronger governmental policy for organic waste collection and pushing for selling blended fuels at higher rate; better subsidy for establishment of biofuel plants; tax credits for biofuel producers and customers; possible technological improvement to improve the efficiency; and value-added byproducts, which could possibly improve the overall production dynamics. Biodiesel produced from different oil types is one such type of liquid biofuel, which showed lower emissions than traditional petro-based diesel and is generally touted as "carbon neutral" fuel. Glycerol is a byproduct of biodiesel production process, which could possibly be used for several applications, such as using it as a substrate for bioethanol production (as shown in current chapter), soap making, and several other beneficial applications.

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Advancement on Biomass Classification, Analytical Methods for Characterization, and Its Economic Importance

10

Veer Singh, Manisha Verma, Nidhi Singh, Jyoti Singh,
Preet Kamal Kaur, Niti Singh, and Vishal Mishra

Abstract

Nowadays, petroleum fuels are primary energy sources and fulfill the energy demand of the world. But these fuels emit large amounts of gases responsible for the greenhouse effect and global warming. The source of these fuels is another major issue due to their limited availability in the Earth's crust and will be depleted in the coming days. Hence, there is a need for an effective alternative of petroleum fuels that can fulfill the need for energy. Biofuels are the emerging energy sources derived from cost-effective raw materials and are considered as renewable energy sources. The efficiency and the quality of biofuels are generally dependent on the material used in biofuel production. Hence, the selection of suitable biomass for bioenergy production is extremely important. The biomass selection is based on the properties such as physical, chemical, and biological. The physical properties like surface morphology can be analyzed by using various instruments like scanning electron microscope, transmission electron microscope, and XRD. The chemical composition of biomass is an important factor for biofuel production. The chemical bonding between biomolecules affects the bioconversion process during biofuel production. Genomic

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V. Singh · M. Verma · J. Singh · V. Mishra (✉)
School of Biochemical Engineering, IIT (BHU) Varanasi, Varanasi, India
e-mail: vishal.bce@itbhu.ac.in

N. Singh
Centre of Bioinformatics, University of Allahabad, Prayagraj, India

P. K. Kaur
Guru Nanak Girls College, Ludhiana, Punjab, India

N. Singh
Vaccine and Infectious Disease Research Centre, Translational Health Science and Technology Institute, Faridabad, India

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characterization has important application in the identification of newly isolated microbial species as well as screening for genetic modification. This chapter focuses on biomass classification, its characterization, and the economic importance of biomass.

Keywords

Biofuel · Physical characterization · Chemical characterization · Genomic characterization · Economic importance of biomass

10.1 Introduction

The population of the world is increasing with time, and energy demand is also increasing for the increased world population. The petroleum fuels are limited on the Earth's crust and may be exhausted after certain time. Another problem is also created due to burning of petroleum fuels (Arku et al. 2020; Khayan et al. 2020; Pehnec et al. 2020). The petroleum products are responsible for several pollutions like air pollution, water pollution, and soil pollution. Hence, it is the need of the world to find out a suitable alternative for energy production (Singh et al. 2021a, b). Biomass derived from various sources are considered as renewable sources of energy production (Trisrivirat et al. 2020; Singh et al. 2020a; Ribas et al. 2020).

Biomass is a renewable energy source because it produced from natural sources such as plant and agriculture (Lauri et al. 2014). Biomass obtained several sources such as industrial waste, domestic waste, agricultural waste, and bioenergy crops (Chen et al. 2020). Biofuels are considered as ecofriendly and cost-effective fuels because these fuels come from renewable energy sources (Singh et al. 2020b; Qin et al. 2020a). These fuels play an important role in the reducing global warming via reduce carbon dioxide emission. Considering environmental health, the Governments of various countries (USA, India, United Kingdoms, etc.) promote the production and use of biofuel. In addition, most of the countries are actively participating in the environmental health mission and are trying to minimize environmental pollutions. There are several bodies such as International Panel on Climate Change (IPCC) that participate in the measures to mitigate air pollutions (Chum et al. 2011; Meena et al. 2020; Babel and Kromer 2020).

Every organic material derived directly or indirectly from photosynthetic process considered biomass. Biomass are classified into several classes such as woody biomass, herbaceous biomass, microbial biomass, and agricultural biomass (Rodionova et al. 2017; Wightman et al. 2020). This classification of biomass is mainly based on their compositions. Several biomaterials like lignin, cellulose, and starch makeup the backbone of biomass and are present in the majority. These biomass components are considered as the raw source of biofuel production (Leong et al. 2018; Li et al. 2020; Qin et al. 2020b). The basic classification of biomass is based on these biocomponents. Biomass characterization is another important process before the use of biomass as a biosorbent or bioenergy source.

