Microorganisms for Sustainability 35

Series Editor: Naveen Kumar Arora

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Biomass, Bioenergy & Bioeconomy

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Microorganisms for Sustainability

Volume 35

Series Editor

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Microorganisms perform diverse roles on our planet most of which are important to make earth a habitable and sustainable ecosystem. Many properties of microorganisms are being utilized as low input biotechnology to solve various problems related to the environment, food security, nutrition, biodegradation, bioremediation, sustainable agriculture, bioenergy and biofuel, bio-based industries including microbial enzymes/ extremozymes, probiotics etc. The book series covers all the wider aspects and unravels the role of microbes towards achieving a sustainable world. It focuses on various microbial technologies related to sustenance of ecosystems and achieving targets of Sustainable Development Goals. Series brings together content on microbe based technologies for replacing harmful chemicals in agriculture, green alternatives to fossil fuels, use of microorganisms for reclamation of wastelands/ stress affected regions, bioremediation of contaminated habitats, biodegradation purposes. Volumes in the series also focus on the use of microbes for various industrial purposes including enzymes, extremophilic microbes and enzymes, effluent treatment, food products.

The book series is a peer reviewed compendium focused on bringing up contemporary themes related to microbial technology from all parts of the world, at one place for its readers, thereby ascertaining the crucial role of microbes in sustaining the ecosystems.

Richa Kothari • Anita Singh •
Naveen Kumar Arora
Editors

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Preface

The three interrelated concepts—biomass, bioenergy, and bioeconomy—from the point of view of sustainable advanced conversion processes are bonded here in this present book to make it available for readers from three different specialized fields. It elaborates on processing routes, i.e., how biomass from various sources can be converted into potential bioenergy options like bioethanol, biodiesel, biobutanol, biogas, etc. There are 13 chapters comprised in the three main sections: "Biomass: Progressive Trends for Bioenergy" is the first part, "Bioenergy: Sustainable Solution for Bioeconomy" is the second part, and "Bioeconomy: Policy Trends, Challenges, and Implications" is the third part.

Chapter 1 reports the scope of biomass and its importance for bioenergy applications. Biomass to energy conversion routes and challenges of biomass to bioenergy are mentioned in this chapter. Chapter 2 explores biomass utilization for biodiesel production. Various types of waste and their utilization for biodiesel production are elaborated with the current global challenges in biodiesel production from biomass. Chapter 3 is based on bioethanol production from biomass. There are three generations of bioethanol production, and advanced technologies such as nanotechnology and genetic engineering are also illustrated with challenges of bioethanol production. Chapter 4 provides the role of thermophilic bacterial enzymes in lignocellulosic bioethanol production. The compositional characteristics and accessibility of lignocellulosic waste are mentioned with the importance of thermophilic enzymes and thermophilic microorganisms in ethanol production. Chapter 5 presents thermochemical and biochemical conversion routes of lignocellulosic biomass in which combustion, pyrolysis, gasification, anaerobic digestion, fermentation, and hydrolysis are illustrated with various challenges and opportunities of lignocellulosic biomass conversion technologies. Chapter 6 examines the importance of catalysts in biodiesel production and process optimization by response surface methodology. The optimization of biodiesel production by the conventional "One Factor at a Time" is used and the combination of feedstock catalysts, the relative proportion of monohydric alcohol, reaction time, and reaction temperature are suggested for optimization of transesterification. Chapter 7 explores bioethanol production technologies and various substrates such as sugar cane, wheat, corn, etc. including knowledge about the consequences and benefits of all generations of bioethanol. Chapter 8 describes biobutanol for biofuel and four generations of biobutanol with their production technologies, recent development in the production of biobutanol, and economics of biobutanol. Chapter 9 examines the energy and exergy analyses of typical cookstove models using different biomass feedstocks. In this study, the analysis is performed with varying quantities of four types of wood which is utilized in the local community for cooking. Chapter 10 deals with biohydrogen production technologies in which the major biological processes for hydrogen production such as indirect biophotolysis, direct biophotolysis, dark, and photofermentation, the sequential dark and photofermentation, and biocatalyzed electrolysis are elaborated. Bioreactors configuration, rate of hydrogen production, rate of hydrogen production and limitations in biological hydrogen production are also explained in this chapter. Chapter 11 lists various technologies of bioenergy and policies of bioenergy that define the roadmap for bioenergy targets for sustainable use of bioenergy. Chapter 12 highlights the concept of bioeconomy, related issues, and its contribution to environmental and bioenergy security. Chapter 13 provides an introduction to global algal biofuel policies and factors affecting the global algal policies.

All scientific and technological challenges with progressive research trends in the area of biomass, bioenergy, and bioeconomy are compiled at one place via this volume by renowned experts of their fields. The interlinks in between the economical and ecological aspects of the selected themes with sustainable routes are clearly expressed in this edited book.

We hope readers will find valuable information provided by the researchers from around the globe. We are thankful to all the authors and team members of Springer for their support and co-operation.

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Part I

Biomass: Progressive Trends for Bioenergy

1 Biomass to Energy: Scope, Challenges and Applications

Shubham Raina, Har Mohan Singh, Richa Kothari, Anita Singh, Tanu Allen, A. K. Pandey, and V. V. Tyagi

Abstract

The enormous use of fossil-based fuels due to industrial growth and rapid population explosion has led to their near depletion and resulted in adverse consequences that are adding to the social, economic and environmental challenges. Problems such as global warming, energy crisis and exhaustion of fossil fuel reservoirs have forced to search for new alternatives that have the potential to provide sustainable and eco-friendly energy in near future. Biomass is abundantly present and a renewable resource of energy, it is being seen as a promising feedstock for the production of biofuels and energy via different routes. This chapter is a brief overview of options for conversion of various biomasses to energy via suitable thermochemical and biochemical conversion routes. Also, the utilization of organic waste for energy production was taken in consideration while framing the chapter. The scope of bioenergy production through different generations of biofuels along with their associated challenges and applications in the present scenario has been summarized.

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Keywords

Biomass to energy · Challenges · Biofuels · Conversion technologies

1.1 Introduction

The new era is facing a huge challenge in terms of energy production, as most of the energy required for running industries, vehicles, offices, homes is still coming from fossil-based fuels. Special emphasis is being paid to limit the use of conventional fuels by replacing them with green energy alternatives. The exploitation of biomass for energy production will provide a path for meeting global energy demands. Apart from fresh biomass, utilization of organic fraction of waste is also a sustainable approach as most of the waste is still untapped for energy conversion. The present paradigm is also shifting from linear economy to circular based economy. In this context, the zero-waste approach is being implemented at a gradual pace that advocates most of the waste as wealth. For example, agricultural waste can be converted into biofuels, sewage can be used for the growth of algae and the production of biogas. Algae can again be used for producing biofuels like bioethanol and biodiesel. Economic prosperous and developed urban outfits have bigger waste generation per capita (Singh et al. 2011). The waste from households has a considerable amount of organic content that is biodegradable. This waste is the breeding house of various disease-causing organisms and vectors. Therefore, the organic fraction of waste from big urban settlements could be easily utilized for energy production rather than just being dumped.

Biomass is the biggest source of renewable energy in the present world that is obtained from plants and animals for desired needs of humans. It includes materials such as wood, crops (Reid et al. 2020) and the residues, animal waste, municipal solid waste (MSW), forest litter, etc., that can be exploited as fuel for the heat and electricity production. The utilization of biomass for biofuels is almost a carbon-neutral process. Unlike fossil-based fuels such as petrol, diesel, and coal, the biofuels are considered as clean source of energy that have low emissions. Thus, the sustainable use of biomass for energy can be beneficial to keep a check on global warming (Bajpai 2019). This biomass in plants is produced through the process of photosynthesis. The radiant energy of sun is stored in the plants as chemical energy in the form of starch. The complex carbohydrates are broken down into glucose that is further used by plants for respiration and growth. Biomass can be used directly as a fuel or as a feedstock for the production of various solid, liquid and gaseous biofuels. Since biomass is a renewable source of energy, therefore, various mechanisms are being modified to improve the yield of biofuels for alternative energy sources (Devi et al. 2020). The proportion of different components of biomass like cellulose, hemicellulose and lignin vary from one plant species to another. Hardwood plants like eucalyptus are rich in lignocellulose, the cellulose fraction can go up to 45% of dry weight, it is low in hemicellulose (12–13%) and high lignin content (25–35%) (Nwokolo et al. 2020).

Softwood such as conifers has biomass content of 40–55% (cellulose), 24–40% (hemicellulose) and 18–25% for lignin (Singh and Satapathy 2018). Grasses like miscanthus also have high lignocellulosic content as up to 40% for cellulose, 18–24% for hemicellulose and about 25% of lignin (Kumar and Singh 2019). On this basis, biomass-based feedstock and biofuels are generally classified into different categories as first generation, second generation, third generation and fourth generation. Aquatic biomass such as algae does not require land for cultivation and even have a high energy yield. Woody lignocellulosic biomass also has high energy content but requires a lot of land area for its growth, moreover, its hydrolysis is also a challenging step (Demirel 2018). Energy shortage and extra burden of carbon dioxide (CO_2) emissions due to fossil fuels are serious problems that need sustainable alternatives (Kothari et al. 2010).

With the overgrowing population, tons of waste is generated on daily basis having a large fraction of organic content. This organic fraction can be utilized for energy production through various available conversion routes and produced energy can be stored in the form of heat and liquid fuels, which can be utilized to meet daily energy demand including electricity generation, vehicular fuelling and heat utilization in industrial establishments. The conversion of waste to energy is a sustainable and green approach that helps to solve waste management problems, and it has the potential to reduce over-dependency on conventional energy resources. Figure 1.1 illustrates the process of photosynthesis and various bioenergy sources such as food grains, energy crops, agricultural, industrial and municipal waste.

1.2 Generations of Biofuels

The technical advancement has shown a gradual pace of development to understand the reaction mechanisms and technical aspects of biofuel production. Sustainable biofuel production faces various challenges in terms of food security, feedstock availability, disposal of waste has pushed the invention of various generations of biorefineries and their subsequent biofuel production. At present, biofuels have been divided into four different generations (Fig. 1.2). A brief overview of them is discussed in the upcoming sub-sections and advantages and disadvantages are mentioned in Table 1.1.

1.2.1 First-Generation Biofuels

The first-generation biofuels use feedstocks rich in sugar including sugarcane, maize, wheat, barley, cassava, soyabean and sugar beet (Ale et al. 2019). Biofuels like bioethanol and biodiesel can be easily produced from them. Apart from biofuels, various main or co-products of first-generation biorefineries are a wide range of polymers, dyes, adhesives, cardboard, paper, detergent, adsorbents, cleaning compounds and paint additives. Despite having enormous benefits and high

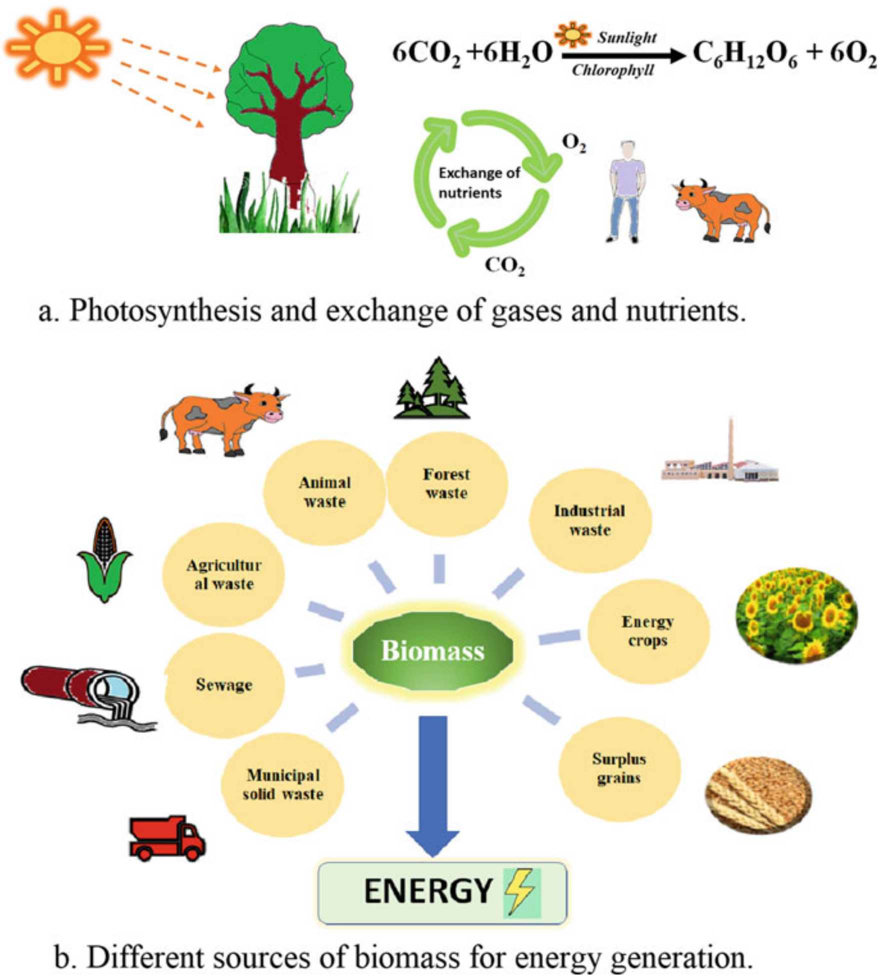

Fig. 1.1 (**a**) Diagrammatic representation of photosynthesis and (**b**) various sources of biomass for energy generation

productivity, the first-generation biofuels are becoming outdated as they are based on crops mainly grown for food. Therefore, for a long time it has triggered a food versus energy debate that led to the evolution in the form of second-generation biorefineries (Ganguly et al. 2021).

1.2.2 Second-Generation Biofuels

The second-generation biofuels process lignocellulosic biomass obtained from non-food crops and agricultural residues such as bagasse, corn stove, rice and

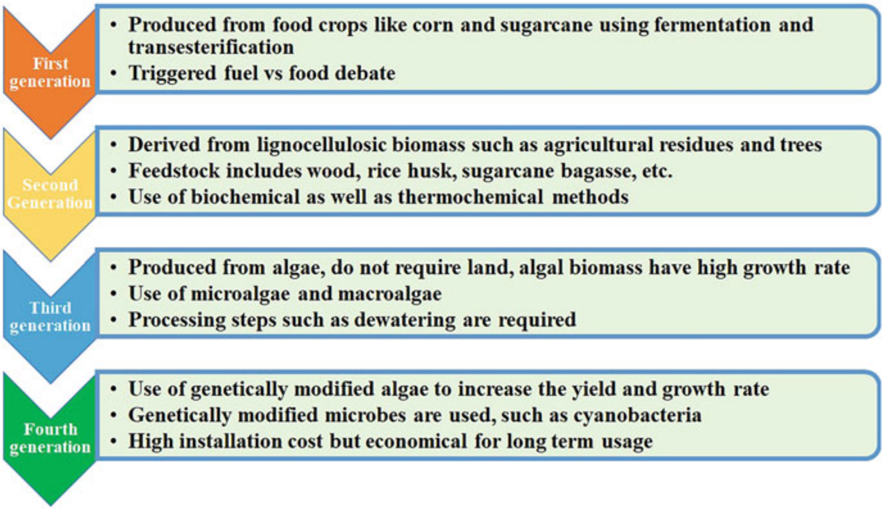

Fig. 1.2 Different generations of biofuels

Table 1.1 Generation of biofuels along with advantages and disadvantages

Biofuel generation	Advantages	Disadvantages
First-generation biofuels	Easy to synthesize, hydrolysis of the feedstock is not a technical hardship	Food crops including maize and sugarcane are primarily used that have triggered the food vs. fuel debate Require high input of nutrients and water supply Requires more area
Second-generation biofuels	Agricultural waste such as crop residues, perennial crops and forest litter can be utilized Feedstock can be grown on less fertile land	Not suitable for the biodiesel production Hydrolysis of biomass is additional step
Third-generation biofuels	Feedstock includes fast growing biomass such as algae that can even be grown on non-arable land	Hydrolysis of lignocellulosic feedstock is a difficult step that requires a big fraction of the total production cost
Fourth-generation biofuels	Genetically modified organisms including feedstock and microorganisms are used to increase the overall efficiency of the synthesis	Still in laboratory scale

wheat straw (Ale et al. 2019). The lignocellulosic biomass is first pre-treated to break down complex polysaccharides such as cellulose and hemicellulose into simple monosaccharides. Pre-treatment of lignocellulosic biomass can be done through various procedures i.e., physical, chemical, biological or physiochemical methods (Ganguly et al. 2021). Physical pre-treatment is given to enhance surface area of the biomass, it includes size reduction through chopping, grinding and milling. Chemical methods include alkali treatment, reaction with ionic solvents and wet oxidation (using oxygen). After this step, they can be converted into desired products using specific routes. Production of biofuels through second-generation biorefineries involves high production cost that is mainly enhanced due to pre-treatment step of lignocellulosic biomass. Other challenges include unavailability of raw materials throughout the year, development of cost-effective methods, the proportion of value-added co-products, biofuel distribution, lack of social acceptance to biofuels like biogas and minimization of possible environmental impacts. Physiochemical methods include autohydrolysis using steam, liquid hot water (LHW) and ammonia recycle percolation (ARP), processing using supercritical fluid carbon dioxide (Ganguly et al. 2021).

1.2.3 Third-Generation Biofuels

The third-generation biofuels use algal biomass. Algae can be obtained from their natural aquatic habitat or grown on a commercial scale in bioreactors and they are further harvested to obtain oil that is present inside their cellular structure. This oil is further processed to convert into biodiesel and de-oiled algal biomass is leftover which can be further use for the production of various types of biofuels such as bioethanol, biomethane and butanol; even it has the potential to provide other valuable products in the form of chemicals and natural fertilizers. Algae is processed for oil extraction using various mechanical as well as solvent extraction techniques. Organic solvents like chloroform/methanol, hexane, pressurized solvent extraction and expeller press are some important oil-extraction methods (Kumar et al. 2019). Algae is regarded as a convenient source of biomass as they have a rapid growth rate, and also do not require an excess supply of nutrients. Moreover, its growth rate can be easily varied by altering parameters such as temperature, water pH, rate of addition of nutrients, etc. Combustion of dried algal biomass can produce electricity. In third-generation biorefineries are also mainly focused on the extraction of metabolites that have various food and medicinal applications (Ganguly et al. 2021).

1.2.4 Fourth-Generation Biofuels

Fourth-generation of biofuels are an extension to already existing third-generation. Fourth-generation biorefineries are being developed for processing genetically-engineered feedstock using genetically modified microbial strains. In fourth-generation biofuels, genetically modified biomass is subjected to genetically-altered microbes such as cyanobacteria for the production of biofuels. Similar to third-generation biofuels, arable land is also not required for the cultivation of fourth-generation energy crops. At present, advanced biotechnological techniques are being invested in the development of fourth-generation energy crops and biorefineries. The fourth-generation biofuels are also carbon-negative fuels as they help in carbon sequestration (Ale et al. 2019). However, these are in the development phase and are expected to run on the commercial model in near future.

1.3 Biofuels Derived from Biomass

In previous times, people have used biomass in the form of wood and straws for fuel. As time passed, they were replaced with fossil fuels such as coal and petroleum. Biofuels can be derived from various types of feedstocks available in the form of crop leftovers, animal waste, plant litter, organic waste from industries and sewage waste. They can also be prepared from specialized crops known as energy crops. On the basis of physical state, biofuels can be categorized into solid, liquid and gaseous forms. Solid biofuels include raw biomass, treated biomass, solid residues after a different types of thermochemical conversions. Liquid and gaseous biofuels include bio-oil, biodiesel and biogas. Biofuels can also be categorized on the basis of feedstocks used into different generations as mentioned in Sect. 1.2. The cultivation of algae requires a lot of fertilizers to meet its demand for nutrients such as nitrogen and phosphorus. This can increase the overall production cost of third-generation biofuels. Various novel species of green algae are being explored from their natural habitat for the biofuel production; Kothari et al. (2013) reported the generation of biodiesel through dairy wastewater using *Chlamydomonas polypyrenoideum.*

1.3.1 Characteristics of Biomass for Biofuels

The choice of the conversion process is decided on the basis of inherent properties of biomass type, and also on the basis of complications arising during the conversion. The technicality of the conversion in combination with the economic feasibility of the final energy form is also kept in consideration. Generally, below mentioned properties are considered for evaluation of best-suited conversion routes.

1.3.2 Moisture Content

Moisture content is an important characteristic that refers to the amount of water present in the biomass, it is usually expressed in percentage of the total mass. Moisture levels range from 15% (cereals) to as high as 90% in a few algal species. This factor is highly important in determining the heating efficiency of a particular feedstock (Sánchez et al. 2019). Usually, feedstocks having low moisture are preferred over biomass having a higher degree of moisture; this is an important factor as higher moisture content will decrease the calorific value of the final fuel. However, in the case of bioethanol and biogas production biomass having high moisture level content are used to ease the conversion technicalities. On the other hand, woody biomass having a low moisture level is best suited for bio-methanol production (Nikolaevich et al. 2016).

1.3.3 Calorific Value

Calorific value or the heating value is the estimation of energy content in the unit mass of a particular substance. It can be calculated by the complete combustion in the presence of oxygen/air. This value refers to the chemical energy bound within the matter and it is the utmost important property that determines its energy value. It is expressed in joules/kg. For the calculative purpose, the calorific value for gases is given in Megajoule per normal cubic-metre (MJ/NM_3) and is calculated in megajoule per litre (MJ/L) for liquid fuels and megajoule per kilogramme (MJ/kg) for solid fuels. There are two calorific values for every fuel, higher calorific value and lower calorific value (net calorific value). A higher calorific value or the gross calorific value is defined as the amount of energy recovered after condensing the water vapours of completely burnt biomass. In lower/net calorific value, the end products of the combusted biomass including water vapours are not cooled to room temperature, therefore only a proportion of energy can be recovered through this mode. The calorific value defines the quality of the fuel, therefore superior fuels have higher calorific values. Calorific value for a particular fuel can be calculated through experimental setup by using a bomb calorimeter and theoretical calorific values can be analysed by proximate and ultimate analysis (Erol et al. 2010). The calorific value of biodiesel is about 41 MJ/kg, for feedstock such as palm and jatropha it can go up to 43 MJ/kg (Kaisan et al. 2017).

1.3.4 Volatile Matter and Fixed Carbon

Volatile matter refers to the gaseous phase produced during the thermal degradation of biomass. It usually contains light volatile gases and tar. The volatile content of biomass helps in its easy ignition. Higher volatile matter content enhances the bio-oil yield (Ullah et al. 2021). On the other side, fixed carbon of biomass is the solid carbon that is present in the char after thermal degradation processes such as pyrolysis and gasification (Basu 2018). Fixed carbon can also be regarded as leftover biomass after removing moisture content, ash content and volatile matter from the original feedstock. Fixed carbon helps in determining the quality of feedstock (Ozbayoglu 2018); the greater the fixed carbon content more is the char production through pyrolysis, 63.3–81% volatile matter if found in wood biomass.

1.3.5 Ash/Residue Content

The chemical breakdown of feedstock is mostly achieved through biochemical and thermochemical methods. In both cases, residue is produced in solid form. The residual end product of combustion is ash (Devi et al. 2020). Ash in combustion processes leads to high levels of polluting emissions and several other problems like difficulty in combustion, increased handling and processing costs during biomass conversion. It also leads to a decrease in the energy content of the total bioenergy production. The solid residues produced during biomass conversion are generally more in comparison to the ash produced by combustion of the same feedstock (Xu et al. 2018). The ash content of petroleum products is commonly low whereas woody biomass is high. High ash content means the incomplete combustion of solid and liquid fuels and 0.03–0.07% of ash content is commonly found by weight of liquid fuel whereas 2.6–18.3% ash content is found with wood biomass.

1.3.6 Alkali Metals Content

The percentage of different alkali metals like sodium (Na), phosphorus (P), magnesium (Mg) and calcium (Ca) is an important factor during thermochemical conversions. Silica (SiO_2) present in ash readily reacts with the alkali metals to form a sticky and mobile liquid that can easily block the air inlet of boiler plants and furnaces, and it results in operational failure. Another phenomenon due to the presence of alkali metals in feedstock may take place, it is called ash melting or ash fusion. It happens due to the high-temperature conditions of boilers. This may corrode the inner linings of the boiler and impact the conversion efficiency. Also, aerosols of alkali matter are formed such as KOH, K_2SO_4, NaCl, KCl. As the temperature of boilers decrease, these aerosols condensate and combine with fly ash to form a slag layer inside boilers (Mlonka-Mędrala et al. 2020). Therefore, pre-estimation of alkali metals in the biomass is an important step that can reduce the chance of failure of the energy conversion process.

1.3.7 Cellulose/Lignin Ratio

Cellulose and lignin ratios are significant in the biochemical conversion process. Plants having higher cellulosic content are easily hydrolysed in comparison to the plants with a higher lignin proportion (Devi et al. 2020). Feedstock with high cellulose to lignin ratio can be easily converted into bioethanol. Current technologies like hydrolysis or enzymatic conversion are not fully matured for converting lignin into syngas. Also, the biochemical conversion of lignin is a complex process due to its chemical composition (Sharma et al. 2021).

1.4 Conversion Routes

Biomass can be transformed into various valuable products such as energy in the form of heat, different chemicals and biofuels. Different factors such as quality of the feedstock, availability of biomass, desired end products, economical aspects of the conversion process, and environmental factors are responsible for choosing the best conversion route. Biomass conversion routes are mainly classified into three types as thermal, thermochemical and biochemical (Fig. 1.3). Sub-types of the different thermochemical and biochemical processes have been discussed in detail.

1.4.1 Thermochemical Conversion

Thermochemical conversion of biomass involves the use of heat for degrading the complex polymeric structure of biomass-based feedstock. Various thermochemical technologies include thermal degradation, pyrolysis, gasification, incineration, etc. and these are further elaborated in the following sections. The various thermochemical conversion processes have their own advantages and operational challenges that have been discussed in Table 1.2.

1.4.1.1 Pyrolysis

Pyrolysis is a thermochemical method through which different types of feedstocks can be broken down in short-chain molecules in the absence or low concentration of oxygen. The operational temperature for pyrolysis lies between 300 °C and 800 °C

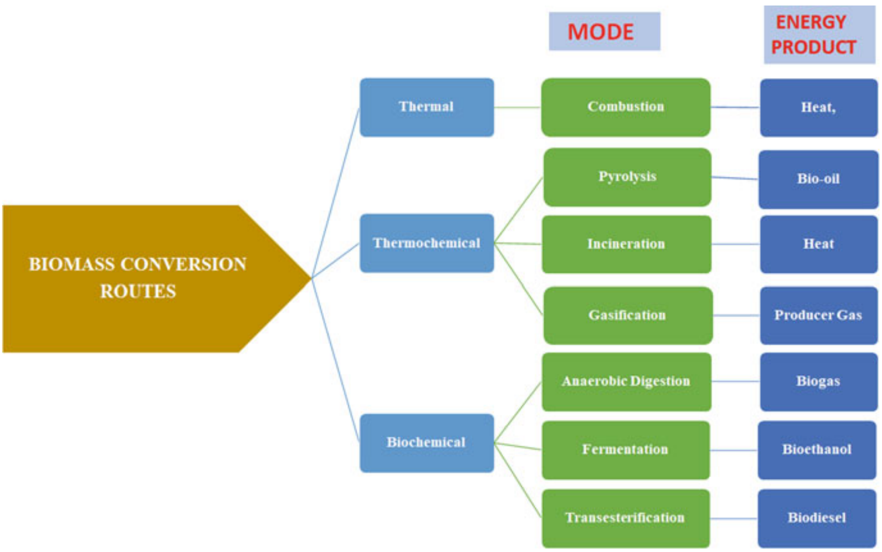

Fig. 1.3 Different routes for biomass to energy conversion

Table 1.2 Comparative study of different technologies involved in waste to energy production along with their preferred operational factors

Technology	Advantages	Challenges	Suitable operational factors
Incineration	Used for waste having high calorific value Requires less land for installation	Release of volatiles such as dioxins and furans Less economical for small scale plants	Continuous oxygen consumption
Gasification/ pyrolysis	Fuel gas and oil are produced as a by-product	Not suitable for waste having high moisture content	The low supply of oxygen and operating temperature range is 300–1300 °C
Anaerobic digestion	Small scale plants can be installed and require less land area Suitable for waste having high organic content	Unsuitable for waste having high inorganic content Segregation of waste prior to feeding in the digester is required	pH 6.8–7.2 and suitable temperature range is 20–37 °C
Fermentation	Bioethanol can be produced through fermentation	Hydrolysis of complex organic matter is a challenging step	Processed feedstock should have high moisture content
Transesterification	Biodiesel is produced through transesterification Reduced emissions in comparison to other technologies	Modified engines are required at higher blending rates	Triglycerides react with alcohols; methanol/ ethanol are preferred

(Gunatilake 2016). The end products of pyrolysis are biochar, bio-oil and gaseous emissions such as methane, carbon dioxide, carbon monoxide and hydrogen (Fig. 1.4). The concentration of these end products will depend on the operational temperature and type of biomass used. It is an ideal technique for the elimination of pathogens and toxic compounds from the waste biomass and biomass can be compressed by the removal of excessive moisture. Pyrolysis is a flexible way to convert biomass into fuel that is easy to store and transport from one place to another in the form of producer gas and bio-oil, which can be utilized for heat, power and valuable chemicals. Like other technologies, it has some disadvantages such as high operational cost, air pollution due to the release of contaminants in the air, heavy metal contamination of soil and groundwater if ash is leached out (Yogalakshmi et al. 2021).

1.4.1.2 Gasification

Gasification is a thermochemical conversion process through which carbonaceous biomass can be converted into various beneficial products including fuels and chemical feedstocks at higher temperatures ranging from 800 °C to 1300 °C (Panwar

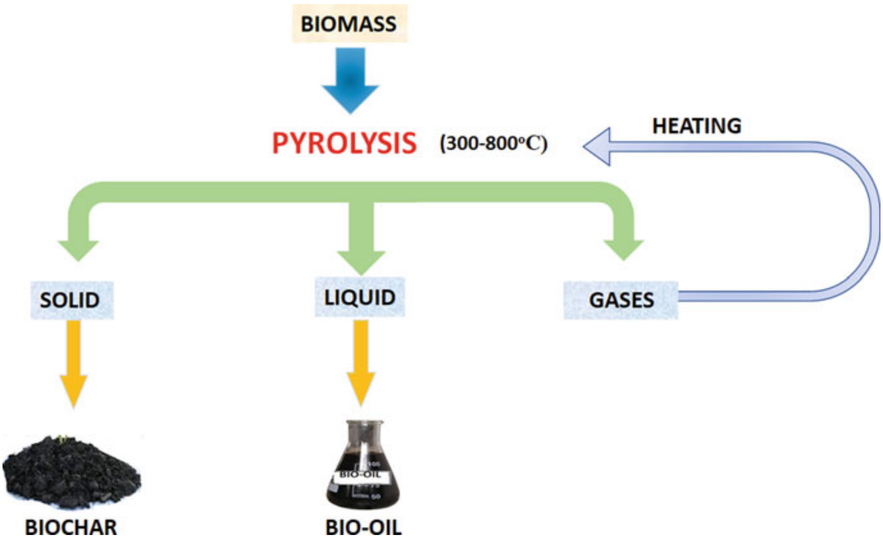

Fig. 1.4 Pyrolysis and its products

et al. 2012) in the limited concentration of oxygen (Fig. 1.5). Syngas or the producer gas is produced through gasification. It is composed of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2) and methane (CH_4). The major difference between pyrolysis and gasification is that, in gasification constant supply of air (oxygen) is required, while pyrolysis is achieved best by proving an inert atmosphere using gases like nitrogen and argon. The major product of gasification is gas (Zhang and Zhang 2019), another important product is oil. Most of the organic substances including wood, plastic, municipal solid waste (MSW), coal can be used for gasification (Gunatilake 2016). During initial times, gasification was employed on small scale for the production of oil through Fischer–Tropsch reaction using coal gas. This equation can be depicted as under (1.1), in this reaction carbon monoxide (CO) reacts with hydrogen gas (H_2) to form oil that is composed of different hydrocarbons (Torres et al. 2021).

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_n\ H_{(2n+2)} + n\ H_2O \tag{1.1}$$

In the present context, integrated gasification combined cycle (IGCC) is being used for the production of eco-friendly fuels. Due to technological advancements, recent times have witnessed a sharp rise in energy production using syngas (Devi et al. 2020). Gasification efficiency depends on a wide range of factors including the type of feedstock, reactor-type, temperature and operational time. Gasification is beneficial for the elimination of waste biomass to produce energy, like pyrolysis it also destroys harmful and toxic constituents and play a significant role in waste management. Limitations include high installation and operational cost of gasifiers, end products that need refining, production of heavy metals (Seo et al. 2018).

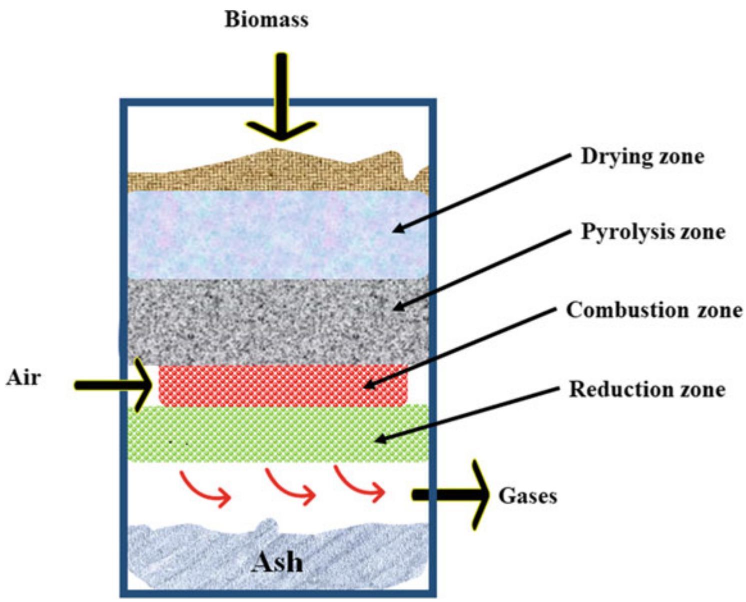

Fig. 1.5 Gasification process in a gasifier (down-draft gasifier)

1.4.1.3 Incineration

Incineration is also a thermal process that requires the combustion of biomass in the presence of air/oxygen. Different types of feedstock having organic origin can be combusted in the incinerator. It is estimated that the volume of municipal solid waste can be reduced up to 90% and the end weight of the burnt biomass is about 25% of the original feedstock. After reaching ignition temperature, feedstock starts burning to produce flue-gases having high energy content that can be used for heating purposes. Various valuable fuels produced as end products include methane, ethanol, methanol, etc. Different types of wastes including municipal waste, biomedical waste, hazardous wastes, waste originating from industrial and packing units, etc. can be processed through incineration (Gunatilake 2016). Temperature is an important factor for any incinerator, high temperature can damage the walls of the incinerator, thereby reducing its efficiency (Mudgal et al. 2014). Incineration reduces the volume of waste to a large extent, requires less installation space. However, there are some limitations associated with it including, high operational and installation cost, the requirement to an external energy source, ineffective handling that can release dioxins and furans into the atmosphere (Dhir et al. 2018).

1.4.2 Biochemical Conversion

Biochemical conversion of biomass involves the use of different enzymes, and microbes such as bacteria for the breakdown of feedstock to produce various biofuels such as biogas and bioethanol. Different chemicals are also produced as by-products during the conversion process. In this subsection technologies such as anaerobic digestion, fermentation and transesterification have been discussed in brief.

1.4.2.1 Anaerobic Digestion

Anaerobic digestion is a biochemical method employed for the production of biogas and biofertilizers. It is performed in oxygen-free chambers known as anaerobic digestors (Gunatilake 2016) and produce biogas mainly comprised of methane (CH_4), and carbon dioxide (CO_2). The biogas could be used as a cooking gas instead of LPG or could be utilized for the generation of heat and electricity. Various types of organic feedstocks such as livestock manure, food waste, sewage sludge, plant litter could be used in anaerobic digesters. Anaerobic digestion consists of four different phases that are mentioned in Fig. 1.6, hydrolytic phase is dominated by hydrolytic bacteria mainly belonging to two phyla, namely *Firmicutes* and *Bacteroides* (Lim et al. 2020). In acidogenesis, various acidogenic bacteria produce short-chain fatty acids from fermentable sugars. Acetogenesis is the third stage that include hydrolytic and fermentative microbes. In the final stage methanogens produce methane gas and carbon dioxide. Temperature (20–7 °C), pH (6.8–7.2) and carbon to nitrogen ratio are vital factors for biogas production (Choi et al. 2020), etc.

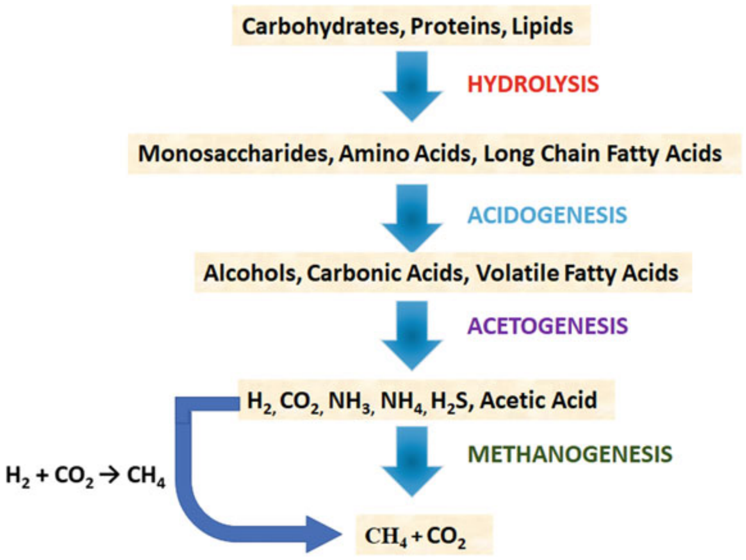

Fig. 1.6 Process of anaerobic digestion

1.4.2.2 Fermentation

Fermentation is largely used for the production of bioethanol using crops rich in sugar and starch such as corn and sugarcane (Gupta and Singh 2019). In the present time, lignocellulosic biomass from cereals and trees is being explored for the production of bioethanol. For this lignocellulosic biomass in the form of hard polysaccharides is first converted into simple fermentable sugar molecules such as glucose, galactose, xylose through the process of hydrolysis and then subjected to fermention. In the end, ethanol is dehydrated through the distillation process (Ruan et al. 2019) (Fig. 1.7). Hydrolysis is usually done through enzymatic action to break down complex chains of carbohydrates (Rezania et al. 2020). However, a lot of improvement is required for the digestion of lignocellulosic biomass to produce simple fermentable sugars. There are various advantages of the fermentation process for the production of bioethanol. Bioethanol is a clean fuel having low particulate emissions and it produces carbon dioxide (CO_2) and water (H_2O) on combustion. It also has higher octane number that gives better burning efficiency to the engine. Bioethanol is a low-cost biofuel having the capacity to limit dependence on fossil fuels. A few disadvantages of bioethanol include its low energy density so a bigger fuel tank is required in comparison to gasoline, has corrosive strength so can corrode conventional engines and storage tanks. Its efficiency is less at lower temperatures; therefore, it has to be used in a blend with gasoline (Dahman et al. 2019).

1.4.2.3 Transesterification

Transesterification for biodiesel is an economical process having a high yield. In this process, triglycerides in the form of fat/oil are reacted with short-chain alcohols to yield alkyl esters in the presence of suitable catalysts. Usually, alcohols like methanol and ethanol are preferred for this process. Transesterification of methanol yields

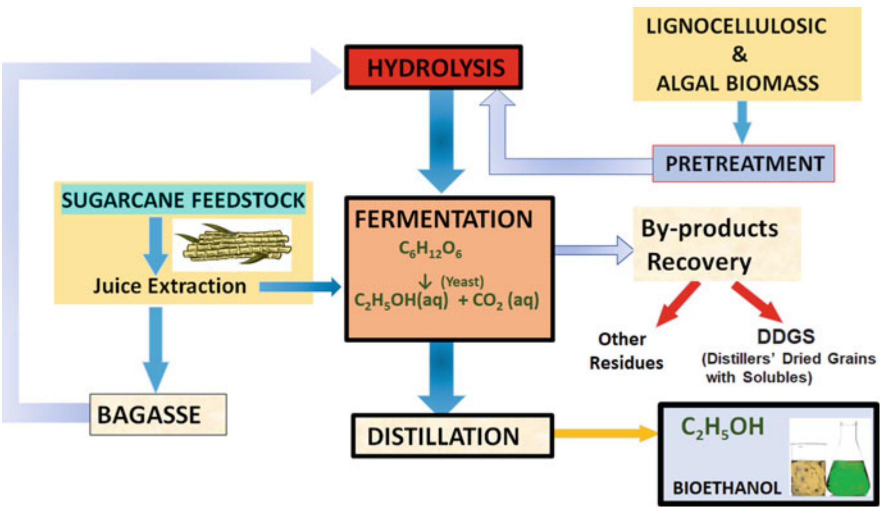

Fig. 1.7 Process of fermentation

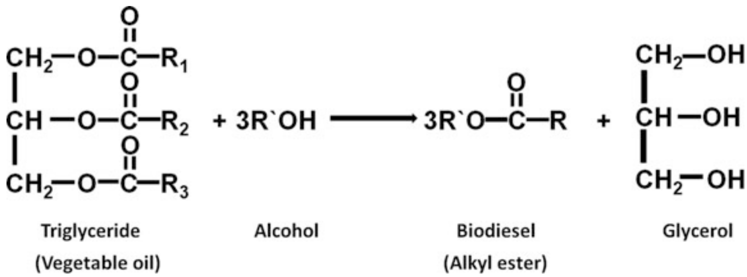

Fig. 1.8 Process of transesterification for biodiesel production

methyl ester, while ethyl ester is produced using ethanol. Glycerol is produced as a waste product that can be used for various industrial applications. In the end, the alkyl ester being lighter is separated from the top of the chamber while glycerol settles down (Debnath 2019). The alcohol to glycerol ratio is a very important factor that decides the rate of transesterification. Theoretically, one mole of triglyceride reacts with three moles of alcohol. But as a practical approach, alcohol is used in excess ratio to enhance the yield of biodiesel (alkyl ester) (Fig. 1.8). However, excessive use of alcohol hinders the easy separation of the alkyl esters (Salaheldeen et al. 2021). Other factors affecting the transesterification process include the type of catalyst used, the temperature of the reactor and the purity level of reactants (Rezania et al. 2019).

1.5 Challenges

The conversion of biomass or organic materials into energy is a very critical and complex process. Various challenges such as feedstock supply, biofuel supply, lack of segregation facilities, food vs. fuel, technical, lack of funds and feasibility hardships have been discussed (Fig. 1.9). If energy has to be produced from fresh biomass such as food grains, food supply can be disturbed, utilization of energy crops has various conversion technicalities. However, in the case where waste has to be utilized as a potential source of bioenergy, challenges are vast that are also discussed further.

1.5.1 Lack of Funds and Planning Failures

Biomass to energy conversion projects lack sufficient financial investments. This financial deficit is a big challenge for the construction of essential infrastructure, training and employment of skilled staff. Lack of dedicated planners due to financial shortages triggers other problems such as poor execution and ineffective financial auditing of the biomass to energy projects. Developed countries can invest better in

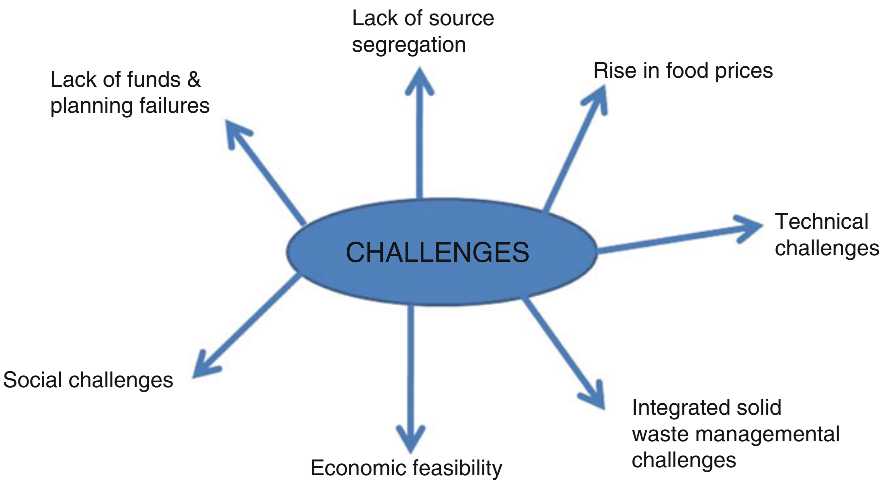

Fig. 1.9 Challenges regarding biomass to energy conversion

biomass conversion facilities; however, poor and developing countries are always in the race of meeting their essential requirements.

1.5.2 Lack of Source Segregation

Biomass is abundantly present but highly diverse in composition. Biomass in the form of wooden logs can be easily utilized for fuel-burning intended for traditional cooking, kilns, commercial bakeries etc. However, a large proportion of this biomass in the form of waste coming out from households and commercial establishments needs segregation before its utilization for energy production. As a result, huge capital is lost during its onsite separation. Waste collection systems in cities are unplanned or outdated, therefore, developing a proper collection system for separate waste types is also a troublesome task. The general public is still lacking proper education for waste segregation. Even people who are aware of the facts, in most cases show carelessness and dump their household trash at wrong places such as empty land plots, river streams, ponds and roadsides.

1.5.3 Rise in Food Prices

Using biomass for energy demands have led to the exploitation of agricultural land as biomass for biofuels require more land for cultivation due to an increase in biofuel production demand. Also, food crops such as corn and sugarcane cannot be used for biofuel production and energy tapping due to their high demand in food industries. The scenario of utilizing food crops can get worse during low harvest seasons affected by low rainfall and bad weather conditions. All these issues can result in a significant increase in food prices (Randhawa et al. 2017). However, lignocellulosic biomass is an alternate of food crops.

1.5.4 Integrated Solid Waste Management Challenges

In energy conversion facilities running on dedicated energy feedstock like wooden logs, energy crops could be fed by biomass of similar composition. For example, bagasse, rice husk etc. can be used with biomass having high lignocellulosic content, and biogas plants along with cow dung could be aided by fruit waste and tree leaves. All this to occur in a synchronized manner, an integrated approach is needed that is often associated with different complexities. Integrated solid waste management (ISWM) is an effective approach that aims at maximum tapping of energy from the waste, thereby promoting its effective utilization and elimination (Sun et al. 2018). However, establishing an ISWM system requires highly skilled staff, high labour for the collection, transfer, segregation and sorting of the waste; also, recovery, treatment and final disposal further add financial burden to the operational cost of the project. To date, no nationwide research has been conducted that covers waste characterization data from all the major cities and different geographical locations. As a result, present policies related to ISWM are formed through the analysis of restricted data only. Moreover, there are chances that the available data is biased; possible reasons for this could be: lack of segregated community bins, non-availability of the waste collection system in rural areas, poor transfer of the waste, untrained staff, low number of transportation vehicles, loopholes in the policies (Kumar and Agrawal 2020) and implementation strategies.

1.5.5 Technical Challenges

Biomass to energy conversion has different technicalities. Biomass having low energy density is not economic for energy extraction. In the second generation of biofuels, easy breakdown of lignocellulosic biomass has to go through complex catalytic reactions. The biological conversion of biomass is not fully efficient; to mark the process economical, better enzymes and catalysts are needed for effective hydrolysis and complete conversion of biomass to energy products. The effective and low-cost extraction of lipids in algal biomass is also a major constraint in bio-oil production (Kumar et al. 2015). Another major obstacle is process optimization. It is quite difficult to maintain optimum reaction conditions. Biomass like algae requires several optimised process parameters, including pH, temperature, nutrient availability, hydraulic retention time, etc. A slight change in these parameters can encompass a significant impact on algal biofuel production. Furthermore, the presence or absence of O_2 in the gasification or pyrolysis of biomass may affect the overall energy production. There are also technical challenges associated with waste-biomass to energy production. Waste to energy technologies are not fully established in developing nations like India; earlier studies show that previously installed waste to energy plants are not successful till date. Probably this could be the result of poor expertise on the authoritarian level, and availability of variable quality and quantity of waste over different locations. Waste generated from different places such as urban, rural, metro cities, industrial areas, residential localities have different energy content; therefore, policies need to be established keeping these differences in the framework. Lack of skilled labour and capital funding in various waste to energy research and development programmes is a major obstacle. Various government body members also suggest that limited land availability for proper exploitation in terms of energy recovery and final disposal is the main hurdle in the case of municipal solid waste (MSW) (Nixon et al. 2015).

1.5.6 Economic Feasibility

The economic feasibility of biomass to energy projects in Asian and African countries is still under question mark. This could be improved a little by encouraging incentives such as financial incentive based energy production. Even the local management system is reluctant in terms of establishing public-private relationships, which acts as a barrier in gaining the trust of industrial investors into waste to energy projects in which biomass is utilized as feedstock. Maintaining a constant supply of biomass feedstock is also a hurdle. Installation of large biomass to energy facilities especially in hilly terrains is also not feasible due to different constraints like small populations, poor transport connectivity and environmental regulations. Also, there are chances of a decrease in forest cover due to excessive deforestation.