There are various physical (scanning electron microscope, transmission electron microscope), chemical (FTIR, XPS, mass spectrometry), and biological (sequencing methods for living organisms) characterization methods used for biomass characterization (Amer et al. 2020; Singh et al. 2020c; Hu et al. 2020; Xia et al. 2020; Weitz et al. 2020; Rathnayake et al. 2020). After characterization, suitable biomass are screened for bioenergy production and wastewater treatment. Biomass are also used for wastewater treatment in several forms like activated carbon or used directly for biosorption of heavy metals (Subramanian et al. 2020). In this chapter, the authors have been focused on the classification, characterization, and economical application of biomass for bioenergy production and waste management.

10.2 Classification of Biomass

Biomass are generated from various natural sources like plants residues, animals, and microorganisms. Due to several characteristics and economic importance, biomass can be classified in different categories. The major classes of biomass are described in Fig. 10.1.

Biomass are also classified on the basis of their origin, function, and their products (Bogota-Gregory et al. 2020; Mitros et al. 2020). Few general groups of biomasses are described as follows:

(a) Woody biomass from higher plants.
(b) Herbaceous.
(c) Animal residues and human waste.
(d) Aquatic weeds and animals.
(e) Mixed biomass.

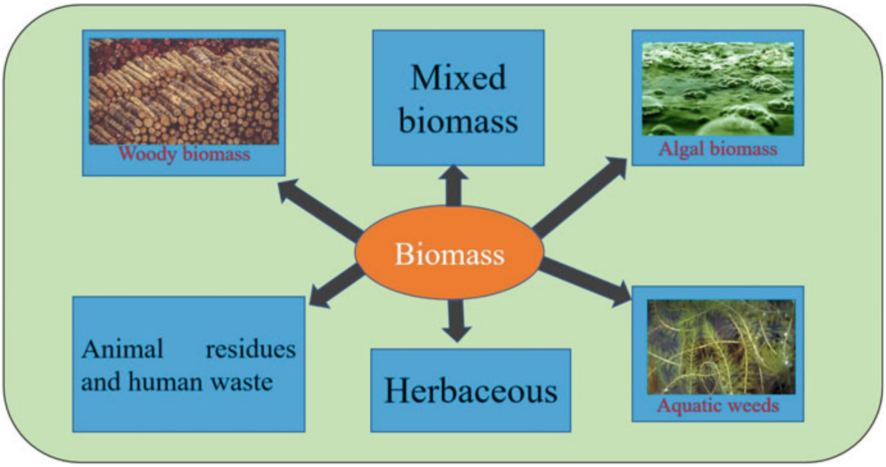

Fig. 10.1 The major categories of biomass used in the production of biofuel

10.2.1 Woody Biomass from Higher Plants

Wood is the hard biomass and obtained from several woody plants. Woody biomaterials contain various components such as carbohydrates and lignin. The woody biomass is obtained from plants and their parts such as the stem of woody plants, leaves, roots, seeds, as well as edible or non-edible fruits (Vassilev et al. 2012; Fan et al. 2020). It can be converted directly into energy through various biomass conversion methods.

Generally, the biomass used for the production of biofuels as well as used for the treatment of wastewater comes from four sources:

(a) Residues of several wood industries.
(b) Industrial and domestic waste.
(c) Production residues.
(d) Urban and agricultural waste.

Woody biomass are considered as simple and very important renewable source of energy due to its wide availability, cost-effectiveness, and ecofriendliness (Lauri et al. 2014).

10.2.2 Biomass from Herbaceous Sources

This type of biomass is obtained from the no-woody stem of the stem of plants. It is degradable in nature. This biomass includes grasses, seeds, grains, as well as residues from several food industries. Industrial by-products are also considered as an option for herbaceous biomass (Tan et al. 2020). Herbaceous biomass generally classified into two classes such as agro-waste and energy crops.

(a) *Agricultural waste*: These include by-products of food materials, agro-waste such as wheat straw, paddy straw, and other agricultural crop residues. The agricultural waste can be directly converted into biofuels through various bioconversion processes. The biofuel production from agricultural waste is considered as an eco-friendly and cost-effective renewable source (Boeken et al. 1998; Molina-Guerrero et al. 2020).
(b) *Energy-based crops*: Jatropha is a good source of herbaceous biomass and utilized for bioenergy production (Trager et al. 2019). Efficient and unique properties of herbaceous biomass can have an important impact at the regional level and will be able to replace petroleum fuels. Thus, they are known as a better alternative of energy source (Shachak et al. 1991; Khan 2020).

10.2.3 Biomass from Animal and Human Waste

This type of biomass is derived from animal bones, meat, and several other products such as animal dung (Vassilev et al. 2012). The waste is also directly used as fertilizer in the agricultural land under the proper waste management processes. Animal and human wastes are considered as better renewable energy sources. The wastes are anaerobically converted into biogas that are used directly as fuel or electricity production or used as fuel for cooking foods (Horan 2018; Veerapandian et al. 2020).

10.2.4 Aquatic Biomass

The aquatic biomass generally includes aquatic plants, algae, and microalgae (Dibenedetto 2011). Algae are multicellular organisms and belong to the kingdom Plantae. These organisms are autotrophic that can synthesize their own food in the presence of sunlight. The microalgae are the microscopic organism which can be divided into several classes such as green, brown, and golden algae. These organisms are few micrometers in size. Diatoms are considered as largest biomass on the Earth. Green algae are generally found in freshwater and brown algae are found in marine water. The algae and the microalgae are the major sources of fatty acids and starch. Algal biomass generates biofuels through several biofuel production methods (Green et al., 2021; Wang et al., 2020).

10.2.5 Mixed Biomass

When biomass comes from multiple sources, it is known as mixed biomass. For example, the domestic waste contains a mixture of biomass such as vegetables, household products, few broken glasses, and plastic waste. This type of biomass cannot be used directly for bioenergy production purposes. Waste segregation is an important process applied for the selection of suitable biomass for application purposes (Gharechahi et al. 2020).

10.3 Major Components of Biomass

The biomass is derived from plants and animals. These biomasses are degradable in nature due to their unique composition. Biomass directly or indirectly converted into biofuel through various conversion methods. The important components of biomass are represented in Fig. 10.2.

The chemical composition of biomass is an important parameter that highly affects the conversion as well as bioenergy production. There are several components like cellulose, starch, hemicellulose, and lignin. These components vary with biomass sources (Che-Zain et al. 2020; Mude et al. 2020).

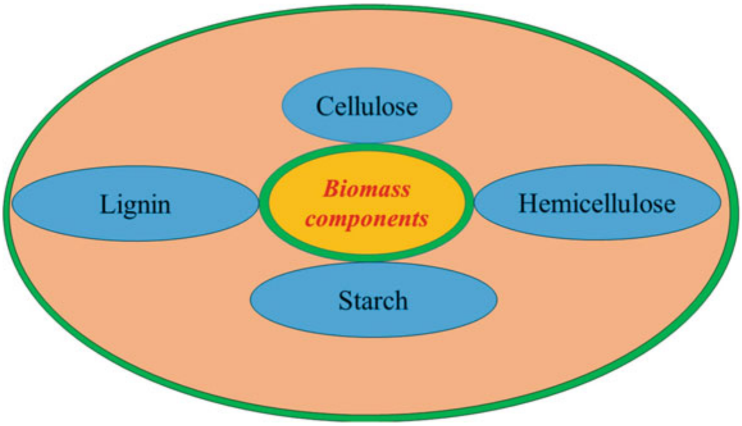

Fig. 10.2 Major components of biomass

10.3.1 Cellulose

It is present in abundance on the Earth. It makes 90% of parts in cotton and about 50% part in woody materials. It is a linear molecule and contains D-glucose monomeric unit. In the cellulose molecules, glucose units are linked with beta-1,4-glycosidic linkage. Carbon, hydrogen, and oxygen play the main role and the general formula of cellulose indicated as $(C_6H_{12}O_6)_n$, where n indicates to the degree of polymerization (Park et al. 2020). The plant cell wall contains major component as cellulose, and this component provides structural function to the cell (Bonechi et al. 2017). The properties of cellulose are influenced by its interchain hydrogen bonding between hydroxy groups and oxygen molecules. Intermolecular hydrogen bonding is responsible for the hardness of cellulose (Chen 2014).

10.3.2 Hemicellulose

It is an important component of plant cells and contains branched and heterogeneous polysaccharides (McKendry 2002). Hemicellulose is generally linked with the cellulose filament on the surface of the cell. It is not necessary for plants to have the same composition and structure as its biomolecules. The composition and structural properties of hemicellulose vary from species to species (Bala et al. 2016). Hemicellulose is composed of five carbon sugar units such as xylose and arabinose with molecular weight about 30,000 (Bonechi et al. 2017). Cellulose is made up of repetitive units of glucose while hemicellulose is made up of several sugar molecules such as, galactans, xylans, mannans, and arabinogalactans (Carpenter et al. 2014). Hemicellulose decomposes at high temperature and produces coal and non-condensable gases. Hemicellulose can be decomposed at temperature between 180 °C and 350 °C (Jindal and Jha 2016).

10.3.3 Lignin

It acts as a binding component or as cementum for cellulose and hemicellulose fibers, and it is also considered as the main component of plant cell wall. It enhances rigidity and competency in the cell wall. If we want to extract cellulose fiber from the cell, it is necessary to first remove lignin component from the cell for the extraction process (Xu et al. 2005). The lignin portion in the plant cell wall varies (30–50%) on the basis of plant species. Carbon (61–65%), hydrogen (6–7%), and oxygen (20–25%) are the main elements present in a plant cell. Carbon covers the major component of the plant cell wall and indicates a good source for bioenergy production. Due to high carbon composition, lignin is also considered as a better option as a biosorbent and activated carbon for wastewater treatment (Fromm et al. 2003).

10.3.4 Starch

Start in the main reserved component of the plants and seeds. Starch is found in the plants in the form of granules that made up of amylose and amylopectin molecules. About 25–27% of amylose and 73–75% of amylopectin are found in the starch of plant cells. The proportion of start in the plant materials is highly dependent on the types of plant materials (Vorwerg et al. 2002; Edwards et al. 2003).