1.5.7 Social Challenges

There is a common thinking of the majority of the population that waste management is the duty of the government only. People are still not educated about the benefits of source segregation. Policies linked with biomass to energy production are still lacking. Segregation of biomass waste at homes and agricultural fields is still not a common practice. Lack of social awareness about the benefits of biomass to energy conversion is also a major factor. Moreover, the teaching curriculum at the elementary level lacks proper knowledge about modern techniques involved in effective utilization of biomass to energy production and waste biomass (agriculture and forest sectors) to energy production. This barrier can be surpassed by providing knowledge about biomass management through school lectures, social awareness campaigns and involvement of the general public in biomass to energy workshops (Malav et al. 2020).

1.6 Conclusion

The energy consumption pattern has grown in recent years. Also, the population explosion has created an extra burden on conventional energy resources and led to climate change in the past few decades. As a result, mankind has started exploring more novel ways to exploit energy resources primarily in the form of renewables. A big fraction of renewable energy is in an untapped form that requires to be explored gradually to meet the energy demands of the future generation. Complete energy exploitation from lignocellulosic biomass requires effective catalysts/enzymes for hydrolysis. Lipid extraction from algae at present is possible by use of high-cost chemical methods, that also need novel enzymes for making this process economical. Bioenergy production from waste biomass also serves as an excellent idea that will help us in the elimination of organic waste fraction, thereby providing energy in a sustainable and eco-friendly manner. However, its effective management is still a matter of concern. Keeping food security in mind, advanced generations of biofuels need more research and development. However, full potential exploration of biomass for energy is very tough at present, but it has enormous scope in near future.

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2 Biomass Utilization for Biodiesel Production: A Sustainable Technique to Meet Global Fuel Demands and Future Scope

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Abstract

In the present era of the global energy crisis, the scientific community is constantly searching for alternate and sustainable energy sources. As the most sustainable energy material, biofuel comes out to be the most appropriate option. Different forms of biofuels include biodiesel, bioethanol, biogas, biobutanol, etc. Out of them, biodiesel is an eco-friendly renewable energy source derived from the trans-esterification of lipid-rich organic waste materials. The identical properties of biodiesel make it a good alternative to fossil fuel-based commercial diesel. Biodiesel is considered useful in various engines as it reduces the emission of greenhouse gases and increases engine lifespan. Biomass being a renewable energy source is a promising feedstock for biodiesel production. Therefore, biodiesel can be obtained from a wide variety of available feedstocks such as lipid-rich animal waste, waste cooking oil, non-edible oil, plant residues, algal biomass, etc. Recent advances in biodiesel production from waste biomass have

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received great attention from the scientific community as global fuel demand has been increasing day by day. Also, fossil fuel reservoirs are being depleted. Therefore, this chapter emphasized on utilization of different waste biomass for biodiesel production along with the latest technologies available for its better production and processing.

Keywords

Biofuel · Biodiesel · Biomass · Feedstock · Trans-esterification

2.1 Introduction

Today, petroleum-based fuels are the world's most important energy source. It is estimated that nearly 159 million gallons per day of fossil fuels were consumed in the year 2020 (USEIA 2021). The excessive consumption rates are resulting in the quick depletion of these petroleum fuels. It has been estimated that the world will face a shortage of petroleum fuel by 2070–2080 (Sharma et al. 2020). Besides this, the increasing prices of petroleum-based fuels in developing countries have also raised a concern to find alternative energy sources. Therefore, a sustainable fuel substitute is required to solve the environmental as well as energy crisis issues. However, the substitute fuel should be easily accessible, economically feasible, eco-friendly, biodegradable as compared to the available mineral-based fuels (Pugazhendhi et al. 2020).

Nowadays, bioenergy production has become an emerging field that utilizes different types of biological waste materials to produce energy materials and therefore, is known as "bioenergy." In this scenario of the energy crisis, bioenergy has emerged as one of the best replacements of the presently available energy sources (Guo et al. 2015). Bioenergy endorses various kinds of energy forms such as biodiesel, bioethanol, biomethanol, biobutanol, bioethers, biohydrogen, biochar, biogas, etc. Being biodegradable, sulfur-free, non-toxic, and renewable, these biofuels serve as the best alternatives to petroleum-based fuels (Rezania et al. 2019).

Amongst these biofuels, biodiesel is the top priority of the transportation industry because of its identical properties with petroleum-based diesel (Bhatia et al. 2017). Biodiesel is an alkyl ester obtained through a trans-esterification reaction of oil and alcohol. Also, biodiesel can be prepared from oil extracted from any organic source (Knothe and Razon 2017). Various feedstocks can be used for biodiesel production like vegetable oil, microbial oils, animal fat, waste oil, algal oil, etc. (Bhatia et al. 2020). However, oil crops are being used for biodiesel production, abundantly. Oil crops used for biodiesel production can be both edible as well as non-edible. However, the use of edible oil for biodiesel production can lead to food security issues, therefore, the focus should be given to the use of non-edible oil for the production of biodiesel (Gashaw and Lakachew 2014). Moreover, biodiesel produced from different feedstock may have different compositions and levels of purity (Singh and Singh 2010). However, there are many techniques of biodiesel production such as pyrolysis, trans-esterification, and the supercritical fluid method. Out of them, trans-esterification is the most commonly used method due to reagent accessibility and shorter reaction time (Knothe and Razon 2017). However, biodiesel can be used in both pure forms or as a blend of petroleum-based diesel. In Europe, a blend of 5% biodiesel is the most commonly used fuel (Lucia and Grisolia 2018). Since biodiesel is compatible with the present diesel engine due to its similar characters to the mineral diesel, therefore; its use can decrease the emission of particulate matter, carbon monoxide (CO), greenhouse gases and also help in decreasing the generation of transferable carcinogens (Nadeem et al. 2017).

2.2 Biomass as a Valuable Resource for Biodiesel Production

Biomass is a renewable energy resource of biological origin that can be converted into energy using different available technologies, thus, the obtained form of energy is known as bioenergy (Namsaraev et al. 2018). However, the utilization of carbon from biomass to convert it into renewable power and bioproducts vary with the type of biomass and technology used. Today, a wide variety of biomass that is often considered as waste can be used to produce biodiesel (Bhatia et al. 2017). Agricultural wastes, oil crops, animal fat, waste cooking oil, recycled grease, microalgal biomass, etc. are some of the most commonly used materials that can be used as feedstock for biodiesel production (Banković-Ilić et al. 2012; Adewale et al. 2015; Paul et al. 2014). In general, biodiesel is a carbon-neutral fuel derived from a variety of biomass which is more similar to petroleum-based diesel (Knothe and Razon 2017). The advantages of biodiesel produced from biomass are given in Table 2.1 (Stephen and Periyasamy 2018; Daioglou et al. 2017; Gebremariam and Marchetti 2018; Živković and Veljković 2018; Saravanan et al. 2020; Singh et al. 2020; Dharma et al. 2016; Chandran 2020).

2.3 Technologies for Biodiesel Recovery from Biomass

2.3.1 Biomass Production

Production of biomass depends on the source of origin of biomass such as oil crops, waste cooking oil, flower waste, microalgae, sewage sludge, animal fat. Figure 2.1 shows the biomass production from different types of biomasses. The most common methods of biomass generation for biodiesel production are given below:

Oil Crops Every plant on this planet contains a certain amount of lipids in its cells. Since the quantity and quality of biodiesel depend on the total lipid content of the biomass, therefore, it would be more beneficial to choose crops that are rich in lipid content. However, oil-bearing crops can be edible and non-edible, choosing edible oil crops such as soybean, sunflower, mustard coconut, peanut, etc. (Jitjamnong 2018) may create additional food scarcity. Hence, non-edible oil crops such as neem,

Table 2.1 Advantages of biodiesel produced from biomass

Advantages	Description	References
Waste management	The utilization of waste material and agricultural residues as feedstock for biodiesel production helps in the management of agricultural waste	Stephen and Periyasamy (2018)
Climate change mitigation and carbon sequestration	Unlike petro-diesel combustion of biodiesel does not produce harmful and greenhouse gases like CH_4, CO_2, etc.	Daioglou et al. (2017)
Economically feasible	Large-scale production of biodiesel is economically feasible since the raw material used for biodiesel production is available in abundance	Gebremariam and Marchetti (2018)
Greener source of energy	Biodiesel is biodegradable having no sulfur and toxic contents	Živković and Veljković (2018)
Available in blends	Biodiesel can be used as such or in the form of blends (B2, B5, B20) with fossil-based diesel fuel	Saravanan et al. (2020)
Renewable energy source	Biodiesel is produced from biomass (crop residue, animal waste) which isa renewable source	Singh et al. (2020)
Diesel engine compatible	Biodiesel produced from any biomass is compatible with the presently available diesel engine	Dharma et al. (2016); Chandran (2020)

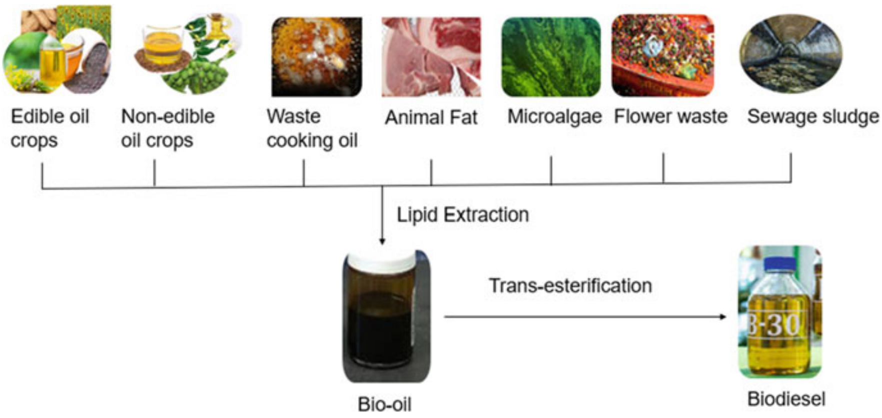

Fig. 2.1 Biodiesel production from different types of biomass as feedstock

linseed, castor, jatropha, Karanja, hemp, *Silybum marianum* have been known as the best feedstock for biodiesel production (Banković-Ilić et al. 2012). Table 2.2 describes the oil content of some edible and non-edible oil crops commonly used for biodiesel production.

Table 2.2 Oil contents of various edible and non-edible oil crops

Edible oils	Oil content (%)	References
Sunflower oil	25–35	(Bet-Moushoul et al. 2016; Luz Martinez et al. 2011)
Soybean oil	15–20	(Rashtizadeh and Farzaneh 2013; Istadi et al. 2015)
Rapeseed oil	38–46	(Aarthy et al. 2014)
Peanut oil	45–55	(Jazie et al. 2013)
Olive oil	45–70	(Sanchez and Vasudevan 2006)
Canola oil	40–45	(Cao et al. 2009; Joshi et al. 2009)
Palm oil	30–60	(Madhuvilakku and Piraman 2013)
Coconut oil	63–65	(Kumar et al. 2010)
Linseed oil	40–44	(Dixit and Rehman 2012)
Non-edible oils		
Jatropha oil	30–40	(Anr et al. 2016; Hashmi et al. 2016)
Castor oil	45–50	(Halek et al. 2013; Dias et al. 2013)
Neem oil	20–30	(Gurunathan and Ravi 2015; Baskar and Aiswarya 2016)
Rubber seed oil	53.74–68.35	(Morshed et al. 2011)
Karanja (*Pongamiapinnata oil*)	27–39	(Kaur and Ali 2011)

Waste Cooking Oil Huge amount of waste cooking oil is generated after the cooking process from food-related industries like hotels, restaurants, commercial complexes, etc. Waste cooking oil can be yellow grease or brown grease-like liquid having high lipid content. Also, waste cooking oil is two- to -three fold cheaper as compared to virgin oils, it can be utilized as a feedstock for biodiesel production (Adewale et al. 2015).

Flower Waste Flowers are widely used in temples, marriages, and many other celebrations, which are discarded afterwards and contribute to organic waste generation (Kumar et al. 2020a). Since flowers are rich in lipid content, therefore, most widely used flowers such as rose and marigold can be used for bio-oil extraction and further production of biodiesel (Waghmode et al. 2018).

Microalgae Microalgae are organisms found in a wide variety of habitats such as ponds, stagnant water, running water, etc. Cells of microalgae are rich in proteins, carbohydrates, and lipid content. Therefore, microalgae such as *Chlamydomonas*, *Scenedesmus*, *Dunaliella*, *Chlorella* sp. can be used as feedstock for biodiesel production (Paul et al. 2014).

Sewage Sludge Sewage sludge is the by-product of wastewater treatment processes. Sewage sludge consists of proteins, fiber, lipids, non-fibrous carbohydrates, and ash. Bio-oil can be produced from sewage sludge through HTL (hydrothermal liquefaction), available in huge volumes. Hence, sewage sludge can serve as feedstock for the production of biodiesel (Qian et al. 2017).

Animal Fat Huge quantities of waste are generated from the meat, leather industry, and fish processing. Waste generated from these industries include mutton fat, broiler chicken waste, chicken feather, microbial oils, waste fish oil, etc. Animal fat is a rich source of lipids, hence, acts as a promising material to produce biodiesel (Paul et al. 2014).

2.3.2 Biomass Pretreatment

Since biomass contains several complex lignocellulosic materials, therefore, prior processing of biomass is necessary to produce biofuel. The process of conversion of complex polysaccharides in biomass into simpler form is called pretreatment (Agbor et al. 2011). There are various methods of pretreatment of biomass such as physical, chemical, and biological methods. Application of physical methods can increase the surface area and pore size of biomass. Physical pretreatment includes the use of pyrolysis, sonication, and mechanical. In the chemical pretreatment method, various chemicals such as acid, alkali, ionic liquids, and ozone gas are used for biomass pretreatment. Physical and chemical pretreatment processes are cost-intensive (Shirkavand et al. 2016). There is another means of biomass pretreatment which is eco-friendly and natural called biological pretreatment. In biological pretreatment, naturally occurring microorganisms such as Basidiomycetes (*Chrysosporium*, *Trametes versicolor*, *Lepista nuda*), and other fungal species (*Ceriporia lacerate*, *Phanerochaete chrysosporium*, *Cyathus cinnabarinus*) are used (Zabed et al. 2019; Kumar et al. 2019).

2.3.3 Lipid Extractions

For the production of biodiesel lipids/bio-oil needs to be extracted from the biomass being used as feedstock. To extract lipid from biomass, cells need to be damaged or ruptured to release their intracellular constituents. The lipid extraction from biomass can be done by using mechanical and chemical methods. The mechanical method includes expeller press, ultrasonic-assisted extraction, microwave-assisted extraction while the chemical method includes solvent extraction, supercritical CO_2, and ionic liquid extraction.

Expeller Press Expeller press is one of the oldest methods that has been used to extract oil from oil seeds. This method involves the application of mechanical pressure that results in the crushing of biomass and cells in such a way that the lipid contents of the cells squeeze out. This method is more commonly used for oil crops as well as algal biomass. This method can extract about 75% of oil (Harun et al. 2010).

Ultrasonic-Assisted Extraction This method involves the generation of intense ultrasonic waves that propagate into the liquid media. It results in alternate high-pressure and low-pressure cycles assisted by ultrasonic waves which damage the cells. The high-pressure and low-pressure cycles result in cavitation which thereby results in the breakage of cells and hence release of lipids (Neto et al. 2013).

Microwave-Assisted Extraction In this method, microwaves are used to generate pressure and heat the whole sample. By this, the inter and intramolecular interactions among the biomass cells take place which helps in the extraction of metabolites from the cells. The advantage of this method is that the obtained oil is of superior quality and high efficiency (Iqbal and Theegala 2013).

Solvent Extraction Method In this method solvents are used for the extraction of lipids from the biomass. However, the solvent can be both polar and non-polar. Non-polar solvents include chloroform, *n*-hexane, benzene, toluene, diethyl ether, while polar solvents consist of methanol, acetone, ethyl acetate, and ethanol. Among the solvents, chloroform and methanol are the most widely used. For example, Bligh and Dyer’s method uses methanol, chloroform, and water for the extraction of lipids from microalgae with high efficiency (Breil et al. 2017).

Supercritical CO_2 Extraction Supercritical fluids can produce solvent-free crude lipids. In the supercritical fluid method, density can vary as per the change in extraction temperature and pressure. Due to moderate critical pressure (7.4 MPa) and low critical temperature (31.1 °C) supercritical CO_2 ($SCCO_2$) is a commonly used solvent for most of the supercritical fluid extractions (Santana et al. 2012).

Ionic Liquids Extraction Due to their non-volatility, thermal stability, and synthetic flexibility ionic liquids are suitable for the extraction of lipids from biomass such as algae.

2.3.4 Biodiesel Production

There are various methods for the production of biodiesel from feedstock such as pyrolysis, supercritical fluid, dilution, trans-esterification, and catalytic distillation (Gaurav et al. 2016). Among all methods, trans-esterification is the most widely used technique of biodiesel production. The process of conversion of lipids/oil to biodiesel in presence of an appropriate catalyst is known as trans-esterification. The catalyst used in the trans-esterification process can be homogeneous (alkaline: H_2SO_4, HCl or acid: NaOH, KOH, $NaOCH_3$), heterogeneous (MgO, TiO_2), and biocatalysts (enzymes-lipase) (Baskar and Aiswarya 2016). According to Indhumathi et al. (2014), the trans-esterification process lowers the viscosity of the oil.

2.3.5 Purification of Biodiesel

Refining crude biodiesel is important for its efficient usage as fuel to remove the various impurities present in it. Various purification techniques for biodiesel include wet washing, dry washing, and membrane technology. Figure 2.2 shows various techniques used for the purification of biodiesel.

Wet Washing The most commonly used method for biodiesel purification is wet washing. Wet washing uses organic solvents, mineral acids, deionized water as solvent. Impurities (glycerol residue, unreacted alcohol, soap, and catalyst residue) in crude biodiesel are water-soluble hence can be removed by extensive water washing.

Dry Washing Dry washing is a method in which impurities are removed by using various adsorbents like activated carbon, activated fiber, ambulate, polite, calcium magnesium silicate, magnesia, silica gel, etc. Adsorbent consists of acidic and basic sites which can attract polar substances such as glycerol and methanol. No water is required in the dry washing technique. Moreover, it improves the quality of fuel and no wastewater is generated, thus, can easily be incorporated with the existing biodiesel plants.

Membrane Technology Membrane technology for biodiesel purification is an emerging technique. Membranes acts as a barrier, therefore, can be used as a medium to separate components of a mixture like crude biodiesel. Separation can occur due to diffusion or convection. Membranes can be organic (polysulphone, polycarbonate), inorganic (Al_2O_3, TiO_2, ZrO_2), and also ceramic. The membrane system can

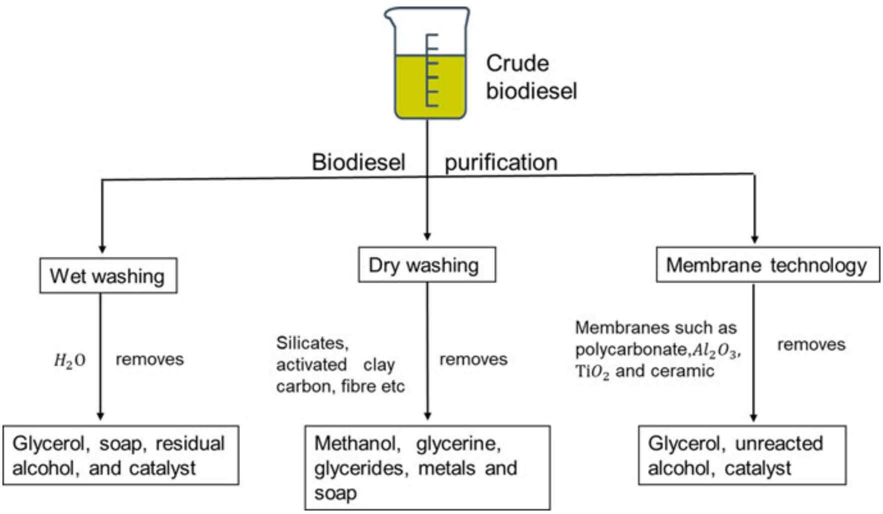

Fig. 2.2 Various methods of purification of biodiesel

enhance the effluent treatment and product recovery hence, helping to minimize the harmful after-effects on the atmosphere due to the purification of biodiesel.

2.3.6 Efficiency Assessment of Produced Biodiesel

Various parameters are used to assess the efficiency of biodiesel such as cetane number, calorific value, density, flashpoint as given below:

Cetane Number Cetane number is the measure of fuel knock tendency of diesel fuel. It is the indicator of the ignition quality of the fuel. A good quality diesel fuel has neither too high nor too low cetane number. Generally, biodiesel is characterized by a higher cetane number as compared to petroleum-based diesel. From their work, Giakoumis and Sarakatsanis (2018) revealed that the cetane number of vegetable oil derived biodiesel ranged between 40 and 52 and then of animal oil derived biodiesel which lied between 60 and 65.

Calorific Value Calorific value is the amount of heat produced as a result of the combustion of fuel at constant pressure under normal conditions. A good fuel should have a high calorific value as it is an important characteristic of any fuel (Ong et al. 2013). In their study, Verma and Sharma (2016) showed that the calorific values of biodiesel derived from corn and peanut-based materials were 39.5 and 39.8 MJ/kg, respectively, which were quite close to the calorific value of petroleum diesel, i.e., between 42 and 45 MJ/kg.

Density Density is an important parameter for any fuel. Higher density means a larger fuel droplet size. Fuel density also affects exhaust emission. Higher fuel density means that fuel will produce more PM and NO_X emissions during its combustion. In their experiment, Kumar et al. (2020b) revealed that the density of biodiesel produced from a blend of Jatropha and algal oil blend was found to be 886 kg/m^3. Also, the B5 blend of Jatropha-alga biodiesel produced minimum CO emission at 1.5 kW load.

Flashpoint It is the temperature at which fuel starts burning upon coming in contact with air. Flashpoint is very important as far as safety, storage, and transportation of fuel are concerned. The flashpoint of biodiesel is always greater than that of diesel (Boz et al. 2009). In a study conducted by Karmakar et al. (2018) on the biodiesel produced from various algal sp. (*Closterium* sp., *Chlorella* sp., *Oscillatoria* sp., *Spirulina* sp., *Navicula* sp., *Pinnularia* sp., *Spyrogyra* sp., *Gomphonema* sp., *Scenedesmus* sp., *Zygnema* sp., and *Frustulia* sp.) showed that the flashpoint of the biodiesel was 150°C which was much better than the flashpoint of petro-diesel, i.e., nearly 93°C.

2.4 Current Global Challenges in Biodiesel Recovery from Biomass

Despite the wide availability of feedstock, still there are many obstacles in the production of biodiesel on a commercial scale. Some of the challenges are given below:

Feedstock From the practical point of view, the cost of biodiesel production from various kinds of waste like waste cooking oil, animal fat, etc. has problems in the oil extraction process and demands a higher cost than that of fossil diesel (Bhatia et al. 2017). Crop-based biodiesel production is easy but it can also lead to food security issues. Therefore, appropriate feedstock needs to be searched which are available throughout the year, easily collected, transported, and requires minimum processing costs.

Infrastructure Currently, there is a lack of sufficient infrastructure for biodiesel production at an industrial scale. The large-scale production of biodiesel requires huge investments for plant installation, storage, and transportation. For commercial scale biodiesel production, there is a need for coordination in production, transportation, distribution, and automobile infrastructure, which also depends on the willingness of investors to finance and buyers themselves (Breitenmoser et al. 2019). Thus, due to a lack of required investment, the biodiesel industry is still limited to a small scale. Moreover, the availability of skilled labor in remote and urban areas is also an issue of concern (Thaba and Mbohwa 2015).

Technological and Financial Barrier The production process for biodiesel is well known but still there are certain technological barriers like reusable catalysts, management of by-products that make the process economical. Therefore, there is a need to develop cost-efficient strategies for biodiesel production (Bhatia et al. 2021). The high cost of installation of bioenergy technology is the major barrier in the biodiesel industry. The technologies needed for larger-scale production are yet not at ground level to support large-scale production. In a study, Fallde et al. (2017) suggested that the technologies for the production of bioethanol from forest-based feedstock have not reached up to the industrial level. Whereas, for the agricultural residue-based bioethanol production, technologies are on the pace of becoming commercial. Due to underdeveloped technology investors fear economic losses for investing in the production of biofuels, therefore, are not willing to invest in renewable energy.

Government Policies Different countries have different policies regarding the production and adaptation of biodiesel. Each country makes policies according to the availability of resources as well as its demands. A country's policy on biofuel has a strong influence on the global biofuel market. Government policies for bioenergy should incorporate environmental benefits, social welfare, and employment opportunities at the local level (Luthra et al. 2015). In their study on bioenergy policy 2018 in India, Kothari et al. (2020) found that some important issues were not considered during the time of policy making which was related to environmental sustainability, technology, coordination among the institutions concerning energy security.

2.5 Future Scope and Recommendations

Biodiesel production can be integrated with other industrial processes to convert the by-products into valuable products; like valorization of by-product glycerol into 1,3-propanediol, citric acid. Biomass-derived heterogeneous catalysts should be utilized more as compared to chemical-based catalysts, since after the biodiesel production biomass-based catalysts can be recovered. Also, the recovered catalysts can be used in bioremediation processes like wastewater treatment. Besides this, the incorporation of nano-catalyst in trans-esterification can result in improved production of biodiesel. Since biofuels are the future energy resources, they are necessary to meet our future energy demands. Therefore, the adoption of bioenergy can provide us with a sustainable and secure future in terms of energy demands.

2.6 Conclusion

Biomass is an energy resource that can be utilized for the production of biofuels like biodiesel. Most commonly oil crops are being used for biodiesel production. But this can lead to feed and fuel issues. The utilization of waste materials as feedstock can help with this regard. Since, the use of wastes like flower waste, waste cooking oil, meat industry waste will not only provide us with the energy sources but also help in the proper management of these wastes. Thus, the use of various non-edible oil crops should be promoted for biodiesel production. In this, various characteristics of biodiesel such as calorific value, cetane number, flash point, density, decide the efficiency of biodiesel produced from any feedstock. However, numerous challenges come across biodiesel production from biomass that include technological and financial barriers, infrastructure, government policies, selection of efficient feedstock. Despite all these challenges biodiesel holds a bright future in the field of bioenergy.

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Conflict of Interest The authors declare that they have no conflict of interest.

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Bioethanol from Biomass: Technologies and Challenges

3

Arti Devi, Anita Singh, Somvir Bajar, and Nilesh Kumar Sharma

Abstract

The increasing demand of energy due to industrialization and urbanization raises the gap between demand and supply of energy. The conventional fuels like fossil fuels are diminishing day by day, and the world is moving towards renewable energy options. Different renewable energy options which are gaining importance are solar, wind, and bioenergy for electricity, transportation, etc. As per the present scenario (COVID-19 pandemic) the increase in personal transportation has gained importance to avoid contactless journey. An increase in transportation boosts the demand of fuel (petrol, diesel, etc.) as these resources are limited and not replenished rapidly. The renewable alternative, biofuel, can be the best option, which can help in decreasing the burden on fossil fuels. Bioethanol is an environmental friendly biofuel that reduces the emission of greenhouse gases from 30% to 85% and reduce particulate emission in the atmosphere up to 50%. There are many processes available for the production of bioethanol. This chapter discusses in detail about different generations of bioethanol and improvisation in bioethanol through the implementation of new technologies, i.e., nanotechnology and genetic engineering.

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Keywords

Bioethanol · Biofuel · Genetic engineering · Nanotechnology · Industrialization · Bioethanol generations

3.1 Introduction

Energy demand has increased due to industrialization and population growth worldwide. The world's energy demand is 80% fulfilled by the fossil fuels and renewables contribute less than 20% (Dalena et al. 2019a, b). Worldwide, there is a search for alternative renewable biofuels. Bioethanol is the renewable biofuel which helps in decreasing the burden on fossil fuels that are not replenished rapidly and hence depleting day by day. Bioethanol is an environmental friendly biofuel which reduces the emission of greenhouse gases and particulate emission in the atmosphere (Di Donato et al. 2019; Agrillo et al. 2013; Barmpadimos et al. 2012). Bioethanol is a liquid fuel which is produced from the living organic matter/biological resource. Compared to other fuels (petrol, diesel etc.), it is better and a cleaner alternative because it possesses distinctive properties and shows a closed CO_2 cycle. Blending of 10% ethanol with petrol diminishes the emission of greenhouse gases at the rate of 2% and fossil fuel energy to about 3% (Chen and Fu 2016). The use of bioethanol is not new; it date backs to the nineteenth century when Simuel Morey used it in IC engine for the first time. Then the policies in different countries developed from time to time to make its use more and more common in the transportation sector so that the dependency on the fossil fuels can be reduced. The USA and Brazil are the two major producers of bioethanol, whereas India has reached to 5.8% blending of bioethanol in petrol (India biofuel Annual Gain Report 2019). The bioethanol production is a multistep process includes three main steps—pretreatment, hydrolysis, and fermentation. There are different generations of bioethanol based on the feedstocks used. The first generation bioethanol production depends mainly on the biomass which is eatable so it creates a debate on the process and food security issues. This can lead to the problem of hunger in developing and poor countries. In spite of that the world production of the first generation bioethanol envisages to reach about 100 billion liters by 2022 (Saini et al. 2015). Brazil largely produces bioethanol from the sugarcane and US from corn, both of which are the leading countries in ethanol production. The second generation bioethanol from the non-eatable biomass overcome this problem of food and fuel but the limitation here is the technical issues in the process. The third generation bioethanol is produced from the biomass of algae extracted by using different methods and converted to ethanol. Each generation of bioethanol has their own advantages and challenges which are discussed below in detail. To make the ethanol production process more efficient and better, some advanced tools (nanotechnological and genetic engineering) are used in the process.

3.2 First Generation Bioethanol

The first generation bioethanol is produced from the edible biomass (sugarcane, corn, maize, etc.). It is mainly produced from C_6 sugars. The production process of ethanol can be divided into two main techniques—one is from the starchy feedstock, i.e. corn, wheat, potatoes, etc. (used mainly by the USA) and other is from the sugar containing feedstock such as sugarcanes (used by Brazilians) (depicted in Fig. 3.1). The ethanol production from starchy substances includes the dry and wet milling process (Kim et al. 2008). The dry milling process includes the grinding phase,

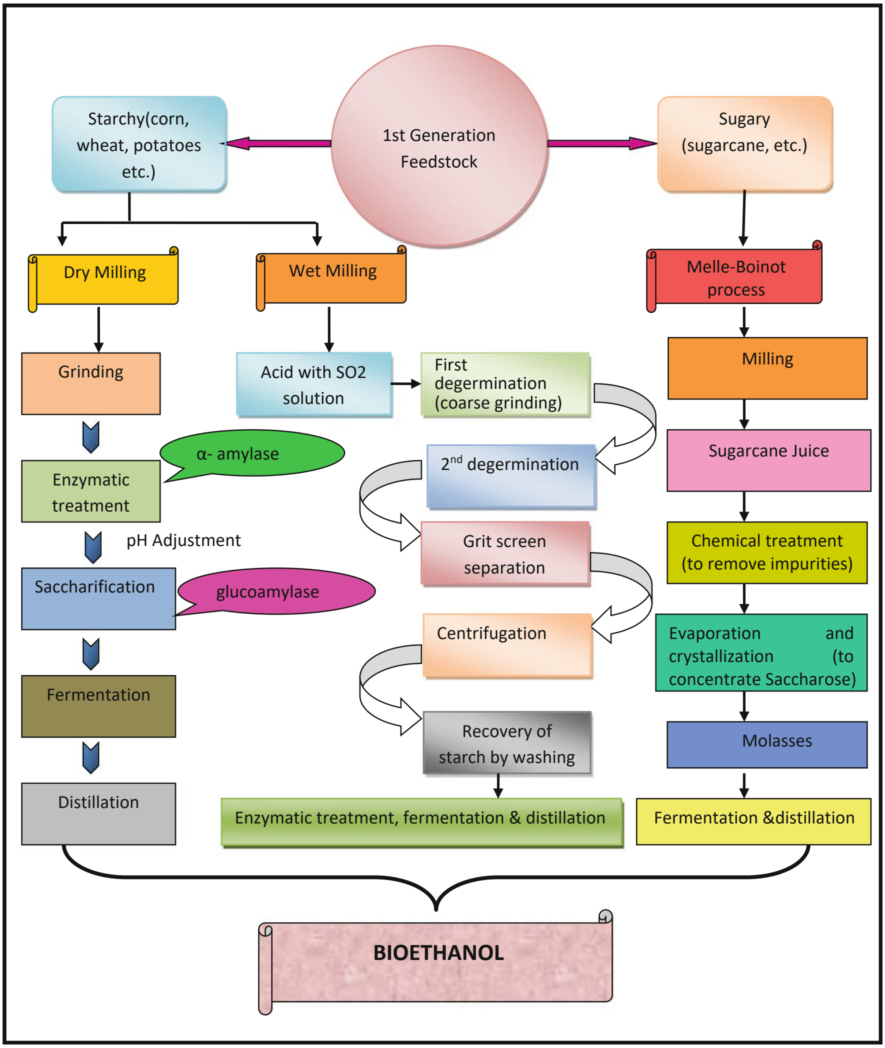

Fig. 3.1 Schematic representation of first generation bioethanol production process

enzymatic treatment, saccharification, fermentation, and distillation step. In the dry milling process, grinding with a hammer mill is required as the particle size is an essential factor influencing the fermentation process. After grinding, the inclusion of α-amylase enzyme is done, which converts the starch into glucose and maltose molecules. After this step pH needs to be adjusted at a range of 4.1–4.2 by 1N sulfuric acid. The saccharification process involves the addition of glucoamylase enzyme, which converts maltose to glucose. The process mixture is then subjected to fermentation process involving the addition of yeast strains, mostly *Saccharomyces cerevisiae*. After the fermentation process ethanol can be recovered by the distillation process and the remaining solid and liquid co-products can also be recovered. The dried grains with solubles are used as the animal feed. The wet milling (WM) process includes the fractionation of the corn components, which was first introduced by Thomas Kingsford as early as 1844 (Ramirez et al. 2008) and was replaced by sulfur dioxide in 1875 (Singh and Johnston 2004). The first steeping step of modern WM is washing with sulfur dioxide solution, and lactic acid to degrade the corn matrix and release starch. Then, a coarse grinding process involves centrifuge and hydrocyclones to separate starchy material from oil-rich components. Purified starch can be obtained by grit separation and centrifuge methods. Then the starchy feedstock is subjected to the enzyme treatment and finally goes for fermentation process to generate ethanol. About 10% of the US ethanol production comes from the use of this technology because it has many advantages like getting the different end products. Although this method has many advantages but the use of SO_2 in huge quantity in this process affects the environment negatively as Environment Protection Agency (EPA) has listed SO_2 as one of the six dangerous air pollutants in the USA (Ramírez et al. 2009). A novel enzymatic wet milling process has been developed to get over this drawback. Proteases behavior (from plant, animal or microorganisms) was studied alone as well as with SO_2 by the researchers. Protease is used in the steeping process, i.e. along with the low SO_2 concentration and also involves in the other stages of the process (after the first degermination process, i.e. coarse grinding). This process assures the protection of the environment due to the little use of SO_2 solution. Dissimilar to the ethanol production from the starchy materials, the technology used by the Brazilians for production of ethanol from the sugar rich plants involves the process of milling and chemical treatments. Two process used chiefly are known as Melle-Boinot process and modified Melle-Boinot process for the ethanol production from sugarcane (Soccol et al. 2005). The process involves the milling to extract the juices, chemical treatment to remove the pollutants and concentrates the saccharose sugars. The saccharose sugars and molasses are subjected to the fermentation process followed by distillation process to produce ethanol and vinasse. In both the processes, the steps are similar but the contrast is in the addition of yeast cells and culture medium as modified Melle-Boinot process involves the simultaneous addition of culture medium and yeast cells but Melle-Boinot process involves the addition of culture medium and yeast cells separately in different stages (Basso et al. 2011). Vinasse is rich in organic substances and was used as a fertilizer in a diluted form in the middle of 1980 in the irrigation process but vinasse has a huge chemical oxygen demand (COD) and biological oxygen demand (BOD) which has made it menacing for the environment. Therefore, the use of vinasse is still a debate among researchers (Senatore et al. 2019). Bioconversion of food crops (starchy or sugary) to ethanol are well established technologies and provide a good share to the total ethanol production i.e. USA using corn and Brazil using sugarcane. The key difference in both the processes is that the energy input for the treatment of sugarcane is less due to the use of bagasse as a co-product while in corn derived ethanol, co-products are not used and also starchy corn material needs a expensive enzyme treatment, which is not required for sugarcane pretreatment (Senatore et al. 2019).

Although there are many advantages of first generation feedstock conversion but still there are some challenges that came across in the use of this technology. The biggest factor is the use of food crops, which is not viable and arises the debate of food versus fuel. The other challenges in the process are the large area of arable land needed for the growth of crops which poses a burden on the land use pattern. The first generation biofuels also have greater carbon footprint contrast to other generations of biofuels. The technological barrier in this process is the physical characteristic of the edible biomass which impacts the overall conversion efficiency (Liew et al. 2014; Dalena et al. 2019a, b).

3.3 Second Generation Bioethanol

To get over the food versus fuel debate, the second generation bioethanol emerged. Second generation bioethanol is produced from the nonedible biomass (i.e. lignocellulosic biomass). Lignocellulosic biomass is composed of three components, i.e. cellulose, hemicelluloses, and lignin. Cellulose is a polymer of six carbon containing group, i.e. glucose linked with β-1,4-glycosidic bonds having chemical formula $(C_6H_{10}O_5)_n$. It was distincted by Anselme Payen in 1839 for the first time from the timber wood by treating it with nitric acid and sodium hydroxide (dos Santos 2013). Hemicellulose is a branched structure contains both five carbon and six carbon groups (D-xylose, D-mannose, D-glucose, or D-galactose). Lignin is an aromatic polymer containing phenolic groups. The production of bioethanol from the lignocellulosic biomass follows three main steps—pretreatment, hydrolysis, and fermentation. Different process steps of second generation bioethanol production are illustrated in Fig. 3.2. The process of pretreatment is needed to remove or degrade the lignin portion from the biomass so that accessibility towards the cellulose and hemicellulose can be increased. Pretreatment are mainly categorized in to four main categories—physical, chemical, physicochemical, and biological. Physical method of pretreatment involves the milling and grinding for the reduction of the size of the particle so that the surface area can be increased, which eases the accessibility of sugars. This treatment method reduces the degree of polymerization of cellulose and degrades its crystalline structure to rupture the lignin (Kumar et al. 2009). Chemical method includes the use of various chemicals like acids, alkalis, and oxidizing agents. Different chemicals have different effects on the biomass structure. Combination of physical and chemical method is used in the

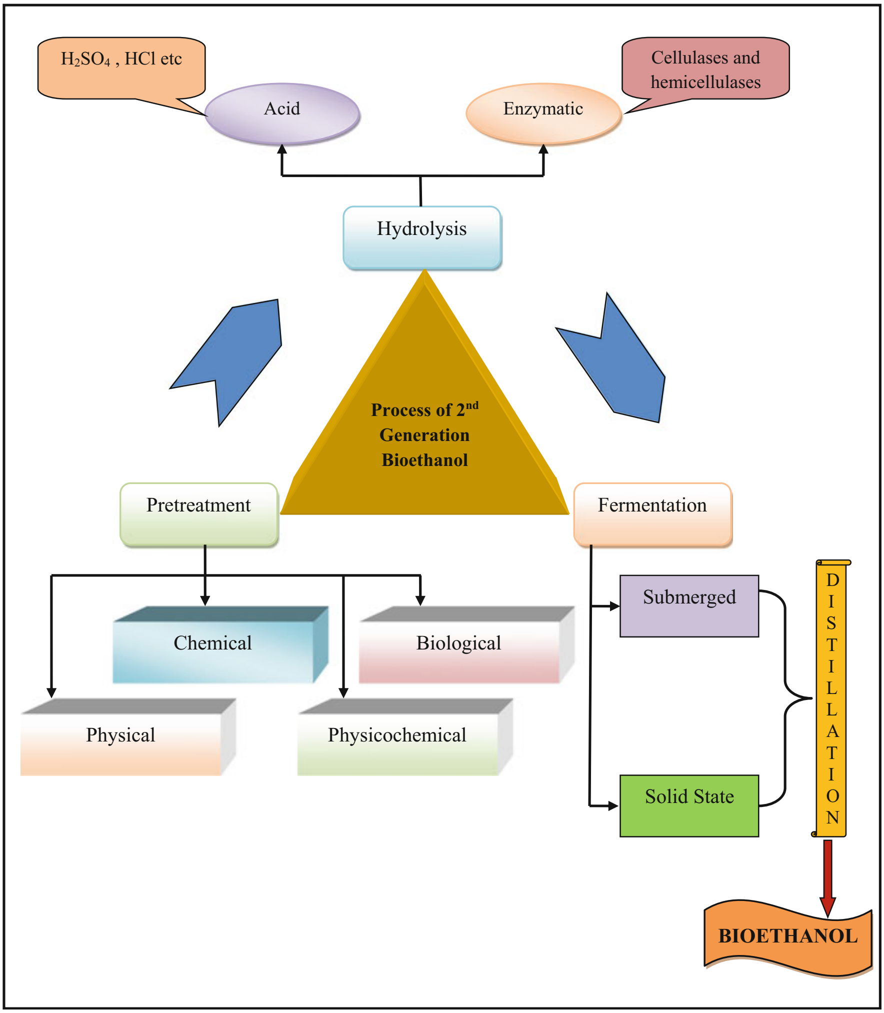

Fig. 3.2 Diagrammatic representation of the process steps involved in second generation bioethanol production

physicochemical method. This method solubilizes the lignocellulose structure at particular pH, temperature, and humidity content. Biological pretreatment method involves the use of microbes that can degrade the structural components of the cellulose and hemicellulose (Dalena et al. 2019a, b). Sometimes integrated approach can be used to enhance the efficiency, which means these methods are used in combinations.

The second stage of the second generation ethanol production is hydrolysis. Hydrolysis is the process of breakdown of the cellulose and hemicellulose into its monomer units. Hydrolysis can be done by acid or enzyme. The hydrolysate quality greatly impacts the subsequent fermentation, so this step is necessary for the overall yield of ethanol (Aditiya et al. 2016). In acid catalyzed hydrolysis, acids like HCl and H_2SO_4 are used at a particular temperature for a specific period of time to disintegrate the cellulose and hemicellulose into their respective sugar units (Dalena et al. 2018). The disadvantage of using acid is its disposal and it also causes corrosion in the bioreactors (Aditiya et al. 2016). The enzymatic hydrolysis entails the use of enzymes. Various enzymes (cellulases and hemicellulases) together work on lignocellulosic biomass and convert it into their monomeric units. Cellulase is a complex of three enzymes–endoglucanase, cellobiohydrolase, and β-glucosidase. Endoglucanse breaks the internal bonds between the cellulose leading to the formation of chains of shorter length. Cellobiohydrolase breaks the bond from the ends forming the cellobiose. β-glucosidase hydrolyses the cellobiose to form glucose. Many other enzymes (Xylanase, acetylesterase, glucuronidase, β-xylosidase) are also used in the degradation of hemicellulose into glucose, galactose, mannose, xylose, and arabinose. Enzymatic hydrolysis depends on the factors like pH, temperature, and the concentration of the substrate (Sun and Cheng 2002). The process of conversion of monomers into ethanol is known as fermentation. Fermentation can be carried out in batch type, fed batch type, and continuous type reactors. In batch type reactor, substrate is once filled at the start of the reaction. Volume remains constant in this type of bioreactor. In the fed batch reactor type, substrate is also added in between the reaction to decrease the substrate inhibition. In continuous type bioreactor, the substrate is added continuously and the product is removed often with the same rate. The glucose and xylose conversion into pyruvate takes place in the process of fermentation through various pathways. Phosphorylation of glucose to glucose-6-phosphate takes place which is followed by some intermediate formation and finally converted to pyruvate by a pathway of EMP (Embden-Meyerhof-parnas). Conversion of hemicellulose into xylose by following the pathway of PPP (pentose-phosphate pathway) which gives fructose-6-phosphate that again converted to pyruvate by EMP pathway through some intermediates. Based on the microorganisms used in the process, the end product varies, as an example if yeast is used it gives end product of alcohol and CO_2 by the process catalyzed by enzymes (Jambo et al. 2016). Microorganisms which have an ability to ferment sugars separately as well as simultaneously are of three types—yeast, bacteria, and fungi (Dalena et al. 2019a, b; Rastogi and Shrivastava 2017). Prior to now, it was thought that the hydrolysis and fermentation takes place in different steps known as the separated hydrolysis and fermentation (SHF) but the inhibition caused by the accumulation of sugars is a drawback of this process eventually impacts the yield of ethanol. So to overcome the drawback, SSF (simultaneously saccharification and fermentation) is a potential method which reduces the energy used in both processes separately and also diminishing the effects of inhibition caused by accumulation of sugars. But this process needs an intervening temperature for both the enzymes and the microorganisms as the optimum temperature required for enzyme hydrolysis is at 50 °C and for the fermentation microbes at a range of 28–37 °C.

The advantage of second generation bioethanol is that it decreases the burden of waste disposal as biomass is found in abundance on earth. It reduces the GHG emission as the agricultural residues are burnt openly in the field which intrudes the high concentration of air pollutants in the air. It is a sustainable method of producing bioethanol as it provides energy as well as solving the problem of food versus fuel. Despite its advantages, the second generation bioethanol production faces some technological challenges like lack of mature technology, expensive enzymes and overall production cost. The other technologically drawback is that the degradation of C6 and C5 sugars simultaneously is not possible for all the microbes which decreases the efficiency of the process and ultimately decreases the yield of the product. So for making this process industrially efficient there is a need to find out the technology with modern innovations which fills these gaps of the process.

3.4 Third Generation Bioethanol

The third generation bioethanol are produced from the feedstock of algal biomass (Chen and Kuo 2011) and its schematic representation was shown in Fig. 3.3. Algae are the tiniest organisms having huge potential. These photosynthetic powerhouses have many applications which play important part in the ecology. They act as nitrogen fixers, source of food due to its metabolic potential (Chew et al. 2017; Tiwari et al. 2019). They are potential feedstock for bioethanol production as their growth rate is high and has a capability of neutralizing the emissions of greenhouse gas. These organisms do not need arable land for cultivation as they can grow on non-arable land/waste water/saline water/fresh water. The algal biomass mainly composed of proteins, lipids, carbohydrates, and several other components (Chen et al. 2014). The production of bioethanol from algae follows certain steps—strain selection, cultivation of the algae, harvesting, fractionation/extraction, and conversion process. The strain should be selected according to the recovery of the product as some strains contain more lipid content than the protein. Different components of the algal biomass give different products (Lardon et al. 2009). Algae can be unicellular (microalgae) and multicellular (macroalgae). Macroalgae is a multicellular aquatic organism which develops attached to the rocks while the microalga is unicellular aquatic organism which floats on the surface of water (Jambo et al. 2016). The multicellular algae are classified into three major groups—green (chlorophyta), brown (phaeophyta), and red (rhodophyta) (Demirbas et al. 2011). The carbohydrate content in green, red and brown algae are 25–50%, 30–60% and 30–50%, respectively. The four major groups of microalgae are categorized widely that are as—chlorophytes, rhodophytes, cyanobacteria, and chromophytes. Some strains of microalgae contain high quantity of carbohydrates and reached up to 70% under specific conditions. The different algal strain gives different commercial products. The microalgae production was started in 1960s in Japan commercially (Varfolomeev and Wasserman 2011). The strains which have high carbohydrate

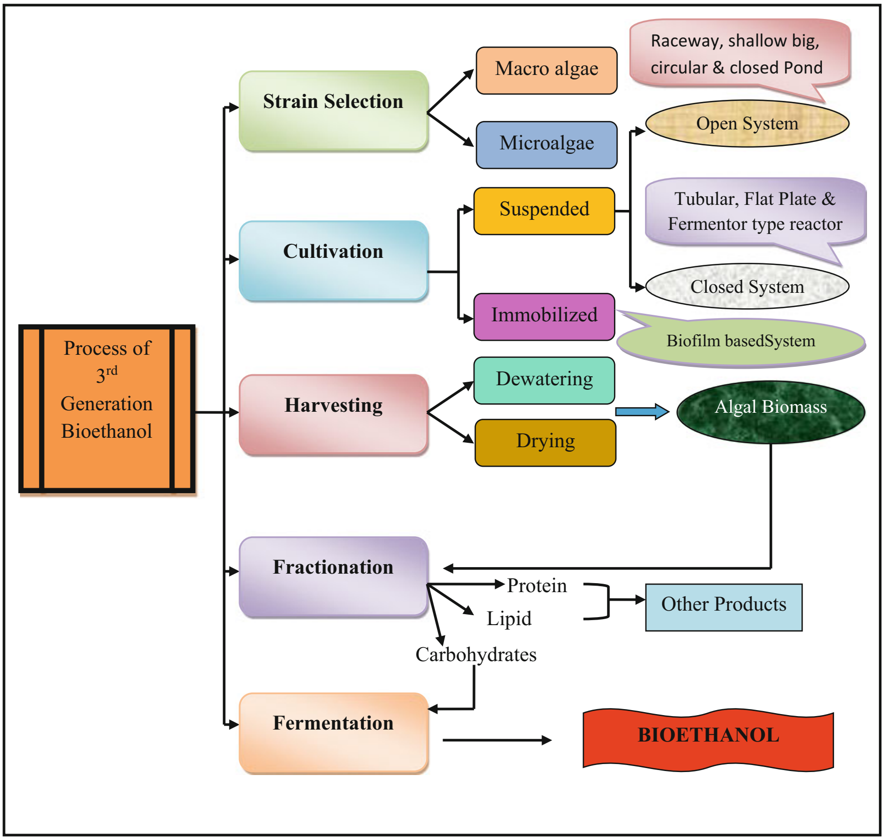

Fig. 3.3 Figure shows the process of ethanol production from the algal biomass

content are the suitable for bioethanol production. The second stage is the cultivation of the algae in which some factors like nutrient, sunlight, pH, and temperature are the major concerns which needs to be taken care. There are different cultivation strategies which mainly includes two systems—suspended and immobilized system. The suspended system includes the open and closed systems. The open cultivation system in the shallow ponds where algae use the atmospheric carbon dioxide effortlessly. The open pond systems generally comprises of the raceway pond, shallow big pond, circular pond tank, and the closed pond. For these systems, the location and availability of the sunlight are the factors which influence its production. The raceway pond system is provided with sufficient carbon dioxide and supply of nutrients. To prevent the sedimentation, this system is fitted with paddle wheels to facilitate mixing (Brennan and Owende 2010). But the disadvantage of this open cultivation system is the chances of contamination by the other photosynthetic organism that may enter through the air or rain and its land usage is more and monitoring is quite difficult in spite of its cost which is very low (Proksch 2013). To avoid contamination of the open system, closed systems provides a good option. It is also known by the name photobioreactor (PBR). The closed system is equipped with controlled conditions and provides the optimum conditions required for the cell growth. Depending on PBR construction and design, it is classified as—flat plate reactor, tubular PBR (horizontal and vertical), helical PBR, and fermentor type reactor. The disadvantage of closed system is, its cost of production. The chief and the biggest difficulty of the tubular and raceway ponds are the harvesting of biomass by dewatering. To overcome this, immobilized systems can be used which is a biofilm based system which removes the difficulties of harvesting (Chisti 2007; Hoffmann 1998). In order to make the cultivation more efficient, researchers develop a hybrid system which removes the disadvantages of open and closed system. It comprised of both systems, i.e. algae first cultivating in PBR and then put in open system to reach the optimum biomass production. The contamination chance is less as when algae is put in open system it becomes dominant and able to compete for resources (Schenk et al. 2008). In reality, no procedure is set to be standard procedure for cultivation; it is based on the conditions and the strain selected for the desirable product.