Amylose is the linear molecules of repetitive units of D-glucose. It adopts a helical structure and makes different forms like A, B, and V. A and B contain six molecules of glucose and form left-handed helical structure. In the V-form amylose structure, glucose combines with iodine, alcohol, and fatty acid molecules and form co-crystallization compound. V-form amylose draws double helical structure which has more rigidity and crystallinity compared to A and B forms (Winger et al. 2009). Amylopectin molecule is the largest molecule which is made up of alpha (1-4) bonding between glucose molecules and branching with alpha (1-6) bonding (Winger et al. 2009).

10.4 Characterization Techniques

It is very important to characterize the prepared biosorbent or biological materials before used in biosorption or bioenergy production. The important methods for biomass characterization have been shown in Fig. 10.3.

10.4.1 Chemical Methods

The determination of chemical structure molecules and the composition of biomaterials vary for different applications. The authors of this chapter summarize important chemical characterization techniques such as FTIR or IR, XPS, NMR, and their applications.

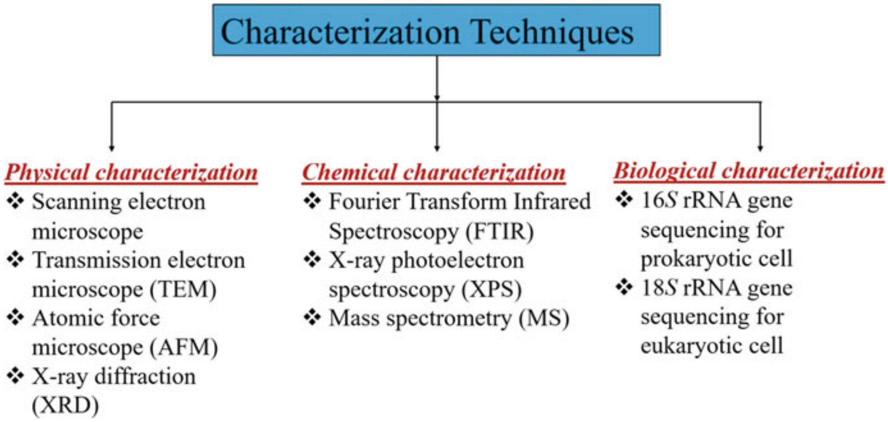

Fig. 10.3 Biomass characterization methods

10.4.1.1 FTIR Analysis

FTIR is an analytical method used for the analysis of lignocellulosic materials. FTIR can analyze using molecular vibrations which can be characteristic to the chemical compound. It is also used for quantitative characterization of chemical compounds in the biomass (Grandmaison et al. 1987; Li et al. 2011). FTIR spectroscopy can be used for characterization of several agro-wastes like rice husk, paddy, and wheat straw [Naik et al., 2010]. In this characterization, the chemical composition of biomass can be classified based on biochemical components. Hence, FTIR analysis is an important analysis for biomass characterization (Acquah et al. 2016; Carballo-Meilan et al. 2014; Chen et al. 2010; Hobro et al. 2010; Meng et al. 2015).

10.4.1.2 XPS Analysis

It is used for characterization of chemical composition as well as elemental composition present in the biomass. This technique is based on the photoelectron effect and bombardment of X-ray photons on the surface of biomass. The electrons are emitted through a monochromatic beam in the vacuum environment. The materials analysis can be determined on the basis of electron kinetic energy and binding energy (eV). This technique is applicable in the determination of elemental analysis of biomaterials and to analyze the quality of biomass for bioenergy generation as well as wastewater treatment (He et al. 2021; Kesavan et al. 2020).

This technique has much application in the detection of elements and their oxidation states. However, it has some limitations in the analysis of biological materials due to its relatively short lifetime in the high vacuum and radiation caused by X-rays (Kesavan et al. 2020).

10.4.1.3 Mass Spectrometry (MS)

Mass spectrometry (MS) is an analytical method for evaluating the characterization of biomass. This method is based on the mass to charge ratio in the gaseous medium

(Ducheyne et al. 2015). The time of flight (TOF) is an important phenomenon in the mass spectrometry technique and highly influences the characterization (Kanazawa et al. 2012). Mass spectrometry combined chromatography technique and shows an advance application for characterization of complex materials. Liquid chromatography mass spectrometry (LCMS) is a combined form of liquid and mass spectrometry. LCMS used for the characterization of biomass extract in liquid phase. Gas chromatography mass spectrometry is another advanced method of using combined techniques for characterization of biomaterials (Vekey et al. 2011).

10.4.2 Physical Method for Biomass Characterization

10.4.2.1 Scanning Electron Microscope (SEM)

The surface morphology of biomass is an important characteristic of biomass. The morphology of biomass is highly dependent on its molecular composition. The surface morphology of biomass can be done using SEM analysis. The roughness, smoothness, and texture of biomass are analyzed using SEM analysis. In the SEM analysis, an electron beam is radiated and scans the biomass surface. Different modes at various resolutions of SEM can be used for better characterization (Sampath Kumar 2013).