After cultivation, the algae is removed from the water and dried to get the biomass for the conversion. The harvesting is done by the different methods—mechanical, chemical, biological, and electrical based systems. The techniques like centrifugation, sedimentation, flocculation, etc. are also used for harvesting. Prior to the conversion to bioethanol, the harvested algal biomass are fractionated in to its constituents—protein, lipid, carbohydrates, etc. The different components of algal biomass give different solid, liquid, and gaseous biofuels and other products on different conversion technologies (fermentation, gasification, pyrolysis, anaerobic digestion, and transesterification). The bioethanol is produced by the process of fermentation (Chowdhury et al. 2019).

The use of algal biomass as a feedstock for biofuel production is environmental friendly as it consumes CO_2 for its growth and neutralizes the CO_2 produced by biofuel on combustion. Another benefit is that it may also bioremediate the excess nutrients if waste water is used for its growth. It does not have conflicts with food and land usage. Even though it has many benefits, but there are some drawbacks associated with the third generation feedstock. The method of using algal biomass is not economically viable as the cost is much higher than other sources. Other drawbacks include the technical and geographical issues. The algae needs water for growth but in some countries where temperature is low it becomes a problem. The high content of water in algal biomass is an issue that necessitates significant dewatering to extract lipids. To make this method sustainable, there is a need for making the harvesting more efficient to reduce the expense of the process (Lee and Lavoie 2013). The Challenges related to different generation of bioethanol production shown in Fig. 3.4.

Fig. 3.4 Representation of different challenges related to different generations of bioethanol

3.5 Advanced Technologies

3.5.1 Nanotechnology

It is the branch of science which deals with the nanoscale. The application of nanotechnology is wide. Nanotechnology is used in the bioethanol production process steps, i.e. pretreatment, enzymatic hydrolysis because it possess some characteristic that makes it beneficial for the process of biofuel production. Pretreatment is the process in which the lignocellulosic biomass degrades into its components—cellulose and hemicellulose. The barrier in the accessibility of cellulose and hemicellulose is lignin (the component of cell wall). Nanotechnology plays a role in the pretreatment process by changing its structure and improving the process efficiency. It has been used in two perspectives—by using nanotechnological instrumentation and catalyzers. Nanotechnological instrumentation provides a good tool for knowing the ultrastructure of lignocellulosic biomass before and after pretreatment. The electron microscopy of the biomass helps to get the information about the morphology, chemical composition and its structure at atomic level. SEM (Scanning electron microscopy), TEM (Transmission electron microscopy) are the tool which works at nanoscale and have better resolution and gives 3D images. Both these instrumentation technology requires a very thin sample size (Bonevich and Haller 2010). Other nanoscale technology includes AFM (Atomic Force microscopy) having low cost and better resolution than SEM and TEM and it does not requires any separate sample preparation (de Oliveira et al. 2017). Another novel pretreatment method is also developed known as Nanoshear Hybrid Alkaline technology (NSHA) in which high speed shear, chemicals, and thermal effect is used synergistically. Commonly used reagent is NaOH and other nonvolatile, ionic liquids are also used. Special type of bioreactor is also used having temperature control mechanism and work axis of high speed. It destroys the ultra-structure of lignocellulosic biomass and chiefly removes lignin (Kim and Holtzapple 2005). Many nanoparticles are used to remove crystallinity of the cellulose. They opened up the cellulose structure and forming a networked structure with nanoparticles. Nanomaterials are also used in the process of enzymatic hydrolysis. Enzymatic hydrolysis involves the conversion of polymers into its monomeric units (Cellulose to glucose) with the help of reaction catalyst-enzyme. To make the enzymatic process inexpensive, immobilization is done. Variety of nanoparticles (Fe_3O_4, SnO_2, TiO_2) are used for enzyme immobilization. The enzyme immobilization on the magnetic nanomaterials gives the benefit of recovering and reusing it up to few cycles after washing. The small size of the particles gives much surface area to the enzyme for the attachment. They provide increased stability to the enzyme and also make the process economically efficient.

Despite its benefits, there are some limitations of using nanoparticles like enzyme denaturation, and reduced efficacy of the enzyme. For industrial usage of this process, it requires a derivative which is stable and may possesses functional properties for specific reaction (Vaghari et al. 2016).

3.5.2 Genetic Engineering

Genetic Engineering is the technology in which the genes of the organism are modified using biotechnological tools. To enhance the production of biofuel, various tools of genetic engineering are used by various researchers in many ways. The different approaches include the enhanced production of starch or sugar, transgenic cellulase production, modification in the cell wall, and lignin content (Saha and Ramachandran 2013). The first generation bioethanol is produced from sugar or starch containing substances. Therefore, the introduction of the bacterial gene sucrose isomerase was done by Wu and Birch (2007) that has a function to convert sucrose in to its isomer (isomaltulose). The accumulation of isomaltulose targeted in the vacuole which doubles the amount of sugar contrast to the control. Cellulase from thermophilic fungi are isolated, modified and expressed in different organism like yeast strains, *E. coli*, etc. The production of cellulase in the plant itself is the another way of reducing enzyme production costs. β-1,4-endoglucanse gene from the *Acidothermus cellulolyticus* was expressed in rice plant that targets its apoplast for accumulation. 6.1% of the enzyme formed to the total leaf soluble protein which is 20-folds higher (Chou et al. 2011). COMT gene (caffeic acid 3-o-methyltransferease) which is responsible for biosynthesis of lignin was downregulated with RNA interference technology in switch grass leads to less lignin production, enhanced sugar release, and improved ethanol production (Fu et al. 2011). The protein that is accountable for the loosening and expansion of the cell wall is "expansins." These expansins aid to loosens the cellulose making the accessibility of cellulase easier during hydrolysis. "Swollenin" is a kind of expansin was isolated from *T. reesei* and cloned in *Kluyveromyces lactis* to get recombinant protein. This results in reduced size of cellulose particle and crystallinity of cellulose leads to the enhanced hydrolysis which in turn is proficient for the increased bioethanol production (Jäger et al. 2011).

3.6 Conclusion

Bioethanol is a potent biofuel that can reduce the stress on fossil fuels. The first, second, and third generation of bioethanol produced from the edible, nonedible, and algal biomass, respectively. Each generation of bioethanol is produced by the different process steps described above in detail. Each of these three generations of bioethanol has its own challenges which need to be overcome for making the process more sustainable and economically viable. Some advanced tools are also used by the researchers for increasing the yield and production of the bioethanol. If the shortcomings and gaps of these processes will be filled, then bioethanol proves to be a promising fuel.

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4

Role of Thermophilic Bacterial Enzymes in Lignocellulosic Bioethanol Production: A Panoramic View

Pankaj Sharma, Somvir Bajar, Narsi R. Bishnoi, and Anita Singh

Abstract

Due to increase in concentration of greenhouse gases, environmental pollution, and climate change, there is an urgent need of some alternate fuels for the sustainable management of the natural resources of earth. Lignocellulose is the biomass which is present in huge quantity on the earth is being used for the production of bioethanol. Besides it, using lignocellulosic material can lower the cost of other material being used for the bioethanol production. The first step to convert these wastes into ethanol is pretreatment. Many pretreatment methods such as mechanical, physico-chemical, chemical, and biological, are being employed which provide maximum accessibility of carbohydrate polymers for simple sugars production during enzymatic saccharification using thermophilic enzymes. Thermophilic enzymes from bacterial species have additional benefits over mesophilic ones like high substrate range and higher operating temperature. Recently, development in search of genetic engineering of thermophilic bacteria gain attention wordlwide and also highlighted in this chapter. Finally, fermentation to convert these mono sugars into ethanol is carried out mostly by baker's yeast, i.e. *Saccharomyces*

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cerevisiae. This review paper focuses on using various techniques for ethanol production by utilizing thermophilic bacterial enzymes.

Keywords

Lignocellulose · Bioethanol · Thermophilic · Enzymes

4.1 Introduction

One of the main challenges being faced by developing world now-a-days is how to meet growing energy demands along with sustainable economic growth without affecting the environment. The global energy markets is largely dependent on conventional fuel resources such as natural gas, oil, and coal, which provide a major part of the total global energy needs but it also contributed to environmental pollution and increased earth average temperature. Hence, researchers have huge interest in discovering non-conventional fuels to substitute the fossil fuels (Bai et al. 2012). The dependency on oil import can be reduced only by production of biofuels. It would also generate jobs for the country as well as abate environmental pollution. Hence, some efficient methods of converting cellulosic substrate into ethanol are required to be developed (Bai et al. 2012). The lignocellulosic biomass (LCB) which is made up of cellulose, hemicelluloses, lignin, and some other components, may serve a good option for the production of bioethanol. For the conversion of this biomass into bioethanol, some suitable and efficient pretreatment methods to break and remove the lignin portion are needed. However, the accessibility of LCB on the earth in huge quantity is of great value for the production of bioethanol (Chang and Yao 2011). Besides being renewable, another benefit of lignocellulosic materials is their ease of access at comparatively lower cost. It does not compete with production of food and fodder for the animal. The present review article focused on importance and role of thermophilic enzymes and thermophilic microorganism in ethanol production.

4.2 Accessibility of Lignocellulosic Waste and Its Compositional Characteristics

To produce bioethanol, lignocellulosic waste acts as an unlimited source for raw material (Sukumaran et al. 2005). LCB is the biological material derived from plants which is composed of cellulose, hemicelluloses, lignin, and other components in different amounts. The composition and quantity of these elements may be different for different plant species (Table 4.1). It has become necessary to produce biofuel and other the value-added products by utilizing these biomass and realize the real economy for today’s societies (Hu et al. 2016; Zhang et al. 2017).

Table 4.1 Structural composition of different lignocellulosic biomass

Substrate	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Banana waste	32.2	14.8	14	John et al. 2006
Corncob	45	35	15	Prassad et al. 2007
Hardwood	40–55	24–40	18–25	Malherbe and Cloete 2002
Newspaper	40–55	25–40	18–30	Howard et al. 2003
Nut shells	25–30	25–32	30–40	Abbasi and Abbasi 2010
Rice straw	32	24	18	Prassad et al. 2007
Softwood	45–50	25–35	25–35	Malherbe and Cloete 2002
Sugarcane bagasse	42	25	20	Kim and Day 2011
Wheat straw	29–35	25–32	16–20	McKendry 2002

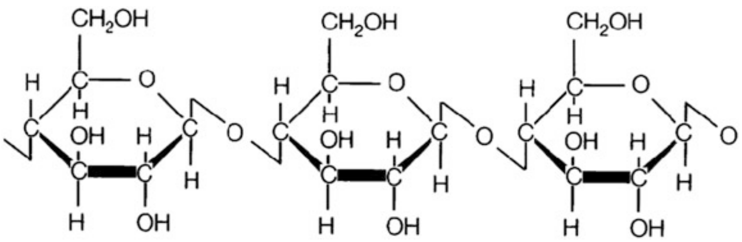

Fig. 4.1 Structure of a cellulose biomolecule (Acharya and Chaudhary 2012)

4.2.1 Cellulose

In lignocellulosic biomass, cellulose is sheathed within hemicellulose and lignin matrix, unlike first-generation biomass (Schmidt 2006). Being about 35–50% of the total biomass by weight, cellulose is the most abundant compound. It is a very firm and solid polymer consisted of nearly 12,000 glucose monomer units united together by β-1,4-glycosidic bond in a linear chain fashion (Anwar et al. 2014). The technical and economic obstacles must be conquered to efficient conversion of LCB to biofuel using biological agents (Srivastava et al. 2014) (Fig. 4.1).

The cellulose is insoluble in most of the solvents due to its structure that makes it resistant to microbial degradation (Jørgensen et al. 2003). The enzymes having potential for cellulose degradation belong predominantly to hydrolases, which can cleave the glycosidic bonds by hydrolysis. Cellulases like β-glucosidase, endoglucanase, 1,4-β-cellobiosidase, etc. are mainly responsible for catalysis of cellulose polymer.

4.2.2 Hemicellulose

After cellulose, hemicelluloses is the most abundant polymer on the earth. It represents nearly 25–35% of the total biomass by weight. It is a heteropolymer made of many pentoses and hexoses attached with β-glycosidic bonds. Unlike cellulose, it is comparatively short heterogeneous polysaccharide consisted of around 200 units of D-Glucose, D-arabinose, D-mannose, D-xylose, etc. Xylan is a very important component of hemicelluloses which can be readily hydrolyzed with the help of an enzyme called β-1,4-xylanase (Chang and Yao 2011) (Fig. 4.2).

4.2.3 Lignin

Being one among the main components of LCB, lignin is the third abundant component after cellulose, and hemicelluloses. It is principally made up of many small alcoholic units like p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol, etc. which are joined to each other by ether bonds. It represents approximately 10–25% of total biomass by weight and is hydrophobic in nature. Lignin generally fills the gap between two other main compounds, i.e. cellulose and hemicelluloses (Anwar et al. 2014) (Fig. 4.3).

Therefore, there is a great interest in finding organisms capable of breaking lignin and cleaving the different linkages existed in between hemicelluloses and lignin. It

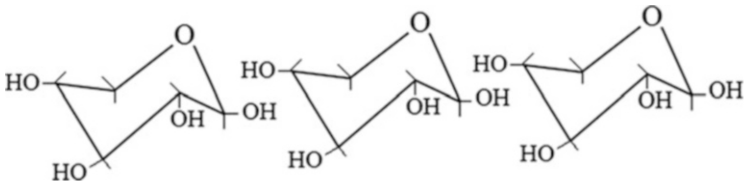

Fig. 4.2 Building blocks of hemicellulose (Shahzadi et al. 2014)

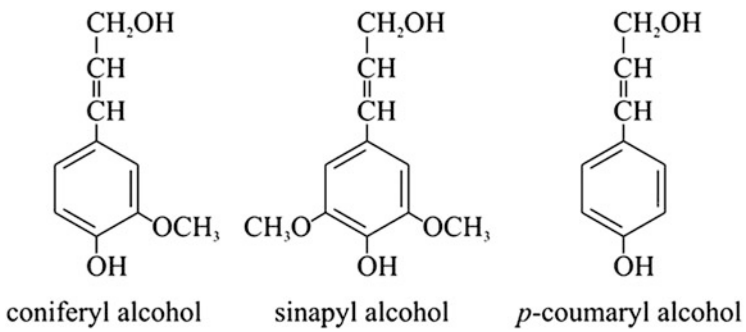

Fig. 4.3 Building blocks of lignin (Shahzadi et al. 2014)

can be effectively broken down by an enzyme unit including manganese peroxidase (MnP), lignin peroxidase (LiP), and laccase (Hofrichter 2002).

4.3 Thermophilic Enzymes

Enzymes have now become essential part in the fuel production. Due to the environmental safety related issues and advances in biotechnology, most of the chemical processes in various industries are being replaced with enzymes (Mahalakshmi and Jayalakshmi 2016). Till date, several enzymes have been discovered with the potential to convert lignocellulosic biomass into some useful products (Nkohla et al. 2017). Though these enzymes are advantageous but their application is restricted due to their limited resistance towards the extreme high temperature, pH, and other conditions but on the other side, thermophilic microorganisms are potent source of such enzymes, which show intense stability towards high temperature conditions. The production of cellulolignolytic enzymes such as endoglucanases, cellobiohydrolases, β-glucosidases, and some other like lignin peroxidase, manganese peroxidase, and laccases have been widely studied and being used in the laboratory at great scale. Cellulase with high activity and stability is usually favored at high temperature for converting lignocellulosic biomass into monosaccharides (Wang et al. 2015; Shirkavand et al. 2016). Most of the thermophilic cellulases work optimally at 50–70 °C, while hyperthermophilic cellulases with optimum temperature around 80–90 °C are not very common (DeCastro et al. 2016). Xylanases are extracellular enzymes produced by different microorganisms such as bacteria, fungi, and a few yeasts which are involved in the catalysis of β-1,4-xylans present in lignocellulosic substances (Udeh et al. 2017) (Table 4.2).

The cellular machinery of these enzymes is thought to be thermo tolerant and these offer considerable guarantee for biotechnological applications at large scale. Such environmental conditions are therefore of great interest because the microorganisms isolated from such environments are good source for thermozymes (Irwin and Baird 2004). Due to which, microbes can acquire high metabolic rates, stable enzymes, and higher product yields than that of mesophilic species. Hence, thermophilic processes are considered to be more stable and rapid reactant activity and product recovery (Sharma et al. 2013).

Table 4.2 Enzymes associated with the degradation of cellulose and lignin

Component	Enzymes
Cellulose	Endoglucanase, β-glucosidase, cellobiohydrolase
Lignin	Lignin peroxidase, laccase, manganese peroxidase

4.4 Ethanol Production Technology

The first step for producing fermentable sugars from lignocellulosic biomass is the breakdown of the lignin–cellulose–hemicellulose complex which is followed by hydrolysis of the cellulosic and hemicellulosic portions of the complex to produce fermentable sugars (Pinar et al. 2017). It is considered to be quite complex due to: (1) the resistant or complex nature of biomass; (2) cost of enzyme necessitates the need to find or genetically engineered organisms efficient in fermenting these sugars to bioethanol; (3) collection and storage costs of low density lignocellulosic materials. Figure 4.4 shows the flow diagram of process for the production of ethanol from lignocellulose material.

4.4.1 Pretreatment

Recalcitrance nature of LCB is the major barrier to enzymatic hydrolysis while using the lignocellulosic material (Kim et al. 2018). Pretreatment of the complex biomass is very important step prior to hydrolysis and effectiveness of the pretreatment in decreasing the lignin crystallinity would avail more and more simple sugars for hydrolysis as well as fermentation (Singh and Bishnoi 2012). The main aim to carry

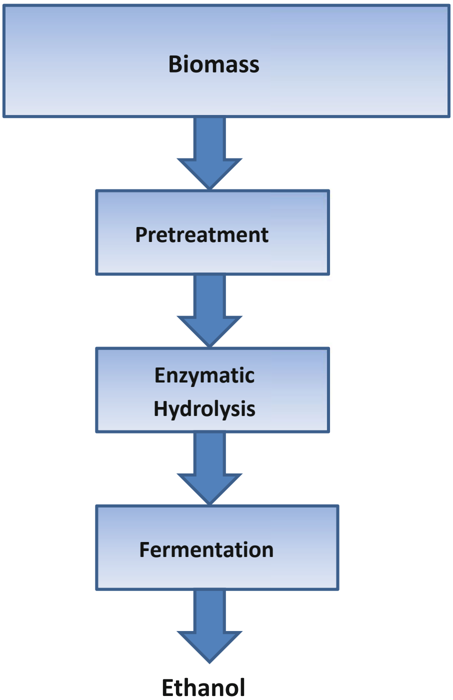

Fig. 4.4 General route of ethanol production using lignocellulosic biomass

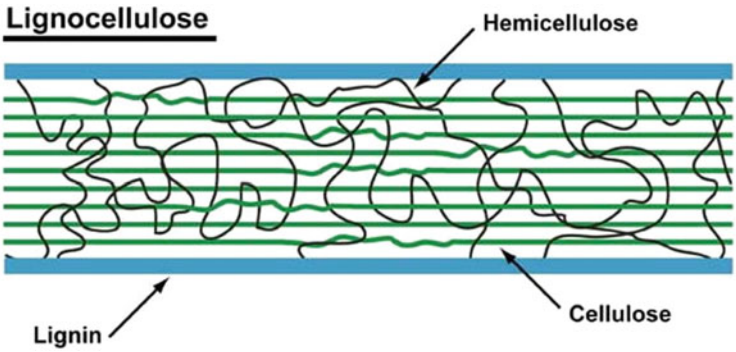

Fig. 4.5 Diagram showing the effect of pretreatment of lignocellulosic biomass

out the pretreatment process is to remove the lignin content and make the cellulose and hemicelluloses free from lignin complex so that the digestibility can be made efficient (Ariana and Candra 2017). Various pretreatments are reported for different kinds of biomass. Some methods are cost-effective especially in which moderate pretreatment conditions are used, but they generally have low ethanol and sugar yields whereas pretreatment methods in which high temperatures and other harsh conditions are employed, have been found to have much more ethanol and sugar conversion yields (Kim et al. 2011) (Fig. 4.5).

According to (Taherzadeh and Karimi 2008), the main requirements for an ideal lignocellulose pretreatment should be: (1) reducing the cost of feedstock, (2) avoiding the formation of various inhibitors, (3) lowering energy input, and (4) consumption of less quantity of chemicals and using cheap chemicals. Besides it, an ideal pretreatment method does not allow reduction in particle size, limits the formation of inhibiting compounds, preserves the hemicellulose fraction and above all, has minimal cost and energy consumption (Mosier et al. 2005; Alvira et al. 2010; Taherzadeh and Karimi 2008).

4.4.1.1 Physical Pretreatment

In physical pretreatment, the following methods are commonly engaged:

Mechanical Comminution

In mechanical comminution, the size of biomass is reduced for removing the cellulose crystallinity by many processes such as grinding, chipping, milling, etc. For reducing the cellulose crystallinity and digestibility of LCB, vibratory ball milling has become an important method than that of ordinary ball milling. This method is capable of increasing the surface area and decreasing degree of polymerization (Zheng et al. 2009).

Pyrolysis

Pyrolysis method is used for converting cellulose and hemicelluloses fraction into fermentable sugars at a higher temperature with excellent yields. It is evident from the previous work when any substrate is pretreated at a temperatures higher than 573 K, then it is quickly decomposed to produce many gaseous by-products (Leustean 2009).

4.4.1.2 Physico-chemical Pretreatment

Following techniques are generally employed under this pretreatment:

Steam Treatment

Steam treatment or explosion or autohydrolysis is also one of the great physico-chemical methods for pretreatment of different lignocellulose biomass. In this method, the biomass is chipped and grinded and treated with steam at high pressure (Devi et al. 2021). After sometime, the pressure is released very quickly due to which explosive decomposition of the material takes place. It is more preferred as it has lesser impacts on the environment, high energy efficiency, low capital cost, and greater recovery of sugar. Here, temperature, residence time, and particle size are some most important factors which affects steam explosion. It is referred as uncatalyzed technique because lignocellulosic biomass is heated very quickly at very high pressure without the adding any chemical and biological agent (Heerah et al. 2008).

Ammonia Fiber Explosion (AFEX) Method

In this method, fast hydrolysis of lignocellulosic material takes place when it comes in contact of liquefied ammonia at high pressure and temperature. The main parameters which can affect this process are temperature, time, loading of ammonia and water, and number of treatment cycles. The complex polymers are attacked then by enzymes to convert them into fermentable sugars which are not liberated directly. This pretreatment method has been found to increase the saccharification rate of numerous lignocellulosic materials. AFEX has been using for many LCB such as rice straw, sugarcane bagasse, newspapers, switchgrass, coconut coir, water hyacinth, MSW, sawdust, etc. (Zheng et al. 2009).

Liquid Hot Water Pretreatment

In this pretreatment method, lignocellulosic materials are heated in hot water which is useful in pulp industries since several decades. The biomass is then treated with hot water for a definite time period which gives foremost recovery rates and generation of less inhibitor. However, 4–20% cellulose, 35–55% lignin, and nearly whole hemicellulose may be removed in this pretreatment (Hu and Wen 2008), but the breaking down of monosaccharide can be lowered if the pH is maintained between 4 and 7.

Supercritical Fluid Pretreatment (SCF)

Supercritical fluid may be a material either any liquid or gas which is used beyond very high pressure and temperature where both liquid and water can show coexistence. SCF shows some elite properties such as density like a liquid, transport property like akin to a gas that makes it special than others (King and Srinivas

2009). The supercritical fluid can penetrate up to the crystalline part of the material. Stabilization of sugars and inhibition of biomass degradation is possible at lower temperature. Alinia et al. (2010) has observed the effect of supercritical CO_2 as pretreating agent alone on wet and dry wheat straw and also in combinations with steam at various conditions which gave best sugars yield.

4.4.1.3 Chemical Pretreatment

Following techniques are generally employed under chemical pretreatment:

Ozonolysis

In ozonolysis method of pretreatment, ozone gas is used to degrade the hemicellulose as well as lignin, and to increase biodegradation of the cellulose. This pretreatment is generally practiced at normal temperature conditions and is effective in removing lignin without generation of any toxic byproducts. This method has been known to break down about 49% and 55–60% of lignin in corn stalks and hydrolyzed corn stalks, respectively. In another study, ozone was applied on wheat and rice straw to boost the enzymatic sachharification to convert the fermentable sugars into ethanol and some other by-products (Kumar et al. 2009).

Alkaline Pretreatment

In alkaline pretreatment method, any alkali reagent (e.g. NaOH, KOH, etc.) is used to remove the lignin portion and other components that may lower the enzyme accessibility to cellulose and hemicelluloses. This pretreatment can be performed at standard conditions and time is taken in hours instead of minutes and seconds (Mosier et al. 2005). Calcium, ammonium, sodium and potassium hydroxides, are some suitable chemicals for pretreatment but NaOH is most common used alkali among these. Alkaline pretreatment with suitable alkali reagent leads to swelling of the LCB which in turn amplify the surface area, reduce the cellulose crystallinity and approximately complete disruption of lignin. It has been reported that lime ($Ca\ (OH)_2$) has low cost as well as less significant safety requirements as compared to KOH and NaOH. Suitable pretreatment conditions are required to make lime as an efficient agent for treatment. It was noticed that lime, water at temperature of 313–423 K, are mixed with lignocellulosic biomass for some hours to weeks as well (Taherzadeh and Karimi 2008).

Acidic Pretreatment

A good amount of monosugars can be yielded from lignocellulosic biomass on treating with acids like hydrochloric acid, sulfuric acid, nitric acid, etc. either at high or low temperature at low or high concentration, respectively. Acidic pretreatment is usually employed to remove lignin and expose cellulose portion to enzymatic hydrolysis. Dilute acid pretreatment may enhance digestibility of cellulose present in biomass (Tucker et al. 2003). Ninety-five percent reduction in xylan of cotton stalk was reported on pretreatment with 2% H_2SO_4 (Silverstein et al. 2007).

Wet Oxidation

This pretreatment method requires oxygen for oxidizing the compounds which can be dissolved into water. Wet oxidation quickly oxidizes lignin, if combined with alkali solution and thus making polymers more prone to enzymatic saccharification. Furfural and hydroxyl-methylfurfural were also not observed during wet oxidation pretreatment (Bhatia et al. 2011).

Organosolv Pretreatment

This is also one of the best promising approaches to pretreat different lignocellulosic wastes. Any strong inorganic acid used in this method enhances the breaking of the bonds present between lignin and other carbohydrate compounds (Margeot et al. 2009; Başakçılardan Kabakcı and Tanış 2021). In comparison with other methods, less chemicals are needed for making the hydrolyzate neutral. (Table 4.3).

Table 4.3 Kinds of pretreatment methods, processes involved and their advantages and disadvantages (Kumar et al. 2009)

Pretreatment method	Process involved	Advantages	Disadvantages
Mechanical or physical pretreatment	Grinding, chipping, and milling	It reduces crystallinity of cellulose structure	Consumption of power is higher
Physiochemical pretreatment	Steam Explosion	Causes auto hydrolysis of hemicellulose and transformation of lignin complex	Production of inhibitory compounds; less effective specially for softwood
	Ammonia fiber explosion (AFEX) pretreatment	Increases the internal area, breaks and separates the hemicelluloses and lignin	Lignin structure cannot be modified
	CO_2 explosion	Inhibitors are not generated in downstream processes	Does not suit the materials having high lignin content
	Ozonolysis	Lignin content is reduced and toxic residues are also not produced	High cost for ozone is required
Chemical pretreatment	Acidic pretreatment	Hydrolyzes hemicellulose into simple sugars and lignin structure is modified	Corrosion of equipment is observed and toxic substances are generated
	Alkaline Hydrolysis	Efficiently removes the lignin and hemicelluloses fraction and surface area is increased	Residual salts in biomass can be found
	Organosolv	Lignin and hemicelluloses is hydrolyzed	Becomes expensive due to recovery of solvents
Biological	Microorganisms	Lignin and hemicelluloses can be broken and less energy is required	Rate of hydrolysis is slow

4.4.1.4 Biological Pretreatment

As far as alternate for chemical pretreatment is concerned, biological pretreatment is considered to be the best, as no change in structure and composition takes place. This method provides biological degradation of hemicelluloses as well as lignin and makes biomass more accessible to enzyme digestion. In this pretreatment, microorganisms consume nearly whole lignin fraction and degrade major portion of hemicellulose. Among all biological agents, fungi, especially the white-rot, are considered to be much effective agent for the biological pretreatment (Bhatia et al. 2011).

The biological delignification of paddy straw, sugarcane bagasse, and corn has been employed using *Cyathus* sp., *Pleurotus florida*, *Pleurotus cornucopiae* strain, *Streptomyces viridosporus*, and *Phlebia tremellosa* (Kumar et al. 2008).

4.4.2 Inhibitors Produced During Pretreatment

If any pretreatment method is made harsher by either increasing residence time or temperature and using more concentrated acids, then mono sugars obtained may further be tainted into different aldehyde groups and other organic compounds which may further cause to loss of yield and create several problems in the path of enzymatic digestion and fermentation (Almeida et al. 2007; Qadoos et al. 2022). Likewise, several different inhibitory compounds like furans, weak acids and phenolics are produced during pretreatment especially chemical one as shown in Fig. 4.6.

Among furans, HMF (5-hydroxymethyl-2-furaldehyde) and furfurals (like 2-furaldehyde) are the two main inhibitors. These inhibitors are degrading products

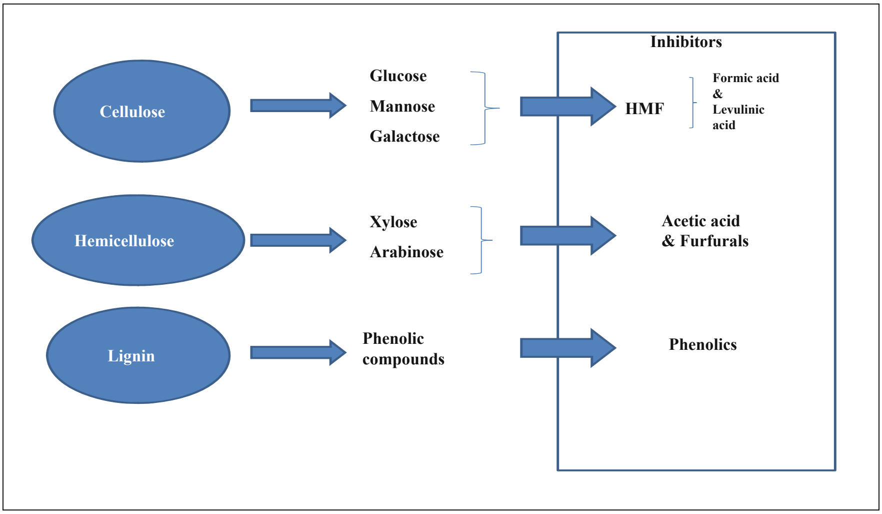

Fig. 4.6 Types of inhibitors produced during different pretreatment methods

of C-6 and C-5 monosugars, respectively. During harsh operating conditions, furans may be further dissociated into levulinic acid and formic acid, whereas phenolics are generated on lignin degradation. On the other hand, acetic acid is somewhat different from other inhibiting compounds with respect to acetyl groups.

4.4.3 Saccharification

Prior to fermentation, saccharification or hydrolysis process takes place which involve breaking down of hydrogen bonds present in celluloses and hemicellulose structures due to which hexoses and pentoses are generated, which are then fermented to produce ethanol. When cellulose is hydrolyzed to glucose, several other substances such as methanol, formic acid, acetic acid, 2-furformaldehyde, etc. are also produced simultaneously but when hemicellulose is hydrolyzed, then galactose, glucose, xylose, mannose, acetic acid, etc. are released. After the pretreatment process, there are two most commonly applied hydrolytic methods to hydrolyze the cellulosic biomass into ethanol: chemical hydrolysis and enzymatic hydrolysis.

4.4.3.1 Chemical Hydrolysis

This process envisages formation of simple sugars from complex polymers when comes in contact with some chemicals at particular temperature for a definite time span. Acids are principally applied in this hydrolysis method. The acid hydrolysis can be performed either by using diluted or concentrated acid. Generally in case of diluted acid hydrolysis, high temperature and pressure is preferred at particular time either in minutes or in seconds. For diluted acid hydrolysis, about 1% H_2SO_4 concentration is used at high temperature (about 488 K). Primary challenge in using this process is how to boost glucose yields greater than 70% with high hydrolysis rate of cellulose and minimal glucose decomposition.

In concentrated acid hydrolysis, the biomass is required to be dried completely and then addition of sulfuric acid with concentration of about 70–90% (Hayes 2009). In concentrated acid hydrolysis, polymers are completely converted into C-5 and C-6 sugars at rapid rate with negligible degradation (Yu et al. 2008).

4.4.3.2 Enzymatic Hydrolysis

It is a process in which suitable enzymes are employed to carry out the hydrolysis. This method is an economic and very effective method in which mono sugars are obtained from pretreated biomass in an eco-friendly way (Wyman et al. 2005). Many enzymes are used to break the hemicellulose and celluloses proportions. To degrade the cellulose portion, a group of cellobiohydrolase, endoglucanase, exoglucanase, and β-glucosidases are employed (Ingram and Doran 1995). Endoglucanase enzyme produces short length polysaccharides chains by attacking on cellulose randomly whereas exoglucanase removes cellobiose moiety from these chains. β-glucosidases produce glucose on catalyzing the cellobiose and other complex polymers. However, this entire process depends critically on some factors like pH, temperature, time, enzymes, substrate concentration, etc. (Anwar et al. 2014). Usually enzymatic hydrolysis is occurred at mild conditions and corrosion problem is caused in it. It has been also demonstrated to be an alternative and environment friendly approach that involved use of carbohydrate degrading enzymes to degrade lignocelluloses into fermentable sugars (Balat 2011).

4.4.3.3 Fermentation

After enzymatic hydrolysis, the final product is composed mainly of some C-6 sugars (viz., glucose, mannose, galactose, fructose, etc.) and some C-5 sugars (e.g., xylose, arabinose, etc.). Total theoretical yield of ethanol from these sugars is found nearly to be 0.51 g/gram glucose which is somewhat greater than that of xylose (Althuri et al. 2018). So many microorganisms are being used to ferment the lignocellulose-derived sugars into ethanol. For example, yeasts (like *Saccharomyces.* and *Pichia* sp.) as well as bacteria (like *Klebsiella*, *Zymomonas*, *E. coli*, etc.) have been used to ferment these simple sugars.

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2CO_2 + ATP$$

Fermentation is conducted in both modes, i.e. batch mode as well as fed-batch mode. Batch mode is considered as a closed system process containing a limited amount of nutrients (Abbasi and Abbasi 2010). Fed-batch reactors are benefited over batch-culture because they gain many advantages than that of other processes/ modes. Increasing the concentration of viable cell and building up of products to a largest level are some of the major benefits in using fed-batch process. The media and feed along with some other nutrients are directly pumped in this process and activated microbes are present into the reactor vessel. Supernatant from bioreactor after fermentation contains bioethanol along with residual sugar.

The major difficulty in achieving greater ethanol yield is production of different acids and phenolic compounds which may cause the process inhibition.

Usually the bioconversion of LCB takes place in two steps and in different reactors in case of SHF (separate hydrolysis and fermentation) process, i.e. saccharification and fermentation take place separately whereas in SSF, both steps are carried out in a single container and cellulose activity is inhibited by glucose that is the major disadvantage of it (Ahmad and Qazi 2014). The production of cellulose degrading enzymes by using SSF (Simultaneously sachharification and fermentation) can be an alternate way to trounce the costs of enzyme which makes it more interesting (Júnior et al. 2017). In this process enzymatic hydrolysis is combined with fermentation simultaneously to achieve ethanol from sugars. However, the steps in SSF are nearly similar to that of SHF but as we know that both process in SSF are employed in same vessel so it reduces the investment cost (Ballesteros et al. 2006). It has been reported in previous reports that SSF is somewhat superior to SHF in terms of ethanol production especially in case of rice straw (Binod et al. 2010).

Biological conversion is consolidated into a single step in which a single engineered microorganism is capable to convert cellulose directly into ethanol using its own enzymatic machinery, which provides a significant contribution in reducing the capital costs and increases process efficiency (Devarapalli and Atiyeh 2015). The term consolidated bioprocessing (CBP) was proposed in 1996. Direct microbial conversion process can be replaced by this CBP in which all the steps (enzyme production, hydrolysis, and fermentation) can be performed in a just single step. Hence, CBP is getting fame now-a-days for conversion of LCB into ethanol by using biological agents (Chang and Yao 2011). By genetically modifying the microorganisms, there is more hope for improvement in biodegradation of biomass and yield of biofuel as well. Lignocellulolytic fermentation using thermophillic microbial enzymes emerge as encouraged approach for development of CBP.

4.5 Ethanol Production Scenario

India is one among the countries in the world who are on top in ethanol production. India started its ethanol blending program in 2003 and satisfactory capacity has been installed for meeting its requirements of E10 (blending up to 10%). Till today, the greater part of India's potential for ethanol has come from molasses. But recently, a few Indian companies have taken the first cautious steps to produce ethanol using alternate feedstock like sugarcane, sweet sorghum, and tropical sugar beet (Table 4.4).

The Indian technology for the production of ethanol from molasses is well recognized now, as there are near 350 distilleries in India. This technology for ethanol production becoming sophisticated day by day as companies located in India are providing technology and energy efficient plants all over the world now.

Although second-generation biofuels are having technical limitations that leads to high cost of production. But in the case of cellulosic ethanol the cost of enzymes has been a problem. However, considerable reductions in production cost have been achieved so far due to intensive efforts and considerable funding in some developed countries. It is believed that this technology may soon start competing with corn-based ethanol production. There are some of the major gaps in algae technology (third generation biofuel) which include algal strain improvement, its growth and hydrocarbon production, programmed downstream processing, spent biomass

Table 4.4 Annual ethanol production by country during 2020 (Source: RFA analysis of public and private data sources)

World rank	Country/region	2020 (Mil. Gal.)
1	USA	13,941
2	Brazil	8080
3	EU	1260
4	China	930
5	India	510
6	Canada	430
7	Thailand	390
8	Argentina	210
9	Rest of World	659
	Total	26,410

utilization, and the evaluation of cultivation systems. Overall, the second-generation biofuel technologies are still to prove their commercial feasibility.

4.6 Genetically Engineered Thermophiles: A New Approach for Ethanol Production

The biological conversion process of lignocellulosic biomass into ethanol has its four major steps; (a) Pretreatment of the biomass, (b) Chemical/enzymatic hydrolysis of pretreated biomass, (c) Fermentation of reducing sugars obtained from hydrolysis, and (d) Separation and purification of the products. As there is urgent need of renewable fuel as an alternate of fossil fuels, so some sincere efforts are to be devoted to improve the feasibility of this process. Till now, simultaneous sachharification and fermentation (SSF) and consolidated bioprocessing (CBP) have been implemented in which all the reactions take place in a single bioreactor. The fermentation process is carried out by various mesophilic microorganisms, viz. *Escherichia coli*, *Saccharomyces cerevisiae*, *Zymomonas mobilis*, etc. which cannot tolerate high temperatures. Hence, research is being done on natural and genetic-engineered thermophiles for ethanologenesis at higher temperatures (Chung et al. 2014).

For the complete degradation of cellulose, generally three enzyme complexes are needed which includes endoglucanase (carboxymethyle cellulase), exoglucanase (avicelase, cellobiohydrolase), and β-glucosidase. These enzymes synergistically catalyze the cellulose. The microorganisms from different environments are the chief sources of these enzymes. Among all microbes, bacteria have gained great attention as they have high growth rate than that of others and have good potential for ethanol production. Several bacterial strains such as *Bacillus*, *Clostridium*, *Cellomonase*, *Micrococcus*, etc. have been reported for having cellulolytic activities. However, researchers have studied thermophiles in certain limits. Thermophilic microbes or their enzymes act at a temperature range of 50–80 °C. Due to their stability and activities at higher temperature, thermophiles are more preferable than mesophiles (Azardian et al. 2017). However, the yields and products obtained by using these thermophiles are not of that grade because of nonavailability of efficient tools for genetic manipulation of microorganisms. This problem can be overcome by using the thermophilic enzymes in a definite pathway in vitro. This in vitro technique of using man made metabolic pathways has been in trend these days as a promising approach to develop biotransformation system which nothing to do with cell proliferation, regulation of metabolism, and recovery of by-products, etc. (Honda et al. 2017). The modern advancement in the field of development of microbial strains for the production of cellulosic ethanol has brought a new era by integrating customary and novel genetic manipulation approaches. *Saccharomyces cerevisiae* has attracted cellulosic ethanol producers due its well-known characterization, feasibility in industrial sectors, and facility of genetic tools for it. However, transition phase from first generation to second generation biofuel production has limited success story due to inability of this fermenting strain towards utilization of xylose sugars

(Nielsen and Keasling 2016). Over the last few years, genetic manipulation technique has passes the traditional approaches to focus on xylose catabolism to enhance the ethanol production yield. The research has been carried out to improve carbon utilization by studying transporter factor engineering and considering the acetic acid as carbon source not an inhibitor. Ko and Lee (2018) in their study, have highlighted the latest genetic engineering strategies to develop more valuable and strong strains of *S. cerevisiae* to higher the cellulosic ethanol production. Target oriented evolution has provided us the generation of mutant xylose transporters that has enhanced xylose utilization rate. For example, $FIVEFH_{497*}$, a mutant xylose transporter from CiGXS1 of *Candida intermedia* has enabled *S. cerevisiae* to fasten the xylose transfer rate (Li et al. 2016). Evolution of $AN_{25,}$ another xylose specific transporter from *Neurospora crassa* also recovered higher xylose transfer rate about more than 40 times (5). Improvement in half-life of mutant transporter has also been advantageous economic and efficient co-fermentation. Genetic manipulation of a common co-repressor of CYC8 has led enhancement in xylose metabolism in *S. cerevisiae* (Ko and Lee 2018). In ancient time, the microbes for ethanol production were improved by their selection, random mutation, screening strategies, etc. which were considered to be quite slow and unpredictable (Derkx et al. 2014). But in recent time, conversion of organic substrates into valuable biofuel via microbial activities can be enhanced by genetic and metabolic improvements. Although, the processes of traditional approaches may not be possible if the general biochemistry of that possible strain is missing. Hence, improvement in microorganisms in many ways depends solemnly on genetic engineering. As a whole, genetic and metabolic engineering of microbes enables modification of microbial strains without causing any unwanted mutations (Liu et al. 2015).

Bacteria Various bacterial strains present in nature have been utilized for the production of different biofuels. Research community still seeks some better strains specifically from thermophilic environments. For bioethanol production, following bacteria have been used.

Zymomonas mobilis This anaerobic strain is a better strain for ethanol production than that of yeasts. In comparison with yeast, *Z. mobilis* converts sugars into ethanol in a much better way (Ajit et al. 2017). However, baker's yeast (*S. cerevisiae*) and *Z mobilis* use the same ethanol production genetic pathway but as far as glycolysis is concerned, then *S. cerevisiae* uses Embden–Meyerhof–Parnas (EMP) pathway whereas *Z. mobilis* uses Entner–Doudoroff (ED) pathway. ED pathway is better than EMP in terms of less consumption of ATPs during the ethanol production process. *Z. mobilis*, due to its high cell specific area, utilizes glucose at a faster rate than *S. cerevisiae*. *Z. mobilis* has only one disadvantage that it cannot utilize the pentose sugars as these cheap sugars are available abundantly. But recently, a recombinant strain was developed with many improved characters which was shown to obtain an ethanol yield of 136 g/L (Wang et al. 2016).

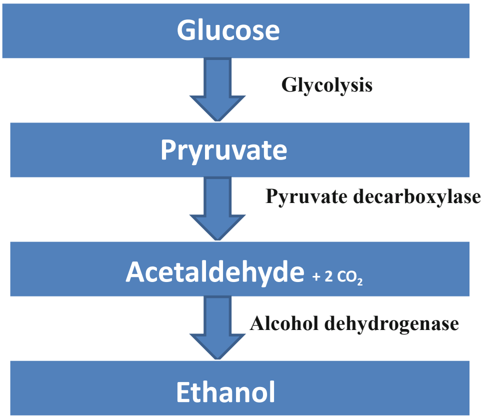

Fig. 4.7 Glucose to ethanol metabolic pathway

Bacillus subtilis Construction of modified *Bacillus subtilis* BS35 produced ethanol and butanol in a good manner but there was reduction in cell growth rate as well as glucose consumption rate. Hence, BS35 was further modified as BS36 by genetic manipulations, and this process enhanced ethanol production by 89%. Another strain BS37 was also developed by inactivating *alsS* gene, and it showed ethanol yield up to 8.9 g/L in the long term (Soo et al. 2017).

Escherichia coli The bacteria *E. coli* has been widely used for ethanol production because its molecular biology is well known to scientists. This strain can utilize a variety of different substrates. It was the first bacterium that was modified successfully through genetic modification for ethanol production (Zhou et al. 2005). *E. coli* was then further modified by introducing some foreign genes in it and eliminating the pathways inhibiting products. It was modified into KO11, which was a novel strain, capable of producing good titer of ethanol. KO11 was having genes from *Z. mobilis* for encoding pyruvate decarboxylase. The engineered *E. coli* strain increased 30% the co-production of hydrogen and ethanol compared to other genetically modified strains (Lopez-Hidalgo et al. 2021) (Fig. 4.7).

Thermophilic Bacteria Thermophilic microorganisms are demanding today to produce a good quantity of bioethanol in a very efficient and economical way. The reasons why thermophiles are more preferable to mesophiles are; poor capability of mesophiles to catalyze the complex carbohydrate polymers, less tolerance towards high pH and temperature (Jin et al. 2014). Due to these shortcomings, mesophiles get contaminated with unwanted microbes very easily, making them unfit for further usage. Due to competence of biofuel with food grains and lands for fodder, we need some processes capable of using lignocellulosic biomass for ethanol production. For obtaining good amount of fermentable sugars, LCB is needed to be pretreated first. Hence, the microorganisms which can hydrolyze the LCB and can simultaneously convert reducing sugars into ethanol are preferred. Therefore, genetic-engineered thermophiles may be useful (Scully and Orlygsson 2014). Besides the prevention

Table 4.5 List of some thermophilic bacteria with their ethanol yield

Microorganism	Substrate	Ethanol yield (Mol/Mol)	References
Clostridium thermocellum	Cellobiose	0.59	Tripathi et al. 2010
T. saccharolyticum TD1	Xylose	0.98	Biswas et al. 2014
T. saccharolyticum HK07	Cellobiose	0.86	Shaw et al. 2009
T. saccharolyticum M1051	Cellobiose	1.73	Shaw et al. 2009
Geobacillus thermoglucosidasius TM242	Glucose	1.73	Cripps et al. 2009
Geobacillus thermoglucosidasius TM242	Xylose	1.34	Cripps et al. 2009
Thermoanerobacter mathranii BG2L1	Wheat straw	1.53-1.67	Georgieva et al. 2008
Thermoanerobacter mathranii BG2L1	Xylose + Glycerol	1.53	Yao and Mikkelsen 2010

from contamination by unwanted species, a thermophilic microorganism also increases the rate of hydrolysis and fermentation. Table 4.5 illustrates the list of thermophilic bacteria with their ethanol yield.

Clostridium thermocellum It is a strict anerobic bacterium which catalyzes and degrades acid pretreated hardwood in CBP and produce ethanol at a temperature range of 60–65 °C. In addition to ethanol, it also produces acetate, lactate, formate, CO_2 without producing butanol (Ellis et al. 2012). First successful transformation of *Clostridium thermocellum* was carried out in 2006 (Tyurin et al. 2006). For ethanol production from cellulose specifically, *C. thermocellum* bacterium is used commonly because of its high cellulolytic capacity. But due to its low ethanol tolerance, the condition may worsen in using this strain but elimination of the synthesis of by-products was achieved. Tripathi et al. (2010) tried and removed the gene phosphotransacetylase (pta) responsible for acetone synthesis.

Geobacillus spp. *Geobacillus* spp. is capable of catalyzing both pentose as well as hexose sugars into ethanol, acetate, lactate, and formate at temperature range of 40–70 °C (Zhou et al. 2005). It can grow by utilizing cellulose as a carbon source and also rice straw and barley by releasing cellulose enzyme complex. *G. thermoglucosidasius*, a facultative anaerobic thermophile, can also produce hemicellulase and can tolerate ethanol concentration up to 10% (v/v) and hence is suitable candidate for production of cellulosic bioethanol. In addition to ethanol, it also produces lactate as a major product. So ethanol titer can be enhanced by deleting this *ldh* gene. Cripps et al. (2009), removed this *ldh* gene from it and ethanol yield was increased from 0.1 g/g to 2.4 g/g (Jiang et al. 2017).

For the improved cellulose degradation and production of desired genes for value-added products, metabolic engineering techniques are being directed now-a-days. It is not easy to engineer an organism that can have all the desired characters in it (Nonklang et al. 2008; Rao et al. 2007). These effects can be seen in consolidated bioprocessing in which a single microorganism can convert the cellulose into desired biofuel. For the proper implementation of CBP, there is need of genetic manipulation of targeted organism. It is an unfortunate coincidence that most of cellulolytic organisms have low yield and are hard to manipulate while microorganisms capable of genetic modification do not have cellulolytic degrading potential. Beside various aspects of CBP, Deng and Fong (2011) developed a thermophilic, aerobic, and cellulolytic actinobacterium named *Thermobifida fusca* capable of bioethanol production. The genetic make-up of *Thermobifida fusca* was sequenced (Deng and Fong 2011).

Raita et al. (2016) in their research article has discussed about a thermophilic strain, namely *Geobacillus thermoglucosidasius* which was developed recently as an effective ethalogen for ethanol production from lignocellulosic biomass. This bacterium was modified by removing its lactate dehydrogenase which improved the fermentation process. Although *G. thermoglucosidasius* is not able to fully utilize the cellulose fraction but are good hemicelluloses degrader. Arabinan, glucan, xylan can be naturally fed upon by some other *Geobacillus* spp. Therefore, Raita et al. (2016) compared some of the basic characteristics of *Geobacillus* spp. with *S. crevisiae* for conversion of palm wastes pretreated with steam into ethanol without using any other supplementary enzyme. Singh et al. (2018) isolated a pentose fermenting thermophilic bacterium strain called DBT-IOC-X_2(from genus *Thermoanerobacter*) from Himalayan hot spring. Batch experiments of their study indicate that the genetically engineered strain was found to have resistance against inhibitors (like HMF, Furfurals, etc.), substrate tolerance as well as high ethanol yield at 70 °C. In this study, pretreated rice straw was used substrate and total sugar conversion of about 83.4% was obtained.

4.7 Impacts of Biofuels on Environment

There is an interface of activities related to the biofuel production which results into both positive and negative environmental impacts. Both ethanol and biodiesel contribute to the reduction in fossil fuels utilization whose extraction and use has environmental implications. In case of biodiesel production from *Jatropha*, utilization of wasteland for the plantations will result in the construction of tree cover for a minimum period of 30–40 years. This will imparts towards enhancing terrestrial carbon sinks and reservoirs. Mostly, the negative environmental impacts of biofuels in India originate from sugarcane cultivation. The environmental concerns of sugarcane cultivation include too much water consumption in cultivation; soil erosion, agrochemical use; decreasing soil fertility; surface and ground water pollution; soil salinity and acidity and farming marginal land. According to the WWF, the production of sugarcane has caused a great loss of biodiversity in many countries. However, it is of less significance for India as there is no land to be cleared for sugarcane plantations. Salinity is also a potential problem especially when over-irrigation, inadequate drainage occurs in a flood plain. Similarly soil acidification is also more rampant in sugarcane growing areas due to excessive use of inorganic nitrogenous fertilizers like urea and ammonium sulfate. The burning of fields after the harvesting of sugarcane is a customary practice in India, which results in air and soil pollution.

4.8 Conclusion

As we know lignocellulosic materials contain several high valued compounds in them like sugars, protein, and other minerals; and fuel ethanol can be produced from different lignocellulosic resources such as agricultural and forestry residues, woody plant, industrial waste water streams, and scrap of municipal solid waste. For the production of lignocellulosic bioethanol, it is usually pretreated by using many different physical, chemical, physico-chemical, and biological method but the selection of the best pretreatment method must be done by considering the value and economical aspects of product produced. The hydrolysate obtained is then fermented with the help of microorganisms especially the baker's yeast. After a long time span of research on utilization of lignocellulosic biomass, it is now understood that enzyme linked technologies for biomass conversions are cost-effective, economically competent, and also eco-friendly. Although a significant development has also been made in search of thermophiles but their factual diversity has not been fully explored so far. Extraction of thermostable enzymes from thermophilic microbes has shown their keen potential which properly suits the bioconversion techniques in large scale industries. The main challenges in bioethanol production in future may include usage of efficient pretreatment methods for better accessibility to microbes, development of genetic-engineered organism to improve thermo-tolerance, cost-effective enzyme production, and finally availability and stability of these enzymes.

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Lignocellulosic Biomass and Conversion Technology

5

Santosh Thapa, Durga P. Joshi, and Bharat Pokharel

Abstract

The research and development of alternative energy sources, especially bioenergy have become extremely important due to increasing demand for energy consumption and fossil fuel use, surged fuel prices, and significantly increased greenhouse gas (GHG) emissions over the last decade. Lignocellulosic biomass garnered public interest as a renewable alternative energy source because of its potential to mitigate greenhouse gas emissions, enhance national energy security, and bolster economic opportunity for rural communities. Nevertheless, its low energy density, high volatile content, low caloric value, and hydrophobic nature make it least preferable as it requires to undergo for a specialize pretreatment while converting it to the value-added energy products. The effectiveness and optimization of biomass to bioenergy conversion technique requires a careful pairing of advanced conversion technologies. For instance, lignocellulosic biomass can be converted to the value-added energy products via exploitation of diverse pathways that include but not limited to: (a) thermo/bio-chemical conversion routes, (b) microbial and enzymatic degradation techniques, and (c) consolidated bio-processing approach. In this chapter, we identified, compared, and assessed those conversion technologies, and further evaluated their applicability, efficiency, effectiveness, and limitations while developing the value-added energy

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products. We believed that the lignocellulosic biofuel will not replace the current use of fossil fuels; it rather complements and reduces their use while meeting the world's ever growing energy demand. To make lignocellulosic biofuel as a viable long-term energy strategy in the United States, there is a need to improve the conversion efficiency at a scale that is sufficiently large for commercial production. The diverse characteristics of lignocellulosic biomass, which requires unique conversion pathway, warrants future biologists, plant scientists, microbiologists, and enzymologists to prioritize the traits and advance the viable conversion pathway for the development and production of next generation of renewable energy for the 21st century.

Keywords

Thermochemical conversion · Bio-chemical conversion · Lignocellulosic biomass · Biofuel · Enzymatic · Microbial degradation

5.1 Introduction

The non-renewable fuels, in particular, fossil fuels (i.e. petroleum, coal, and natural gas) serve approximately 80–90% of today's global energy needs, both energetically and commercially (Hayes 2009). Nevertheless, they are non-renewable, are limited, and have reached to a "Hubbert Peak" in terms of their production and in some cases are in the verge of rapid depletion. Growing public interest and awareness on clean energy, the crude oil production is anticipated to decline from 1033 billion gallons in 2010 to 206.6 billion gallons in 2050 (Campbell and Laherrère 1998). Despite this projected decline in crude oil production, the reservoir of crude oil, natural gas, and coal are estimated to be exhausted in the next 50, 60, and 120 years, respectively (Tissot and Welte 2012).

Secondly, anthropogenic activities such as land use and land cover change, and fossil fuel combustion contributed an increased in concentration of greenhouse gases (GHG) in the atmosphere. In 2018, the USA accounted for about 5.42 billion ton of the total CO_2 emission (Lal 2004; Ritchie and Roser 2017). The liquid fuels from fossil fuels are projected to induce the carbon dioxide emissions from 14,740 Million Tonnes of Oil Equivalent (Mtoe) (2002) to 27,364 Mtoe (2030), which is in fact a very serious concern (Asia Pacific Energy Research Centre (APERC) 2007). According to United States Environmental Protection Agency (EPA) 2018 report on inventory of US greenhouse gas emission and sinks, total GHG emission has increased by 3.7% and CO_2 emission from fossil fuel accounts for 6.2% increase for the last 28 years (baseline year 1990).

As of 2007, the number of cars and light trucks on the road were about 806 million, which is projected to increase to 1.3 billion and over 2 billion by 2030 and 2050, respectively (World Business Council for Sustainable Development

(WBCSD) 2004; Balat 2011). This results in anthropogenic loading of GHG such as carbon dioxide, nitrogen oxide, and methane in the atmosphere will be a significant contribute towards climate change and global warming (Sun et al. 2012).

As such, the dwindling supply of commonly used traditional energy resources (i.e. fossil fuel), coupled with global warming as a foremost environmental concern have added new immediacy to the renewed interest in the pursuit of accessible, affordable, and eco-friendly sustainable energy source (Crutzen et al. 2016). Such challenges may be an opportunity for researchers and policy makers to promote renewable source of energy to meet our ever-growing energy needs, mitigate climate change, enhance environmental quality, uplift rural livelihoods, and strengthen global economy.

In regard to the above-mentioned scenarios, hydroelectric, geothermal, wind and solar approaches are some of the current methods to satisfy the renewable power needs through electricity generation. According to the International Energy Agency (IEA) report 2019, these sources account for 25.6% of total electricity generation (IEA, International Energy Agency 2019). Hydropower has the highest shares of 63% to global electricity generation among these approaches, followed by Wind (18.1%) and solar photovoltaic (8.3%) (IRENA, International Renewable Energy Agency 2020). The electricity generated through hydropower is supposed to reduce 4 billion tons of GHG emission per year (Association 2019). Similarly, another approach of electricity generation—geothermal approach has very low (103 g CO_2e/kWh) GHG emission from power generation compared to coal (1235 g CO_2e/kWh) and natural gas (485 g CO_2e/kWh) (Sullivan et al. 2010). While looking over the statistics provided by World Wind Energy Association (WWEA), the total global wind power energy has reached 650.8 GW in 2019 ultimately resulting to lowest GHG emission (8 g CO_2e/kWh) and air pollution after hydropower (5 g CO_2e/kWh) (Sullivan et al. 2010). Also, it is productive to state that the solar energy provides 2.5 $\times$ 10^{21} Btu/year (1 British thermal unit (Btu) = 1055.05585 joules), more than 12,000 times the current human requirement of 2.0 $\times$ 10^{17} Btu/year and approximately 4000 times the energy projection expected to use by humans in 2050 (Demain et al. 2005; Kumar et al. 2008). The energy obtained from the sun is utilized via photovoltaic conversion or by exploiting plant biomass as solid or liquid fuels (Armaroli and Balzani 2007). Regardless of it, none of these approaches can suffice the global energy needs. Thus, unlike merely a single technology, a basket of complementary technologies is helpful to stimulate the production of eco-benign renewable fuel sources. The best alternative method to strategically substitute the consumption of fossil fuel and meet energy demand is through the use of biomass (Piemsinlapakunchon and Paul 2019). The production of renewable liquid fuels from cellulosic biomass is considered to be the utmost effective approach. As a further matter, the microbial conversion of cellulosic biomass into ethanol is an often-touted route in an alternative fuel industry (Alper and Stephanopoulos 2009; Das et al. 2020).

Biofuels evolved over time, and they are classified as first, second, third and fourth generations based on the feedstock production and use. Biofuels produced from edible food crop feedstocks that contain starch are first generation biofuels

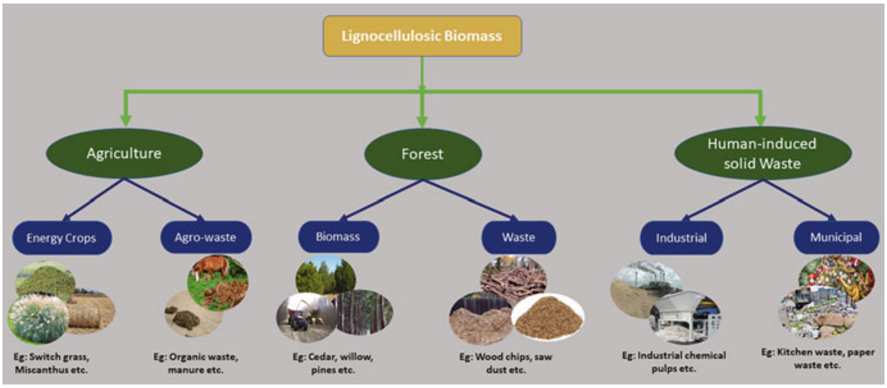

Fig. 5.1 Sources of lignocellulosic biomass

(Bhatia et al. 2017). High cultivation cost and competition with foods make the first generation biofuel feedstocks unreliable and unsuitable alternative for fossil fuels (Alalwan et al. 2019). Inedible lignocellulosic biomass mainly from forest, agricultural residues and industrial waste are second generation biofuels. These sources of biomass have higher possibility to become best alternatives for fossil fuel despite their limitations in scaling up the production (Alalwan et al. 2019). Third generation biofuels are produced from the algae that lead to the high yielding biofuel (Bhatia et al. 2017). Fourth generation biofuels are produced from genetically engineered, low lignin and cellulose containing feedstocks to solve the possible limitations of second and third generation biofuel feedstocks production. The metabolic engineering pathways used for the fourth generation feedstock production which can be a prominent strategy for high yielding biofuel in near future (Dutta et al. 2014).

Out of all types, biofuels from second generation feedstocks are found to be feasible and environmentally sustainable. While looking over the abundance of the feedstock to produce these different generations of biofuels, second generation biofuels are found to be ubiquitous, eco-friendly, and easily accessible. Also, they are derived from the non-food sources and do not compete with food production. A sustainable production of lignocellulosic biofuel minimizes the risk of environmental problems that include but not limited to deforestation and land degradation, unsustainable land and water use, global warming, and natural resources depletion. Also, forest and crop residues, major sources of feedstock of second generation biofuels are found to be carbon neutral and have high carbon capturing ability. They do not add additional carbon to the atmosphere while burning. The heating value is about 3×10^6 kcal/Mg, which is twice of that of coal and thrice of that of diesel (Larson 1979).

Lignocellulosic biomass is a carbon rich biodegradable plant and animal materials, especially obtained from agricultural, industrial and municipal wastes, substantial forest residues, and wastewater treatment plants as explained in Fig. 5.1 (Deublein and Steinhauser 2011; Yousuf et al. 2020). The paucity of global energy (from fossil fuels) in the near future, the global warming and environmental concerns have propelled to a resurgence in the production of sustainable fuel sources. Biomass receives notable significant concern as an alternative viable and environmentally sustainable feedstock for the production of biofuel in an industrial scale. The singular attributes of biofuel from cellulosic biomass such as environmentally benign, lower hygroscopicity, and competitiveness with the existing transportation fuels can circumvent the associated problems due to fossil fuels (Sakimoto et al. 2016).

Cellulosic biomass is the most ubiquitous class of biomass available on earth and it is the forest that accounts for about 80% of the world's plant biomass (Sakimoto et al. 2016). Perlack et al. (2005) stated that forest-based woody biomass represents nearly 370 million tons per annum of cellulosic biomass in the USA. Hadar (2013) proposed that 154 l of bioethanol can be produced from 1 ton of fiber representing municipal solid waste. Kim and Dale (2004) suggested that 491 Gallon/year can be produced from the crop residues. Taking into consideration a viable conversion technology, the biofuels from cellulosic biomass could replace about 30–40% of the total annual transportation gasoline in the USA (Wu et al. 2010).

The process of conversion of cellulosic biomass into liquid or gaseous fuel is a very meandering phenomenon. The route for conversion of cellulosic biomass into the biofuel has about 45–50% conversion energy efficiency (Fajardy et al. 2019). Consumption of the products from these routes releases only about 25–30% of the carbon dioxide to the atmosphere which is relatively very low to that of fossil fuel consumption. In the USA, according to the 2018 data produced by EPA, 75.4% of the total carbon dioxide emission in the atmosphere was from the combustion of fossil fuels (Hockstad and Hanel 2018). As of today, the thermochemical and the biochemical are the two prominent conversion routes exploited for the processing of cellulosic biomass. Each of them has its own merits, demerits, and the technological pathway. Biochemical conversion is preferred for high efficiency during conversion as well as high selectivity whereas, the major advantage of thermochemical conversion is the ability to accept wide range of feedstocks and robust technology while conversion. The pyrolysis, and gasification/liquefaction incorporate in the latter approach, where the fermentation, hydrolysis, and anaerobic digestion are the former approach.

The economic aspects, environmental standards, type and amount of the biomass feedstock, its size and shape distribution, and the required form of energy are some of the fundamental aspects that play an important role while selection for the suitable cellulosic biomass conversion approach (Kenney et al. 2013). The infancy of the current understanding of the mechanistic and biochemistry attributes of commercial enzymes, its costly nature and the slow specific enzymatic hydrolysis are the major impediments for large scale biofuel production.

Thermo-chemical routes, also referred to as biomass to liquids (i.e. BTL), are basically the incorporation of heat energy and chemical catalysts for the breakdown of cellulosic biomass into its intermediate components. The thermochemical conversion route encompasses combustion, pyrolysis, and gasification; yielding intermediates (i.e. bio-oils by pyrolysis and syngas by gasification). To the contrary, in bio-chemical conversion route, several enzymes and micro-organisms are

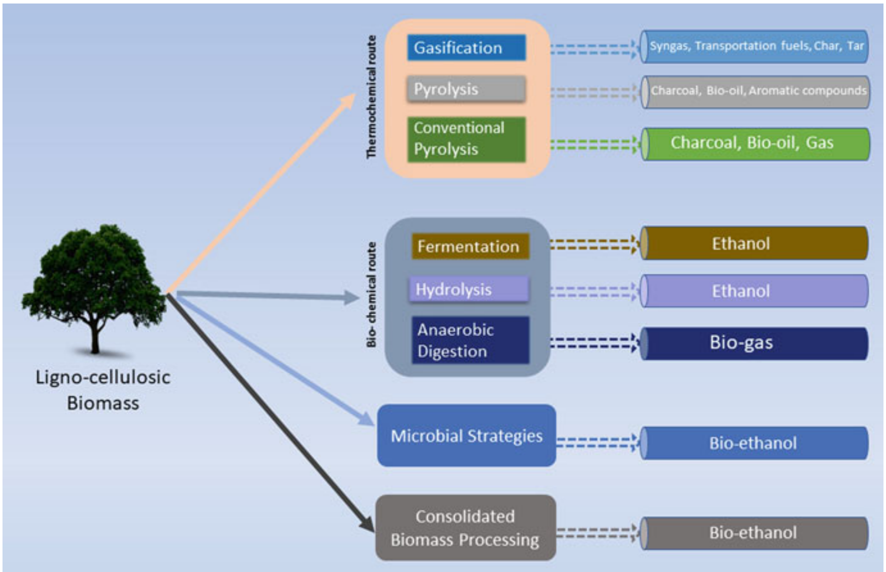

Fig. 5.2 Types of lignocellulosic biomass conversion routes and their final products

employed for the breakdown of biomass into desirable products (i.e. ethanol). Bio-chemical route is sub-categorized into anaerobic digestion and fermentation. Here, we examine challenges and opportunities of both the thermo-chemical and bio-chemical pathways for the biomass conversion. A brief description of the diverse routes in the lignocellulosic biomass conversion and its end products is manifested in Fig. 5.2.

5.2 Thermo-Chemical Conversion Routes

5.2.1 Gasification

Gasification is the thermochemical conversion process of biomass into a combustible gaseous mixture such as syngas. It primarily involves the use of high temperature (800–900 °C) and a controlled environment for the conversion of biomass into a combustible gas mixture such as producer gas or syngas. The producer gas or syngas is a mixture of hydrogen, carbon monoxide, methane, carbon dioxide, and nitrogen (Demirbas 2004; Naik et al. 2010; Piemsinlapakunchon and Paul 2019; Yu et al. 2019). The oxidizing agents also known as gasifying agent such as air, steam, CO_2, O_2, and N_2 play an utmost prominent role in the decomposition of large polymeric molecules of biomass into lighter molecules and ultimately to permanent gases, ash, tar, char, and other minor contaminants. The incomplete conversion of biomass lead to the production of char and tar (Kumar et al. 2009).

The production of syngas is possible through two different pathways, namely catalytic (requires high temperature for operation as high as 1300 °C) and non-catalytic (involves low temperature comparatively) (Naik et al. 2010; Carvalho et al. 2017). The syngas can be upgraded to liquid hydrocarbons such as diesel and gasoline through Fischer–Tropsch (FT) synthesis (Alonso et al. 2010). Sasol South Africa is an example that incorporates FT synthetic facilities to produce liquid fuels, chemicals, and electricity. Carbon monoxide and hydrogen, the major components of syngas, are the building blocks of essential products such as chemical-fertilizers and fuels; thereby, syngas is primarily used to make a range of power transportation fuels, fertilizers, chemical intermediates, and substitute natural gas (Naik et al. 2010).

Biomass gasification is a promising biomass conversion process and has significant potential due to its flexibility to use irrespective of feedstock nature and to convert into energy, and broad range of transportation fuels and chemicals (methanol, urea). In addition, gasification process aids in reducing methane emissions from landfills and production of ethanol from non-food sources. The use of syngas from gasification coupled with the gas turbines and fuel cells is being used to enhance the efficiency and cut off the investment costs of electricity generation through biomass (Demirbaş 2001; Kumar et al. 2009). On the contrary, the amount of water in the biomass and cleaning the impurities in the product gas from various contaminants such as alkali compounds, and tar are the technical bottlenecks in the commercialization of fuels and chemical production.

The operation of gasification reactors encompass four steps, namely drying, volatilization, reduction, and combustion (Damartzis and Zabaniotou 2011). In a nutshell, the biomass gasification despite the fact being a prominent technology in the production of second generation automotive biofuel, it is still in its infancy in terms of commercialization.

5.2.2 Pyrolysis

Pyrolysis, the precursor of combustion and gasification of biomass, is the conversion phenomenon of biomass into a fuel source in the absence of oxygen. It comprehends the thermal anaerobic destruction of biomass into a carbon rich solid residue (charcoal), an oil-like liquid (bio-oil or crude oil) and a hydrocarbon rich gaseous products, acetic acid, acetone, and methanol by heating the biomass to about 700–800 K (Demirbaş 2003). The thermal environment and the temperature have a significant effect on the pyrolysis yield. Bio-char is the by-product of pyrolysis at longer reaction times (i.e. temperature around 450 °C), whereas gaseous compounds are produced at high temperatures around or greater than 800 °C. An intermediate temperature is optimum for the production of bio-oil (Alonso et al. 2010). Thus produced bio-crude is considered not only to be used in engines and turbines, but also has been regarded to be efficient as feedstocks refineries (McKendry 2002). The conversion of biomass into its subsequent products yield around 20–30% aromatic compounds in the presence of H-ZSM-5 (Carlson et al. 2009).

5.3 Conventional Pyrolysis

Conventional pyrolysis is a slow and irreversible process for the disintegration of organic matters in biomass into various pyrolysis products. This traditional technique has been used mainly for the production of charcoal (Yaman 2004). In developing nations, charcoal is used as a domestic fuel source because its energy density content is relatively higher and is smokeless (Demirbaş 2001). On the contrary, fast pyrolysis (thermolysis) or flash pyrolysis also known as ultra-pyrolysis is considered an innovative design with promising characteristic as an alternative for efficient pyrolysis of biomass feedstock that includes seaweed and algae (Shuttleworth et al. 2012). As suggested by name, fast pyrolysis is a rapidly occurring thermochemical conversion of biomass with 60–70% bio-oil yield and 20% bio-char and syngas simultaneously; depending upon the nature of feedstock (Naik et al. 2010). Hayes (2009) has reported 60–70% bio-oil yield and obtain increased yield of bio-crude products. Here, the expedition decomposition of biomass induces the production of vapors, aerosols, and gaseous products. Flash pyrolysis is a thermochemical biomass conversion route performed in the range of 1000–1300 K in order to change the small fraction of dried biomass into bio-crude.

Biomass pyrolysis is at utmost prominent attention as an alternative for a thorough exploitation of cellulosic biomass due to its inherent attributes such as significant economic benefits over other existing thermal conversion processes in addition to the notable logistical aspects. However, the major impediment for direct bio-oil use are the poor thermal stability, high acidity, low energy, density, and corrosive nature that perils equipment lifetime once used in existing engines (Demirbaş 2003; Alonso et al. 2010).

5.3.1 Bio-Chemical Conversion Routes

In spite of the fact that the thermochemical conversion is employed for biomass conversion, the use of promiscuous biological enzymes has gained a significant attention in industrial setting due to its efficient and selective nature in the biochemical reaction (Jaeger et al. 1999). Nevertheless, the factors such as poor stability, increased cost, low activity of the currently available enzymes trigger the uncertainty in the feasibility of biomass conversion for sustainable fuel production. On this account, the need for the development of novel enzymes is of prime significance for bio-economy (Barnard et al. 2010). The biochemical conversion technology assists the conversion of cellulosic biomass into different intermediates through the aid of bio-catalysts, novel enzymes or microbes. At present, the exploitation of biochemical pathway inherited into the native micro-organisms can be often touted route for the proper biomass utilization and its conversion in industrial processes (Alper and Stephanopoulos 2009). So far, the two divergent microorganisms, namely *Escherichia coli* and *Saccharomyces cerevisiae* have produced a promising organisms of choice for biotechnological applications in biofuel industry.

Fermentation and anaerobic digestion are the two major processes in bio-chemical conversion pathways.

5.3.1.1 Fermentation

Basically, this process is used in commercial scale for the large scale production of ethanol from different crops such as sugarcane, sugar beet, corn, and wheat (McKendry 2002). Mostly, yeast is used for converting sugars into ethanol. The batch processes, semi-continuous processes, and continuous processes are the three different fermentation processes deployed for ethanol production (Saxena et al. 2009). The use of transgenic micro-organisms can enhance the efficiency of fermentation process. The insertion of genes into a micro-organism possess the ability to ferment both 5-carbon sugar (pentose) and 6-carbon sugar (hexose) (Ingram et al. 1991). Nevertheless, it is of prime importance for the lignocellulosic biomass to undergo hydrolysis due to its recalcitrant nature.

5.3.1.2 Hydrolysis

The hydrolysis comprises of acid treatment and enzymatic hydrolysis of biomass. The acid treatment incorporates both concentrated as well as the dilute acid hydrolysis process. The concentrated hydrolysis mainly de-crystallize cellulose with concentrated acid, followed by the dilute acid hydrolysis into sugars (Kyoung Heon Kim and Nguyen 2002). The later hydrolysis process more efficient for ethanol production from biomass, where 0.7% sulfuric acid is used at 190 °C to hydrolyze the hemicellulos present in the plant biomass at a first stage. In addition, the second stage yields cellulose fraction by using 0.4% sulfuric acid at 215 °C (Brennan et al. 1986).

Unlike acid hydrolysis, during enzymatic hydrolysis, the synergistic actions of multifunctional cellulolytic enzymes screened from the various micro-organisms are of fundamental significance for the microbial degradation of cellulosic biomass and its downstream applications. The cellulase enzymes are considered as the most prominent among them so far (Saxena et al. 2009). The microbes deploy their extracellular cellulases to hydrolyze and metabolize the recalcitrant nature of plant carbohydrates into sugars which is then fermented by bacteria, yeast or other micro-organisms to produce ethanol (Ando et al. 1986; Lynd et al. 1999, 2016; Thapa et al. 2020).

5.3.1.3 Anaerobic Digestion

Anaerobic digestion is the natural biological conversion of organic wastes into bio-fertilizers or bio-gas by the use of bacteria in anaerobic condition. Thus, produced bio-gas encompasses an energy content of about 20–40% of the lower heating value of feedstock and can be used in gas turbines, and as a natural gas substitute. This is a reliable commercial technology for the organic waste and cellulosic feedstock treatment. The energy produced through anaerobic digestion can be used for both electricity and heating purposes.

5.4 Microbial Strategies for Lignocellulosic Degradation

The different cellulolytic and xylanolytic enzymes derived from various cellulolytic and xylanolytic bacteria, fungi can be exploited for the biomass conversion to feedstock chemicals. A study done by Benedict C. Okeke stated the strain of *P. janthinellum* FS22A and *T. virens* FS5A proved to be promising for the co-production of cellulolytic and xylanolytic enzymes in a research lab scale; yet further investigations are required to enhance their enzyme production (Okeke et al. 2015). The holistic approach in engineering the microbial enzymes, their proper isolation, identification, expression, characterization, and final assay can aid further to achieve tailor-made cellulases and xylanases for various industrial applications.

The bacterial species present in soil, marine, herbivore guts possess multi-functional novel enzymes that can efficiently hydrolyze the plant cell wall constituents (Medie et al. 2012). The bacterial glycosidase hydrolases enzymes enhance functions and synergistic effects and hence are often multi-modular (www.cazy.org). Sigoillot et al. (2012) stated that Basidiomycota and Ascomycota fungi demonstrated effective ability to produce wide range of lignocellulolytic enzymes to deconstruct lignocellulosic materials. Soft-rot fungi degrade plant polysaccharides; brown-rot fungi such as *Gloeophyllum trabeum*, *Coniophora puteana,* and *Postia placenta* degrade cellulose and hemi-cellulose; white-rot fungi are efficient in the degradation of wood components (Daniel et al. 2007; Irbe et al. 2011; Sigoillot et al. 2012). Hyperthermophiles archaea domain and thermophilic bacteria like *Thermotoga* and *Aquifex* have the ability to grow on crystalline cellulose and unprocessed plant biomasses (Yang et al. 2009).

The enzymatic hydrolysis of plant cell wall takes place through the combined action of three different glycol-hydrolyze (GH) enzymes, namely endoglucanase (EC 3.2.1.4), exo-glucanase also known as cellobiohydrolases (EC 3.2.1.91) and β-glucosidases (EC 3.2.1.21). All these enzymes hydrolyze the β-1, 4 covalent bonds where the glucose units are connected in the cellulose fiber. Endoglucanase belong to families GH5, GH6, GH7, GH9, GH12, GH45, and GH74. β-glucosidases belong to families GH1 and GH3. The two important synergistic action endo-exo between endoglucanases and cellobiohydrolases and the exo-exo between two cellobiohydrolases are of phenomenal importance during the hydrolysis of cellulose. Hemicellulose hydrolysis also requires the intervention of several functional enzymes along with the complementary activities at various levels. GH and carbohydrate esterase (CH) are involved in the hemi-cellulose hydrolysis by cleaving ester bonds between the acetyl groups and hemi-cellulose chains (Shallom and Shoham 2003).

The production of better competitive enzymes cocktails through the exploration of fungal bio-diversity with their Secretomes is one of the new approach in isolating the multi-functional enzymes to increase the saccharification efficiently in biomass conversion. In addition, the library of new microbial genome sequencing, the proteomic and transcriptomic analysis and thorough studies of various bacterial, fungal and other microbes thriving in harsh habitats and enzymes isolated therein, can definitely be the kernel of hope to open new avenues for lignocellulolytic/xylanolytic discovery.

5.5 Consolidated Bio-processing

The economic aspects related with the hydrolysis of cellulosic biomass in producing ethanol is one of the major bottlenecks that needs to be unlocked. Consolidated bio-processing (CBP) reduces the lignocellulosic bioprocessing operation cost with improved cellulosic conversion efficiency through the integration of the enzymatic hydrolysis of cellulose and the subsequent fermentation by the production of single cellulolytic enzyme or microbial consortium.

The efficient operation of CBP requires the engineering of a CBP enabling microbe, which is being made primarily through two different strategies: strategy I incorporates the engineering of a micro-organism that produce cellulase that can ferment sugars; Strategy II is engineering the ethanologenic micro-organisms that exhibit cellulolytic attributes with high product yields and enable cellulose utilization (Amore et al. 2012; Daniel et al. 2012). In regard to CBP strategy I, owing to the high level production of cellulase activity, the filamentous fungi, namely *Trichoderma reesei* is considered as the best potential candidates due to their broad range of tools for genetic manipulation (Xu et al. 2009). Unlike, as far as CBP strategy II is considered, the bacteria like *E. coli* and *Zymomonas mobilis* (Edwards et al. 2011) and fungi *Kluyveromyces marxianus* and *Saccharomyces cerevisiae* are the most interesting candidates (Jung et al. 2013).

Despite being a favorable candidate, both bacteria and yeast are unable to sufficiently produce cellulolytic enzymes in terms of quantity and quality for lignocellulosic biomass degradation. Filamentous fungi are proven to be prolific in production of high amount of cellulolytic enzymes and therefore, the genetic engineering of these fungi is of prime need for enhancing ethanol yield.

5.6 Conclusion and Future Perspectives

Biomass is the most ubiquitous renewable carbon source that can be processed in an integrated biorefinery. Hence, the production of various biofuels and other value-added co-products based on lignocellulosic biomass is now a global primacy. Nonetheless, the exploitation of lignocellulosic biomass in the production of biofuels and bio-based chemicals is neither new nor is an historic artefact. The pre-treatment of recalcitrant nature of cellulosic biomass and the expensive biomass conversion technology is a prime bottleneck in its bioprocessing for biofuels and other bio-products. The crucial economic and technological impediment in bio-ethanol production includes but not limited to pretreatment process, enzymatic hydrolysis, fermentation strategy, and distillation process. Even though some of the biomass conversion strategies deliver some apparent advantages, it is considered that none of the technique has become the strategy of choice at this point at least not for all feedstocks. The bio-chemical complexity, increased oxygen concentration, and elevated stability are some of the pre-eminent factors to be considered during the biomass pre-treatment. Likewise, high processing costs are perceived as the most impediment to commercialization for biomass conversion technologies. The cocktail of biomass pre-treatment technologies could enhance the biomass digestibility while reducing the inhibitory product formation. Similarly, the synergistic action of multi-functional novel cellulolytic/xylanolytic enzymes could improve the biomass conversion efficiency. A coordinated research on the biomass pre-treatment strategies, feedstock digestibility, conversion strategy, enzymatic hydrolysis, and fermentation technology could impart a fundamental understanding in optimizing the robust integrated biorefinery approach in the near future. The successful commercialization of multitude conversion strategy advances necessitates the catalysts synthesis and its optimum performance, kinetic evaluation of the various chemical reaction pathways, comprehensive in situ enzyme characterization as well as theoretical studies comprehending state of the art "omics" approaches.

Despite innumerable challenges, biofuel is the most promising as well as viable energy portfolio not to replace the use of fossil fuels rather complements to meet the world's ever-growing demand of energy. The current and emerging conversion technologies such as pyrolysis, gasification, and cellulosic ethanol production bestow extensive opportunities while improving the biomass conversion efficiency while reducing greenhouse gas emission in the atmosphere, bolstering rural economy, and enhancing the national energy security.

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Part II

Bioenergy: Sustainable Solution for Bioeconomy

Catalysts in Biodiesel Production and Process Optimization by Response Surface Methodology

6

Dipesh Kumar and Bhaskar Singh

Abstract

There is a growing awareness regarding the use of environmentally benign products and processes. The utility of biodiesel as an alternative fuel is well recognized and catalysts play an important role in the production of biodiesel. In this work, we highlight the types and importance of catalysts in biodiesel regime and how they affect the techno-economic and sustainability dimensions of biodiesel production. For any given combination of feedstock and catalyst, the process variables including the concentration of the catalysts, relative proportion of monohydric alcohol, reaction time, and reaction temperature have a profound influence on the conversion of the feedstock. As a result, the settings for these variables are usually optimized toward maximum response. The optimization of biodiesel production by the conventional "One Factor at a Time" and more reliable "Response Surface Methodology" is also presented in this chapter.

Keywords

Biodiesel · Transesterification · Catalyst · Response surface methodology · Process optimization

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6.1 Introduction

The incompatibility of straight vegetable oil (SVO) or other oleaginous feedstock for direct use in diesel engines is primarily attributed to their high viscosity (Guo et al. 2015). Combustion of SVO in diesel engines leads to a host of issues, including carbon deposition, coking, plugging of fuel lines and filters, and poor atomization (Ma and Hanna 1999). Since the original design of the compression ignition engine was modified to run on a low viscosity fuel (diesel), SVO are no longer compatible with modern engines (Dey and Ray 2020; Simsek and Uslu 2020). Although different strategies to reduce the viscosity of the SVO have been put forth, transesterification remains to be the most commonly adopted technique (Meher et al. 2006). In fact, esterification/transesterification of oleaginous feedstock is the only method to produce fatty acid alkyl esters (FAAE), which is commonly referred to as biodiesel. Others methods such as blending in diesel/kerosene, development of microemulsions, transformation to pyrolytic oil, or hydrotreatment also facilitate viscosity reduction of the oleaginous feedstock, but such fuels cannot be termed as biodiesel (Knothe 2010).

The oleaginous feedstock are usually enriched in tri-esters (triacylglycerol; TAG) of long-chain fatty acids. The process of transesterification involves the sequential release of the glycerol backbone in the TAG molecule and the esterification of the individual fatty acid chains with a monohydric alcohol. The process involves vigorous mixing of the oleaginous feedstock with monohydric alcohol under elevated conditions of temperature and is usually a catalyzed process (Kusdiana and Saka 2001). The oleaginous feedstock often contain a significant proportion of free fatty acids (FFA), and their content often dictates the preferred choice of catalyst (Fjerbaek et al. 2009).

6.2 Transesterification Catalysts

The process of catalyzed transesterification may involve either homogeneous or heterogeneous catalysts and can either be supported by an acidic or alkaline/basic catalyst (Ma and Hanna 1999). There are several drawbacks of using homogeneous catalysts, and such challenges have supported worldwide research and development efforts on developing heterogeneous catalysts (Kumar et al. 2018). There is a growing body of knowledge on the utility of heterogeneous transesterification catalysts (acidic/basic/enzymatic) (Borges and D’iaz 2012; Sani et al. 2014; Kumar et al. 2018). In addition to these, research on supercritical transesterification (usually does not require a catalyst) has also gained momentum.

6.2.1 Conventional Homogeneous Catalysts

Homogeneous catalysts remain in the same phase as the reactants or are soluble in the reactants. The conventional approaches of transesterification involve homogeneous catalysts, and these can either be a proton abstractor or a proton donator. However, these catalysts, unlike the conventional catalysts, cannot be recovered and reused as they are majorly inseparable from the products of transesterification (Lam et al. 2010). After the transesterification, these catalysts are usually washed off from the crude biodiesel and glycerol. In the process, vast amounts of wastewater are generated, and their characteristics (pH, Acidity, Alkalinity, etc.) are dependent on the choice of a transesterification catalyst (Sani et al. 2014).

6.2.1.1 Homogeneous Alkaline Catalysts

Hydroxides and methoxides of Na/K are the most common types of homogeneous alkali catalysts in transesterification. These are highly active and form the bulk of the industrial consumption of transesterification catalysts in current use (Granados et al. 2009). These catalysts are highly suited for high-quality refined feedstock such as the dried and de-acidified edible oils (soybean, sunflower, oil palm, etc.) (Meher et al. 2006). The alkali/base-catalyzed transesterification is reported to operate around 4000 times faster than their acid counterparts (Ma and Hanna 1999; Meher et al. 2006). The attractiveness of high purity feedstock for homogeneous alkali-mediated transesterification is ascribed to the negligible content of moisture and FFA in such feedstock. The presence of alkali in a moist environment promotes the hydrolysis of oil and fats, and as a result breakdown of TAG is affected (Chai et al. 2014). An excess of FFA reacts with alkali leading to saponification and consequently results in wastage of FFA and the catalyst. Moreover, saponification complicates the separation of phases after transesterification (Kaur and Ali 2014). These issues limits the application of WCO, spent oil, and other feedstock rich in the content of FFA for their direct alkali-catalyzed transesterification. To circumvent these challenges, primarily two approaches are employed. These include (1) the prior esterification of FFA to FAAE with a monohydric alcohol and (2) their transformation to glycerol esters. The former approach usually involves H_2SO_4 as a homogeneous catalyst for esterification and operates under conditions similar to that of alkali-catalyzed transesterification. Alkyl esterification being a single-step reaction proceeds at a faster rate than the transesterification of triacylglycerol (that involves three reversible elementary reactions), and the solubility of free fatty acids in low chain alcohol is higher than acylglycerols (Kumar and Singh 2018). Moreover, compared to the acid-catalyzed esterification, the acid-catalyzed transesterification conditions are more severe in terms of requirement of the higher molar ratio (typically $\geq$20:1), high reaction time (typically $\geq$4 h), and high reaction temperature (typically $\geq$80 °C) (Aranda et al. 2008). These technicalities limit the conversion of TAG to FAAE during pre-esterification to negligible levels. The pre-esterification reaction necessitates the neutralization/washing of the excess acid (if any) and removal of the water formed as a reaction by-product. The esterified oil is amenable to alkali-catalyzed esterification. An alternative approach is the esterification of FFA with glycerol to produce glyceridic ester (MAG) (Felizardo et al. 2011).

6.2.1.2 Homogeneous Acid Catalysts

H_2SO_4 remains to be the most frequently cited catalyst for the (homogeneous) acid-mediated transesterification. Despite operating at severe conditions than the alkali-catalyzed process, the acid-catalyzed transesterification is appealing, as it extends greater feedstock flexibility (Lam et al. 2010). The process is tolerant to high FFA and moisture levels in the feedstock, which are frequently present in excess quantities in low-cost recycled feedstock and in a majority of non-edible oils. The single-step acid process for the transesterification of recycled feedstock extends greater economic return over the two-step alkali process (Marchetti and Errazu 2008). However, the environmental desirability of the process is somewhat compromised due to the involvement of a hazardous acid, associated acid-resistant infrastructure, and the neutralization and/or washing steps. Moreover, the reaction conditions for the process are less desirable in terms of the requirement of a higher concentration of alcohol, residence time, and reaction temperature.

An alternative approach involves hydrolysis of oleaginous feedstock to yield corresponding fatty acids and glycerol followed by the esterification of the former to FAAE. In this process, the production of FAAE from FFA involves a singular reaction (unlike the transesterification of TAG, which involves three sequential steps), and the backward reaction of glycerol and FAAE is avoided (Atadashi et al. 2013).

6.2.2 Unconventional Catalysts

Perhaps the most significant drawback of homogeneous catalysts is their non-reusability and the necessity of product neutralization and/or washing. The dose of such catalysts should be carefully determined (through optimization studies) so as to limit the excess to a bare minimum. The excess is usually neutralized and/or washed off the product by means of several cycles of hot water wash, and the process in effect generates large quantities of wastewater of undesirable characteristics (Faccini et al. 2011). The unconventional catalysts broadly fall into three categories, that includes (1) heterogeneous base catalyst, (2) heterogeneous acid catalysts, and (3) biocatalysts (lipases) (Lam et al. 2010). These catalysts offer several significant advantages over conventional catalysts, which are primarily reflected in their ease of recovery, reusability, simpler phase separation, and high product purity.

6.2.2.1 Heterogeneous Base Catalysts

The heterogeneous base catalysts overcome some of the limitations of their homogeneous counterparts, including easy recovery, reusability, high product purity, environment-friendly downstream processing, and in many cases, their ease of production. However, their utility for feedstock rich in water and FFA remains limited, just like the homogeneous alkali catalysts. The utility of alkali metal oxides, mixed metal oxides, perovskite like materials, and related materials having a proton extraction tendency have been reported (de Lima et al. 2016).

6.2.2.2 Heterogeneous Acid Catalysts

The attractiveness of the heterogeneous acid catalysts is attributed to their greater feedstock flexibility and the avoidance of the use of a hazardous acid (viz. H_2SO_4), and the associated acid-resistant infrastructure (Faruque et al. 2020). Solid acids have been cited as one of the most attractive choices of catalysts for mass-scale biodiesel production. The efficiency of the catalyst (usually characterized as the turnover frequency), catalytically active sites (strength, distribution, and abundance), specific surface area, porosity, and nature of catalyst (bronsted/Lewis acid) usually characterize a solid-acid catalyst and are responsible for the preference of certain materials over others (Pandian et al. 2020). The morphology and related surface characteristics of a heterogeneous catalyst exhibits a dynamic nature as these properties tend to change in response to the changing reaction conditions. Such observations have been characterized by the in situ operando spectroscopic studies and have also formed the basis for describing such materials as "non-equilibrium" or "dynamic" catalysts (Topsøe 2003; Frenken and Groot 2017). It also highlights the importance of optimizing process variables for chemical reactions employing such catalysts. The homogeneous catalysts offer definite acidic characteristics, while the diversity of acidic sites on the solid catalyst surface is an added advantage (Sheikh et al. 2013).

Mixed oxides, mixed metal oxides, catalysts with introduced sulfonic acid groups, polyoxometalates and heterospory acids, ionic liquids, and zeotype materials and zeolites have been used in the production of biodiesel (Sani et al. 2014). Moreover, there is a growing body of knowledge on bi-functional solid catalysts which combine the advantages of both acid and base catalysts (Mansir et al. 2017). Bi-functional catalysts perform the esterification (of FFA) and transesterification (of TAG) reactions in a simultaneous fashion (Al-Saadi et al. 2020). However, a detailed analysis on the synthesis, characterization, mechanism of action, and other related properties of such materials are due.

6.2.2.3 Biocatalysts

The utilization of biocatalysts (enzymes) in transesterification has emerged as one of the most appealing opportunities to overcome the problems of homogeneous catalysts (Xu 2000). Enzymatic transesterification is by far the most eco-friendly approach toward biodiesel production. Biological origin (renewable catalyst), low (close to stoichiometric) demand for methanol, low reaction temperature, ease of recovery, and recyclability of the enzyme are among the most prominent advantages of enzymatic transesterification (Fjerbaek et al. 2009).

It involves lipases (TAG acyl hydrolase EC 3.1.1.3) typically sourced from yeast, fungi, and bacteria. Depending on the source, the lipases exhibit different regioselectivity. On the basis of the specific regioselectivity, lipases have been categorized into: (1) fatty acid-specific lipase, (2) non-selective lipase, (3) sn-1,3 specific lipase, and (4) sn-2 specific lipase (Fjerbaek et al. 2009).

A vast literature on enzymatic transesterification has accumulated over time after its first reported use in 1990, wherein the enzyme sourced from *Pseudomonas fluorescens* and *Mucor miehei* was employed in the production of FAAEs from sunflower oil (Santos et al. 2020; Lv et al. 2021). Despite the mentioned advantages, the enzymatic transesterification is not a very popular choice as the cost of the enzyme (lipase) is high; its activity is inhibited in the presence of alcohol, its susceptibility to denaturation at a higher temperature, sensitivity toward pH fluctuation, and exhibits a slow reaction kinetics (Marchetti and Errazu 2008).

6.3 Transesterification Variables

In addition to the choice of feedstock, alcohol, and catalyst, the final conversion to biodiesel is governed by four independent variables, including the concentration of the catalyst, molar ratio, reaction time, and reaction temperature (Eevera et al. 2009). The miscibility of the reactants (oleaginous feedstock and alcohol) is poor, and in the absence of a vigorous mixing of the reactants, the mass transfer limitations compromise the overall conversion efficiency. As a result, several studies have also accounted for the effect of the rate of stirring on the conversion of the feedstock. However, it is well recognized that if the rate of stirring is maintained at sufficiently high levels ($\geq$700 rpm), the relative effect of stirring is apparently insignificant (Hamze et al. 2015). Therefore, for all practical purposes, the process is assumed to be dependent on only the four variables listed above.

6.3.1 Optimization of Transesterification Variables

6.3.1.1 Conventional Approach

The convention optimization design is based on the one factor at a time (OFAT) approach, wherein, one of the controllable variables is varied over its predefined range, while the remainders are held constant at a particular level. The optimum setting for a given variable is reflected by the level at which the response is most favorable. The process is continued until it is replicated for all the variables under investigation. Therefore, the optimum setting is believed to lay at one of the predefined levels of the variable (Czitrom 1999). The challenges involved in the OFAT approach become more apparent with an increase in the number of independent variables or for a given combination of variables, the range of operation and the number levels for the individual variables are increased. Clearly, for multi-factor problems (each at several levels), the number of experiments to reach the optimum combination of factor levels will be too many. Under such circumstances, the OFAT approach will prove to be resource and time-intensive. Moreover, the OFAT approach fails to decipher and quantify the potential interaction between process variables (Czitrom 1999). Interaction between factors is a very common phenomenon wherein an independent variable fails to produce a similar effect on the process output (response) at different levels for another independent variable. In cases where the factor interaction is significant, the results obtained by univariate optimization are significantly different from those obtained by multivariate optimization, and the results obtained by the latter are more reliable (Khuri and Mukhopadhyay 2010).