10.4.2.2 TEM Analysis

This instrument is used for the study of surface morphology, crystal structure,—— and biomass composition. TEM gives more appropriate results and better resolution compared to SEM. In the TEM analysis, electrons are emitted from the electron gun in the vacuum chamber. The emitted electrons are targeted at the sample; few electrons are absorbed by the sample, and the remaining electron transmitted from the sample. Transmitted electrons are detected by detection and analyzed. The transmission of the electron is mainly depending on the depth and texture of the sample (Agrawal et al. 2013).

10.4.2.3 AFM

It is a very advanced analytical instrument providing images in three dimensions (3-D). AFM can be performed on all kinds of surfaces, including conducting, insulator, synthetic, or natural. AFM provides high resolution at nano and angstrom range (Haugstad 2012; Agrawal et al. 2013).

In the AFM imaging sharp tip is automatically dragged through a material surface and captures the topographic image of material. The tip is connected with a flexible beam, and the force between material and tip deflects to the beam. An optical system records the beam deflection and that deflection is proportional to the interatomic force (Sampath Kumar 2013). There are several models available, and the difference in these models is based on the tip-surface interaction.

10.4.2.4 XRD Analysis

XRD is an important and advanced type of instrument used for the study of biomass composition and structure. In this technique x-rays are emitted through x-rays generator in the controlled way. X-rays target at the sample, and these x-rays are analyzed through detector which is connected to the computer. In this analysis monochromatic electron beam is used for the material detection (Agrawal et al. 2013).

In this technique, X-ray beam is radiated toward the material and the intensity of the beam (diffracted beam is calculated as a function of the angle of incident) (Agrawal et al. 2013).

10.4.3 Biological Characterization

Genomic characterization method is used for the identification of an unknown microorganism. In bacteria, 16 S rRNA genes remain constant within a species. Hence, bacterial species are classified based on 16S rRNA gene sequencing. In an eukaryotic cell, 18S rRNA genes remain constant; hence, eukaryotic cells like fungi and algae characterization are based on sequencing of 18S rRNA gene. In this chapter author mainly focused on genomic characterization methods. Genomic sequence is the unique characteristic of any individual, be it either eukaryotes or prokaryotes or archaebacteria. It defines the physical characteristics of bacteria. There are different methods to characterize the whole genome sequence of bacterial DNA (Singh et al. 2017). The most advanced technique used nowadays is next-generation sequencing which has wide application in metagenomics also. The approaches for genomic characterization of microorganisms are as follows (Singh and Mishra 2020; Singh et al. 2020d; Ryu et al. 2020; Djemiel et al. 2020).

10.4.3.1 Maxam-Gilbert Sequencing

This was discovered by Allan Maxam and Walter Gilbert in 1976–1977, and it is also known as chemical-based method. This sequencing is performed using chemical modification in DNA molecules and cleavage in the DNA backbone at modified nucleotides. It requires radioactive labeling at one $5'$ at end nucleotide and uses gamma-^{32}P ATP for DNA labeling. This method is also called chemical cleavage method. The advantage of this method is its application to read purified DNA; DNA-protein interactions, epigenetic modifications, and nucleic acid structure can be analyzed using this method. The major disadvantage of this method of sequencing is the use of hazardous chemicals for modification, complex technical set up, difficult scale-up facility, and only up to 500 bp can be sequenced (Verma et al. 2017; Liu and Zhu 2018).

10.4.3.2 Sanger Dideoxy or Chain Termination Sequencing Method

This method was described by Fredrick Sanger in 1977, hence the name the Sanger Sequence. In this method, DNA primer is used to start DNA synthesis. Four deoxynucleotide triphosphate, the polymerase extends the primer by adding dNTPs. Four dideoxynucleotide triphosphate labeled with several fluorescent dyes are used for the determination of nucleotide added into the chain of nucleotides. After synthesis, it can be loaded into the gel, and gel electrophoresis is performed. DNA sequence was determined on the basis of size. 99.99% base accuracy of Sanger sequencing by considering the “gold standard“for confirming DNA sequences. The advantage of this method is more efficient and uses fewer toxic chemicals. The disadvantage of Sanger sequencing is that it can sequence only short pieces of DNA up to 300–1000 nucleotides. Initial 15,040 and 700–900 nucleotide sequences are not good (Waldmuller et al. 2015; Sikkema-Raddatz et al. 2013).

10.4.3.3 Automated DNA Sequencing

Automated DNA sequencing is PCR-based method for sequencing DNA. This method is also called cycle sequencing or PCR sequencing. In this method, unknown DNA sequence can be amplified using PCR followed by *Taq* polymerase. In this method, the efficiency of *Taq* polymerase was increased including its proofreading ability. PCR mixture includes all components such as four deoxynucleotides, dideoxynucleosides, primer, DNA template, and polymerase enzyme. The fluorophore used this method for visualization of reaction. Template DNA can be amplified and made into thousands of copies, with each stopping at several nucleotides. The mixture was separated on the gel and recorded for each fluorescence tag labelled nucleotide. Automated sequencer is an expensive instrument and involved costly materials in this analysis; however, in this method, multiple samples run at one time, and thus the cost per sample is quite low (Dougas et al. 2020; Van Brempt et al. 2020).

10.4.3.4 Pyrosequencing

The principle of pyrosequencing is based on sequencing-by-synthesis. During DNA synthesis, a chain of enzymatic reaction takes place to incorporate a nucleotide as a result inorganic pyrophosphate (PPi). ATP is used for this reaction. The overall reaction in this method from amplification to light recognition takes 3–4 s at room temperature according to Ronaghi. At a wavelength of 560 nm more than 6×10^9 photons are generated by using 1 pmol of DNA which could yield 6×10^{11} ATP molecules. Types of pyrosequencing are liquid phase pyrosequencing and solid phase pyrosequencing. This method is having the potential advantage of accuracy and flexibility. The challenges of pyrosequencing are the short read length and false signal capture (de Melo Pereira et al. 2020; Guerrini et al. 2020).

10.5 Economic Importance of Microbial Biomass

Three types of microbes are used for microbial biomass production: bacteria, fungi, and microalgae (Singh et al. 2021c). The use of microorganisms as a tool for producing a wide range of food products, antibiotics, beverages, and bioenergy is significant. In ancient times, the ability to make vinegar and was well known and widely used. Likewise, converting a yeast suspension into beer or a crushed grapes suspension into the wine was the most common practice (Hui et al. 2004). These economic uses of microorganisms are the earliest examples of biotechnology. Microbial species are used in a fermentation reaction to make yogurt, cheese, paneer, curd, kefir, and other types of food. Fermentation provides flavor and aroma and inhibits undesirable organisms (Hui et al. 2004). They are utilized for bread and to convert saccharides into alcohol (wine and beer). Microbes are used in baking, brewing, winemaking, pickling, and other food industry processes (Hui et al. 2004). In the agricultural field, utilization of *Rhizobium* sp. to convert atmospheric nitrogen into a useable form of nitrogen (fixed nitrogen) by crops, led to the use of the microbes as a living biofertilizer that grew in association with the crops (Mmbaga et al. 2014). Composting process is based on a wide range of aerobic microbes and is also known as aerobic reaction. This reaction is widely used for the conversion of several types of wastes via microbial consortia. In this process complex organic waste converted into a more simple, safe, and stable form which is further useful in various agricultural practices (Mondal and Palit 2019). A wide range of bacterial species having ability to degrade hydrocarbons (Kafilzadeh et al. 2011). Some studies reported removal of pesticides toxic pollutants by bacterial species such as *Staphylococcus* sp., *Streptococcus* sp., *Corynebacterium* sp., *Klebsiella* sp., *Shigella* sp., *Acinetobacter* sp., *Alcaligenes* sp., *Enterobacter* sp., and *Escherichia* sp. (Struthers et al. 1998). Studies found that DDT can be degraded by some of *Stenotrophomonas* sp. and *Bacillus* sp. from several contaminated sources such as agricultural field (Kanade et al. 2012). Bacteria and microalgae play a major role in the treatment of wastewater. The majority of microbial species are facultatively and obligatorily living in either presence or absence of oxygen (Cydzik-Kwiatkowska and Zielińska 2016; Kshirsagar 2013). Algae are a potential microorganism used for treatment wastewater because these organisms are able to accumulate several pollutants such as heavy metals, pesticides, and organic or inorganic pollutants within cells (Singh et al. 2021d; Lloyd and Frederick 2000). In order to tolerate organic pollutants, the most tolerant genera used are *Chlamydomonas, Euglena, Chlorella, Oscillatoria, Scenedesmus, Nitzschia*, and *Stigeoclonium* (Palmer 1969). Degradation of organic substrates by microbial activities and utilization of its by-products to generate sustainable green energy or biofuels has a significant value nowadays, e.g., biodiesel, biogas, and ethanol from algal biomass (Verma and Mishra 2020). The lignocellulose-containing agricultural wastes and plant biomass could be used as fermentative feedstocks for certain yeast strains to obtain bioethanol (Zhang 2020). Electrochemically active metal-reducing bacteria such as *Shewanella and Geobacter* sp. are used in microbial fuel cells for generating green electricity along with wastewater treatment. It has not become commercial, yet it has drawn a lot of attention of researchers toward the green electricity on a large scale (Logan and Regan 2006). At a glance, microbial biomass has huge significance in food industry, fermentation industries, agriculture sector, organic waste management, wastewater treatment, bioenergy-biofuel production, etc.