The OFAT approach remains to be the most commonly used optimization tool, as the alternative statistical modeling-based approaches demand technical know-how and expertise. Nonetheless, OFAT experiments are invariably less efficient than statistical modeling-based optimization tools.

6.3.1.2 Response Surface Methodology

Response surface methodology is an optimization tool based on factorial designs, wherein, the independent variables are varied together. Depending on the type of design, the number of variables, and their desired levels for the purpose of experimentation, the factorial experiments may involve a few to several experiments (Chelladurai et al. 2021). For designing and analysis of such experiments, several statistical packages such as those offered by Minitab® and Design Expert® are frequently being used. The process begins with a screening factorial design-based experimentation having the prime objective of identification of the significant variables. The analysis of the experimental design helps identify the significant variables and the potential relationship between the variables and the response (linear, quadratic, or interaction). In the beginning, the operational range is usually far away from the optimum, and under such circumstances, a first-order model performs satisfactorily (Mäkelä 2017). A first-order model with only the main effects for two factors is shown as Eq. (6.1). The first-order model guides the next sequence of experiments by following the method of steepest ascent/descent depending on the type of desired response. The step size for one of the variables is decided, and the regression coefficients for the rest of the variables are used to estimate a proportionate step size for such variables. Using the determined step size for all the variables, additional experiments are carried out in a manner that follows the fastest approach toward reaching the optimum (steepest ascent/descent). Such experiments are continued until there is no favorable increase in the response. It suggests that the region of optimum response is close by, and the first-order model is no longer adequate for such regions. The analysis of the results is likely to indicate a curvature and/or an interaction. Until this point, factorial designs are used. Special response surface designs are then used to model higher-order (usually a second-order model is adequate) relations after a curvature and/or interaction becomes a significant player (Chelladurai et al. 2021). A representative second-order polynomial model for k factors is shown as Eq. (6.2). These specials designs include the central composite, Box-Behnken, Taguchi, and Mixed designs.

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \tag{6.1}$$

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots \beta_k x_k + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \ldots \beta_{kk} x_k^2 + \beta_{12} x_1 x_2 \ldots + \beta_{k-1,k} x_{k-1} x_k + \varepsilon \ldots \tag{6.2}$$

where Y is the response, β_0 is the intercept, β_1 and β_2 are the coefficients for the main effects, β_{11} and β_{22} are the coefficients for the quadratic effects, β_{12} is the coefficient for two-factor interaction, and ε is the random noise.

Central composite designs (CCD) are two-level factorial (2^k) or fractional factorial ($2^{k\text{-}f}$) designs augmented by a few experiments at the center point and those at the axial points. The levels of factors are usually represented in coded units where +1 represents the highest, 0 represents the center point, and −1 represents the lowest setting for a variable. The axial points (α) represent those experimental runs where one of the variables is set at their mid-level (canter point; level 0). The axial points for a 2^2 factorial design thus include the runs at −1 & 0, +1 & 0, 0 & −1, and 0 & +1 levels. In terms of the coded values, a CCD design involves the following five levels $-\alpha$, + α, −1, 0, and +1 for all the variables. Depending on the distance of the axial point from the center point, different CCD are realized (face centered CCD, spherical CCD, etc.), and for $\alpha > 1$, a CCD is said to be rotatable. A rotatable design maintains a constant variance of the response in all the directions of the operation as long as the observation points are at identical distances. A CCD can easily be incorporated in a simple 2^k factorial design as only the runs at axial points are additionally required. The 2^k or $2^{k\text{-}f}$ designs allow the estimation of all the coefficients for the second order polynomial model. The total number of experiments (N) required for the estimation of the entire model terms using the CCD is $N = 2^k + 2k +$ *runs at center points*. The significance of the regression coefficients is then determined by the student's t-test, while the validity of the model is analyzed by the analysis of variance (ANOVA). R^2, adjusted R^2, and Predicted R^2 help assist in determining the adequacy and accuracy of the model for predicting the outcomes of additional experiments within close proximity of the range of operation. The cut-off p-value can be used to identify the nature of the relationship and the significant model terms. The insignificant terms can be dropped from the model to attain higher predictive power. The 3-D response surface plots are generated and help decipher the effect of two of the independent variables on the response at a fixed level for the remainder of the variables (if any). The model (full/reduced) is used to predict the combination of factor levels for attaining optimum response. The predicted optimum is then validated by performing a few experiments at the predicted optimum (Chelladurai et al. 2021).

Another important design that is frequently used is the Box-Behnken design (BBD), in which each of the factors at set at three levels (−1, 0, and +1) and includes the two-level factorial designs with balanced incomplete blocking (Mäkelä 2017). The BBD does not involve an embedded factorial (or fractional factorial) and is thus an independent design. The treatment combinations in BBD lie at the midpoint of the edges and center of the design space. BBD is rotatable or nearly rotatable and are all spherical designs. These designs are more efficient than the CCD as the number of experiments to estimate all the second-order model terms ($N = 2k\ (k\text{-}1)$ + *runs at center points*) are less in the former. Thus for a three, four, and five-factor design with three runs at the center points N = 15, 27, and 43, respectively, while for a corresponding CCD design N = 17, 27, and 45, respectively. The effect is highly pronounced for three-factor experiments, but the difference is less significant for experiments with a higher number of factors. Unlike the CCD, the BBD does not involve runs at axial points, and it is an added advantage as such points are many a time difficult to run or expensive.

Table 6.1 Process variables and examined levels for $BaZrO_3$ catalyzed production of Pongamia biodiesel (reproduced from Kumar and Singh 2018)

Factor	Symbol	−1	0	+1
Catalyst loading (wt %)	A	0.5	1.25	2
Molar ratio	B	10:1	20:1	30:1
Time (h)	C	1	2	3
Temperature (°C)	D	55	62.5	70

An example for a BBD-based optimization of biodiesel production from *Pongamia* oil using $BaZrO_3$ as a basic heterogeneous catalyst is being presented here (Kumar and Singh 2018). The independent variables (factors), their designated symbols, and examined levels (−1, 0, and +1) in actual terms are provided in Table 6.1. The levels of the examined factors were decided after a screening experiment. The experimental design consisted of a total of 27 experiments and included 24 experiments at the factorial points and the remainder at the center points (Table 6.2). The experiments were performed in a randomized order, and the responses (% conversion of *Pongamia* oil to biodiesel) as determined through ^1H NMR spectroscopy are presented in Table 6.2.

The experimental data was fitted to a second-order model, and the regression coefficients were estimated. All the main effect and quadratic terms were significant, but among the interaction terms, only CD (time × temperature) was significant at a confidence level of 95%.

The insignificant model terms were then dropped (cut-off of $p < 0.05\%$), and the resultant coefficients for the model terms, along with the original coefficients, are presented in Table 6.3. The adequacy of the reduced model was then assessed by ANOVA (Table 6.4). The reduced model with an F-value of 103.64 ($p = <0.0001$) was highly significant. Among all the model terms, the effect of catalyst loading was disproportionately large ($F = 628.14$, $p = <0.0001$).

The reduced second-order model in coded and actual terms are shown in Eqs. (6.3) and (6.4), respectively. The response surface plot of conversion of *Pongamia* oil plotted against catalyst loading and the molar ratio is shown in Fig. 6.1.

$$\text{Conversion }(\%) = +91.60 + 31.17 \times A + 7.29 \times B + 6.13 \times C + 3.84 \times D + 6.12 \times CD - 24.62 \times A^2 - 18.86 \times B^2 - 17.17 \times C^2 - 8.91 \times D^2 \tag{6.3}$$

Table 6.2 Experimental design for $BaZrO_3$ catalyzed transesterification of Pongamia oil, and the obtained responses (reproduced with permission Kumar and Singh 2018)

Std	Run	Catalyst loading (wt. % with respect to oil)	Molar ratio (alcohol to oil)	Time (h)	Temperature (°C)	Experimental conversion (%)	Predicted conversion (%)	
							Full quadratic model	Reduced model
8	1	1.25	20:1	3	70	87	81.62	81.62
11	2	0.5	20:1	2	70	26	27.79	30.74
9	3	0.5	20:1	2	55	27	26.01	23.06
3	4	0.5	30:1	2	62.5	24	22.42	24.24
25	5	1.25	20:1	2	62.5	92.7	91.6	91.6
19	6	0.5	20:1	3	62.5	21	23.75	24.77
16	7	1.25	30:1	3	62.5	67	70.49	68.99
17	8	0.5	20:1	1	62.5	15	13.53	12.5
15	9	1.25	10:1	3	62.5	50	52.91	54.41
1	10	0.5	10:1	2	62.5	12	11.48	9.66
5	11	1.25	20:1	1	55	57	61.67	61.67
14	12	1.25	30:1	1	62.5	53	55.22	56.72
27	13	1.25	20:1	2	62.5	93	91.6	91.6
21	14	1.25	10:1	2	55	58	54.65	52.7
13	15	1.25	10:1	1	62.5	42	43.64	42.14
24	16	1.25	30:1	2	70	78	76.91	74.96
23	17	1.25	10:1	2	70	60	58.43	60.38
12	18	2	20:1	2	70	89.9	96.02	93.07
20	19	2	20:1	3	62.5	91.1	88.13	87.1
4	20	2	30:1	2	62.5	88.6	88.4	86.57
18	21	2	20:1	1	62.5	81	73.81	74.84
7	22	1.25	20:1	1	70	57	57.1	57.1
10	23	2	20:1	2	55	79.1	82.44	85.39

26	24	1.25	20:1	2	62.5	89.1	91.6	91.6
6	25	1.25	20:1	3	55	62.5	61.68	61.68
22	26	1.25	30:1	2	55	68.2	65.33	67.28
2	27	2	10:1	2	62.5	69.3	70.17	71.99

Table 6.3 Regression coefficients for the quadratic models used to optimize $BaZrO_3$ catalyzed biodiesel production (reproduced from Kumar and Singh 2018)

Term	Coefficients		*p*-Value	
	Full quadratic model	Reduced model	Full quadratic model	Reduced model
Intercept	91.60	91.60	<0.0001	<0.0001
A-Catalyst loading	31.17	31.17	<0.0001	<0.0001
B-molar ratio	7.29	7.29	0.0001	<0.0001
C-reaction time	6.13	6.13	0.0005	0.0001
D-reaction temperature	3.84	3.84	0.0114	0.0067
AB	1.82	–	0.4293	–
AC	1.03	–	0.6541	–
AD	2.95	–	0.2107	–
BC	1.50	–	0.5141	–
BD	1.95	–	0.3993	–
CD	6.13	6.12	0.0178	0.0112
A^2	−24.62	−24.62	<0.0001	<0.0001
B^2	−18.86	−18.86	<0.0001	<0.0001
C^2	−17.17	−17.17	<0.0001	<0.0001
D^2	−8.91	−8.91	<0.0006	0.0002

Table 6.4 ANOVA of the quadratic model (reproduced from Kumar and Singh 2018)

Source	Sum of squares	df	Mean square	*F*-Value	*p*-Value
Model	17,309.93	9	1923.33	103.64	<0.0001
A-catalyst loading	11,656.33	1	11,656.33	628.14	<0.0001
B-molar ratio	638.02	1	638.02	34.38	<0.0001
C-reaction time	451.41	1	451.41	24.33	0.0001
D-reaction temperature	177.10	1	177.10	9.54	0.0067
CD	150.06	1	150.06	8.09	0.0112
A^2	3232.99	1	3232.99	174.22	<0.0001
B^2	1896.73	1	1896.73	102.21	<0.0001
C^2	1572.47	1	1572.47	84.74	<0.0001
D^2	423.24	1	423.24	22.81	0.0002
Residual	315.47	17	18.56		
Lack of Fit	306.05	15	20.40	4.33	0.2034
Pure Error	9.42	2	4.71		
Cor Total	17,625.39	26			

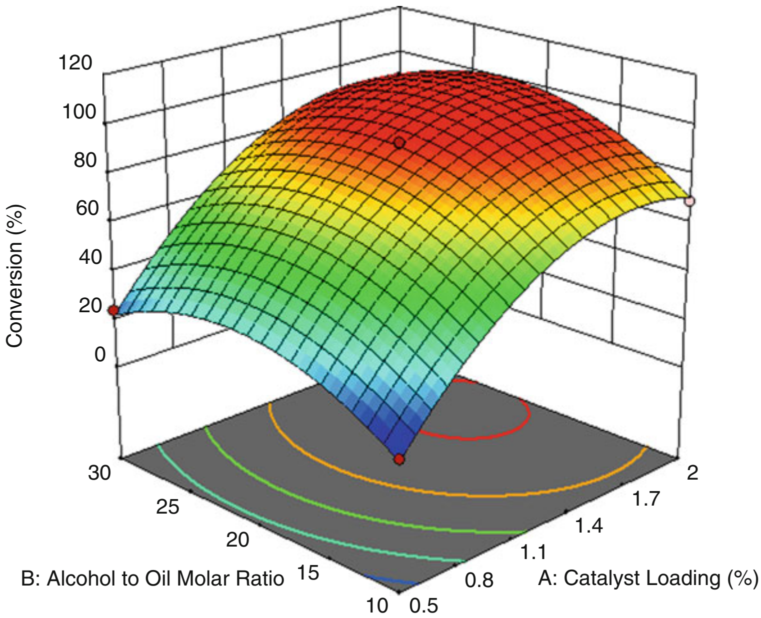

Fig. 6.1 Response surface plot of the influence of catalyst concentration and the molar ratio on conversion of *Pongamia* oil to biodiesel (reproduced from Kumar and Singh 2018)

$$\begin{aligned}\text{Conversion }(\%) = & -748.26713 + 150.98148 \times \text{Catalyst}\% + 8.27250 \\ & \times \text{oil} \\ & : \text{alcohol ratio} + 23.77500 \times \text{Time} + 18.67519 \\ & \times \text{Temperature} + 0.816667 \times \text{Time} \times \text{Temperature} \\ & - 43.77037 \times \text{Catalyst}\%^2 - 0.188583 \times \text{oil} \\ & : \text{alcohol ratio}^2 - 17.17083 \times \text{Time}^2 - 0.158370 \\ & \times \text{Temperature}^2 \end{aligned} \tag{6.4}$$

The high p-value of the model's lack of fit suggested that the data adequately fits the model. The response surface plot indicates the quadratic nature of the relationship between the catalysts concentration and the conversion of *Pongamia* oil. The response surface plots are similar to contour plots, except for the fact that the response variable is also included on the Z-axis, and as a result, a 3-dimensional graphical representation is obtained. The F-value along with the p-value can be consulted to identify the variables (and their relative influence) having the most profound influence on the response variable. An optimality tool embedded in the software platform can be used to determine the optimal setting for the process variables, and the model is then validated by performing a few replicate experiments at the predicted optimum conditions. The predicted and actual response for the case of $BaZrO_3$ is given in Table 6.3. When operating under the region of optima, close collinearity between the predicted and experimental response is expected.

Although the response surface methodology is a quite useful tool in process optimization, the use of newer tools, including artificial neural networks, is gaining momentum due to their reportedly better accuracy in process optimization (Bacs and Boyaci 2007; Maran and Priya 2015; Garg and Jain 2020).

6.4 Conclusion

The homogeneous catalysts continue to remain the most commonly employed transesterification catalysts in an industrial setting. High activity, low residence time, moderate reaction conditions and established downstream separation and purification strategies for homogeneous catalysts continue to outweigh the environmental appeal of their heterogeneous counterparts. The conventional OFTA optimization design suffers from the requirement of large number of experiments, ignorance of non-linear effects and factor interactions and as a result advanced statistical designs such as the RSM is now becoming a routine exercise.

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Bioethanol Production Technologies: Commercial and Future Perspectives

7

Meenakshi Suhag

Abstract

The demand of energy is continuously increasing, which is also increasing the demand of conventional fuel. The major demand of any country till date is fulfilled by conventional fossil fuels, however, the use of renewable energy, waste to energy and other non-conventional energy technologies are in progress. The conventional source of liquid fuels is limited to few countries and sources are getting exhausted in near future, so the alternate source of liquid fuel is current need of research. One such fuel is ethanol which is gaining importance nowadays due to its wide range of substrate and production methods. Ethanol is one of the most acknowledged engine fuels capable of partially substituting gasoline for the purpose of making gasoline-ethanol mixture in different ratios. Bioethanol production is one of the renewable methods of producing ethanol from different biological substrates and various routes. Bioethanol can be produced from various substrates such as sugar cane, wheat, corn, etc. Various countries are producing bioethanol from different routes and substrates. This chapter deals with all such possible technologies available for bioethanol production through different routes. The chapter also provides knowledge about the consequences and benefits of all generations of bioethanol.

Keywords

Bioethanol · First generation fuel bioethanol · Second generation bioethanol · Third generation bioethanol · Lignocellulose biomass · Organic waste

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7.1 Introduction

Transportation sector generally associated with increasing energy demand (Fig. 7.1b) and emissions of harmful gases. Issues such as energy security, depleting fossil resources and phenomena like global warming and climate change motivate the researchers all over the world to focus towards the exploration of more reliable, alternative and sustainable source of energy. Biofuels are the sustainable alternative

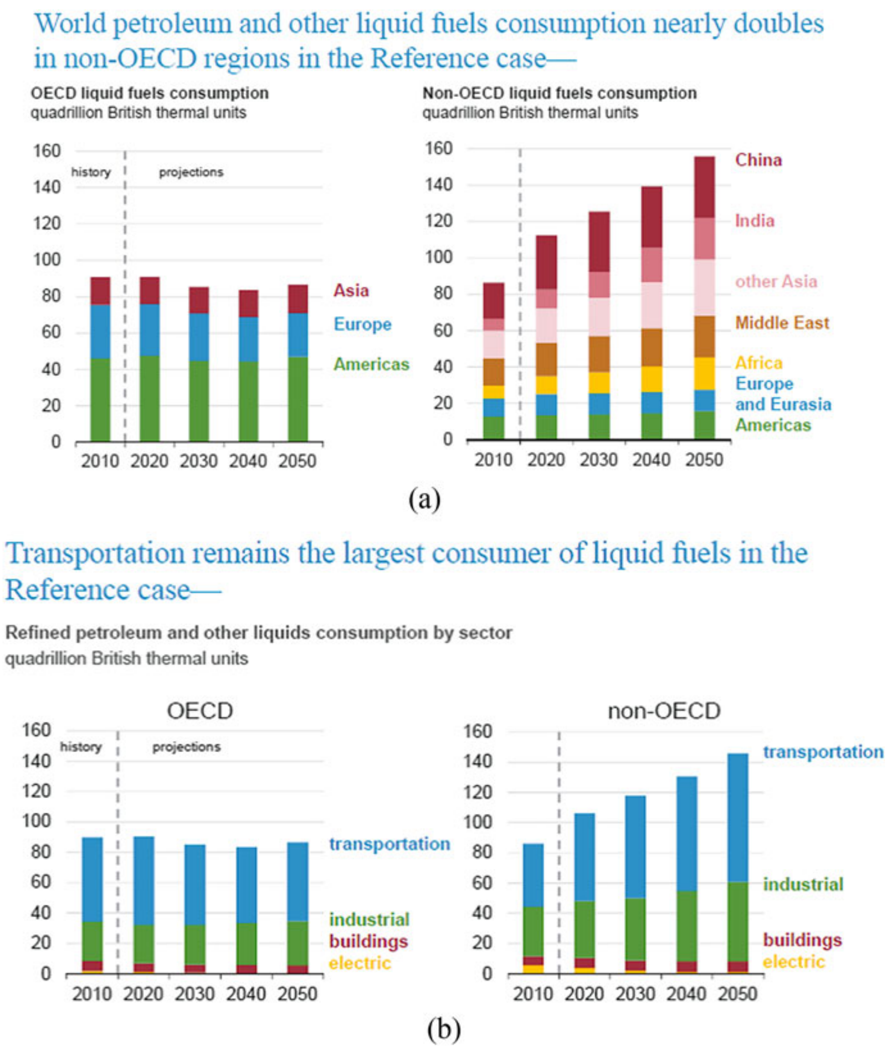

Fig. 7.1 (**a**) World petroleum and other liquid consumption trends and (**b**) Transportation sector as largest consumer of liquid fuels (Source: U.S. Energy Information Administration Office of Energy Analysis 2019; İnan and Ozçimen 2019)

fuels (solid, liquid or gaseous), produced mainly from renewable sources unlike conventional fuels. In today's scenario, where global demand for liquid fuels like petroleum is on rise (Fig. 7.1a), biofuels (mainly as bioethanol and biodiesel) seem to be attractive alternatives for reducing dependency on fossil based fuels and dropping possible CO_2 emissions (Yuan et al. 2008; Demirbas 2009). In the past years lots of work has been done in this direction, where production of liquid biofuels mainly bioethanol appeared to be a very promising candidate (Farrell et al. 2006).

Ethanol (CH_3CH_2OH) is the most acknowledged engine fuel capable of to partially substituting gasoline for the purpose of making gasoline-ethanol mixture, i.e. gasohol viz E15 (85% gasoline and 15% ethanol) E85 (15% gasoline and 85% ethanol). Higher oxygen content of ethanol acts as gasoline enhancer and helps in its cleaner combustion (Elfasakhany 2016). Bioethanol produced by sugar fermentation and/or starch enriched biomass sources using microorganisms, considered to be renewable, less toxic, having good adaptability and pollutant free thereby reducing CO_2 emission and air pollution (Zakaria et al. 2016). Moreover as reported by Renewable Fuel Association (RFA) in 2019, bioethanol lowered down CO_2-equivalent emissions of greenhouse gases from transportation sector by 54.1 million metric tons. That is equals to the removal of 11.5 million cars for an entire year from the roads or annual elimination of emissions from 13 coal-fired power plants.

Therefore, a strong constrain is apparent worldwide towards exploration of different bioethanol feedstocks and conversion technologies such as sugarcane in Brazil (Consuelo et al. 2010), conversion of ethanol from corn in the USA (Ulgiati 2001) and wheat in China (Ren et al. 2015). In 2019 the global production of ethanol (Fig. 7.2) recorded as 29 billion gallons, where USA contributes to 54% (16 billion gallons) of global output and Brazil contributes to only 30%.

7.2 Bioethanol Feedstocks

A range of raw materials have reported being used for the ethanol production (Table 7.1) primarily belongs to edible feedstocks such as sugarcane (*S. officinarum*)) in Brazil (Gupta and Verma 2015), corn (*Zea mays*) in the USA and cassava (*Manihot esculenta*) in Thailand and China (Deesuth et al. 2015). However, they are categorized as sugar, starch and cellulosic biomasses on the basis of their composition (Fig. 7.3) and further categorized in first, second and third generation bioethanol on the basis of their sources used.

- First generation bioethanol comprises sugar rich (such as sugar cane, sugar beet, sweet sorghum, etc.) and/or starch containing (viz., wheat, cassava, rice, corn, etc.) feedstocks.
- Second generation bioethanol derives from non-edible biomasses mainly lignocellulosic materials such as straws, organic residues, grasses, etc.
- Third generation bioethanol emanates from microalgae, macroalgae and seaweeds (Nigam and Singh 2011).

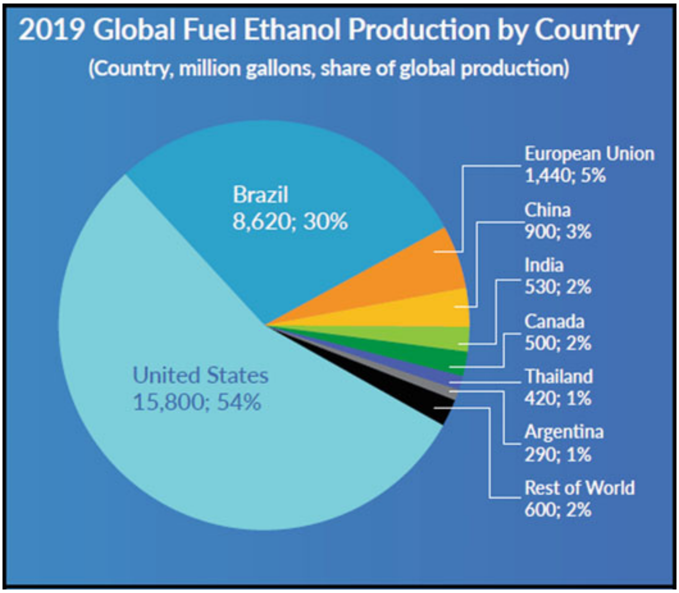

Fig. 7.2 Global fuel ethanol productions (Source: 2020 outlook, RFA analysis of public and private data source)

7.2.1 First Generation Bioethanol Production

Normally, lucrative bioethanol production governed by fermentation of glucose rich raw materials, viz. sugarcane, molasses or starch rich crops (Davis et al. 2006; Bhatia et al. 2017). Although, superior ethanol yield per hectare remains associated with sugar crops only firstly, because of higher sugar amounts per hectare compared with starch crops and secondly, ease in direct fermentation of sugar while in case of starch before fermentation it must be hydrolysed (Bessou et al. 2011).

7.2.2 Bioethanol Production from Sucrose Based Feedstocks (Fig. 7.4)

Sugar cane (*Saccharum of cinarum*) (Limtong et al. 2007), sugar beets (*Beta vulgaris*) (Razmovski and Vučurović 2012) and sweet sorghum (Barcelos et al. 2016) are reported to be used as raw materials for producing ethanol. However, in developing world sugarcane dominates ethanol production where molasses efficiently converted into ethanol (Hasan and Nurhan 2004). In case of India, molasses are used by distilleries for production of approximately 2.7 billion litres ethanol (Sukumaran et al. 2010).

Table 7.1 Different feedstocks reported for bioethanol production

Feedstock used for bioethanol production	References
First generation bioethanol feedstock's	
Sugarcane	Amorim et al. 2011; Huang et al. 2020
Sugarbeet	Foteinis et al. 2011
Sweet potatoes, cassava, corn	Ziska et al. 2009
Sweet potatoes	Zhang et al. 2011
Cassava	Cardona and Sánchezó 2007
Second generation bioethanol feedstock's	
Bamboo	Sun et al. 2011
Corn straw	Adelabu et al. 2019
Sugarcane leaf waste (SLW)	Sindhu et al. 2011; Go et al. 2020
Grass	Liu et al. 2017
Sugarcane bagasse	Pandey et al. 2000; Bian et al. 2014
Wheat Straw	Zhu et al. 2006; Talebnia et al. 2010; Hammond and Mansell 2018
Eucalyptus bark	Matsushita et al. 2010
Corncob	Yah et al. 2010
Rice straw	Wi et al. 2013; Singh et al. 2016
Lantana camara	Kuhad et al. 2010
Rapeseed straw	Karagöz et al. 2012
Switchgrass	Kennes et al. 2016
Sago pith waste	Thangavelu et al. 2019
Rape straw	Mathew et al. 2011
Sorghum	Chen et al. 2012
Argane pulp	Zouhair et al. 2020
Miscanthus	Aravindhakshan et al. 2010
Waste newspaper	Byadgi and Kalburgi 2016
Wheat bran	Cripwell et al. 2015
Rye straw and bermudagrass	Sun and Cheng 2005
Mushroom spent straw	Balan et al. 2008
Rye straw	Petersson et al. 2007
Sorghum stover	Vermerris et al. 2007
Coconut coir fibres	Ebrahimi et al. 2017
Rice hulls	Dagnino et al. 2013
Banana peels	Gebregergs et al. 2016
Pine wood chips	Cotana et al. 2014
Cotton stem waste	Patel 2017
Sugarcane residues	Dawson and Boopathy 2007
Rice husk	Favaro et al. 2017
Water hyacinth	Bayrakci and Koçar 2014
Third generation bioethanol feedstock's	
Sargassum muticum, seaweed	Pablo et al. 2019
Chlorella vulgaris	Kumar et al. 2016

(continued)

Table 7.1 (continued)

Feedstock used for bioethanol production	References
Chlorococcum sp.	Harun et al. 2011
Chlorococcum littorale marine green algae	Ueno et al. 1998
Porphyridium cruentum	Kim et al. 2017
Chlamydomonas reinhardtii	Nguyen et al. 2009
Scenedesmus obliquus	Miranda et al. 2012
Gelidium amansii (red seaweed)	Park et al. 2012
Chlorococcum sp.	Klochkova et al. 2006
Euchema Spinosum waste	Alfonsín et al. 2019
Ulva lactuca macroalgae	İnan and Ozçimen 2019
Microcystis aeruginosa microalga (cyanobacteria)	Khan et al. 2017
Gracilaria verrucosa, red seaweed	Kumar et al. 2013
Ulva rigida green seaweed	El Harchi et al. 2018

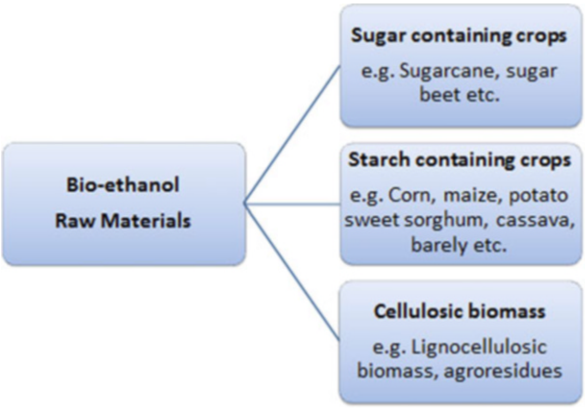

Fig. 7.3 Bioethanol feedstock's categories

7.2.3 Bioethanol Production Using Starch Rich Feedstocks

Traditionally starch based bioethanol production technologies consist of several stages (Fig. 7.5). First, the starch in the raw material is subjected to a gelatinization process which is followed by liquefaction of the starch. This involves the addition of heat and enzymes to accelerate the process. Liquefaction can be carried out under pressurized or non-pressurized conditions. This is followed by the saccharification of starch to fermentable sugars (Wang et al. 2007).

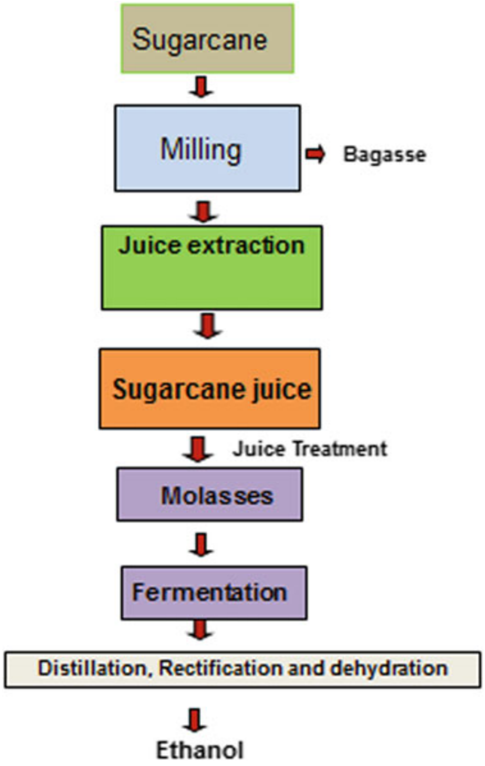

Fig. 7.4 Production flow of ethanol from sugarcane

7.2.4 Problems Associated with First Generation Ethanol

The production of first generation bioethanol from food crops has attracted criticism due to rising food prices as a result of the food and feed industry competition with the biofuel sector for raw materials and the global food shortage (Hasegawa et al. 2010).

7.3 Second Generation Bioethanol Production

Being most plentiful organic matter on earth, lignocellulosic biomass is a promising renewable resource for sustainable bioethanol production (Remond et al. 2010; Balat 2011; Sarkar et al. 2012; Ariyajaroenwong et al. 2016). In general, lignocellulosic biomasses are divided into three categories: (1) agricultural residues (e.g., crop residues and sugarcane bagasse), (2) forest residues and (3) herbaceous and woody energy crops (Carriquiry et al. 2011).

Cellulose, hemicelluloses and lignin are the three major components of lignocellulosic biomasses provide structural strength to plant cell walls (Rubin 2008). Cellulose and hemicelluloses are constituted approximately two-third of the dry biomass components can be easily fermented to ethanol whereas lignin cannot.

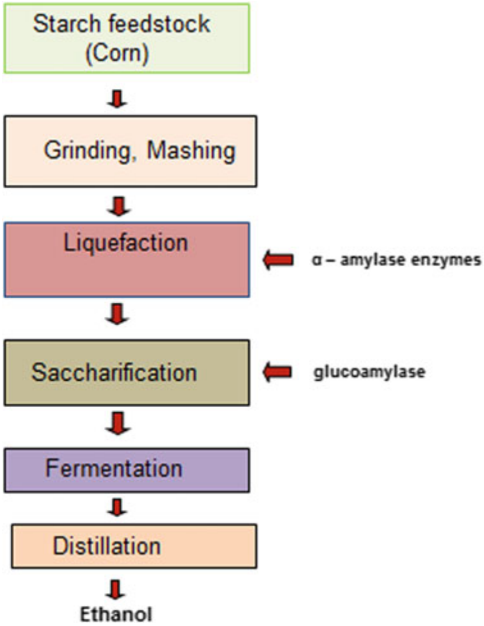

Fig. 7.5 Production flow of ethanol from starch feedstock

Therefore, due to the recalcitrant properties of lignocellulosic biomass microorganisms are unable to hydrolyse cellulose into glucose (Moodley and Kana 2019).

7.3.1 Conversion Paths for Lignocellulosic Feedstocks to Ethanol

Researchers have reported two different pathways referred as (Gonzalez et al. 2012):

- Sugar platform or Biochemical conversion route: in this platform, pretreated lignocellulosic materials are subjected to enzymatic conversion into sugars, the later fermented into ethanol.
- Syngas platform or Thermochemical conversion route: Solid biomass undergoes thermochemical conversion reactions at elevated temperatures to produce gaseous fuel called syngas (CO, H_2 and CO_2), which are having wide applications. The later may be converted into ethanol chemically employing chemical catalysis or using microbes through biological reactions (Datta et al. 2011).

7.3.2 Biochemical Conversion Route

The biological conversion processes appealed to be more beneficial include a suitable pretreatment followed by enzymatic saccharification/hydrolysis of polysaccharides into monomeric sugars and their further fermentation to ethanol and finally distillation (Sonderegger et al. 2004).

The conversion route of bioethanol production from LCB comprises different stages (Fig. 7.6):

- Pretreatment (to disrupt the cell wall structure and to facilitate the polysaccharides accessibility).
- Hydrolysis of cellulose and hemicellulose (enzymatic hydrolysis to break polysaccharides down into fermentable sugars, followed by their fermentation into bioethanol)
- Sugar fermentation and distillation and purification of the ethanol to meet fuel specifications (Demirbaş 2005).

7.4 Pretreatment

Owing to structural complexities, lignocellulosic raw biomass first undergoes a pretreatment so as to increase the susceptibility of cellulose content towards successive enzymatic hydrolysis process (Kim and Han 2012; Zabed et al. 2017).

The important goals of pretreatment step are as follows:

- Lignocellulose fractionation and solubilization of hemicellulose (Rocha et al. 2014).
- Decrease crystallinity of the cellulose and improve porosity of lignocellulosic biomasses (Van Dyk and Pletschke 2012).
- High degree of cellulose degradation and to remove lignin and improve the enzymes accessibility to polysaccharide (Mikulski and Kłosowski 2020).

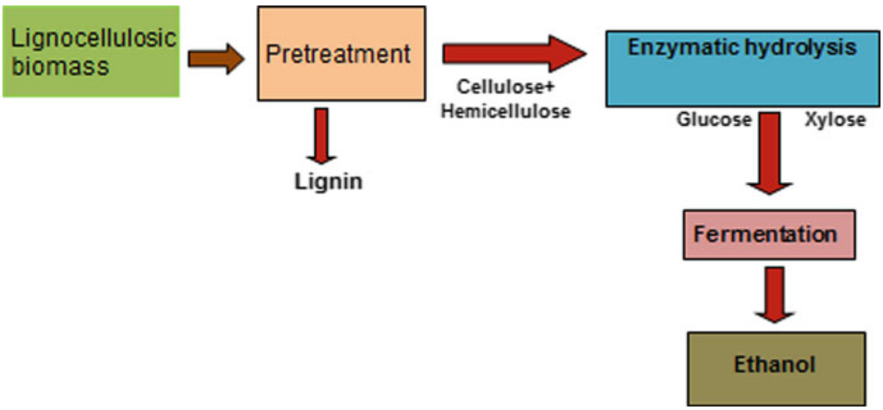

Fig. 7.6 Ethanol production from lignocellulosic biomass

The key challenge in emerging cost-effective technologies for producing bioethanol is to choose a suitable pretreatment technique. An effective pretreatment process in spite of cost-effective in nature must meet up with the following necessities (Kumar et al. 2009a):

a. enhance the sugar production efficiently during hydrolysis,
b. circumvent the loss or deprivation of carbohydrate,
c. hinder by-products inhibition throughout hydrolysis and fermentation processes.

Different methods of pretreatment have been reported by different researchers like acid pretreatment (Avci et al. 2013) alkali treatment (Chen et al. 2013; Cheng et al. 2010), ammonia explosion (Chiaramonti et al. 2012), Organosolv pretreatment (Teramoto et al. 2008; Huijgen et al. 2011), steam explosion (Horn et al. 2011), etc. In biological treatment microorganisms usually white-rot fungi (*Phanerochaete chrysosporium*) degrading both lignin and hemicellulose (Kennes et al. 2016) are employed. While, dilute acid pretreatment has received lots of appreciation for pretreating diverse biomasses (Kootstra et al. 2009; Singh et al. 2015).

7.5 Hydrolysis

Foremost objective of hydrolysis is conversion of polysaccharides (cellulose and hemicellulose) into soluble monomers to obtain sugars for further fermentation process (Chandel et al. 2007). Generally, acid and enzymatic hydrolysis are used for the saccharification/hydrolysis of lignocellulosic biomass. As one of the oldest and cheap methods, dilute or concentrated acids may be employed during acid hydrolysis. However, degradation of saccharides, more acid consumption and appearance of chemical compounds such as aldehydes make it less attractive. On the other hand there is growing concern for transformation of glucose from cellulose, pentoses (xylose and arabinose) and hexoses (glucose, galactose and mannose) from hemicellulose using enzymes mainly cellulases and hemicellulases via enzymatic reactions (Hu et al. 2011).

7.6 Cellulases and Xylanases

Cellulases are assembly of enzymes including *endoglucanase*, *exoglucanase* and *β-glucosidase* that acts synergistically and hemicellulases (xylanase) are essential for effectively hydrolysing cellulose to soluble oligosaccharides (Gottschalk et al. 2010; Kubicek et al. 2009). Whereas, complete xylan cleavage requires action of β-xylanase and accessory enzymes, i.e. β-xylosidase, α-arabinofuranosidase, α-glucuronidase and acetyl xylan esterase (Angel 2017; Carvalho et al. 2013).

Based on catalytic activity cellulases further characterized in three prime classes (Sukuruman et al. 2009):

- endo-β-1,4-glucanases: this enzyme splits bonds of inner amorphous areas of cellulose to dislocate the polymer chains.
- exo-1,4-β-glucanases (cellobiohydrolases): which acts on terminal of chains releasing cellulose oligomers and cellobiose.
- Cellobioses than hydrolysed to glucose molecules by β-glucosidases (Sharma et al. 2019).

7.7 Production of Hydrolytic Enzymes

Cellulolytic enzyme production has acquired great importance as commercial cellulases production is energy intensive and their cost adversely affected the economics of lignocellulosic ethanol conversion route (Cardona et al. 2010; Lever et al. 2010). Large quantities of enzymes are essential for cellulose hydrolysis along with hemicelluloses in to fermentable sugars. For microbial enzyme production lignocellulosic biomass mainly agricultural wastes are recognized to be an outstanding carbon source. Many microbes such as bacteria and fungi capable to produce cellulolytic enzymes while multidirectional research is being done regarding their strain improvement, use of cheap substrate which makes biomass to bioethanol method further cost-effective (Saini et al. 2015). Amid them, strains of *Aspergillus*, *Trichoderma* and *Penicillium* are conforming major studies related to cellulases production (Singh and Bishnoi 2012; De França Passos et al. 2018). *Aspergillus* sp. is rich *β-glucosidase* producer (Ahamed and Vermette 2008) contradictory to *T. reesei* as deficient of this enzyme that leads to accumulation of cellobiose during hydrolysis resulting in repression and end-product inhibition. Therefore, external adding of *β-glucosidase* can eliminate inhibitory effect of end-product (Fang et al. 2010).

Hydrolases are formed by submerged cultivation or by solid-state cultivation. Traditionally, submerged fermentation is carried out in excess amount of water and used for industrial production of cellulases due to better monitoring and easy handling (Singhania et al. 2010). Solid-state fermentation (SSF) method as rapid cellulases production now seems interesting as it offers cost-effective alternative. In SSF sufficient moisture is available so as to maintain microbial metabolism (Orzua et al. 2009). Utilizing inexpensive agro-based residues like wheat bran, wheat straw, etc. as substrate (Ghoshal et al. 2012); lower capital and operating costs; reduced down-stream processing and reduced stirring (Martins et al. 2011; Farinas 2015) are some of the major benefits of SSF. Effectiveness of hydrolysis is affected by various parameters, viz. pH, temperature, enzyme loading and substrate concentration (Canilha et al. 2012). Adding of Tween 20 or Polyethylene glycol (PEG) reducing the sorption of cellulase enzyme on lignin polymer which enhanced efficiency of saccharification (Joshi et al. 2011).

7.8 Fermentation

Pretreated of LB is accompanied with production of hexose and pentose mixture after enzymatic hydrolysis that fermented by microorganisms to ethanol (Alvira et al. 2010). Here, choice of appropriate microorganism proficient to utilize different types of sugars for production of ethanol is important such as yeasts (*S. cerevisiae*, *S. pombe)*, fungus (*F. porum)* and bacteria (*Z. mobilis*) (Chaudhary and Chincholkar 1986; Balat 2007; Bettiga et al. 2009). Yeasts as compared to others, are easier to harvest, recycle and are not easily be contaminated. Traditionally *Saccharomyces cerevisiae* is employed for fermentation step (Behera et al. 2010) as accompanying high ethanol yield (12.0–17.0% w/v; 90% of the theoretical yield), wide pH tolerance range (Lin et al. 2012) and efficiently ferment range of sugars (Azhar et al. 2017). Subsequently *Pichia stipitis* can further augment yield of ethanol from xylose conversion. Thus, all produced sugars need to be co-fermented to ethanol and is a key research objective (Chen 2011). In this regard, widespread studies are going on to isolate and screen microorganisms which facilitate fermentation of pentoses and hexoses and withstand inhibitory situations.

Separate hydrolysis and fermentation and simultaneous saccharification and fermentation (Carrillo-Nieves et al. 2017) (Fig. 7.7) schemes could be adopted after pretreatment step (Lu et al. 2013; Guerrero et al. 2018).

Hydrolysis and fermentation steps are carried out separately at optimized conditions in (SHF). However, during this process end-product inhibition effect was observed that resulted in poor sugars yield (Kumar et al. 2009a, b).

Now-a-days another proficient technique observed like simultaneous saccharification and fermentation. Herein single reactor both hydrolysis and fermentation

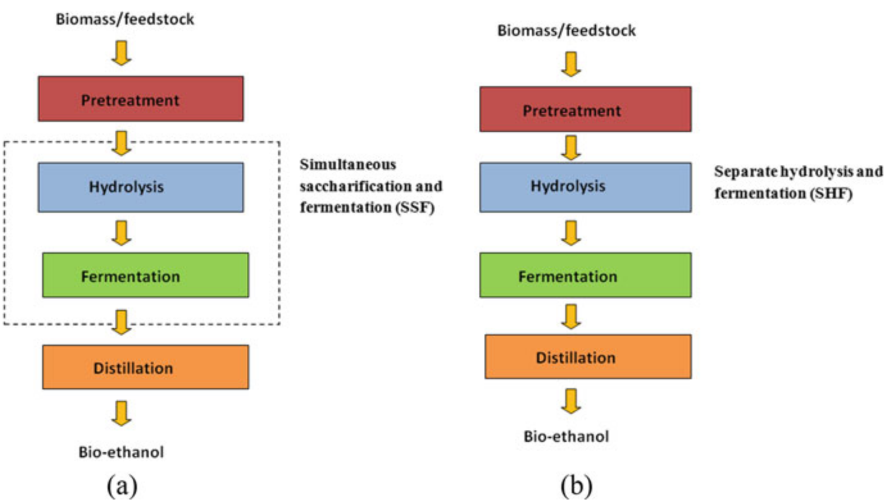

Fig. 7.7 Process flow for (**a**) simultaneous saccharification and fermentation (SSF) and (**b**) separate hydrolysis and fermentation (SHF)

operated simultaneously. This helps to reduce the costs and evading the production of inhibitory substances by eliminating time-consuming processes (Sewsynker-Sukai and Kana 2018). Furthermore, SSF process found additional prominent for enhancing rate of hydrolysis and ethanol yield as compared to SHF (Ko et al. 2017).

Few issues for progressive 2G sustainable bioethanol industry that need to be addressed appropriately (Mishra and Ghosh 2019; Aguilar-Reynosa et al. 2017).

- Effective utilization of the pretreated low cost substrates for extraordinary fermentable sugar yield.
- Withdraw higher amount of sugars through lignocellulosic structure during enzymatic hydrolysis step.
- Screening of more tolerant microorganisms and optimized fermentation procedures for maximum amount of sugars conversion fermented into ethanol (Zabed et al. 2017).
- Integration of steps involved in overall production to minimize number of processes.

State-of-the-art technologies reduce the costs through the use of quality feedstock's, effective pretreatment methods that generates less by-products and more versatile fermenting organisms (Arora et al. 2016). Although simultaneous fermentation of glucose and xylose associated with increased ethanol concentration, it is still a long way to achieves meaningful level in commercial (Narra et al. 2018). Thus, innovative approaches and substantial research and development efforts are required to improve efficiency and economy of whole conversion.

7.9 Syngas Platform or Thermochemical Conversion Route

The other emerging approach is thermochemical route that can utilize widespread varieties of biomass with numerous hybrid schemes. Production of syngas and pyrolysis of lignocellulosic biomass are the key steps under thermochemical pathway (Nanda et al. 2014).

National Renewable Energy Laboratory (NREL) developed indirect gasification process for ethanol and mixed alcohols production (Phillips et al. 2007; Munasinghe and Khanal 2010). Mixture of CO and H_2 produced during indirect gasification called syngas or synthesis gas. Formerly alcohol conversion, raw gas cleaning is required to remove catalyst-fouling contaminants. Then cleaned gas conversion to alcohols mixture (ethanol and propanol) performed using molybdenum catalyst (Daystar et al. 2015) (Fig. 7.8). Whereas, in case of fast pyrolysis process, biomass decomposition was conducted oxygen deficient conditions to yield flammable gas (syngas), liquid bio-oil and carbon-rich solid (biochar).

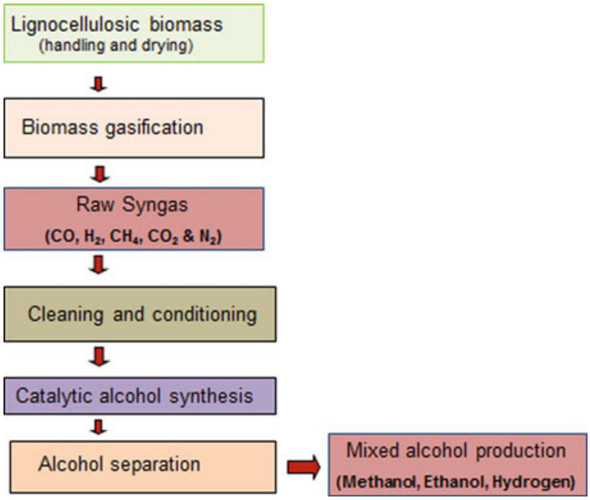

Fig. 7.8 Biomass gasification pathway for mixed alcohol production

7.10 Third Generation Bioethanol Production

In the last few decades microalgae, macroalgae and seaweeds are acquiring wide consideration for bioethanol production grouped for third generation biofuels production. Microalgae has multiple benefits as contain high carbohydrate content (Cesario et al. 2018), have great atmospheric CO_2 fixing ability (Wang et al. 2008) besides not upsetting food or feed chain (Hossain et al. 2019).

Promising methods for bioethanol production from microalgae processing are:

- Traditional processes including pretreatment, hydrolysis and fermentation (Fig. 7.9).
- Dark fermentation (Magneschi et al. 2012): some algae species helps to produces ethanol directly through dark-anaerobic fermentation.
- Through “photo-fermentation” using light energy from carbon dioxide produces bioethanol (Dexter et al. 2015).

Although above mentioned technologies can possibly provide solutions but currently conventional fermentation technology from microalgae biomass obtains the most consideration (Lakatos et al. 2019). John et al. (2011) investigated *oleaginous* microalgae which after oil extraction generates high amount of waste as cellulose biomass hydrolysed to produce ethanol production. However, requirement of large amount of water, more energy consumption and costly along with complicated algal biomass farming are some of the limitations (Medipally et al. 2015). Moreover, it was observed that amount of carbohydrates formed found to be insufficient for large-scale bioethanol production.