10.5.1 Solid Waste Management

Waste management is the process which include collection and conversion of waste into suitable products. The major aim of waste management is to minimize the harmful effects of waste materials on human and animals' health and the surroundings. However, challenges are rising day by day with a rapid increase in population, industrialization, and urbanization. Waste management has basically four types of waste: biomedical, electronic, industrial, and municipal. The 4R theory, refuse, reduce, reuse, and recycle, helps to minimize the accumulation of waste materials. Microbial biotechnology in waste management has huge significance in the process of waste degradation via utilization of a wide range of microbes in controlled condition. A wide range of microbial communities such as *Chlorella vulgaris, Corynebacterium* spp., *Staphylococcus* spp., *Scenedesmus platydiscus, Streptococcus* sp., *S. quadricauda, and S. capricornutum* (Singh et al. 2020e) have been involved effectively for the waste management. The most common and efficient strategies adopted for various types of waste at different levels of waste management are biodegradation, bioremediation, and composting. Some important microbial communities used for waste degradation have been listed in Table 10.1.

Plastics are most common and contribute to a major portion of waste material. Proper management of nondegradable wastes like plastic waste is a major component. The degradation of plastic polymer can be done using various ways like

Table 10.1 Microbial communities and their application in different types of wastes degradation

Process	Waste material	Microorganisms	References
Biodegradation	Aromatic hydrocarbons present in soil	*Acinetobacter and Microbacterium* sp.	Simarro et al. (2013)
Biodegradation	Crude oil	*P. Cepacia, B. cereus, B. coagulans, C. koseri, S. ficaria*	Kehinde and Isaac (2016)
Composting	Organic matter	*Bacillus* sp., *Cellulomonas* sp., *Pseudomonas* sp., *Klebsiella* sp., and *Azomonas* sp.	Gajalakshmi and Abbasi (2008), Nakasaki et al. (1996), Strom (1985a, b)
Biodegradation	Textile dyes	*M. luteus, L. denitrificans, N. atlantica*	Hassan et al. (2013)
Plastic biodegradation	Polyethylene bags	*P. aeruginosa, P. putida, B. subtilis, S. marcescens, B. cereus, S. aureus, M. lylae*	Aswale and Ade (2009), Nwachukwu et al. (2010)
Plastic degradation by fungi	PVC (polyvinylchloride)	*P. versicolor, P. chrysosporium, P. sapidus, P. eryngii, P. florida*	Kirbas et al. (1999)
Plastic degradation by fungi	Polyurethane	*C. globosum, A. terreus, C. senegalensis, F. solani*	Boubendir (1993), Crabbe et al. (1994)

catalytic and biodegradation, photo-oxidative, mechanochemical, and thermal. Among all the above strategies, plastic waste management process has a feasible potential because it is an eco-friendly reaction. Biological degradation of plastic is the natural process based on some microbial communities and their enzymatic activity (Albertsson et al. 1987). Such microbes will contribute in degradation of natural and synthetic plastics waste (Gu et al. 2000). The degradation of plastics polymer is a very slow process which further depends on various environmental conditions like pH and temperature. Bacteria and fungi play a major genera involved as degraders in plastics waste degradation. Plastic biodegradation involves many subsequent steps, among them hydrolysis and enzymatic reactions are the most important (Schink et al. 1992). In agricultural sector, agricultural residues act like organic waste. Major portion of agricultural wastes (plant biomass) are made up of complex carbohydrates such as cellulose, lignocellulose, lignin, and hemicellulose. Mesophilic aerobic and anaerobic microbial communities such as *B. brevis, B. cereus*, *B. circulans, B. firmus, B. licheniformis, B. megaterium, B. polymyxa, B. pumilus, and B. subtilis* are cellulose and hemicellulose degraders (Strom 1985a, 1985b). Hence, the ability of microbes to assimilate organic waste depends on their capacity to produce the enzymes needed for the degradation, i.e., if the substrate is complex, then complex and more extensive enzymes are required (Singh et al. 2016; Golueke 1991).

10.5.2 Bioenergy Production

Dealing with the dangers of the global warming is a serious matter for the whole world. Simultaneously, there is a problem to minimize consumption of fossil fuels as the storage of fossil fuel is depleting day by day. Uncontrolled consumption of conventional fuels is the main reason behind accelerated accumulation of CO_2 and CO in the atmosphere because of industrial and human activities. Microbial biomass is the great answer to generate novel, renewable green energy and could be a potential solution as alternative energy resource. Algae and microalgae are considered as a potential choice to generate biofuels (Verma and Mishra 2020). Table 10.2 represents utilization of microbial biomass in bioenergy production through different processes.

Algal biomass is a great source of complexed saccharides such as hemicellulose, lignocellulose, and cellulose. Treatment of algal cell biomass before biofuel production is very important for the conversion of complex carbohydrates into fermentable simple saccharides (Ho et al. 2013; Asada et al. 2012; Kim et al. 2012; Jang et al. 2012; Balat et al. 2008; Sanchez and Cardona 2008). After pretreatment the obtained saccharides are processed further for the production of biofuel in the form of bioethanol by several yeast and bacterial strain like *S. cerevisiae, Z. mobilis, C. brassicae,* and *M. indicus* (Bjerre et al. 1996; Talebnia et al. 2010; Sukumaran et al. 2010; Girio et al. 2010; Li et al. 2008; Moniruzzaman 1995; Nigam 2001). Lipid content is about 20–60% dry weight of algal biomass (Chisti, 2007; Meng et al. 2009; Terme et al. 2017). Microalgal oil contains triacyl glycerides, which is

Table 10.2 Production of green energy by different microbial mass

Substrate	Microorganism for processing	Process	Product	References
Pretreated and saccharified agricultural residues	*S. cerevisiae, Zymomonas mobilis, P. stipitis, C. brassicae, M. indicus, P. tannophilus, E. coli*	Fermentation	Bioethanol	Bjerre et al. (1996), Balat et al. (2008)
Pretreated and saccharified algal biomass	*S. cerevisiae, Pichia angophorae, Escherichia coli, Zymomonas mobilis,*	Fermentation	Bioethanol	Sanchez and Cardona (2008), Kim et al. (2012)
Algal biomass	*Chlamydomonas reinhardtii, Dunaliella salina, Thalassiosira pseudonana, Nannochloropsis Isochrysis* sp. *Chlorella* sp., *Botryococcus braunii,* and *Phaeodactylum tricornutum*	Transesterification	Biodiesel	Scott et al. (2010)
Wastewater or organic waste substrate	*Geobacter* sp., *Proteobacteria, Bacteroidetes, Actinobacteria, Firmicutes, Chloroflex*	Microbial fuel cell	Bioelectricity biohydrogen	Zhang et al. (2012) Rahimnejad et al. (2015)

esterified by using glyceride molecule. For biodiesel production, these triacyl glycerides undergo for a reaction known as transesterification. Transesterification involve any of the acids, alkali, or lipase as a catalyst with methanol, which is actually biodiesel (Fukuda et al. 2001). The concept of biofuel production was identified in 1950s, and is known as a better alternative green energy. However, biofuels production on large scale is not commercially viable because of fluctuating behavior of funding in this sector. Nowadays, biofuel production from algal biomass is at its beginning and requires huge investments and some attention from the automobile sector, oil companies, and algaculture farms. Electroactivity of *Shewanella putrefaciens* (a metal-reducing bacteria) was reported in the microbial fuel cell (MFC) (Kim et al. 1999). The microbial communities which are used to develop these systems have great diversity ranging from *Shewanella* sp., *Geobacter* sp., *Pseudomonas* sp., *Proteobacteria, Bacteroidetes, Actinobacteria, and Firmicutes* (Rahimnejad et al. 2015). Such electroactive microbial community is also known as exaelectron. However, power generated from these MFC systems are not efficient. However, this method catches attention of researcher's due novel alternative option for bioenergy production as well as wastewater treatment (Singh et al. 2020f).

10.5.3 Wastewater Treatment

Wastewater treatments include chemical and biological methods to clean up the impurities. Biological treatment is found to be more effective as compare to the chemical treatment. This method is also cost-effective and environment friendly. Several microorganisms like bacteria, algae, and fungi played a major role in the treatment of various industrial effluent. Microbes efficiently remove or degrade various toxic compounds such as NH_3 and H_2S. Bacteria in wastewater treatment system are a potential degrader of nitrogen and phosphorus. Most of the microbial communities involved in wastewater treatment are respirate facultative either aerobic or in anaerobic conditions (Yadav et al. 2019; Spellman 1997). Heterotrophic microbes are the most dominant ones present and use the organic compound present in wastewater as a substrate. Bacterial species such as *Acinetobacte, Alcaligenes, Achromobacter, Arthrobacter, Citramonas* spp., *Pseudomonas* spp., and *Zoogloe* spp. are commonly used in biological treatment of wastewater (Oehmen et al. 2007). Some algal species like *Chlamydomonas* sp., *Oscillatoria* sp., and *Euglena* sp. are also involved in wastewater treatment. Microalgae are a suitable organism to eliminate and degrade organic compounds, pesticides, and heavy metals, from wastewater. Fungi play an effective part of the sewage effluent treatment. Some of fungal species can oxidize NH_3 into the nitrite. *Zoogloea* sp. and *S. natans* are generally used in sewage wastewater treatment (Le-Chevallier and Au 2004; Painter 1970). Some fungal species such as *Absidia* sp., *Fusarium* sp., and *Penicillium* sp. have been used to remove carbon and other nutrient content from wastewater (EPA 1996; Akpor et al. 2013).

10.6 Conclusion

In this chapter, authors focused on biomass major components of biomass, classification of biomass, and characterization technique. Biomass are classified on the basis of their component such as cellulose, hemicellulose, lignin, and starch. The components also vary with biomass used. Biomass can be classified into several categories like woody, herbaceous, microbial, and agricultural waste. Various types of techniques are used for characterization of biomass such as surface morphology determined by SEM, TEM, and XRD. Chemical characterization can be done through FTIR, mass spectrometry, and XPS analysis. Biological characterization can be performed in the term of genome characterization, and it can be done through several sequencing methods. Biomass has emerging application in the field of bioenergy production as well as wastewater treatment. In this chapter authors summarized biomass classification, characterization, and its important application in the waste management and bioenergy production.

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