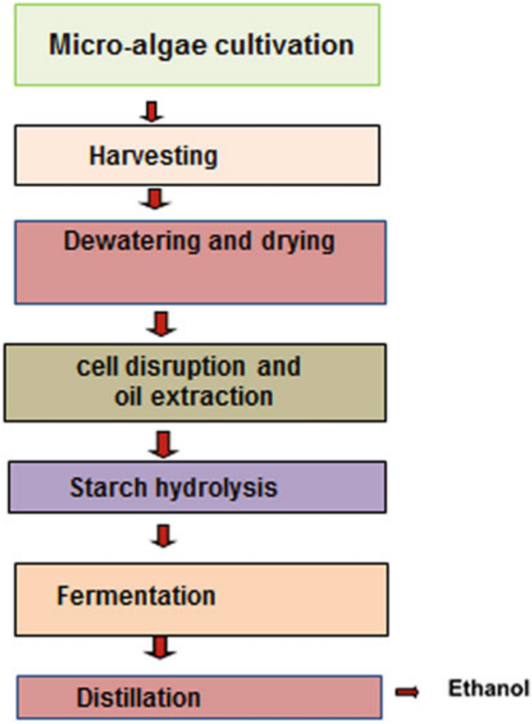

Fig. 7.9 Pathway of ethanol production from algal biomass

7.11 Integrated Approaches and Future Perspectives

To utilize biomass more cost-effectively, bio-refinery platform using agro-industrial waste products as feedstock leads to improved environmental sustainability. Studies suggested that the biorefinery approach offers an ecofriendly route that convert biomass to range of bio-products via several integrated processes (Kaur et al. 2019). Using integrated biorefinery technologies primary benefit is the production of valuable co-products along with the increased substrate use, more income for agriculturists and zero release of waste can be achieved (Offei et al. 2019). Linares et al. (2017) suggested microalgae biomass can be used for bioelectricity, methane, biohydrogen, bioethanol and biodiesel by using integrated processes.

Although screening of unique better altered yeasts with enhanced fermentative properties is still an immense task (De Souza et al. 2018). However, efforts to construct superior engineered yeasts using some previous strain like *S. cerevisiae* with desirable traits using groundbreaking genetic engineering technologies for large-scale fermentations may be possible (Lee et al. 2017). Moreover, consolidated bioprocessing technology for producing second generation bioethanol researched progressively.

7.12 Conclusion

Increasing energy demand, rapid exhaustion of fossil based fuels and aggravated environment issues has resulted to the progress of various sustainable technologies based on renewable energy sources. In this regard, first generation bioethanol production technologies are well-recognized with high bioethanol productivity but are competing with food-based feedstocks. On the other hand prospects of using non-food-based raw materials are associated with second generation bioethanol production. In which lignocellulosic waste materials represent a favourable feedstock while major restrain for bioethanol commercialization is the complex structure, use of expensive enzymes and lack of cost-effective conversion technologies. Further recommendations are proposed for attention in future research for making relevant production costs and improving production efficiency.

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Biobutanol for Biofuel: Technologies and Commercial Approach

8

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Abstract

Depletion of fossil fuels and elevated cost of fuels has caused unfavorable effects, global warming, strange weather conditions, unfavorable air quality, and so on. Biobutanol is now preferential alternative for fossil fuel. In fact world's dependency on alternative fuel move towards biobutanol. Among all other biofuels, biobutanol is at the forefront as a reasonable, renewable, and lucrative alternative fuel. Low butanol titers, accessibility of companionable feedstocks are the hurdles for biobutanol production. Set on these hurdles modified genetic engineering techniques and metabolic engineering strategies helps to produce economic biobutanol production using cost-effective lignocellulosic materials and microalgae as feedstocks. Strain improvement and highly developed downstream processing are in pipeline for large scale production of biobutanol to meet the up-to-date requirements.

Keywords

Biobutanol · Genetic engineering techniques · Metabolic engineering · Lignocellulosic materials · Microalgae and strain improvement

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8.1 Introduction

Globally, consumption of petro-fuel will reach to 136.8 million barrels/day by 2030, due to decrease in crude petroleum reserve. With the depletion of conventional fuel resources and increase in global warming, there is a need for renewable and eco-friendly product to solve the crisis. Liquid biofuels such as biodiesel, biobutanol, bioethanol, biogas, biohydrogen, and syngas seem to be potential replacement of petro-fuels (Kushwaha et al. 2019). In 2018, global production of biodiesel has increased around 5% to 41.3 billion L/year [Renewable Energy Policy Network for the twenty-first Century (REN 21), Global Status Report, 2019]. Global demand for biofuel will reach 51.1 billion gallons/year by 2022, according to the report by Navigant Research, USA 2014. Biofuels are in general considered as carbon neutral fuels as CO_2 emitted can be reused for biomass growth. Till date, ethanol is considered as a better alternative to fossil fuel due to its simplicity in production through basic fermentation means. However, as a biofuel, ethanol is not an excellent choice due to its high vapor pressure and hygroscopicity. Biobutanol, a renewable biomass based fuel possess similar characteristic to that of gasoline, can be used as an alternative to B85 ethanol/gasoline. Butanol, a C4 hydrocarbon produced via the fermentation of various biomass feedstocks such as energy crops, lignocellulosic biomass, algae, etc. Microbial production of butanol through ABE (Acetone-Butanol-Ethanol) fermentation was initiated in 1910, achieved its peak in 1950, but in last few decades its requirement declined on account of the availability and growth of different petrochemical pathways. Nevertheless, due to increase in crude oil prices, over consumption of petroleum products and its effect on global warming, bio-based chemicals, and biofuels including butanol has gained global attention.

Butanol is the most auspicious biofuel among conventional fuel alternatives because of its certain advantages over the other known biofuels, such as low water absorption, high energy content, and better blending with gasoline. Also, because of similar air-to-fuel ratio and energy content, it can completely replace gasoline without any modifications in engines (Fivga et al. 2019). Its less hygroscopicity nature indicates low degree of corrosivity to engines, also the presence of –OH group in butanol increases its oxygen content as a result of which decreased smoke release (Prakash et al. 2016).

8.2 Production Methods of Butanol

Butanol can be obtained by chemical synthesis (as petro-butanol) from fossil fuels or by microbial fermentation (as biobutanol) from biomass. However, the chemical synthesis is futile due to over consumption of petroleum-based products (Tsvetanova et al. 2018). By chemical technologies butanol can be obtained through Oxo-synthesis, Reppe synthesis or crotonaldehyde hydrogenation and aldol condensation. Some fossil oil derived materials such as ethylene, propylene, and triethylaluminium or carbon monoxide and hydrogen are used in butanol production.

Of the above methods, Oxo-synthesis has edge of raw materials and underlined ratio of *n*-butanol to isobutyl alcohol than the other chemical processes. Hence, Oxo-synthesis process is widely used for commercial production of *n*-butanol.

The biological process involves production of butanol from the biomass through fermentation by bacteria, hence called biobutanol. Since the key products of this fermentation are acetone, butanol, and ethanol, this type of fermentation is called ABE fermentation. ABE fermentation pathway employs an anaerobic conversion of carbohydrates to acetone, butanol, and ethanol (ABE), by various species of strictly anaerobic bacteria belonging to the genus *Clostridium*, e.g. *C. acetobutylicum* or *C. beijerinckii*. Production of biobutanol by *Vibrio butyrique* was first recorded by Pasteur in 1861. Later, Chaim Weizmann isolated *Clostridium acetobutylicum*, which produced quantities of acetone, butanol, and ethanol in the ratio of 3:6:1 from potato starch and patented for ABE fermentation process in 1915 (Weizmann 1919). In earlier days, ABE fermentation was used by UK for manufacturing acetone which can be used as a solvent in cordites (Fernández-Naveira et al. 2016). Later during World Wars I and II, this process spread along the world and contributed for production of butanol. By the last century, large scale production of butanol was done by fermenting starch and sugar residues. However, in 1950s, when the global oil prices decreased, the oxo process (Chemical synthesis) which hydroformylates and hydrogenates propylene to butanol, uprooted the ABE process as the most provident feasible method of butanol production. By 1970s, ABE industry in US ended, and nearly all the ABE industries throughout the world were closed within 20 years and in 2004, the China's last large scale ABE plant was ended. But in recent days with the worldwide increase in crude oil prices owing to its high demand and along with environmental concern, the need for ABE fermentation has renewed (Jiang et al. 2015).

China has recommenced ABE production in 11 plants, of which Cathay Industrial Biotech is a 30,000 ton/year facility in Jilin China. In the US, Gevoat Luverne, Minnesota is operating a 10 million gallon/year of iso-butanol facility (Kolesinska et al. 2019). Despite many advantages, ABE fermentation is limited by the high cost of the fermentation substrates, end product inhibition and by the low yield of butanol, as well as by the high downstream processing costs (Fu et al. 2021). Despite its advantages, traditional method of biobutanol production provides low yields and end product inhibition, so the use of genetically modified strains, use for various feedstocks and make use of advanced downstream processing are in trials for large scale production of biobutanol to meet the current needs.

8.3 Applications of Butanol

At present, butanol synthesized from petroleum derivatives is used as a solvent and as a chemical intermediate for many important products. As a solvent, butanol is used in the production of dyes, paints, rubber, and chemical stabilizers. In pharmaceutical industries, butanol is used as an extractant for drugs and natural substrates like antibiotics, vitamins, and hormones. As an eluent, butanol is used in TLC and paper chromatography. Also butanol is used as a precursor in the production of acrylic esters, butyl acetate, butyl amines, and glycol ethers. In textile industry, it is used as de-icing fluid for solubilization, and can be used as a supplement in polishes and cleaners for domestic and industrial cleaning (Mahapatra and Kumar 2017). In chemical industry, it is used in the production of various polymers and plastics such as safety glass, hydraulic fluid, and detergents and as a perfume base in cosmetics. Lastly, as a transportation fuel, it can be used with gasoline in blended proportions. Owing to its high energy content, less corrosive nature, low volatility, low affinity to moisture, high octane number (96), and similar air-to-fuel ratio, it can completely replace gasoline without any alterations in engines.

8.4 Feedstocks and Technologies for Different Biofuel Generations with Respect to Biobutanol Fermentation

Biofuels are generally classified into four generations based on the type of biomass feedstock. Each generation feedstock has its own merits and demerits and their biofuel production technologies vary due to the nature of feedstock.

8.4.1 The First Generation Feedstock

Back in Weizmann process (ABE fermentation) period, the primary substrate corn was used for butanol production. However, for industrial scale ABE fermentation, molasses were a preferred source. In both the cases, the bacterium used for fermentation was *C. acetobutylicum*. The first generation feedstocks, primarily used for butanol production for commercial scale, were starchy agricultural crops (corn, maize, potatoes, wheat starch, etc.) and cheap sugar sources (cane and beet molasses). In addition, food industry wastes such as sago, apple pomace, palm oil mill effluent, cheese whey, soy molasses, etc. were also used as carbon sources for butanol fermentation. Also Jerusalem artichokes and cassava were found to be suitable substrates for ABE fermentation (Tigunova et al. 2017; Jiang et al. 2020).

Later, when the molasses were also used as cattle feed, the competition increase, and also by the arrival of petrochemical industry, the option of using molasses as substrates seems to be costly process. On the economy point of view for butanol production the cost of raw material pose a direct impact; hence the choice for raw material choice was shifted to second generation feedstock. The biofuel production flowchart from first generation feedstock is depicted in Fig. 8.1.

The earlier known bacterial species for butanol fermentation is *C. acetobutylicum*. This bacterium can ferment wide spectrum of carbohydrates to synthesize organic compounds, acids, alcohols and other solvents. Other species include *C. aurantibutylicum*, *C. beijerinckii*, *C. saccaroperbutylacetonicum*, and *C. saccharoacetobutylicum* and *C. tetanomorphum*, which are known to produce butanol with high fermentation yields.

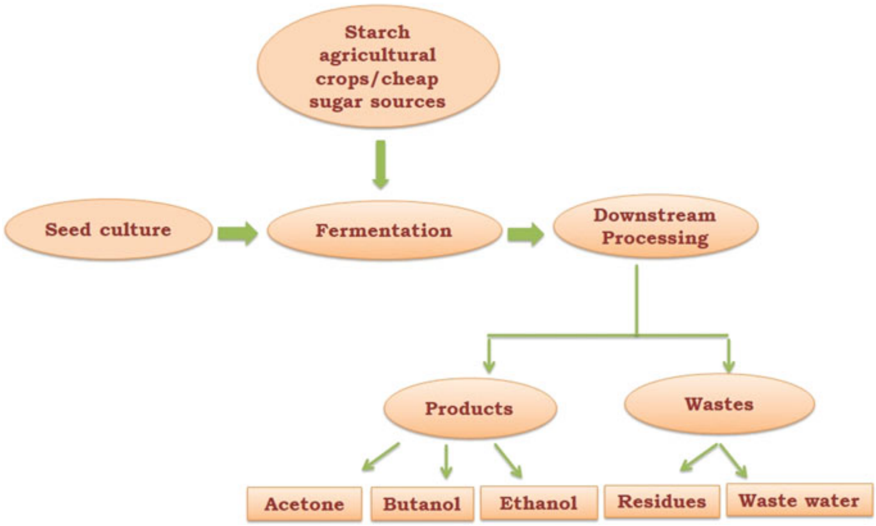

Fig. 8.1 Technologies involved in the first generation of biofuel

C. acetobutylicum is a Gram-positive, strictly anaerobic organism. In general, ABE fermentation process is biphasic containing both acidogenesis (conversion of sugar into organic acids) and solventogenesis (solvent production) phases. During exponential phase, accumulation of free acids causes the pH to drop. In order to survive at low pH condition, this bacterium switches to solventogenesis phase at the end of log phase. Acetate and butyrate which are produced during first phase are once again utilized by the microbe and metabolized into acetone and butanol. By converting acids to solvents, the pH in the medium increases again. Since, this bacterium is sensitive to butanol, they starts to form endospores at the same time. Butanol, ethanol, acetone, acetic acid, butyric acid, CO_2, and H_2 are the common end products of ABE fermentation process. At the end of solventogenesis, the bacterial metabolism stops upon the butanol and other products concentrations reaches a level (Kolesinska et al. 2019; Xie et al. 2019).

The conventional method of fermentation is often restricted by certain factors such as low butanol yield (around 16–17 g/L) due to production of other end products (acetone and ethanol), substrate inhibition, end butanol toxicity, therefore low cell density. As a challenge to these problems, researchers have developed genetically engineered strains capable of improved biobutanol yield and tolerance. The use of some notable mutagens includes UV exposure, butanol, *N*-methyl-*N*-nitro-*N*-nitrosoguanidine (MNNG), and ethyl methane sulphonate, enhances the capabilities of *Clostridium* species. For example, productivity of C. *acetobutylicum* ATCC 824 can be improved with 121% higher butanol tolerance by prior exposure to butanol (Pugazhendhi et al. 2019). Also metabolic engineering of biosynthetic pathways for alcohol production can improve productivity. The genes involved in butanol synthesis are *thl*, BCS operon, *add*, *bdh*, etc.

Over-expression of *aad* gene alone has enhanced butanol production (Hocq et al. 2019). In *C. tyrobutyricum*, the over-expression of alcohol dehydrogenase not only enhanced the butanol production (to 27–30%) but also increases its tolerance towards butanol. Higher production of 1-butanol and 1-propanol in *Escherichia coli* is done by modifying its amino acid biosynthetic pathway (Dong et al. 2017).

8.4.2 Second Generation Feedstock

Due to limited availability and high cost for food crop as substrate for ABE fermentation, the use of lignocellulosic biomass has been practiced. It includes agricultural and forest residues such as rice straw, wheat straw, waste wood, corn stover, etc. Lignocellulosic biomass contains 20–40% hemicellulose (mainly D-xylose) and cellulose, which can be degraded and utilized effectively. According to the United Nations Environment Program (UNEP 2015), about 140 billion tons of agricultural biomass is generated annually which is analogous to 50 billion tons of oil. Countries such as Costa Rica, Cambodia, and India are largest agro-waste producers, of which India alone produces 415.5 million tons of agricultural biomass (analogous to 103.9 million tons of oil).

Other sources include non-edible oil seeds and waste cooking oil. Bagasse and rice straw are found to be suitable substrates for the solvent production, since hydrolysates contain, besides hexose sugars, cellobiose, cellodextrins, and pentoses, which can be utilized by solvent-producing *Clostridia*. Of which rice straw is found to have a good source of fermentable sugars for biobutanol production (Chen and Li 2018). Theoretically these biomass sources can supply energy as much as 100 EJ/year. Other alternatives include vegetative grasses (Miscanthus, switchgrass) and some less usable forest species (Eucalyptus, Poplars, Robinia) are favored, since they can grow even in marginal and degraded lands.

The main drawbacks with second generation feedstock are the requirement of large arable lands, water supply, and high lignin content of biomass, which affect the conversion to biobutanol economically (Ibrahim et al. 2018). Also the presence of various complex molecules such as cellulose, hemicellulose, and lignin, in the second generation feedstocks, an extensive pretreatment is required to remove lignin, reduce cellulose/hemicellulose and thereby improve the porosity of the feedstock to achieve maximum accessible sugars.

The biobutanol production process from lignocellulosic feedstock is shown in (Fig. 8.2). Firstly, the biomass should be pretreated for easier accessibility to sugars. Various pretreatment methods are widely used which includes alkaline peroxide pretreatment, dilute sulfuric acid pretreatment, steam explosion pretreatment, hydrothermal pretreatment, organic acid pretreatment, and many more. The production/presence of inhibitors, such as acetic acid, furfural, 5-hydroxymethyl furfural, phenols during butanol production process, are to be detoxified by using activated charcoal, overliming, electrodialysis, and membrane extraction. Different feedstock requires diverse pretreatment methods. At the end of fermentation, the desired product is recovered and purified (Dharmaraja et al. 2020).

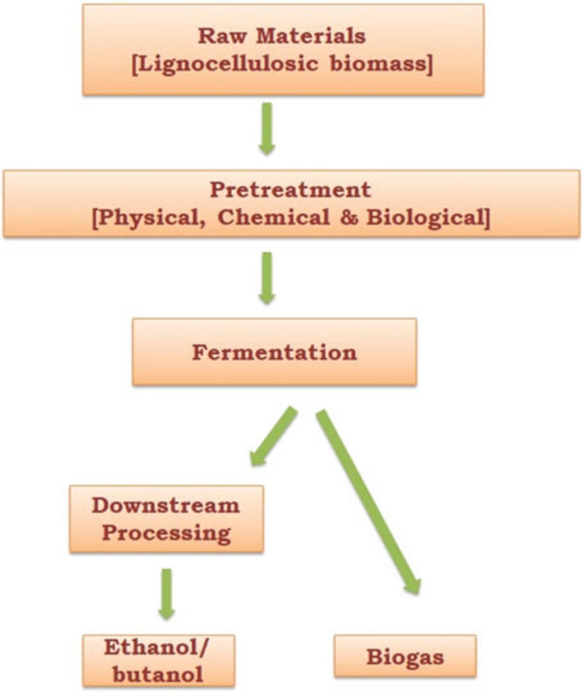

Fig. 8.2 Technologies involved in production of second generation biofuel

When compared to ethanol and petroleum-based fuels, biobutanol produced from a variety of waste lignocellulosic biomass feedstocks demonstrates superior capability as an unconventional fuel in terms of both market value and technical requirements. The rising scope of process growth may be analyzed in terms of developing novel continuous systems, feedstock pretreatment, and effective integrated biobutanol recovery for increasing biobutanol fermentation productivity. Advanced recovery tools for the separation and purification of biobutanol can improve the yield and output of ABE products or biobutanol (Dharmaraja et al. 2020). The most extensively studied form of feedstock is lignocellulosic biomass that includes agricultural wastes and energy crops, which typically contains cellulose (40–45%), hemicellulose (20–30%), lignin (10–25%), ash, and extractives (Gottumukkala et al. 2017).

Currently, the ABE fermentation process has been changed through the use of increased pretreatment and genetic modified methods. To reduce inhibitor formation, which results in the production of a partially disrupted substrate that is then converted to monomeric sugars by enzymatic hydrolysis, moderate pre-treatment methods are frequently used. Pretreatment with a high degree of severity is an alternate strategy that entails methods of detoxification such as excessive liming, diluting with water, and adsorption onto activated carbon and resins (Birgen et al. 2019).

When four prospective lignocellulosic biomass feedstocks such as wheat straw, barley straw, corn stover, and switch grass were compared to a glucose control, it was discovered that wheat straw hydrolysates produced better fermentation outcomes than the glucose control. Wheat straw hydrolyte produced 0.60 g/L/h, compared to 0.31 g/L/h for glucose control. However, no conversion occurred when corn stover hydrolysate was used on pretreatment investigation revealed that over-liming of hydrolysate for detoxification increased butanol concentration and productivity by 26.27 g/L and 0.31 g/L/h, respectively. Switchgrass had the highest concentration and productivity, with 14.61 g/L and 0.17 g/L/h, respectively. Thus, for butanol fermentation, substrate selection, pre-treatment, and hydrolysate detoxification are important criteria to consider (Huzir et al. 2018; Alavijeh and Karimi 2019).

8.4.3 Third Generation Feedstock

The third generation biomass includes photosynthetic bacteria and algae. Higher carbohydrate (low lignin content) and high lipid content (approx. 70% of dry weight) in algal biomass makes it a suitable feedstock for biofuel production including biobutanol (Abomohra and Elshobary 2019). Also, they can be grown in wastewater streams (saline/brackish/coastal seawater) and do not require any cultivable land and assorted farming inputs. Some potential algal species include *Botryococcus braunii*, *Chaetoceros calcitrans*, several *Chlorella* species, *Isochrysis galbana*, *Nanochloropsis*, *Schizochytrium limacinum*, and *Scenedesmus* species are used for biofuel production (Wang et al. 2017).

The strain *C. pasteurianum* has reported to produce 14–16 g/L of mixed solvent, including butanol, while microalgae *Dunaliella* can produce up to 40 g/L of butanol along with glycerol mix (Kolesinska et al. 2019). Though there remains a factor that fast growing algae (*Spirulina*) have low oil content while high lipid containing algae are slow growers. Therefore, suitable species with high biomass plus high lipid content are to be identified for industrial production of algal biofuel. Microalgal carbohydrates are easily accessible and converted to alcohols than from macroalgae (Hong et al. 2020). Also, detoxification of algal hydrolysate is not necessary as it contains very little amount of toxins while *Clostridium* species can't tolerate above 1 g/L of furfural and 2 g/L of 5-hydroxymethyl furfural (Fig. 8.3).

As a third generation biofuel, biobutanol can be produced from microalgae which can be used as substrate. In general, algae-to-biofuel technology entails the chemical or biological processing of algal biomass as a feedstock or substrate for the generation of biofuels, viz., biodiesel, ethanol, or butanol. Recent developments in genetic and metabolic engineering have played a vital role in designing the algal host to function as a "microbial cell factory" for generating biofuels via oxygenic photosynthetic pathways (Antil 2019). Microalgae, as promised, addresses the major difficulties of economically sustainable feedstock production methods. Currently, genome engineering strategies for enhancing butanol metabolic expression from microalgal feedstock rely on (a) optimal expression of heterologous genes under

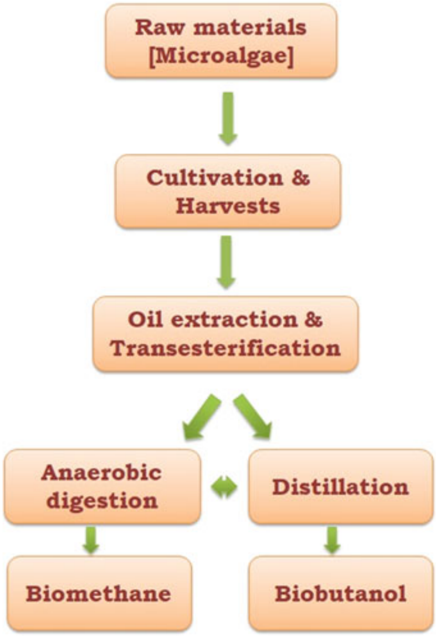

Fig. 8.3 Technologies involved in the production of third generation biofuel

various promoters/regulators expressing in exogenous pathways, (b) balancing the metabolic network by eliminating competitive pathways with knock-in or knock-out genes to regulate metabolic reflux, and (c) increasing cellular tolerance to butanol toxicity by hosts (Dębowski et al. 2020).

Integrating and applying synthetic biology and metabolic engineering, microalgar can be made capable of producing biobutanol from CO_2 and solar energy. Through the use of modern genome engineering techniques, a heterologous gene or a whole pathway can be introduced into native microalgae, modulating the CO_2 fixation pathway and utilizing its metabolites (ATP, NADPH) for the generation of butanol. Furthermore, the fusion of phototrophic and fermentative metabolism in order to produce microalgae chimaeras capable of directly converting CO_2 to biobutanol without using solar energy. As a result, photo fermentation is based on the efficient use of photosynthetic machinery and fermentative enzymes for the direct conversion of CO_2 into biobutanol using solar energy, making the use of fourth generation biofuels attainable. Besides that, by implementing sequential strategies to integrate the production of microalgal biobutanol with the co-production of value-added products or by utilizing the by-products of other fermentation processes as the substrate, this single-stage process can be converted into a multi-terminus process capable of providing a more economical industrial production (Shanmugam et al. 2021).

Addition to these developments, microalgal fuel also integrated with nano-additive applications. Numerous nano-additives were developed to prepare strategies for microalgae cultivation and harvesting, biofuel extraction, and uses in microalgae-biofuel nanoparticle blends. In terms of solid nano-additives, microalgae biomass not only converts to biofuel but also improves the combustion of biofuel, enabling revolutionary breakthroughs (Hossain et al. 2019).

Macroalgae (Seaweed) of marine environment were recently looked as an alternative feedstock for biobutanol production. Seaweeds such as red, green, and brown algae were experimented as feedstock for biobutanol production using *Clostridium* sp. (Huesemann et al. 2012; Van der Wal et al. 2013; Sunwoo et al. 2018). The different types of seaweeds were tried individually and also as mixed feedstock. They show potential for biobutanol production and especially brown algae supersede the other two. However, the need for pretreatment and removal of inhibitors adds a significant cost for biobutanol production. Further insights into developing a suitable strain for fermenting and utilizing this feedstock can be a viable option for economics production.

8.4.4 Fourth Generation Feedstock

In general, third generation feedstock offers less complications when compared to other generations for biobutanol production. However, the production process is quite costly. Therefore, the use of genetically modified strains to maximize lipid content and biomass are in trials. In *Chlamydomonas* starchless mutant, ADP-glucose pyrophosphorylase inactivation led to tenfold increase in triacylglycerol (TAG). Here the shunting of photosynthetic carbon partitioning from starch to TAG synthesis appears to be an efficient strategy than the direct gene manipulation in lipid synthesis pathway to overproduce TAG (Anandharaj et al. 2020). In cyanobacterium *Synechococcus elongatus*, modification in CoA-dependent 1-butanol production pathway leads to direct production of butanol from CO_2 (Fig. 8.4) (Rathour et al. 2018).

8.5 Recent Developments in Biobutanol Production

8.5.1 Strain Improvement

Strain improvement refers to any changes made to the butanol production strain through random mutagenesis and selection, such as in adaptive laboratory evolution, or through directed, rational, and/or systems biology guided genetic modification using metabolic engineering and synthetic biology to improve fermentation performance by increasing tolerance to toxic components, butanol selectivity and productivity, and improving substrate utilization and range (Li et al. 2020). Table 8.1 refers to various strains and their strategies to enhance the biobutanol production.

In recent research, recombinant *C. cellulovorans* produced 1.42 g/L of butanol through a genetically modified approach that included the integration of an aldehyde/alcohol dehydrogenase (*adh*E2) stem from *C. acetobutylicum* utilizing cellulose as a feedstock (Yang et al. 2015). When compared to lignocellulose

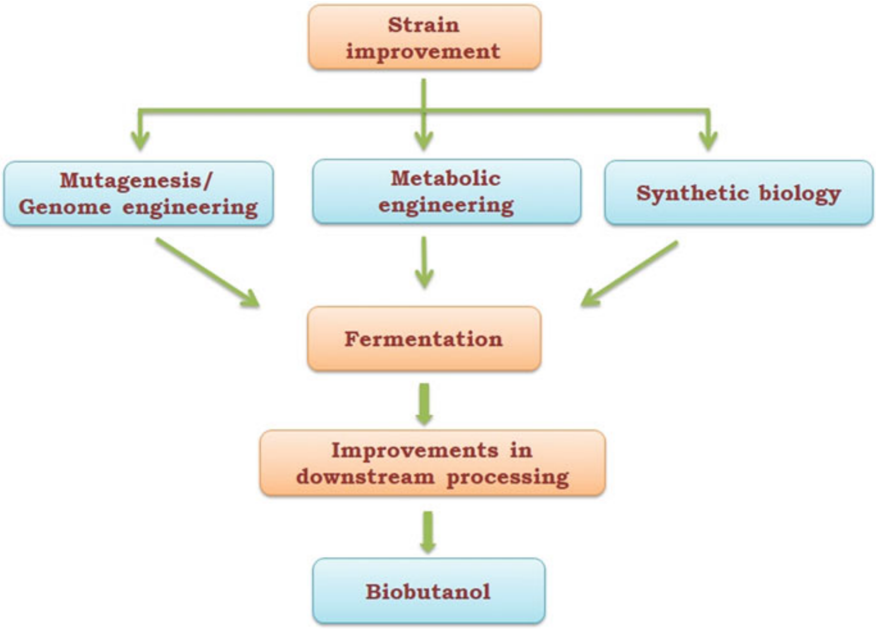

Fig. 8.4 Technologies involved in the production of fourth generation biofuel

pre-treatment, consolidated bioprocessing (CBP) is an approach in which enzyme synthesis, substrate hydrolysis, and microbial fermentation are all accomplished in a single reactor. Using xylan as a feedstock and CBP, a thermophilic *Thermoanaerobacterium* sp. M5 with exceptional xylan breakdown ability, 1.17 g/L of butanol was produced (Jiang et al. 2018).

Co-culture has recently become the preferred method for producing lignocellulosic butanol via CBP, but the mechanism and cell-cell communication are still being investigated. The CBP process can use a variety of microbial communities from the same or other species to produce butanol from lignocellulose. The co-culturing system of *C. thermocellum* and *C. saccharoperbutylacetonicum* N1-4 resulted in the synthesis of 7.9 g/L butanol from 40 g/L avicel cellulose after 9 days. This was comparable to when starchy substrates were used as feedstocks (Jiang et al. 2019).

8.5.2 Downstream Processing of Biobutanol

The major techniques involved in the biobutanol separation process are liquid–liquid separation, pervaporation, and gas stripping. In liquid–liquid separation process, the water insoluble organic solvent is mixed with the fermentation broth to selectively separate the butanol. Organic solvents are most preferable because they separate the butanol without disturbing the other things present in the broth. This process has to be done with a high accuracy. Oleyl alcohol is mostly suggested for the butanol

Table 8.1 Strategies used to develop strains for biobutanol production

Strain	Strategy	Physiological characteristics (control/ engineered strain)	Reference
Mutagenesis strategies			
C. beijerinckii BA101	Treated with *N*-methyl-*N*-nitro-Nnitrosoguanidine (NTG)	butanol: 10/19 g/L	Qureshi and Blaschek (2000)
Clostridium acetobutylicum JB200	Evolution in fibrous bed bioreactor	butanol: 12.6/21 g/L	Xu et al. (2015)
Clostridium acetobutylicum BKM19	Screening cells on fluoroacetate plates; random mutagenesis	butanol: 10.7/20.1 g/L	Jang et al. (2013)
Clostridium acetobutylicum GX01	NTG; genome shuffling and butanol exposure	butanol: 16.3/20.1 g/L	Li et al. (2016)
Metabolic engineering strategies			
Improve butanol tolerance			
C. acetobutylicum ATCC 824	Expression of SA1 and SA2	Improve butanol tolerance with 121% (SA1) and 27% (SA2)	Lin and Blaschek (2013)
C. acetobutylicum ATCC 824	Overexpression of *gro*ESL	Improve butanol concentrations to 17.1 g/L	Tomas et al. (2003)
C. acetobutylicum DSM1731	Overexpression of *gsh*AB genes from *E. coli*	Increase aero and solvent tolerance from 14.5 to 18 g/ L	Zhu et al. (2011)
Substrate utilization			
C. tyrobutyricum	hydrolysis of α-1,4-glycosidic bonds in maltose	butanol: 11.2/17.2 g/L	Yu et al. (2015a)
C. tyrobutyricum	Coexpression of glucose and xylose genes from C. *acetobutylicum*ATCC824	butanol: 12.1/15.7 g/L	Yu et al. (2015b)
Enhance butanol production			
C. acetobutylicum JB200	Disrupting acetoacetate decarboxylase gene *adc*	20 g/L butanol, increase butanol ratio from 70% to 80.05%	Jiang et al. (2009)
C. tyrobutyricum ATCC 25755	Overexpression of *adh*E2 from *Clostridium acetobutylicum* ATCC 824	Butanol titer obtained about 1.1 g/L higher than *E. coli*	Yu et al. (2011)
Saccharomyces cerevisiae	Elimination of glycerol synthesis pathway	Enhanced 1-butanol production to yield 14.1 mg/ L after 48 h of cultivation	Sakuragi et al. (2015)

separation due to its low toxicity and extraction efficiency. By mixing the benzyl benzoate and dacohl, the efficiency of butanol increase to 60% and 72%, respectively. Other chemical used in the butanol separation is 4-*n*-butylphenol. Ionic liquids are not suitable for the due to the possession of anions to use in in situ recovery of butanol. Pervaporation process is a cost-effective and commercially useful technique for the butanol separation and this is the only process having the membrane phase transition. Advantages includes single step and simple separation process, energy efficient and disadvantages are biocompatibility and membrane fouling. This process involves the mechanism of selective sorption through membrane and desorption into vapor state on permeate. Among the various membrane, the silicate membrane proves to be best membrane for the separation of butanol. Gas stripping is a physical method of separation; the gas steam is added as separating agent. Due to its versatility this method is one of the reliable separation methods for butanol (Bharathiraja et al. 2017).

Biomass like wheat straw, sweet sorghum bagase, food waste, and yellow top press cake are major substrates for the production of butanol. The production cost of butanol from lignocellulose waste like sweet sorghum bagasse (SSB) through the fermentation process is estimate by two process. The number one is separate hydrolysis, fermentation, and recovery (SHFR) and second one is simultaneous scarification, fermentation, and recovery (SSFR). In the first process (SHFR), the pretreatment and hydrolysis processes were done in two isolated tanks and the other processes like fermentation and recovery were combined done in the one reactor and the butanol and other solvents were recovered through the vacuum process. In the second one (SSFR), the whole process of scarification, fermentation, and recovery were performed in single reactor. From the both process, the butanol is separated from the other solvents like acetone and ethanol by distillation process (Qureshi et al. 2020). In the butanol production from the yellow top press cake require pretreatment with the condition of 160–190 °C compared to sweet sorghum bagasse but it needs the half amount of enzymes when compared to sweet sorghum bagasse. Using the food waste for the butanol production does not require the pretreatment, starch hydrolysis enzyme (Arabi et al. 2019).

8.6 Economics of Biobutanol

The Life Cycle Assessment (LCA) methodology is used to analyze the environmental constraint associated with a product, process or activity, through identification and quantification of material, energy and waste released, besides evaluating the environment impact on a scientific and quantitative basis. The ISO standards 14040 and 14044 describe the general route map to conduct an LCA (Arabi et al. 2019). The biofuel engines release less carbon monoxide than conventional engines and thereby minimizing greenhouse gas (GHG) emission. Also, the net GHG emission varies with different sources of biofuel. A 33% of reduction in GHG emission is reported for corn stover-derived biofuel when compared to switchgrass-derived biofuel. Of all the sources, the least GHG emission has been noted for algal biofuel

(Ashani et al. 2020). Also, the overall GHG emission from a fuel is not only based on the effects on consumption of fuel but also on the production process. In case for lignocellulosic biofuel, GHG emission of the enzymes used for the pretreatment process and from the production of process chemicals are taken into account.

Global Warming Potential (GWP) is the measure of quantity of heat captured by GHG in the atmosphere up to a specific time horizon, relative to CO_2. In a study, it has been shown that algae cultivated in raceway ponds are more environmentally sustainable than fossil fuel and the biofuel produced from this method has 80% low GWP than fossil fuels (Yeong et al. 2018).

Another environmental concern is the requirement of water and nutrient resources. Apart from the biofuel regeneration process, biomass cultivation requires water and nutrients. As first and second generation feedstocks (plants and crops) are hard to grow in raw waste water, algae can grow in waste and sea water, utilizing the nutrients present and thereby reducing the demand for fresh water. As an integrated system, algae can both used for waste water treatment and biofuel production (Trilokesh and Uppuluri 2021).

Overall biofuel production cost = [Feedstock value over time + Conversion cost (capital cost, chemicals, enzymes and energy) + Operational cost + Maintenance cost] − Co product value over time.

Among these, the feedstock production cost is the most predominant one. The high cost of edible crops makes the first generation biofuel more lavish while the second generation use low cost feedstock but the requirement of pretreatment, detoxification increases its cost value. When compared to other two generations, third generation feedstocks are very cost-effective since they can grow in waste/sea waters, low land utility and usage of limited resources. Though due to the complexity of algae growth and production systems, the process remains costly. Improving the downstream processes and production of other more valuable products will notably reduce algae biofuel costs.

With reference to economic performance, currently first generation biofuel is considered to be a cost-effective one, whereas the second and third generation biofuels are costly due to low conversion efficiency and high investment costs. By improving and optimizing the conversion technologies, second and third generation biofuels can be made more economic.

The total capacity of butanol production plant in the USA, Brazil, and European union is 170,000–171,000 ton/year with the production rate of 58,561 (acetone), 99,330 (butanol), and 13,406 (ethanol) ton/year. The abundance of agri waste like whey permeate, wheat straw, sugarcane bagasse helps to run the production plant about 350 days/year. For the production of butanol by using sweet sorghum bagasse with the SHFR plant, the fixed capital, working capital and startup cost is $\$165.26 \times 10^6$, $\$40.2 \times 10^6$, and $\$8.26 \times 10^6$ and in total the amount of $\$213.72 \times 10^6$ investment is required. Comparing with SHFR the SSFR require a fixed capital of 153.22×10^6. The feedstock amount of 609.80×10^6 kg of SSB is used per year, 53.66×10^6 kg of hydrolytic enzymes and 76.58×10^6 kW h of electricity is used for the butanol production. And the selling cost of butanol is $1.14/kg and $1.05/kg for SHFR and SSFR, respectively (Qureshi et al. 2020). The rate of

Table 8.2 Comparison table for biobutanol production using different substrates (Qureshi et al. 2020, 2013)

S. No	Feedstock	Total raw material cost (per ton) ($)		Total capital investment ($)		Butanol selling price (per kg) ($)	
		SHFR	SSFR	SHFR	SSFR	SHFR	SSFR
1.	Sweet sorghum bagasse	100	100	213,720,627	198,160,002	1.14	1.05
2.	Food waste	–	10	–	107,257,000	–	0.49
3.	Yellow top press cake	25	25	132,205,000	122,579,000	0.79	0.73
4.	Wheat straw	24	24	193,073,000	193,073,000	0.95	0.88

butanol produced from wheat straw as substrate is \$0.95/kg and \$0.88/kg when using SHFR and SSFR, respectively. The price reduction is due to the price of wheat straw (\$24/ton) (Qureshi et al. 2013). When using the food waste the capital investment is estimated to be $\$107.26 \times 10^6$ and the butanol selling price is to be \$0.42/kg. This low selling price is mainly because the food waste does not require the pretreatment step and hydrolysis enzymes. YTP is a best substrate for the butanol production due to the capital investment of $\$132.21 \times 10^6$ and selling price is \$0.79/kg (Table 8.2) (Qureshi et al. 2020).

8.7 Global Biobutanol Producers and Consumers

Butanol produced today is mainly by the petrochemical route (oxo process). Major global producers of butanol are Dow, BASF, Celanese, and Eastman, as well as Sasol in South Africa, and KH Neochem in Japan and Elekeiroz in Brazil. During 2014–2019, the global butanol market is estimated to grown more rapidly driven mainly by the Asian-Pacific countries. The worldwide chemical market for *n*-butanol is approximately 950 million gallons, produced mainly by Dow, Dupont, BASF, and Oxea group, whereas China is the leading producer of biobutanol through fermentation with production approx. 100,000 tons. At present, China is increasing the butanol market and the expected demand estimated to them is about 1.64 million tons by 2021. Due to its advantages over ethanol and biodiesel, the global butanol market is expected to reach \$247 billion by 2020.

Gevo Inc., a Colorado based company uses genetically modified yeast which produces iso-butanol only from glucose to be used a gasoline blend stock. Cobalt Technologies, a California based biofuel company has assembled technologies in microbial physiology, strain development, fermentation, to produce more efficient biofuel. Their current holding of technologies is aimed at advancing the mercantile production of biobutanol from plant material. BP and DuPont are also developing a butanol production facility through a company named Butamax™ Advance

Biofuels, a joint collaboration of BP and DuPont are developing a butanol production facility with expected production in 2014.

Syntec Biofuel Inc. a Canada based company has entered into a joint development program with the Energy and Environmental Research Center (EERC) in Grand Forks for converting a wide variety of biomass and waste into biobutanol. Butalco, Switzerland based company uses genetically advanced yeasts which enable increased production yield of biobutanol from lignocellulose, using C5/C6 sugars for fermentation. The Hohenheim pilot plant is a unique project in Germany, which uses genetically modified yeasts. Apart from that, there are many pilot scale and small scale industries all over the world working on the production of biobutanol.

8.8 Conclusion

In recent years only, the biobutanol production has arisen after a long time due to its increasing need and environmental concern. Biobutanol is a promising biofuel alternative which possess all the properties to the conventional gasoline. The use of biomass for butanol production has less carbon foot print on environment. Ever since, its establishment first and second generation feedstocks are commonly used at industrial scale; now the focus has gone to utilization of algae for biobutanol production. Though the described biobutanol concentration from algal biomass is still lower, improvements in the metabolic pathways for biobutanol production or the use of genetically modified strain are still in trials for commercial production. Further, the upstream and downstream process which includes the use of high efficient microbe and feasible recovery technologies are to be upgraded to make biobutanol a future global fuel.

Declaration Authors have no conflict of Interest.

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9 Energy and Exergy Analyses of Typical Cookstove Models Using Different Biomass Feedstocks

K. Pal, Himanshu, and S. K. Tyagi

Abstract

Biomass cookstove is widely used in remote and rural areas of most of the developing countries around the world for space heating and cooking applications since ancient times. The most popular traditional cookstoves such as three stone and U-shaped mud stoves are highly inefficient as they are able to transfer only 10–15% of the total energy available in the fuel to the cooking vessel. Besides, these inefficient cookstoves release the harmful pollutants into the environment which are hazardous for human health and also, aid the climate change. Furthermore, the pollutants that are being released from the cookstove during its operation strongly affect the health of cook and their family members specially, the children below the age of 5 years. Nowadays, a wide range of improved cookstoves are available in the market that are designed and developed by various scientific and non-scientific organizations around the globe and having efficiency in the range of 30–40% with limited emission of pollutants. Most of the studies presented so far and available in the literature are based on energy analysis only. Therefore, in this chapter, the exergetic evaluation of biomass cookstove has been presented for a few cookstove models developed by the group in the last few years. Furthermore, the exergy analysis of the different cookstove models developed by the group has been carried out to analyze the different losses that could not be assessed through energy analysis. The results of the present study revealed that the exergy analysis could work as a new scientific technique that may assist

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in the development and performance evaluation of the cookstoves. Therefore, the exergy analysis can be very helpful in the development of improved cookstoves leading to better design in terms of performance, economy and convenience in the long run.

Keywords

Gasifier cookstove · Exergy efficiency · Energy efficiency · Biomass combustion

9.1 Introduction

Most of the countries around the world are using wood as a primary source of energy for fulfilling their daily energy requirements (Honkalaskar et al. 2013). Annual fuelwood consumption of Asia and Africa is more than 75% of the global fuelwood consumption, mostly for cooking and to a lesser extent for cottage industries such as brick making and food drying and space heating applications (Quaak et al. 1999). Every day more than three billion people are cooking food with traditional or improved cookstoves (Ruiz-Mercado et al. 2011). The growing global population, particularly in the developing and poor countries increases the demand of fire wood which leads to the problems of human health, deforestation, and climate change. In most of the developing countries, people cannot afford fossil fuels due to a number of constraints. At the same time, the significance of cooking is forcing to rely on solid biomass in the majority of the rural areas, globally. According to World Health Organization (WHO), high emissions of CO, hydrocarbons, and particulate matter is the reason for the premature death of millions of people annually around the world (World Health Organization (WHO) 2009). Incomplete combustion of biomass in the traditional cookstove leads to many health problems due to smoke from open fires, dirty environment household kitchen, unhealthy situation, eye and respiratory problems, fire hazard from flying spark, and the soot-blackened area is also unhealthy to live in. As per the estimation, around 2% of the world's GHGs emissions are due to the biomass combustion only (Urmee and Gyamfi 2014). According to WHO, smoke from open fire or cookstove leads to the problems of pneumonia, chronic respiratory disease and lung cancer (Clean Cooking Alliance 2015).

In developing countries, the difficulties faced by indoor smoke are comparable to that of the difficulties faced by life-threatening diseases such as malaria and tuberculosis (Office Energy Efficiency and Renewable Energy 2011). The second largest source for current global warming is released by the biomass cookstoves (22%) and fossil fuel cookstoves (7%) (Ramanathan and Carmichael 2008). One estimate says the only 18 g of equivalent wood is sufficient to cook 1 kg of food in the ideal case, therefore, a huge wastage is going on globally (Baldwin 1987). On the other hand, if one uses the open fire with the controlled testing conditions, the amount of fuel wood required is only 268 g, whereas the improved cookstoves (ICS) consume only 160 g of fuel wood that is nine times of ideal requirement. This statement symbolically says that there is a huge potential to reduce wood consumption globally by using the improved cookstove. However, the dissemination of improved cookstoves through proper project design and better planning, which is otherwise a complex phenomenon and may be an important key to reduce global CO_2 emissions up to large extent.

However, only technically designed cookstove is not enough to achieve 100% penetration of the improved cookstove in the field. The poor adoption rate by the end users is also associated with number of other parameters such as the availability of processed fuel at affordable cost, high cost of cookstove, social issues, and behavioral aspects. Some of these issues can be addressed through awareness and outreach programs, effective financial, and women empowerment models to play the catalytic role, which is otherwise will end up with poor dissemination. Furthermore, there are number of other issues and reasons that need to be addressed and tackled by effective measures to overcome including but not limited to develop the mechanism for ensured supply and availability of affordable biomass fuel, rural employment generation, providing operation and maintenance, meeting the user's expectations with multiple usages other than cooking, overcoming insufficient networking, and distribution channels (Ramanathan and Carmichael 2008; Thacker et al. 2014; Mukhopadhyay et al. 2012; Barens et al. 1994; Tyagi and Prakash 2019). In some cases, the end users also consider that the biomass cookstove should be upgraded to a level where it can compete the LPG stove with the convenience of cooking, operating, and maintenance, however, no one wants to pay the higher cost involved in the development of such technology and/or in buying the processed fuel to compete with the high-grade fuel like electric or gas-based stove (Mukhopadhyay et al. 2012; Barens et al. 1994; Tyagi and Prakash 2019).

The thermal efficiency of improved cookstoves, viz. natural draft top lit updraft and forced draft cookstoves was found to be higher than the traditional cookstoves while using coconut shells, fuel wood, and wood pellets as fuel (Tyagi 2018; Sonarkar and Chaurasia 2019). Many studies indicated that the improved cookstoves have significant reduction potential for harmful pollutants such as particulate matter and carbon monoxide (Mitchell et al. 2019; Padilla-Barrera et al. 2019). The stove and fuel type greatly influence the composition of emissions particularly particulate matter and it has been found that the use of gasifier stoves can reduce the fuel consumption and hence, saving both the fuel and the harmful emissions drastically (Lai et al. 2019). Also, improved cookstoves can drastically reduce cooking time, and hence decrease the exposure levels of toxic pollutants to the users (Chakraborty and Mondal 2021; Pratiti et al. 2020). The use of improved cookstoves could lead to the savings of 1.72–2.08 tons of fuelwood per household annually, which in turn can reduce the emissions of 2.82–3.43 tons of carbon dioxide equivalent per cookstove (Wassie and Adaramola 2021; Memon et al. 2020).

According to some observers including the World Bank (Gitau et al. 2019; World Bank 2011; Obara et al. 2008), improved cookstoves, may become a "game changer" in climate change mitigation through the development of new generation of biomass cookstoves, if the end users adopt them. Nowadays, a wide range of improved biomass cookstoves are available in the market which are designed and developed by various scientific and non-scientific organizations around the globe and having efficiency in the range of 30–40% with limited emission of pollutants. But most of these cookstoves are not adopted by rural people because of their high market price and required processed fuel, which is not freely available, unlike the traditional stoves. This is putting a big barrier in the adoption and hence, a lot of efforts are required from all walk of people to contribute in these social and environmental causes.

Numerous studies on exergy and energy analysis of agricultural, herbaceous, and woody biomass have been published in the literature (Zhong et al. 2002; Park et al. 2014; Himanshu et al. 2021; Tyagi et al. 2021, 2013). The exergy efficiency of conversion of biomass to liquid fuel has been calculated (Pal et al. 2019). It has been concluded from the literature survey that the main source of exergy loss from various biomass is methanation, gasification, and CO_2 removal. The present study has been carried out to analyze the energetic and exergetic performance of two different cookstove models, while utilizing the different types of biomass. The effect of varying the quantity of biomass has also been analyzed on the performance of the cookstove.

9.2 Material and Methodology

The present study is focused to determine the energetic and exergetic performance of two different cookstove models as per the procedure given in BIS (IS 13152 (Part 1): 2013) (Bureau of Indian Standards 2013). Four different woody biomass fuel wood such as Bakana Neem (Persian Lilac), Shahtoot (Mulberry), Sheesham (Dalbergia sissoo), Eucalyptus (Eucalyptus Globus) were utilized to analyze the performance of both cookstove models. The selection of fuel was based on the ease of availability to the end users and in the particular region of the country. The performance of both the cookstoves were compared in terms of energy and exergy efficiencies by using the varying quantities of biomass.

9.2.1 Experimental Set-Up and Procedure

The pictorial view of the cookstove testing laboratory is shown in Fig. 9.1. The experiment was started by placing the cookstove in the standard cookstove testing hood. Approximately 10–15 mL of diesel/kerosene was sprinkled on the top of the fuel kept inside the combustion chamber in a honeycomb fashion to ignite the fire initially and starting time of the experiment was noted down manually. The water kept over the cookstove in the cooking pot was permitted to heat-up gradually till it attained a temperature of around 95 °C. Also, the temperature of water was recorded in the logbook manually at an interval of 5 min. The total time consumed by water to reach the final temperature in the pot was also noted down manually. The pot was interchanged with a fresh pot having water at ambient conditions and the experiment was repeated until the entire flame got vanished completely. Some of the essential parameters particularly temperatures of water, flame, handle of cookstove, and

Fig. 9.1 Cookstove test center showing different measuring equipment with cookstove testing hood

cookstove outer surface, etc. were measured periodically by using digital temperature sensors. However, the ambient temperature was recorded with the help of a glass thermometer. Each experiment was repeated at least six times for making the consistency of each parameter. The laboratory conditions were maintained at the temperature of 25 ± 5 °C during the experiments.

9.2.2 Cookstove Models

Cookstove models 1 and 2 were designed on the basis of gasification principle and based on the survey carried out in the various states of Punjab (India). These are the unique models so far developed in the country as per the requirement of rural household people. Models 1 and 2 are the domestic size cookstove models for a family of 4–6 members. Model 2 is a two pot cookstove or modified version of the traditional cookstove, developed based on the requirement of a local community.

9.2.2.1 Gasifier Cookstove (Model-1)

The basic design principle behind this cookstove model is down-draft gasification of biomass in which secondary air holes are provided throughout the length of the combustion chamber. The height and diameter of this model were evaluated as per the power output rating. The photographic view of this particular model can also be seen in Fig. 9.2i. Mild steel and galvanized iron sheets were used in the manufacturing of combustion chamber and other parts of the cookstove; however, cast iron was used for making grate, handle, and legs of the cookstove. A half-inch square cross-section iron mesh was provided at the outside surface of the cookstove to avoid any burn injury to the end users of the cookstove. The testing of this model was also done as per the revised BIS (IS, 13152 (Part 1): 2013) (Bureau of Indian Standards 2013) protocol and the various results obtained are given in Table 9.1.

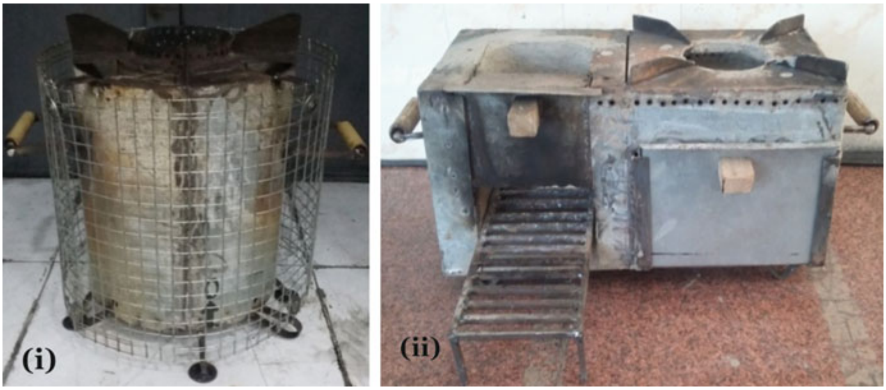

Fig. 9.2 Photographic view of cookstove models (i) Gasifier Cookstove (Model-1), (ii) Modified, Two Pot Cookstove (Model-2)

Table 9.1 Average value of energy efficiency and exergy efficiencies of cookstove models with different quantity feedstocks

Quantity (kg)/ Types of wood	01		02		03		04		05	
	η (%)	ψ (%)	η (%)	ψ (%)	η (%)	ψ (%)	η (%)	ψ (%)	η (%)	ψ (%)
Gasifier Cookstove (Model-1)										
Eucalyptus	28.24	3.83	28.00	3.57	26.97	4.06	26.83	3.92	24.27	5.01
Sheesham	30.53	3.92	29.30	4.12	27.36	4.45	26.66	4.89	25.83	4.56
Dek	29.46	3.32	27.87	3.74	28.63	4.19	27.91	4.73	23.25	4.16
Shahtoot	28.71	3.80	27.63	4.10	28.78	4.24	27.33	3.85	22.48	4.32
Modified, Two Pot Cookstove (Model-2)										
Eucalyptus	21.87	3.12	22.44	3.98	23.54	4.37	26.19	3.82	25.76	3.65
Sheesham	23.79	3.10	25.08	3.24	27.59	4.44	26.68	4.14	25.96	3.90
Dek	22.62	3.02	23.82	4.12	27.97	3.98	25.88	3.81	27.13	4.19
Shahtoot	25.35	3.00	24.02	3.07	24.53	4.19	24.77	3.75	26.47	4.11

This one is the unique model, modified on the basis of gasification principle. All the parameters of this cookstove model are within the permissible limit of the BIS protocol.

9.2.2.2 Modified, Two Pot Cookstove (Model-2)

This is a modified version of the traditional cookstove, which is having two pot openings (two cooking burners) such that one can cook two dishes at the same time. This cookstove was designed and developed based on the requirement of the local village people of Kapurthala district. This cookstove model has the facility to use the heat of first cooking burner into second cooking pots by single fuel inlet or by single combustion chamber as can be seen from Fig. 9.2ii. This is one of the unique models developed/modified so far, as it has the option to roast the chapatti from the direct contact of the flame and has the option to cook two food items at the same time and also has the option to store cooked food items in the oven space provided in the cookstove body, for better recovery of the heat, as can be seen from Fig. 9.2ii. Although, there are many two pot cookstove available/developed so far in the country but it has the uniqueness of supply of primary and secondary air at particular space and at a particular amount. All the parameters of this cookstove model satisfy the BIS protocols.

9.3 Performance Analysis

The methodologies as per new BIS (IS 13152 (Part 1): 2013) (Bureau of Indian Standards 2013) were used and the details are as follows:

9.3.1 Thermal Efficiency Test for Cookstove Models

The thermal efficiency for any cookstove is expressed as ratio of the useful heat delivered to the cooking pot to the heat ideally produced which further relies on the amount of the fuel being burnt and its net calorific value (Bureau of Indian Standards 2013).

9.3.1.1 Laboratory Room Conditions

- Laboratory temperature should be maintained at 25 ± 5 °C during the experiment.
- The test room should be free from forced draft air.
- All the cooking vessels, cookstove, wood, etc. should be at room temperature at the beginning of the experiment.

9.3.1.2 Required Equipment

- Bomb calorimeter.
- Standard cookstove testing duct.
- Digital Thermocouple (Pt-100).
- Mercury in glass thermometers (0–150 °C).
- Cooking vessels of required size.
- Weighing balance (100 kg capacity and least count of 10 g).
- Measuring jars of capacity 1, 2, and 5 L.
- Stopwatch.
- Pairs of tong.
- A piece of clean cloth/globes.

9.3.1.3 Fuel Preparation

The fuel used for the testing of both the cookstoves was woody biomass which was available locally. The fuel was prepared according to BIS protocols for the cookstove testing by cutting pieces of square cross-section of area 3 cm × 3 cm and length equal to the half of the diameter of the combustion chamber in order to place the fuel in a honeycomb manner. The percentage of the moisture content in the fuel used was kept between 4% and 6% (drybasis) by using a hot air oven.

9.3.1.4 Burning Capacity Rate

The burning capacity rate is defined as the capacity of cookstove to burn the particular amount of fuel biomass in 1 h. The burning capacity can be found out from the following stepwise procedure:

- Put the biomass fuel in the combustion chamber up to 75% of its volume in a honeycomb manner.
- Sprinkle the small amount of kerosene over the fuel bed (approximately 10–15 mL).
- Weight the cookstove with fuel (say it as W_1 kg).
- Light up the fuel by putting the cookstove inside the testing duct and left it to burn for half an hour.
- After half an hour burning measured the weight of cookstove with burning wood/ charcoal (say it as W_2 kg).
- The burning capacity rate and the heat input per hour than can be calculated as follow:
  - **Burning capacity rate** $= 2(W_1 - W_2)$, kg/h
  - **Heat input** $= 2(W_1 - W_2)c_1$, kcal/h.
    where: c_1 = calorific value of biomass fuel in kcal/kg.

9.3.1.5 Selection of Vessels

Based on the heat input rate of a particular cookstove model, the size of the cooking vessels and the amount of water that need to be taken during the experiment was determined by using the standard procedure described in BIS protocol.

9.3.1.6 Water Boiling Test (WBT) Procedure

- Measure the amount of fuel according to the burning capacity rate of the cookstove.
- Divide the measured fuel into ten equal parts and place one or two parts of fuel in the cookstove in a honeycomb fashion.
- Take the suitable size pots (2–3 nos.) in accordance with the burning capacity rate and fill the water as per the heat input rate.
- Spray 10–15 mL of kerosene on the wood and start lighting of fuel by simultaneously start the stopwatch.
- Put the first cooking vessel immediately on the cookstove and not down the initial time.
- The other fuel lots were fed into the combustion chamber at an interval of 6 min.
- The temperature of water, the surface of the cookstove, cooking vessel, cover plate, and flame were recorded at an interval of 5 min.

- As soon as the water kept in the cooking pot attained the temperature of water 95 °C, another pot having water at ambient temperature was interchanged with the first pot and the time of boil was recorded immediately.
- The experiment was continuing until the end of fuel by changing the vessels of fresh water.

9.3.2 Calculation of Thermal Efficiency

The thermal efficiency of the cookstove can be calculated by dividing the heat actually utilized to the heat produced ideally as follows (Bureau of Indian Standards 2013):

$$\text{Heat utilized} = \{(n-1)(W \times 0.896 + w \times 4.186\,8)(T_2 - T_1) + (W \times 0.896 + w \times 4.186\,8)(T_3 - T_1)\}, \text{ kJ}$$

$$\text{Heat produced} = 4.186\,8\,\{(X \times c_1) + (x \times d \times c_2/1000)\}, \text{ kJ}$$

$$\eta = \frac{\{(n-1)(W \times 0.896 + w \times 4.1868)(T_2 - T_1) + (W \times 0.896 + w \times 4.1868)(T_3 - T_1)\}}{4.1868\{(X \times c_1) + (x \times \rho \times c_2/1000)\}} \times 100 \tag{9.1}$$

where w is the amount of water taken in the pot, in kg; W is the total mass of pot along with the cover plate, in kg; and n is the total number of vessels used in a complete experiment, c_2 is net heating value of kerosene (kcal/kg), ρ is the density of kerosene kg/m^3, x is the total volume of kerosene utilized in m^3, X is the quantity of fuelwood.

9.3.3 Power Output

The amount of fuel being burnt; the net heating value (c_1) and the thermal efficiency of the cookstove influences the power output obtained from any cookstove. It can be defined as the total useful energy obtained from combustion of certain amount of fuel in unit time and evaluated by using the following equation (Bureau of Indian Standards 2013):

$$\text{Power output} = \frac{X \times c_1 \times \eta}{3600 \times 100}, \text{ kW} \tag{9.2}$$

9.3.4 Exergy Analysis

It is a qualitative analysis based on the second law of thermodynamics in contrast to the energy analysis, which is quantitative only. Exergy analysis accounts for irreversibility in any system or process, and indicates the available energy that can be obtained from a system/process. Therefore, exergy can be defined as the maximum work potential that could be generated by a system corresponding to specific operating conditions, which in general are the ambient temperature and pressure especially, for thermal applications. The thermal exergy input to any cookstove can be calculated by using the following equation (Tyagi et al. 2007; Kotas 1985):

$$\mathrm{Ex_{in}} = (m_{\mathrm{wd}} c_1 \times \eta_{\mathrm{c}} + x \times d \times c_2)(1 - T_{\mathrm{a}}/T_{\mathrm{fuel}}) \tag{9.3}$$

where T_{fuel} is the temperature of burning source/fuel and T_{a} is the ambient temperature. Also, the exergy input can be defined in terms of chemical exergy stored in the fuel. For certain fuels such as biomass, petroleum products, etc. and can be expressed by using the following equation (Kotas 1985):

$$\xi^0 = \left[(\mathrm{NCV})^0 + w_{\mathrm{moistue}} h_{\mathrm{fg}}\right] \varphi_{\mathrm{dry}} \tag{9.4}$$

where h_{fg} is the enthalpy of evaporation of H_2O at standard temperature ($h_{\mathrm{fg}} = 2442$ kJ/kg at $T = 298.15$ K), $(\mathrm{NCV})^0$ is the net heating value of the moist fuel and w_{moisture} is the mass fraction of moisture present in the fuel. The term φ_{dry} for dry organic substances such as woody biomass having C, H, N, O as its constituents and ratio of oxygen to carbon (by weight) ranged between 0.667 and 2.67 ($2.67 > o/c > 0.667$) can be calculated by using the following equation:

$$\varphi_{\mathrm{dry}} = \frac{1.0438 + 0.1882 \times (h/c) - 0.2509(1 + 0.7256 \times (h/c)) + 0.0383(n/c)}{(1 - 0.3035 \times (o/c))} \tag{9.5}$$

where c, h, o, and n are the mass fractions corresponding to the amount of C, H, O and N, respectively, within the fuel. Exergy output of any cookstove can be expressed as the product of the energy delivered to the cooking pot and the Carnot factor and is represented as follows (Tyagi et al. 2013, 2007; Pal et al. 2019; Kotas 1985):

$$\begin{aligned}\mathrm{Ex_o} = {} & m_{\mathrm{w}} C_{\mathrm{p}} (T_{\mathrm{fw}} - T_{\mathrm{iw}})(1 - T_{\mathrm{a}}/T_{\mathrm{fw}}) + m_{\mathrm{pot}} C_{\mathrm{p,pot}} \left(T_{\mathrm{fp}} - T_{\mathrm{ip}}\right) \\ & \times \left(1 - T_{\mathrm{a}}/T_{\mathrm{fp}}\right)\end{aligned} \tag{9.6}$$

Hence, the exergy efficiency that could be defined as ratio of exergy output to exergy input can be calculated by using Eqs. (9.3) and (9.6) as given in the following (Tyagi et al. 2013, 2007; Pal et al. 2019; Kotas 1985):

$$\psi = \frac{\text{Exergyoutput}}{\text{Exergyinput}} = \frac{\text{Ex}_o}{\text{Ex}_{in}} \tag{9.7}$$

9.4 Results and Discussion

The experiments for evaluating the different performance parameters were carried out with the varying quantity of Sheesham (Sh), Shahtoot (Sa), Dek (Bakana Neem), and Eucalyptus (Eu) wood from 1 to 5 kg. The software tools developed by the research group were used to analyze the experimental data. The values of energy and exergy efficiencies calculated from the average of six experiments are listed in Table 9.1. The results indicated that the energy efficiency of the cookstove model-1 was in good agreement with the BIS permissible limit (i.e. ≥25% for natural draft cookstove models). The performance of cookstove model-1 was found to be satisfactory for varying the quantity of different wood from 1 to 4 kg, however, the energy efficiency with 5 kg of wood was lower than 25%, the limit (≥25%) set by BIS. The char formation could be the possible reason for lower energy efficiency with 5 kg of wood. When the char builds up in the combustion zone, it hindered the circulation of primary air which is responsible for biomass gasification. Incomplete gasification/combustion during the last 15 min of the experiment results in lower energy efficiency with a higher quantity of wood. It was also observed that with the increasing quantity of wood the amount of unborn char collected at the end of the experiment was also increased.

9.4.1 Performance Analysis of Gasifier Cookstove (Model-1)

The different performance parameters of this cookstove model with increasing quantities of biomass are shown in Figs. 9.3, 9.4, 9.5, 9.6, 9.7, 9.8, 9.9, 9.10, 9.11, 9.12, 9.13, and 9.14. The values of both the efficiencies are fluctuating throughout

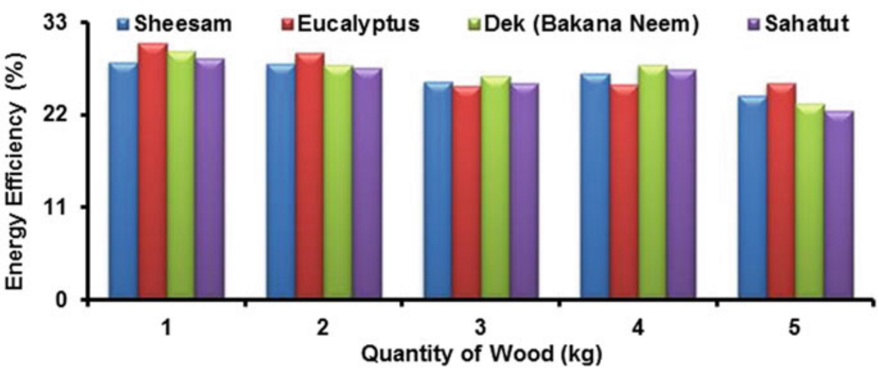

Fig. 9.3 Energy efficiency with varying quantities of different wood for cookstove model-1

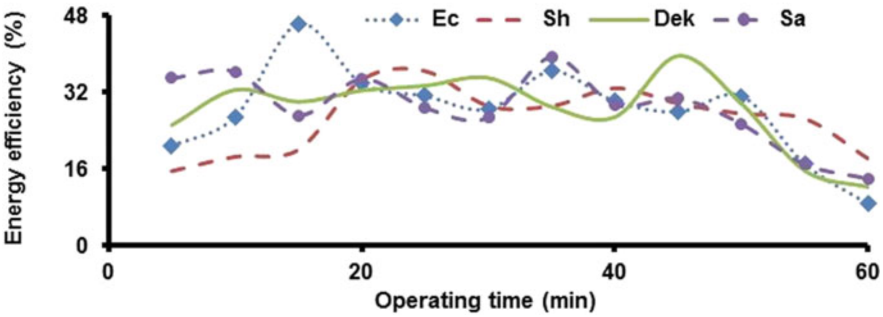

Fig. 9.4 Variation in energy efficiency with 01 kg wood for model-1

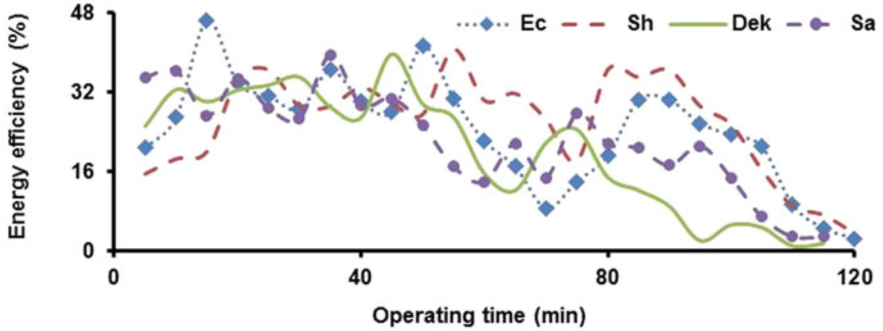

Fig. 9.5 Variation in energy efficiency with 02 kg wood for model-1

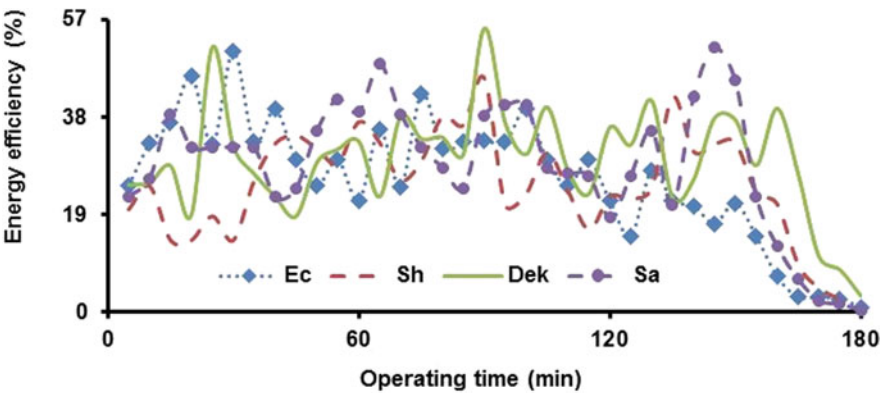

Fig. 9.6 Variation in energy efficiency with 03 kg wood for model-1

the experiment. The values of energy and exergy efficiencies first increase, and thereafter decrease with an increase in the operating time. The peak values of energy and exergy efficiencies are different because of the various reasons like energy input

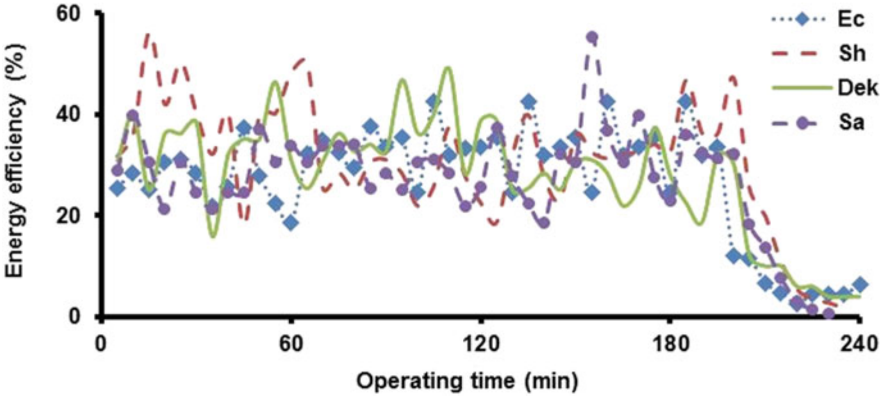

Fig. 9.7 Variation in energy efficiency with 04 kg wood for model-1

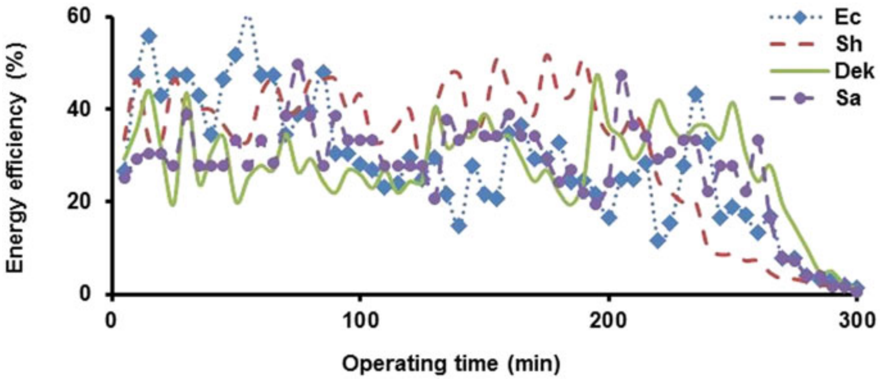

Fig. 9.8 Variation in energy efficiency with 05 kg wood for model-1

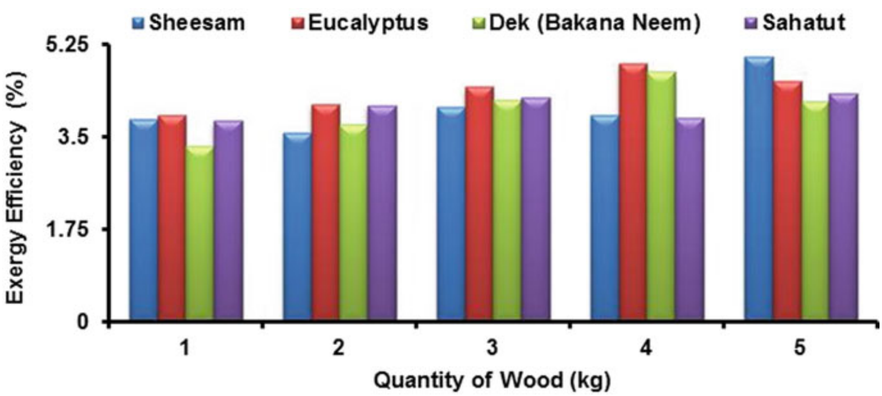

Fig. 9.9 Exergy efficiency with varying quantities of different wood for Cookstove model-1

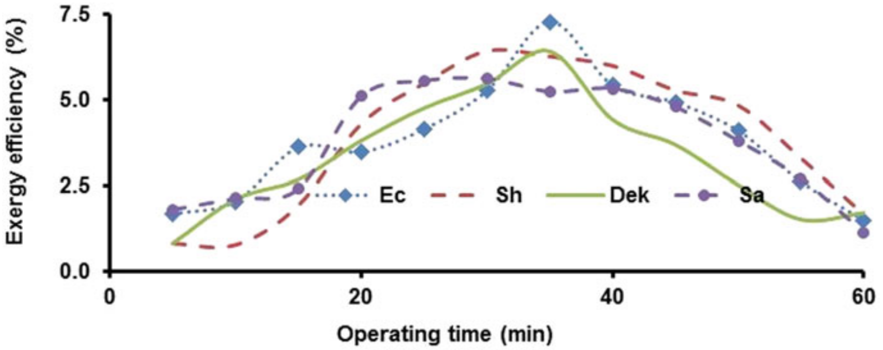

Fig. 9.10 Variation in exergy efficiency with 01 kg wood for model-1

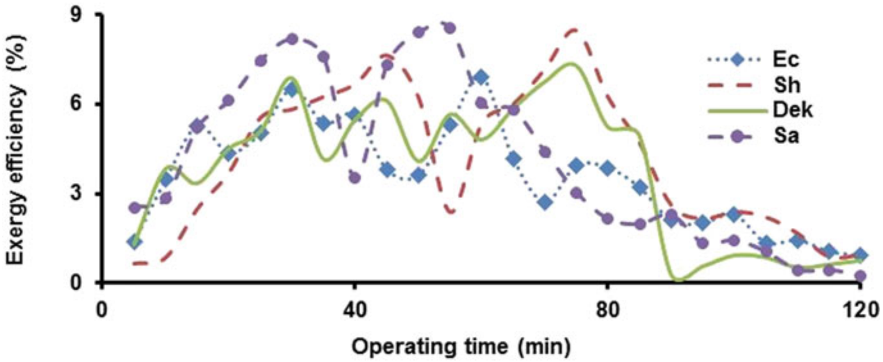

Fig. 9.11 Variation in exergy efficiency with 02 kg wood for model-1

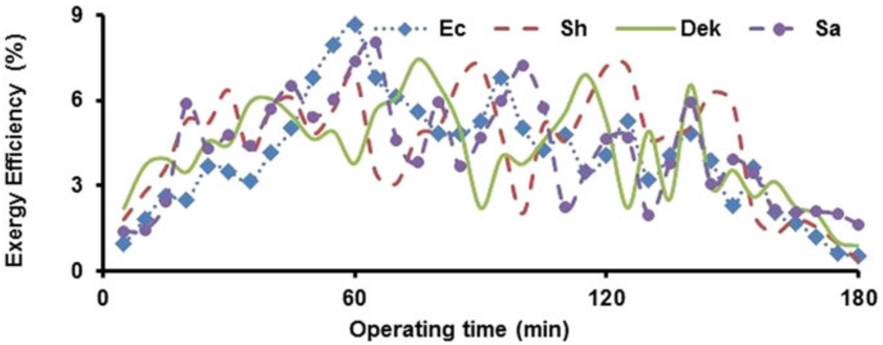

Fig. 9.12 Variation in exergy efficiency with 03 kg wood for model-1

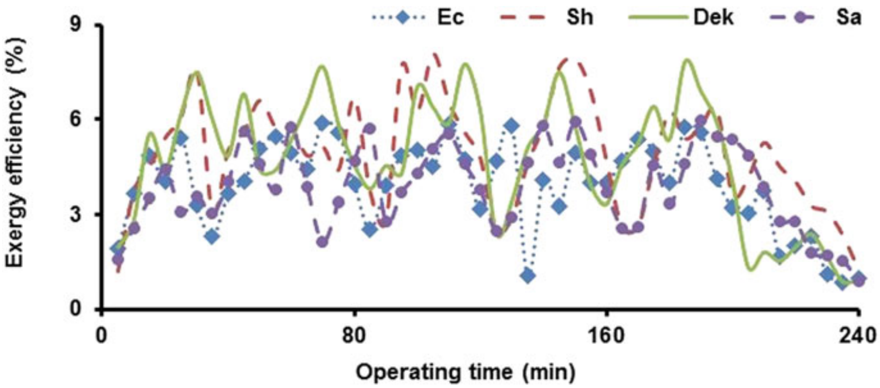

Fig. 9.13 Variation in exergy efficiency with 04 kg wood for model-1

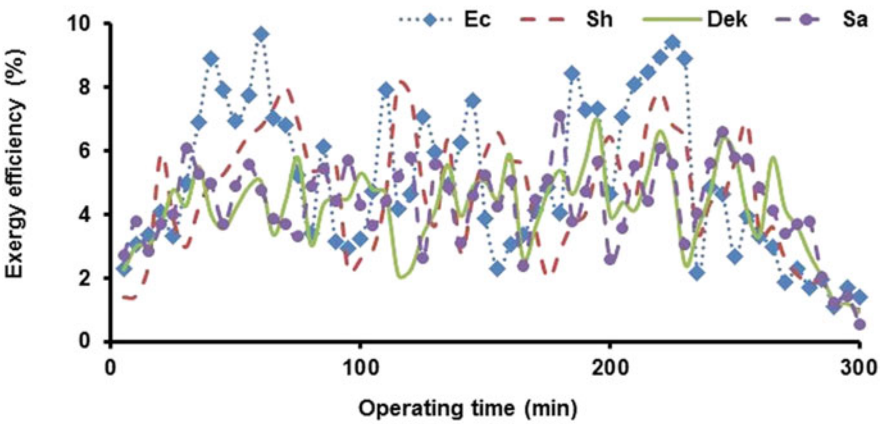

Fig. 9.14 Variation in exergy efficiency with 05 kg wood for model-1

at the time of the beginning of the experiment is less as compared to the energy input during after some time of starting the water boiling test. This is because of the fact that the amount of volatiles released and the temperature of the combustion chamber was different at a different stage of time.

The energy efficiency of cookstove model-1 was evaluated with varying quantities of different wood and the comparative results are shown in Fig. 9.3. The energy efficiency was found to be highest with the 1 kg biomass wood, while the value of energy efficiency decreased with further increase in the quantity of fuel-wood. The maximum value of energy efficiency was 30.53% corresponding to 1 kg of Eucalyptus wood. The results indicated that the energy efficiency lied in the range of 25.36–30.53% for varying amount of Eucalyptus wood from 1 to 5 kg. The value of energy efficiency was found to be lowest with 5 kg of Shahtoot wood. With varying amounts from 1 to 5 kg of Sheesham wood, the energy efficiency resulted in the range of 25.97–28.24%. In contrast, the energy efficiency was found in the range of 23.25–29.46% with an increasing quantity of Dek wood. This variation in the values of energy efficiency could be attributed to the variation of different physical and chemical properties of biomass wood. The energy efficiency not only depends on the heating value of biomass but also relies on other properties of biomass such as moisture content, volatile matter content, etc.

The fluctuations in the values of thermal and exergy efficiency may be because of the availability of heat or the absorption of heat energy at the starting time of the experiment and at the time of changing the pot is different and it first increases with the temperature of the water, and thereafter decreases with further increase in the temperature. This also justifies the physical significance of the results obtained as shown in Figs. 9.6, 9.7, and 9.8 and Figs. 9.12, 9.13, and 9.14 which are having several speaks adding fluctuations throughout the individual experiment especially, when the mass of cooking wood is higher and/or the cooking time was prolonged. The average values of energy and exergy efficiencies were found to be highest for the Eucalyptus wood (Eu), while these values were lowest for Shahtoot wood (Sa) with some exceptions elsewhere, which is evident from results given in Table 9.1.

9.4.2 Performance Analysis of Modified, Two Pot Cookstove Model-2

This cookstove model is also a domestic size cookstove model, having unique operating characteristics such as two cooking burner, higher power output, better combustion characteristics, use of different types of biomass fuel, etc. This cookstove model can be operated with varying sizes and types of biomass and also with a variable quantity of biomass fuel. The energy and exergy efficiencies of this particular cookstove were also evaluated with varying quantities of different biomass as can be seen from Figs. 9.15, 9.16, 9.17, 9.18, 9.19, 9.20, 9.21, 9.22, 9.23, 9.24, 9.25, and 9.26.

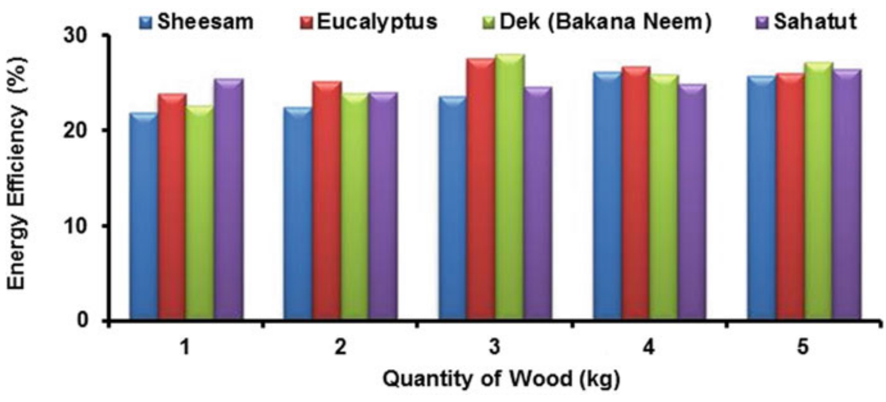

Fig. 9.15 Energy efficiency with varying quantities of different woods for cookstove model-2

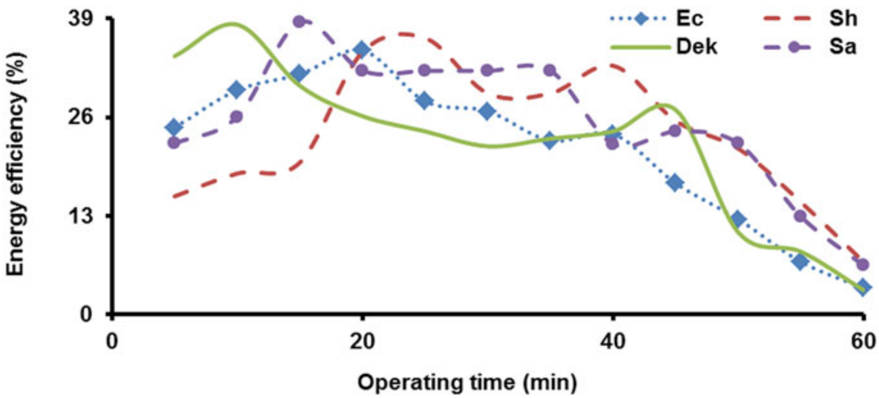

Fig. 9.16 Variation in energy efficiency with 01 kg wood for model-2

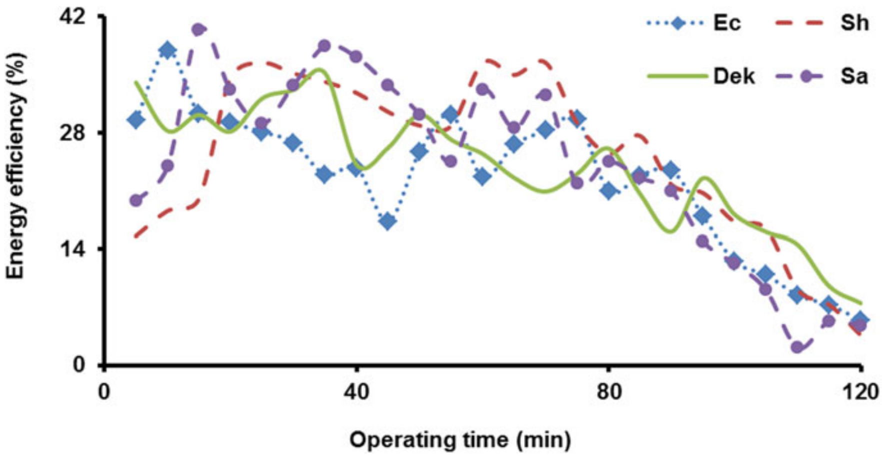

Fig. 9.17 Variation in energy efficiency with 02 kg wood for model-2

Similar to the results obtained from previous cookstove models, the fluctuations of readings of both the efficiencies were also found throughout the experiment. The maximum reading of both the efficiencies was found with 3 kg of Dek wood followed by Eucalyptus, Shahtoot, and Sheesham wood. The values of both efficiencies first increased, and thereafter decreased with the operating time from the initial stage toward the end of the experiment. The fluctuation of the values of both the efficiency was due to the variation of fuelwood physical and chemical properties as discussed in the results of the previous cookstove model. At the starting phase of the experiment, the amount of heat produced was less, and as the combustion of biomass wood builds up to its maturity level the amount of heat production increased with the increasing temperature of combustion bed material. The increasing temperature of combustion bed material stimulates the production of

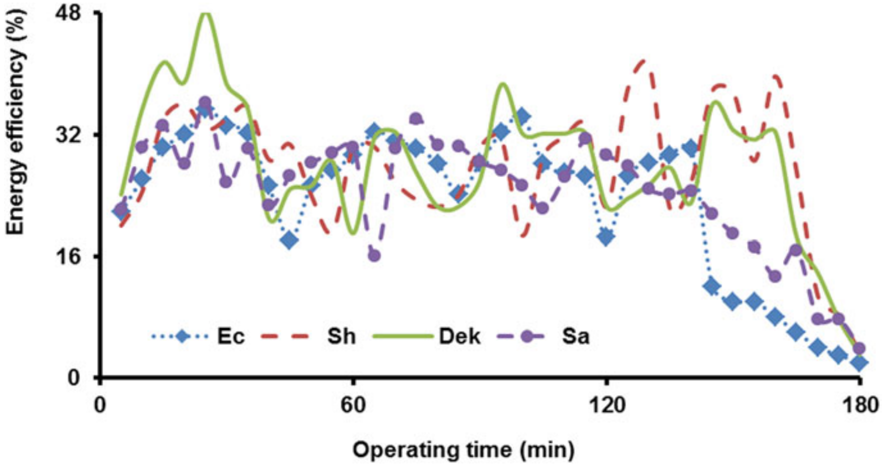

Fig. 9.18 Variation in energy efficiency with 03 kg wood for model-2

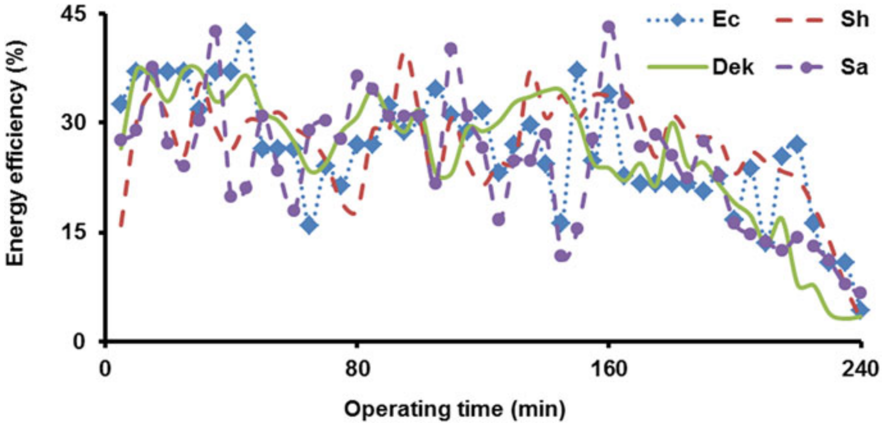

Fig. 9.19 Variation in energy efficiency with 04 kg wood for model-2

combustible gases at a faster rate. More heat was produced as soon as these evolved volatile gases came in contact with the secondary air. Also, the temperature of water in the cooking pot was at lower level, which absorbed the heat at a faster rate because of the large temperature difference. The gain of temperature stimulates the value of energy efficiency at a faster rate during the initial stage of the water boiling test.

The value of both the efficiencies was found to be in the fluctuating nature during the experiment, however, the value was higher during the mid-time of each experiment and for each new pot, and this can be seen from Figs. 9.15, 9.16, 9.17, 9.18, 9.19, 9.20, 9.21, 9.22, 9.23, 9.24, 9.25, and 9.26, respectively. It is clear from Figs. 9.16 and 9.17 and Figs. 9.22 and 9.23 that the numbers of peaks obtained with less amount of fuelwood were less and as soon as the quantity of wood

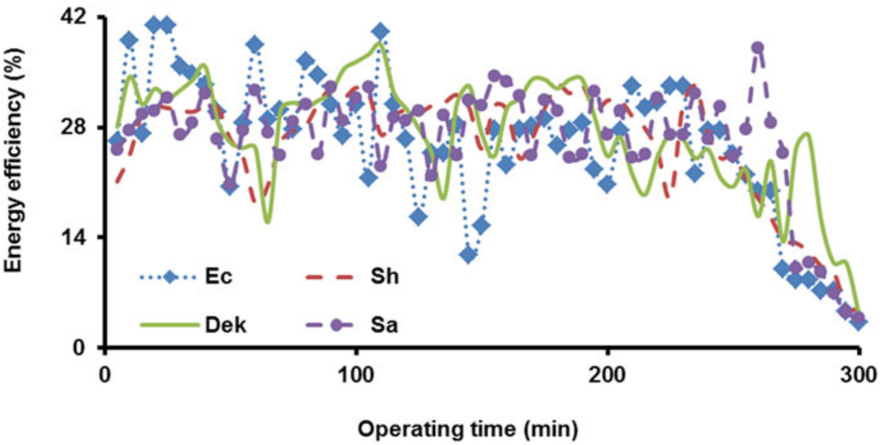

Fig. 9.20 Variation in energy efficiency with 05 kg wood for model-2

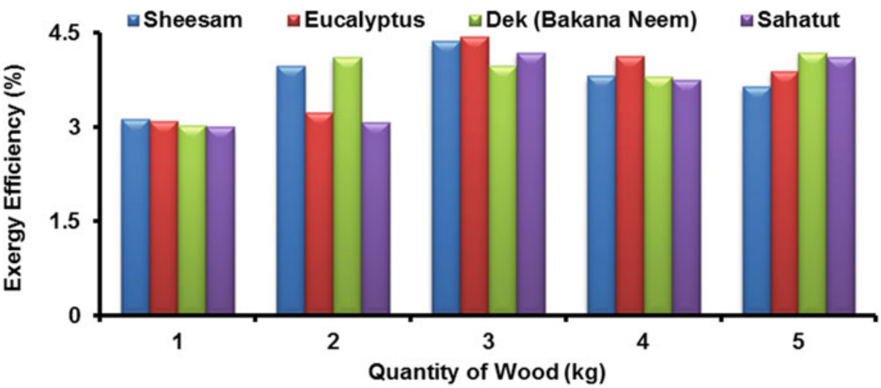

Fig. 9.21 Exergy efficiency with varying quantities of different wood for Cookstove model-2

increases the numbers of peaks also increases as can be seen from Figs. 9.18, 9.19, and 9.20 and Figs. 9.24, 9.25, and 9.26. From the results, it was also observed that the value of both the efficiencies decreases toward the end of the water boiling experiment. This is due to the mismatch of produce energy with excess air supply.

Some of the typical results were also observed for different types of wood with varying quantity leading to some interesting conclusions. The energy efficiency for Sheesham (Sh) wood increased with increasing the amount of wood from 1 to 4 kg, however, it was decreased for further increase in the quantity of wood from 4 to 5 kg. The maximum value of energy efficiency was found to be around 26.19% with 4 kg of wood, while the exergy efficiency was increasing from 1 to 3 kg of biomass wood. However, the value of exergy efficiency was found to be in the decreasing order with further increase in the amount of wood. The maximum values of energy and exergy efficiencies for 3 kg of Eucalyptus (Ec) were 27.59% and 4.44%, respectively, while;

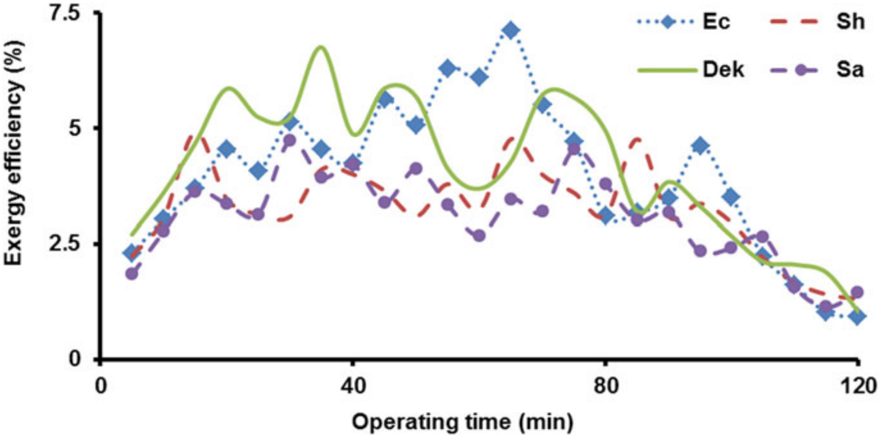

Fig. 9.22 Variation in exergy efficiency with 01 kg wood for model-2

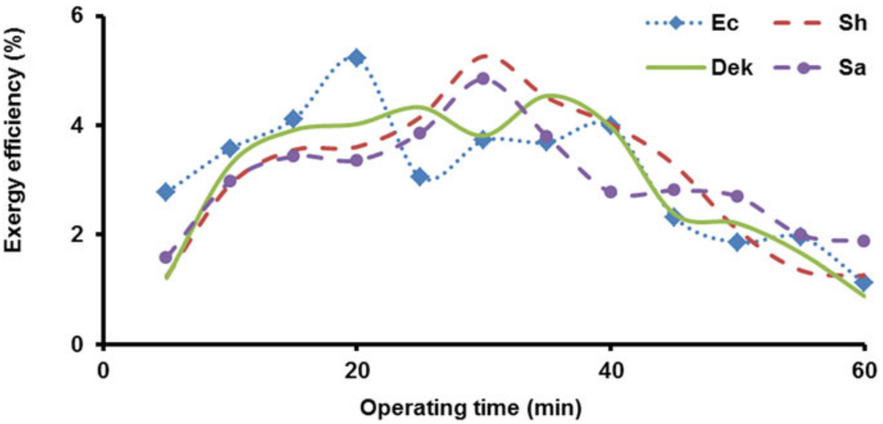

Fig. 9.23 Variation in exergy efficiency with 02 kg wood for model-2

the lowest values were 23.79% and 3.10% for 1.0 kg of fuelwood, respectively. In contrast for Dek wood, the maximum values of energy efficiency and exergy efficiency were 27.97% for 3 kg and 4.19% for 5 kg, while the maximum value was 26.47% for 5 kg for Shahtoot (Sh) wood and 4.19% with 3 kg wood, respectively.

9.5 Conclusions

The analysis of energy and exergy efficiencies of two different cookstove models is present in this study. The analysis was performed with varying quantity of four different types of wood which is generally used in the local community for cooking.

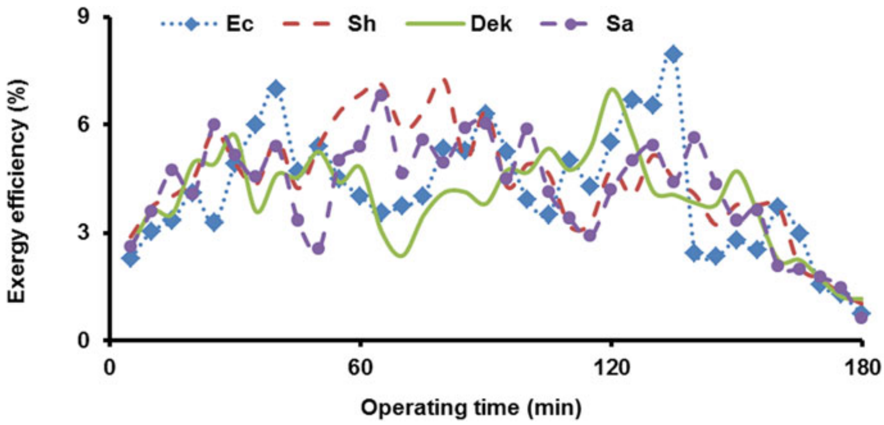

Fig. 9.24 Variation in exergy efficiency with 03 kg wood for model-2

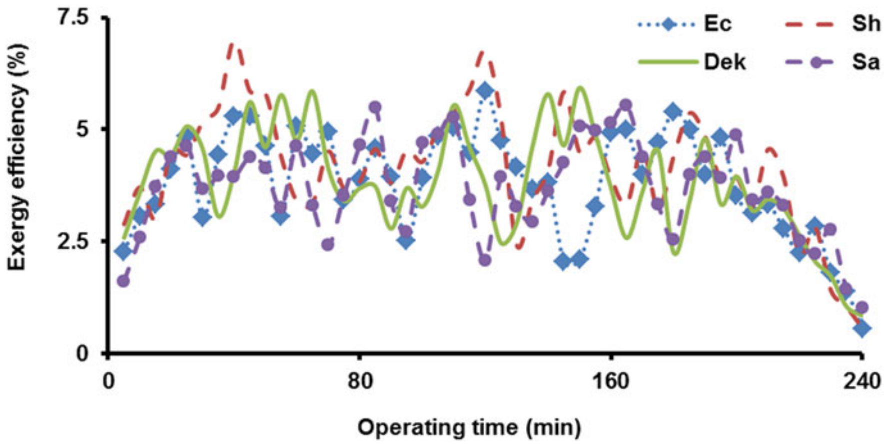

Fig. 9.25 Variation in exergy efficiency with 04 kg wood for model-2

The performance parameters of both the cookstoves were determined following the standard testing protocol (IS 13152 (Part 1): 2013). The results obtained from the standard water boiling test were analyzed and discussed in detail. Based on the result and discussion the performance parameters of both the cookstove model was rated out and also various markets and demerits were listed out for both the models. According to experimental observation, it was found that with varying quantities of different woods both the cookstoves exhibit some specific quality. The detailed experimental investigations carried out in this work led to the following conclusions:

- The values of energy efficiency of cookstove model-1 w.r.t. the operating time and varying quantity of biomass fuel ranged between 25.83% and 30.53% with

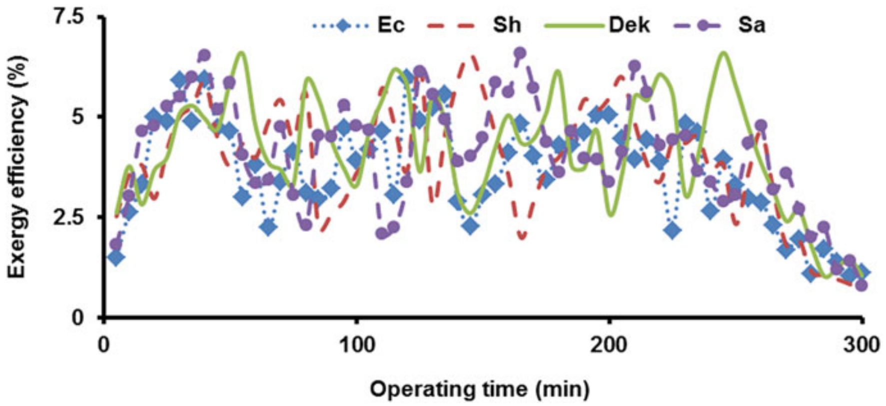

Fig. 9.26 Variation in exergy efficiency with 05 kg wood for model-2

Sheesham wood, while the exergy efficiency was found to be in the range of 3.83–5.01%.

- The variation of energy efficiency of cookstove model-2 w.r.t. the operating time and varying quantity of biomass fuel was found to be in the range of 22.62–27.97% with Dek wood, while the maximum value of exergy efficiency ranged between 3.10% and 4.44%.
- On comparing the above results of both the cookstove models, the values of energy and exergy efficiencies of gasifier type cookstove models-1 are always greater than that of the cookstove model-2.
- The values of energy efficiency are found to be much higher than the exergy efficiencies for both the cookstove models.

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Biohydrogen Production Technologies: Past, Present, and Future Perspective

10

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Abstract

Biohydrogen is considered as the attractive future energy sources and clean energy due to its high energy content and eco-friendly conversion methods. Hydrogen energy sources became the most valuable energy as the current demands gradually begin to increase. Global temperature is increasing due to increasing pollution and hydrogen energy is an important key solution. Nowadays, technology related to hydrogen production is commercially available, and advancements are also under developmental stages. Currently, most hydrogen is produced by the electrolysis of water and by the steam reformation of natural gas. However, other conventional methods can be used for hydrogen production process such as thermo-chemical gasification, solar gasification, pyrolysis, and supercritical conversion process. However, to produce energy in sustainable manner, it is utmost important to go for the biological route for the hydrogen production as fuel. Biological production of hydrogen has significant advantages over thermochemical and electrochemical processes. This chapter discussed the major biological processes for hydrogen production such as indirect biophotolysis, direct biophotolysis, dark and photo fermentations, the sequential dark and photo fermentation, and biocatalyzed electrolysis. Major constraints include lower hydrogen yields and rate of hydrogen production, bioreactor

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configuration, intrinsic limitations in light conversion efficiencies, etc. To overcome all these constraints, the advancements in the scientific research such as development of efficient bioreactor design, engineered hydrogenase enzyme, and genetic modified microorganisms are, therefore, strongly recommended for the enhancement of hydrogen yields and production rate. The future status of the biological hydrogen generation not only depends upon the research advances but also considering economic and social acceptance.

Keywords

Biomass · Dark fermentation · Photo fermentation · Bioreactor · Biocatalyzed electrolysis

10.1 Introduction

In the current scenario, most emerging areas in the environmental and energy sector are environmentally friendly approaches, i.e. energy and renewable sources. Previous study shown that presently 80% of the global energy requirements for the economy are met by the fossil fuel (oil, coal, and natural gas) (Ghimire et al. 2015). Excessive use of fossil fuels leads to the depletion of reserve energy resources and enhances the environmental pollution by releasing the by-products due to fossil fuel burning. Thus, it is considered as prime challenge not recently but in future as well (Akinbomi et al. 2015). It can be seen that energy consumption is growing fast at the rate of 2.9% in 2018 and fastest since 2010. However, presently, it is double on comparison with the 10-years average of 1.5% per year (BP 2019). On the other hand, one report highlighted on energy consumption that it will increase drastically to 35% from year 2014 to 2035, fossil fuel has significant contribution of 80% of the total energy supply (BP 2016). Thus, it is necessary to develop alternatives such as renewable and clean energy source to resolve the future energy demands by preserving our environment. Therefore, various research studies are going to explore and enhance the use of renewable energy options such as wind, solar, tidal, and geothermal energy, etc. In fact, remote areas still have challenges associated with the proper power supply which is heavily dependent upon the climate, geographical locations, high energy storage, and transportation cost (Wang and Yin 2018). Thus, the biomass-based energy has significant contributions in the global renewable energy sector which is the rapidly growing area and has a major share in the power production worldwide (Rathore et al. 2016). Thus, biofuels present a biodegradable, eco-friendly, sustainable, and cheaper and promising alternatives for the fossil fuels. Hydrogen among the biofuels is considered as a clean energy fuel (Lubitz and Tumas 2007). Hydrogen is a potential future alternative fuel which produces only water as a by-product when combusted and nearly zero air pollutant emissions. The hydrogen has high energy conversion efficiency with an energy yield of 142.35 kJ/g and considered as major source of energy (Bakonyi et al. 2013; Zhang 2010; Chowdhury et al. 2018).

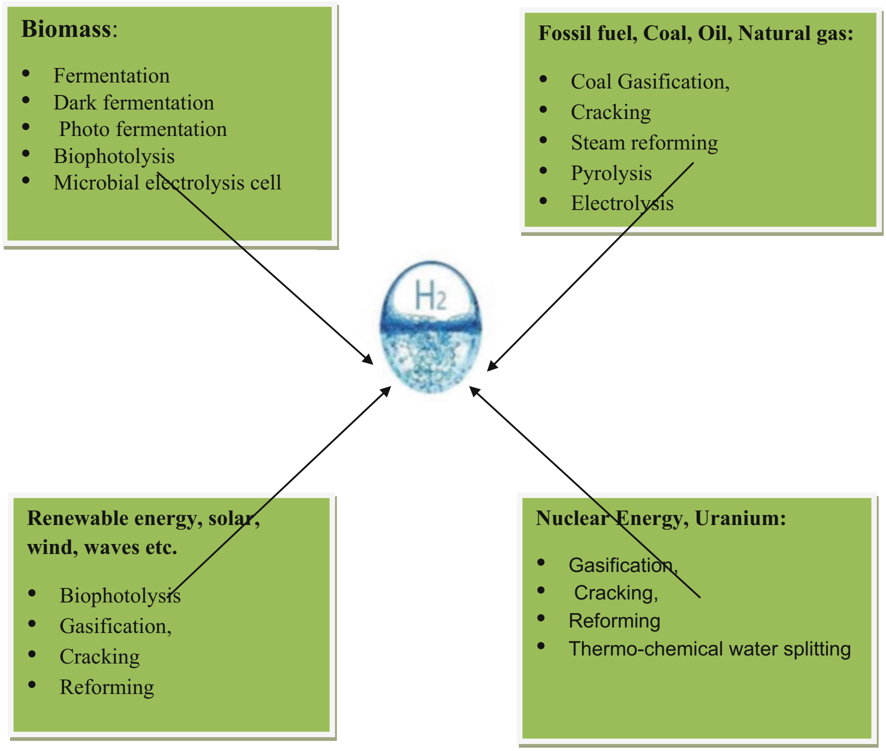

Fig. 10.1 Various sources of raw materials and method for the hydrogen production

Hydrogen can be generated using a variety of sources through many processes, technologies, and pathways (Fig. 10.1), and currently, main source of hydrogen production is based upon the fossil fuels (Das and Veziroglu 2008). Depending upon the initial raw materials, hydrogen can be produced by various ways like thermo-chemical conversion and biological way. Currently, most of H_2 used in industrial application is derived from natural gas (48%) and oil (30%) by steam generating systems, coal gasification (18%), and remainder from electrolysis of water (4%) (Bharathiraja et al. 2016).

The principal technologies of hydrogen production via conventional energy sources comprise steam reforming of natural gas and petroleum (50%), a process which leads to enormous emissions of greenhouse gases, natural gas catalysis, partial oxidation of heavy hydrocarbons, coal or coke gasification, and fractions of petroleum. These process technologies are based upon the high-energy intensive systems and require higher temperature, i.e., more than the 700 °C. For instance, all these processes have big environmental concerns by releasing the large amounts of the oxides of nitrogen, sulfur, and carbon as well as fly bottom ashes containing radioactive materials and heavy metal ions (Kapdan and Kargi 2006; Momirlan and Veziroglu 2002). However, two other processes such as plasma and electrolysis methods reveal a high efficiency for the hydrogen production which unfortunately expensive processing due to the higher energy demand (Holladay et al. 2009).

One of the earlier works cites the major advantage of biological process for hydrogen production due to less energy intensive as well as the ambient operating temperature and pressure (Basak and Das 2007a). Various renewable sources, i.e., biomass, organic waste, wastewater used for the production of hydrogen by biological methods, are known as the "biohydrogen." Biohydrogen can be produced by utilizing two major processes, i.e. photosynthetic (photo-autotrophic) and fermentative processes (dark and photo fermentation). Biohydrogen production process comprises with the indirect photolysis, direct photolysis, and photo and dark fermentation (Rai and Singh 2013). Several photosynthetic microorganisms such as photosynthetic bacteria, microalgae, and protists produce hydrogen (direct or indirect photosynthetic hydrogen generation) in which solar energy is directly utilized by these microorganisms involving photo-reactions. As far as, photosynthetic hydrogen generation can be seen practical and challenge to control and low utilizations of the solar light and problems in the designing of the reactors for hydrogen production (Pandu and Joseph 2012). In photo fermentation and dark fermentation process hydrogen production take place during the waste organic substrate conversion into the simpler organic compounds. The role of photosynthetic microorganisms and anaerobes leads to the transformation of carbohydrates into the end product as biohydrogen (Ghimire et al. 2015). Due to simple operation, high efficiency of hydrogen production and having capability to use various organic wastes, fermentative hydrogen process is beneficial as compared with the photosynthetic hydrogen production (Pandu and Joseph 2012). However, in dark fermentation process, biohydrogen production rate depends upon certain factors such as amount and type of substrate used, nature of microorganisms, bioreactor, metabolic pathway taken, and which type of end products formed (alcohols and acids). The formation of inhibitors inhibits the bacterial growth which directly reduce the hydrogen production rate (Nath et al. 2005; Rai et al. 2012; Rai et al. 2014a, b). Over the last many years, integrated systems involving both the dark and photo-fermentative process have got significant attention for biological H_2 production. Currently, researchers are focusing and started working on the integration of anaerobic waste processing having dark fermentation with the photo fermentation using the industrial wastewater as substrate for the photosynthetic purple microbes. Rai and Singh (2016) has investigated the strength of several microorganisms and their individual capabilities may be explored to overcome the shortcoming and weaknesses in the process. The present review deals with the different biohydrogen production technologies from the biomass used in past and recent years' progress made by the various researchers along with the future perspectives and scope.

10.2 Biohydrogen Production Technologies

Biomass as a sustainable resource could be employed for the production of bioenergy utilizing a number of various processes. Basically, there are mainly two routes used to transform the biomass into the hydrogen rich gas as final product. Two processes are (1) thermo-chemical conversion method and (2) biochemical or biological conversion method.

10.2.1 Thermo-Chemical Conversions

Thermo-chemical conversion involves the high temperature and chemical reactions during the production of hydrogen. Broadly, biomass is converted into clean fuel as hydrogen through the following processes:

1. Pyrolysis
2. Biomass gasification
3. Supercritical water gasification (SCWG).

10.2.1.1 Pyrolysis

Pyrolysis process entails the gasification of organic material at a certain pressure and temperature range of 0.1–0.5 MPa and 500–900 °C, respectively. The process takes place in the absence of air or oxygen, and thus, the formation of air pollutants in gaseous emissions such as dioxins, carbon monoxide, and carbon dioxide can be eliminated. The pyrolysis process is divided into the three processes from low (up to 500 °C), medium (500–800 °C), and high (over 800 °C) depending upon the temperature range (Demirbas and Arin 2004). The pyrolytic reactions are performed in the pyrolyzer or reactor where biomass enclosed with the long chains of hydrogen, oxygen, and carbon which are transformed into the small molecular chains for example tars, gases, and biooils (Shen et al. 2016). The rate of degradation of organic biomass wastes is frequently affected by the several operating process parameters, i.e. pressure in reactor, reaction temperature, biomass composition, heating rate of biomass, and the reactor configuration (OliveiraMaia et al. 2018). Biomass pyrolysis is one of the recent processes which transformed organic material into gaseous, liquid, and solid products with higher energy content (Gallezot 2012). One of the significant disadvantages of the pyrolysis approach is the fouling by the carbon formed at higher temperature and it needs to be controlled by the appropriate design of the reactor.

However, this technology has the potential to lower emissions in the form of the CO and CO_2 and the process could be operated in such a way for the efficient recovery of the solid carbon generated and furthermore easily sequestered (Muradov 2003; Demirbas and Arin 2004). However, the advantages of pyrolysis are compactness, fuel flexibility (wood waste, agricultural residues, and municipal solid waste, etc., as feedstocks), relative simplicity, clean carbon by-product, significant emission reduction, and higher efficiency.

10.2.1.2 Biomass Gasification

Biomass gasification is a controlled condition process that utilizes the steam, heat, and oxygen for the conversion of biomass waste into the synthetic gas at higher temperature via partial oxidation (Parthasarathy and Narayanan 2014; Barbuzza et al. 2019). The gasification system typically suffers from the lower thermal efficiency since moisture content of biomass needs to be vaporized at particular heating (Yamada 2006). The experiments carried out in the presence or absence of catalyst in the fluidized or fixed bed gasification reactor where fluidized bed gasification reactor always have better performance in hydrogen yielding. Furthermore, the oxygen or steam addition to the gasification system or process resulting into the steam reforming and steam reforming and producing a synthetic gas (H_2 to CO ratio of 2:1), which could be used as the feed to a Fischer–Tropsch reactor to make higher hydrocarbons or to a water gas shift (WGS) for the hydrogen generation (Chen et al. 2004; Asadullah et al. 2002; Demirbaş 2003; Hao and Guo 2002). It has been observed that hydrogen yield increases with increased temperature in the gasification reactor and partial pressure of the steam in the reactor. The formation of tars and CO_2 is the major technical limitation of the biomass gasification which are further major sources of the impurities to the produced synthetic gas (Zribi et al. 2019). In this scenario, various optimization parameters and final products for example in situ process of tar removal or post-gasification treatment which will decreases the challenges associated with the biomass gasification (Rios et al. 2018).

10.2.1.3 Supercritical Water Gasification (SCWG)

Biomass gasification in supercritical water is a clean and efficient way to transform the biomass into the hydrogen rich synthetic or producer gaseous products. Direct conversion of biomass into biohydrogen takes place without using highly intensive drying process to achieve efficient energy (Yoshida et al. 2003). Different types of wastes (e.g., agricultural wastes, leather wastes, sewage sludge, algal manure, black liquor, etc.) have increased interests in SCWG (supercritical water gasification). The main products of the SCWG process are H_2, CH_4, CO_2, and CO contents (Jin et al. 2018).

Most of the hydrogen bonds break above the water critical conditions, i.e., temperatures of 374.15 °C and 22.1 MPa, because of its unique physical properties (Antal et al. 2000; Adschiri et al. 2000). Thus, it has excellent transport characteristics that depend upon their high diffusion capability, lower viscosity, and the new reaction alternatives for the oxidation or hydrolysis. Furthermore, the system offers a better controlling mechanism depending upon these conditions and the operating parameters (Savage 1999; Bermejo and Cocero 2006). It was investigated that produced hydrogen content ranged between 26% and 57% when temperature reached at higher than the 700 °C and total conversion of corn silage and clover grass took place in supercritical water gasification (D'Jesús et al. 2006). The important concern about the modifications in the supercritical water gasification process by using some catalysts such as Ru, Ni, Pt, and alkali metal-based materials which can reduces the operating temperature and pressure. Furthermore, it will decrease the heavy initial equipment cost and operating costs as well (Azadi and

Farnood 2011). But during supercritical water gasification of biomass, poisoning, and deactivation of the catalysts further enhances the process costs which needs to optimize and studied accordingly. In supercritical gasification of biomass at higher pressure and temperature were found to be critical issues during hydrogen generation (Correa and Kruse 2018). It can be concluded that due to complex nature and interplay system of supercritical water gasification, designing of the an efficient and low-cost supercritical for raw materials such as biomass is still under investigations.

10.2.2 Biochemical/Biological Conversion Technologies

Biohydrogen production via biological route is one of the most suitable techniques where the processes can be operated under the normal room temperature and pressure. The other associated advantages of biological process are less energy demands and more environmentally friendly process (Mohan et al. 2007a, b). Therefore, biological route for hydrogen production utilizes the natural capabilities of microorganisms to produce hydrogen as important metabolic products. In modern era, this technology offers a variety of renewable raw materials sources or waste for the production of potential hydrogen in usable form (Tamagnini et al. 2002; Cheong and Hansen 2006). Biological conversion process from biomass and waste materials are basically dependent in the presence of hydrogen producing enzymes. The reactions involved in the enzymes catalyze are

$$2H^{+} + 2e^{-} \leftrightarrow H_2 \tag{10.1}$$

Three enzymes operate this reaction: Fe-hydrogenase, nitrogenase, and NiFe-hydrogenase. Biophotolysis processes utilize Fe-hydrogenase enzyme, whereas photo fermentation processes consume nitrogenase (Hallenbeck and Benemann 2002). Biological hydrogen production can be classified into the following groups: (1). Direct photolysis, (2). Indirect biophotolysis, (3). Photo fermentation, (4). Dark fermentation, (5). Two-stage or coupled process (integration of dark and photo fermentation), and (6). Biocatalyzed electrolysis.

10.2.2.1 Direct Biophotolysis

In biophotolysis process, the dissociation of water takes place by photoautotrophic organisms such as cyanobacteria and algae to produce hydrogen (Pandu and Joseph 2012). A direct biophotolysis for hydrogen production involves microorganisms which utilizes the solar energy and photosynthetic systems of algae and cyanobacteria to transform water into the chemical energy. The process of biohydrogen generation takes place though the absorption of solar radiations and shifting of electrons from the two groups of enzymes mainly nitrogenases and hydrogenases (Manish and Banerjee 2008). Biophotolysis technology has advantages as water is used as a primary feedstock, which is inexpensive and abundantly available in nature (Manish and Banerjee 2008). Under two conditions, a few microorganisms expel the surplus electrons by means of a hydrogenase enzyme which transform the hydrogen ions to hydrogen gas, (a) anaerobic conditions and (b) when large amount of energy is captured in the process (Sorensen 2005; Turner et al. 2008). One report highlighted the observations that the water-splitting process extracts the protons and electrons which are further recombined by a chloroplast hydrogenase for producing the molecular hydrogen gas with a purity of 98% (Hankamer et al. 2007). However, oxygen is act as the limiting factor for the process with the low yields and inhibition of the hydrogenase enzyme (Skonieczny and Yargeau 2009).

Researchers have been engaged into the laboratory engineered algae and bacteria focused upon the higher utilizations of the solar energy to hydrogen production. Furthermore, scientific communities are investigating on the identification or engineering of less sensitive microbes, isolation of the hydrogen and oxygen cycles, or changes in the ratio of photosynthesis to respiration to reduce the oxygen buildup (Milliken 2007). In the presence of sun light, culture preparation of green algae under anaerobic conditions and energy obtained under the deprivations from the sulphur would enhances the “hydrogenase pathway” which lead to the photosynthetically hydrogen generation (Melis 2002). Considerable amounts of internal starch and protein are consumed by cells under such sulfur deprivation hydrogen production condition (Zhang et al. 2002).

The reducing sites of the photosystem I are used to produce hydrogen gas along with the production of oxygen as by-product at the oxidizing sites of the photosystem II. The oxidation process of water molecules leads to the formation of electrons and to flow to ferredoxin (Fd). This further transfers the electrons to the hydrogenase for the generation of the hydrogen gas. Several green micro algae such as *Chlorella fusca*, *Platymonas subcordiformis*, *Chlamydomonas reinhardtii*, *Chlorococcum littorale*, and *Scenedesmus obliquus* have [Fe-Fe]-hydrogenase enzymes activity for the hydrogen generation (Eroglu and Melis 2011).

$$2H_2O + \text{Light energy} \rightarrow 2H_2O + O_2 \tag{10.2}$$

However, the hydrogen production rate through direct biophotolysis is relatively low. The dissociation of water and the use of solar energy only provide a working model for biohydrogen production. Hence, it is required to develop knowledge and technical innovations in the hydrogen enzymes (Pandu and Joseph 2012).

10.2.2.2 Indirect Biophotolysis

Indirect biophotolysis process, photosynthetic bacteria involves the utilization of carbon dioxide (CO_2) formed carbohydrates in the presence of light. These are subsequently fermented in the presence of the solar light to produce light energy and thereby released hydrogen molecules as by-products (Arimi et al. 2015). This is the two-stage process, in which the first stage, photosynthesis and carbohydrates storing taken place in the form of biomass. Furthermore, another stage, i.e., second stage, the fermentation process for the stored carbohydrates leads to the generation of the hydrogen gas. In these two process or stage system, carbon fixation and its evolution takes place (Benemann 2000). The process details of the indirect biophotolysis are presented in the following equations:

$$12H_2O + 6CO_2 + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (10.3)$$

$$C_6H_{12}O_6 + 12H_2O + \text{light} \rightarrow 12H_2 + 6CO_2 \qquad (10.4)$$

Cyanobacteria is an example among the all microorganisms that can produce hydrogen through the indirect photolysis method. For example, *A. variabilis*, a species of Cyanobacteria, was tested and reported as a potential candidate for the production of hydrogen through indirect photolysis. One challenge is observed in this process is the sensitivity of the carbon dioxide consuming microbes to oxygen which further inhibits the process (Arimi et al. 2015).

10.2.2.3 Photo Fermentation

In this process, photosynthetic microorganisms (anaerobic bacteria) are able to convert volatile organic acids including lactic acid, butyric acid, and acetic acid into the hydrogen gas in the presence of sun light. One type of bacteria is an example of purple non-sulfur (PNS) bacteria. These organic acids formed are utilized by the microbes as a carbon source for their metabolic activity thus releasing hydrogen as by-products (Ren et al. 2006). On comparison with the photosynthetic system of purple nonsulfur bacteria which is comparatively simpler to the green algae. This is composed of only light-based photosystem which is fixed in the intracellular membrane (Akkerman et al. 2003). Biological hydrogen production yield can be enhanced by the purple nonsulfur bacteria (PNS) through the suitable process parameters, e.g., light intensity, bioreactor configuration, carbon-to-nitrogen ratio, and inoculum time (Basak and Das 2007a, b). Green algae produced hydrogenase enzymes via photosynthesis, whereas photosynthetic bacteria produced nitrogenase enzymes, both plays a vital role in the biohydrogen generation. The major PNS microrganisms contributes in the hydrogen generation are, i.e., *Rhodobacter sphaeroides*, *Rhodopseudomonas palustris*, *Rhodobacter sulfidophilus*, *Rhodospirillum rubrum*, *Rhodobacter sphaeroides RV* and *Rhodobacter capsulatus* etc.

One study in this connection on the three various pure strains of the *Rhodobacter sphaeroides* (NRLL, RV, and DSZM) has been done to investigate the hydrogen yield and hydrogen production rates. The results observed that *R. sphaeroides* RV *strain* have increased the cumulative hydrogen gas generation (178 mL), hydrogen yield (1.23 mol H_2 mol^{-1} glucose), and the specific hydrogen production rate (46 mL H_2/g biomass/h) at 5 g/L of initial sugar concentrations among the other pure cultures (Kapdan et al. 2009). The hydrogen generation rates taken place through the activity of the nitrogenase enzyme which further leads to the generation of the hydrogen and works under the absence of the molecular nitrogen. The following Eq. (10.5) provided the hydrogen gas formation by the nitrogenase enzyme.

$$\rightarrow 2H^{+} + 2e^{-} + 4ATP \text{ Light nitrogenase} \rightarrow H_2 + 4ADP + Pi \tag{10.5}$$

The nitrogenase enzyme proper functioning requires the large number of ATP energy along with the strict environmental conditions. Several operating parameters such as temperature, light intensity, pH, and substrate concentrations are optimized and are necessary for the desired growth of the microorganism, e.g., PNS. It is also evident that the optimum value of the suggested parameters varies from substrate to substrate used and strain to strain, etc. (Koku et al. 2002). Furthermore, several other issues such as lesser number of nitrogenase (turnover), lower light transfer efficiencies, and higher cost of the photo-bioreactor yet to be managed. These issues could be mitigated by the enhancement and scale-up of the photo-hydrogen generation on the industrial level (Mishra et al. 2019).

10.2.2.4 Dark Fermentation

Dark fermentation is an anaerobic digestion process, in which hydrogen, carbon dioxide, and low weight organic acid are released in the presence of anaerobic microorganisms, dark environment grown, which utilize carbohydrates-rich substrates like glucose in the absence of light. Hydrolysis of higher carbohydrate such as hemicelluloses, cellulose, starch, or molasses converted into hexoses or pentoses (Hallenbeck et al. 2012). Dark fermentation process employs the facultative anaerobic or anaerobic bacteria, considered as the realistic approaches for the biohydrogen production (Levin et al. 2004; Brentner et al. 2010). It can be further classified into two systems: (a) Obligate and (b) Facultative anaerobic bacteria on the basis of their anaerobically biomass degradation capacity. Various microbe's species such as *Clostridium*, *Ethanolugenes*, and *Desulfovibrio* are known as strictly anaerobes, whereas *Citrobacter*, *Enterobacter*, *Klebsiella*, *Escherichia coli*, and *Bacillus* species are known as facultative anaerobes. One report cites that around 70% of hydrogen production was carried out the correlated with the strict anaerobe's genus *Clostridium* (Mishra et al. 2019). Biohydrogen production from this process can be accomplished in the presence of a mixed culture or pure culture of acetogenic-acidogenic microorganisms. The application of pure culture is advantageous due to easier detect/control of metabolic changes and also to disclose the condition that enhance the biohydrogen production at highest rate. While, from a technical point of view, mixed culture is advantageous because it does not involve sterile condition (cheaper raw materials can be used as substrate), may produce synergies between microorganisms and metabolization of complex substrates (De Sa et al. 2011; Niu et al. 2010; Elsharnouby et al. 2013).

This method uses pure sugars such as glucose, pentose, and hexose along with the organic matter as a substrate for the biohydrogen generation which makes the process environmentally friendly and less costly. Fermentative anaerobic bacteria break down the organic matter via oxidative methods to further increase their biomass and metabolic activity. During anaerobic environmental conditions, the electrons produced during the oxidation of substrates are disposed by the reduction of protons to hydrogen. This will help in maintaining the electrical charge neutrality of the cell systems (Levin et al. 2004; Das and Veziroğlu 2001). Basically, two hydrogenases' enzymes, i.e., [FeFe]-hydrogenase and [NiFe]-hydrogenase, are responsible for regulating the hydrogen metabolism. These enzymes catalyze the reversible reaction [FeFe]-hydrogenases are more active than [NiFe]-hydrogenases, in the production of molecular hydrogen whereas [FeFe]–hydro-genases are generally susceptible to oxygen (Mishra et al. 2004; Hallenbeck 2009). It was found that the theoretical maximum hydrogen yield from glucose (and other hexoses), and pentose in the dark fermentation is 32–33% (4 mol H_2/mol hexose) and biohydrogen production depends upon the metabolic pathways (ethanol, acetate, butanol, butyrate, format degradation or decomposition etc.) (Hallenbeck et al. 2012; Gómez et al. 2011). While as, when used mixed culture for biohydrogen production, the theoretical maximum yield of hydrogen is the roughly only 21%, with the butyrate as the major by-products (2.5 mol H_2/mol hexose) (Guo et al. 2014; Rafrafi et al. 2013). Various operational parameters such as temperature, partial pressure, metal ions or pH, affect the efficiency of dark fermentation (Trchounian and Trchounian 2015; Vasmara and Marchetti 2017). The reactor type and feed depend upon the particular parameters such as pH, temperature, substrate concentration, etc. Maximum efficiency of biohydrogen production from dark fermentation can be achieve by the optimization of parameters so that to avoid methane production at that condition and inhibiting Ni Fe-hydrogenase (Rai et al. 2014b). It was observed that biohydrogen production from dark fermentation has low yield but purification of hydrogen is achieved by using suitable mixed cultures and substrates. It could be further enhanced or maximized the conversion rates of biohydrogen by the combination of the fermentation in dark environment with the other processes (Parthasarathy and Narayanan Parthasarathy and Narayanan 2014; Singh and Wahid 2015).

10.2.2.5 Two-Stage Process (Integration of Photo and Dark Fermentation Process)

It was found that both dark and photo fermentation processes and technologies for biohydrogen production were significant. However, lower hydrogen yield along with accumulation of short chain organic acids is the main disadvantage of both the fermentation. These problems can be tackled by adopting the two-stage dark and photo fermentation technique. The waste matter dark fermentation is used as the substrate for photosynthetic bacteria of the photo fermentation process (Perera et al. 2010; Afsar et al. 2011). Two stage system can be separated into the combination of the photo and dark fermentation processes into the sequential single (co-culture) and two-stage process systems.

Sequential Two-Stage Process System (Photo and Dark Fermentation Process)

As compare with the single stage system and sequential two stages system of photo or dark-fermentation, the latter is considered to be the more effective mode of hydrogen production. In this system, two separate bioreactors are required in sequential manner to operate fermentation process under respective optimal conditions (Argun and Kargi 2011). In this process, hydrogen production is high because photo-fermenting bacteria consume the organic acids as substrate generated during dark fermentation by anaerobic bacteria. Highest theoretical hydrogen yield of 12 mol H_2/mol hexose sugar observed in this process (Singh and Wahid 2015). For instance, photo-fermentative bacterium utilizes acetic acid as a substrate produced during dark fermentation and gives overall hydrogen yield of the 12 mol/mol of glucose (Chen et al. 2008).

Stage-I: Dark fermentation (Facultative anaerobes):

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 \uparrow + 4H_2 \uparrow \quad (10.6)$$

Stage II: Photo fermentation (Photosynthetic bacteria):

$$2CH_3COOH + 4H_2O \rightarrow 8H_2 \uparrow + 4CO_2 \uparrow \quad (10.7)$$

The remarkable application of sequential two-stage systems is the utilization of industrial wastewater and organic wastes. Renewable biomass materials such as cellulose and starch have been investigated in various studies on the two-stage processes. Pre-treatment process can be done by utilizing acid or enzyme of starch and cellulose comprising biomass resources which reduce the appropriate substrates for the two-stage processes (Rai et al. 2014a, b). A lot of works have been reported for the hydrogen production from industrial and agricultural wastes via two stages, i.e., dark and photo fermentation up to till now (Kumar et al. 2017, 2016; Zong et al. 2009) studied the feasibility of hydrogen generation through sequential two stage system by utilizing cassava and food waste as substrate. On comparison with the single stage dark fermentation process, overall hydrogen yields were observed to increase by 4.08- and 3.05-fold for the food and cassava wastes when using two stage sequential photo and dark fermentation process. Mishra et al. (2016), confirmed the applications of the sequential two stages process by using palm oil mill wastewater as substrates. It was observed that in dark-fermentation process the hydrogen yield of 0.784 ml H_2/mL achieved by means of *Clostridium butyricum* LS2 as inoculum. When dark fermented effluents, subjected to the photo-fermentation by means of *Rhodopseudomonas palustris* as inoculum in the optimal physico-chemical environments and hydrogen yield increased to 3.064 mL H_2/mL POME (Mishra et al. 2016). However, the theoretical H_2 yield should be 12 mol/mol glucose via sequential dark and photo-fermentation but the practically it is very difficult to accomplishes that the standard values. Such invariability can be explained by suggesting the glucose uptake by bacterium for their metabolic process. Various inappropriate operational parameters i.e., pH, temperature, and the performance parameters of the system (conversion rates of inoculum) etc. can be expected constaints to attains the theoretical hydrogen yields (Fig. 10.2) (Ren et al. 2011).

Single Stage (Co-culture) Process

One important parameter related to increasing cost in the sequential two stage reactor, in which two separate bioreactors are required. However, in most of the cases pre-treatment of industrial effluents in dark fermentation is necessary that could be expensive. The advantages of integrating the dark and photo fermentations, is only single stage co-culture process where both the fermentation process taken

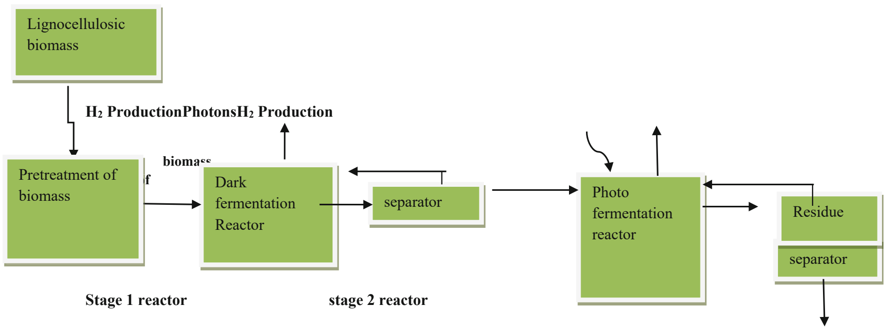

Fig. 10.2 Sequential dark and photo fermentation system for the hydrogen generation using biomass

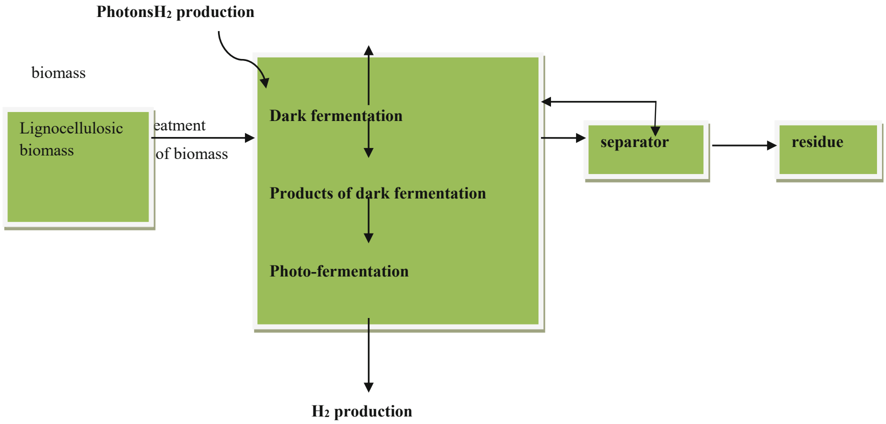

Fig. 10.3 Schemes of the combinations of both the dark and photo fermentation process for hydrogen generation utilizing the biomass

places by instantaneously in the similar reactor (Yokoi et al. 1998; Ozmihci and Kargi 2010). Microbes involved in the dark fermentation process used up organic wastes as substrates to yield hydrogen and volatile fatty acids (VFAs). Thus, volatile fatty acids (VFAs) generated via dark fermentation were consumed in situ through the photo fermentation microbes as substrates for the hydrogen generation. Besides these, no additional requirements of the outdoor pH alteration, inhibition of substrates, and decreased in the operational time duration having benefits of the co-culture process over the two stages sequential dark and photo-fermentation and process is investigated on the single stage process (Ozmihci and Kargi 2010). Figure 10.3 presents single stage (co-culture) processes for the hydrogen generation from biomass.

10.2.2.6 Biocatalyzed Electrolysis

Microbial electrolysis cell (MEC) utilizes various types of microorganisms to activate the reactions on the electrodes, also known as biocatalyst electrolysis (Sabourin-Provost and Hallenbeck 2009). MEC process is frequently manufactured from various polycarbonate plates. Various bacteria such as *Shewanella*, *Pseudomonas,* or *Geobacter* are growing on the surface of the anode on the MEC (Gómez et al. 2011). Furthermore, the community composition and function of the microorganisms at the cathode are not well understood (Logan et al. 2008). Electrochemically assisted microbial fuel cell (MFCs), bioelectrochemical systems (BES), and microbial electrolysis cell (MECs) utilize various types of microbial species to catalyze the biochemical reactions at the cathode and/or anode. Furthermore, this process during the electrolysis can generate the electrons and protons from the oxidations of organic materials (Liu et al. 2005; Logan et al. 2008; Jeremiasse et al. 2010).

The following equations represent the reactions involved in the evolution of hydrogen in BESs:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{10.8}$$

$$\text{Anode} : CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \tag{10.9}$$

$$\text{Cathode} : 8H^+ + 8e^- \rightarrow 4H_2 \tag{10.10}$$

The voltage required to degrade the water in microbial electrolysis systems is around 1.2 V (Liu et al. 2010) and the hydrogen generation rates were 0.2–3 m^3 of hydrogen per m^3 of water per day (Gómez et al. 2011). According to Yang et al. (2021) the potential produced by bacteria is too low for water-splitting and needs to be reinforced by an external energy source to generate hydrogen. According to Logan and Regan (2006) potential 0.3 V produced by bacteria should be increased to 1.23 V for water-splitting. To solve this problem MREC (Microbial Reverse-Electro Dialysis Cells) system was designed. It is also evident that on comparison with the dark fermentation process, hydrogen generation rates are lower in case of microbial electrolysis cell. Hydrogen production technology via MEC system is estimated to increase drastically in the upcoming years. The major challenge associated during the formation of MEC system practically, is the requirements of the outward power supply to increase the energy of the generated electrons, replacement of costly electrodes, decrease in the voltage output etc. and all these hurdles have to be removed (Hallenbeck and Ghosh 2009).

10.3 Limitations in Biological Hydrogen Production

In this section, we have given some details about the smooth change in the economy from fossil fuel based to the renewable energy (hydrogen) based economy as follows:

- Thermo-chemical conversion technology such as pyrolysis, gasification, SCWG, although attractive, but all are energy intensive process. Low hydrogen yield is the major disadvantage of the process.
- Direct bio photolysis processes, is although environment friendly biological process, but the oxygen sensitivity, low hydrogen yield and intrinsic limitations in the light conversion efficiencies are the major obstacles.
- In indirect bio photolysis process, the utilizations of nitrogenase enzyme activity with its inherent high energy demands, and the low solar irradiation with the conversion efficiencies are the insurmountable parameters.
- The major drawback of photo fermentation process involved low photochemical efficiencies (3–10%), lower nitrogenase turnover number and requires the expensive photo-bioreactor.
- Some biomass feedstock processing is too expensive and thus, it is needed to develop the less cost-based techniques from the growing, harvesting, transporting, and pre-treatment of the biomass.
- It was a key challenge to develop metabolically engineered microorganisms which was proficient to induce the hydrogen production rate.
- In dark fermentation, the by-products, for example, acids and alcohols deposition outside a certain restriction of the microbial growth. Therefore, it will further inhibit the hydrogen generation and process termination with reduction in the hydrogen yield. However, the feedstock waste or substrates is not entirely used and the process leaving behind the large quantity of wastewater from the bioreactor overloaded with the higher amount of the VFAs. The system can be made more efficient to substrate utilizations and environmental preservation, and therefore, a second stage is essential to improve the energy from the wastewater and its bioremediations.
- Various engineering problems and issues requires to be addressed which include the appropriate bioreactor design, substrate concentration, and separation and purification of hydrogen.
- The hydrogen productivity and yield from any of the processes mentioned above having low commercial applications.

To overcome all these challenges and limitations, further improvement in the research design needs to be done. The advancements in the scientific research for example development of bioreactor design, engineered based hydrogenase enzymes, and genetic modified microorganisms furthermore needs investigations and research to increase the yield and production rate of biohydrogen. Several researchers are working to carry out the scientific and technical advancements for the better output for biohydrogen as a futuristic fuel.

10.4 Conclusions and Future Prospective

Biomass is considered as one of the major renewable sources of the energy in global and it is sustainable, large quantity availability, and regeneration potential. Biomass accounts for the primary energy source and major portions of biomass consumption in the developing countries. The biomass-based hydrogen production could be utilized to achieve the challenge faced in the present scenario to search alternatives for future energy demands as well as the greenhouse gases emission. The present chapter focused on several thermochemical and biological techniques that have been investigated to produce biohydrogen such as pyrolysis, gasification, dark fermentation, photo fermentation, biophotolysis of water, etc. The thermochemical processes are energy intensive and operational cost is high. Biologically hydrogen production methods are environment friendly, require input of low energy, and easy handling processes. Still, there are some limitations and hurdles in the process; therefore, a proper planning, execution, and updates in the recent technologies are the need of hours. Furthermore, several types of waste could be utilized for the production of hydrogen fuel and its rate and yields could be enhanced by utilizing knowledge and development of the process optimization, industrial microbial strain and metabolic engineering. By seeing the recent scenario, the recent advancements in the area of the hydrogen technologies, and this could be that hydrogen era have been already started. In fact, there are various other sources of renewable energy which are available in the market, but in realistic situations, one kind of energy source cannot be completely replaced the fossil fuel. The changing energy requirements in developing and developed world could be mitigated by the incorporationof latest technologies, processes, and energy sources. The future scenario of biohydrogen production not only dependent upon scientific advancements i.e., the improvement in efficacy though the genetically modified microorganisms. Moreover, the bioreactors developments and economic considerations (at the cost of the fossil fuels), social acceptance along with the hydrogen energy sources.

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Part III

Bio-economy: Policy Trends, Challenges and Implications

Bioenergy: Technologies and Policy Trends 11

Har Mohan Singh, Shubham Raina, Atin Kumar Pathak, Kajol Goria, Richa Kothari, Anita Singh, Ashish Pathak, Sanjeev Anand, and V. V. Tyagi

Abstract

Fossil fuel-based energy economies are shifting towards a renewable energy-based economy. Renewable energy comes from naturally replenishing sources with low carbon emissions. Solar, wind, bio and geothermal are well-accepted renewable energy sources. Among renewable energy, bioenergy is the prominent energy source that is utilized in the form of biofuels for transportation, bioenergy for heat and power applications. Most of the bioenergy is obtained from biomass and crop residues, and wastes materials, energy crops as the main feedstock. There are several bioenergy conversion technologies employed at the commercial level which are combustion, gasification, pyrolysis, torrefaction, hydrothermal processes, anaerobic digestion, fermentation and transesterification. The roles of bioenergy conversion technologies are to provide reliable and sustainable energy that have needed a policy framework. Bioenergy policies define the target based for technology-specific policies to regulate energy production, distribution and utilization. This article is focused on bioenergy technologies and bioenergy policies.

Keywords

Bioenergy · Bioenergy policies · Bioenergy conversion technologies

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11.1 Introduction

Solar is the 'mother' of all kinds of renewable energy on the earth and the primary component of nutrition for green plants. Biomass is the storage form of chemical energy which forms by the process of photosynthesis between green plants and sunlight (Abbasi et al. 2011) (Fig. 11.1). Energy is considered an essential tool in the development of social and economic activities in the origin of human civilization. The rapid economic growth of the world and demand for energy is increasing day by day. Conventional energy sources such as coal, petroleum oil and natural gas play an important role in the present time. These energy sources create the massive gaseous substance that changes the constitutional model of the atmosphere, i.e., pollution. This changing model is a serious concern of many international bodies because it adversely impacted on flora and fauna.

Depletion of fossil fuels is the paradigm shift toward renewable energy sources like biomass, wind, solar and tidal energy. Renewable energy sources are the resources that can be used to produce energy again and again and are also often called alternate energy sources. Renewable energy is considered a locally abundant, clean and inexhaustible source of energy and optimum use of these sources can minimize environmental impacts. As time passes, the share of renewable energy is gradually increasing and in 2019 it reached 27% of the global electricity production (Renewables 2020) and it is continuously increasing. The most important and challenging task for energy policymakers is to better understand the developing world like India, Brazil and China. Energy consumption in the non-Organization for

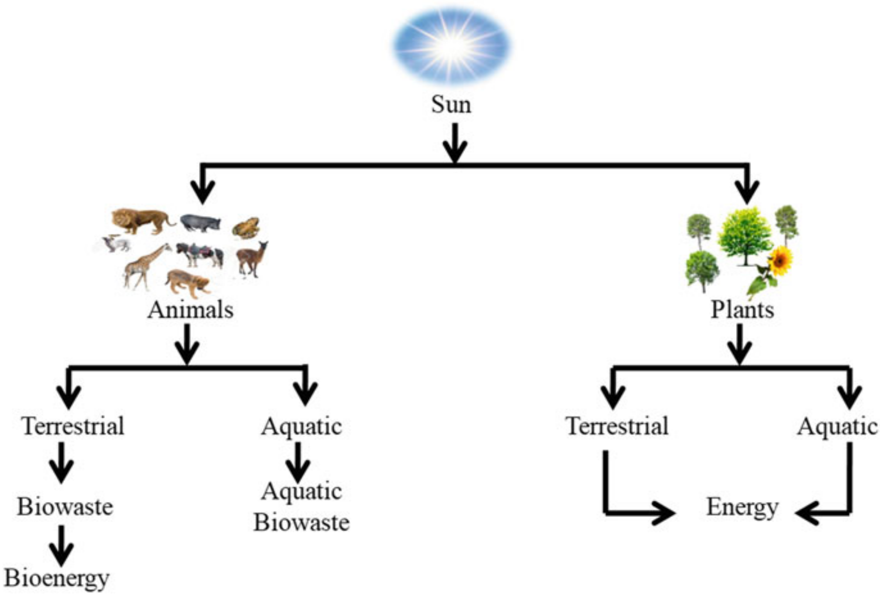

Fig. 11.1 Pathway of solar energy on the earth (Abbasi et al. 2011)

Economic Co-operation and Development (OECD) countries exceed in 2008 and is predicted to grow by fivefold much as much over the upcoming next 25 years (US Energy Information Administration 2013). Many developed and developing nations have been involved to promote renewable energy options for clean sources by making financial incentives policies. These policies have shown fruitful outcomes and make sure the cost of renewable electricity generation and energy conservation efficient technologies have come down over the past few decades.

In India, biomass fuel is dominated in rural energy consumption culture. Biomass-based fuels are playing a key role in rural energy security and most of the components of biomass energy comprise crop residues, cattle dung and forest wood. Energy shortage and rising fuel prices are altering the pattern of biofuel consumption. Due to this reason, biomass energy conversion is becoming dependent on various crop residues and animal dung. It may be a better solution of deforestation and other environmental degradation. Therefore, bioenergy technologies such as biogas, gasifiers are low-cost solutions for energy security in the country.

Bioenergy policy and programmes are the documents of future vision that define the roadmap for bioenergy targets. Various programmes and policies are prepared by the Government of India from time to time so that low-cost sustainable energy security is ensured in the country. Apart from national wide programmes, some regional or state-wise policy programmes are also run by states based on their need for energy. The present article is categorized into two main parts bioenergy technologies and bioenergy policy and programmes.

11.2 Carbon Neutral Biomass Energy

Biomass-based fuels are the first-ever energy feedstock utilized by humans and it was the backbone of the fuel economy in the eighteenth century. Although carbon emissions of biomass-based energy conversion technologies are high (such as biomass gasifiers) but net carbon emission of biomass conversions technologies are considered almost zero because biomass produced by the photosynthetic process which requires solar radiation and atmospheric carbon dioxide. Thus, carbon emission is almost equal to carbon sequestration in the form of biomass (Fig. 11.2) (Sinha et al. 2019). It is defined that biomass is a renewable energy source, easily grow on the earth. Plants have natural mechanisms that provide better environmental tolerances and robustness to enhance photon efficiency during the wide life span. Presently solar technologies such as photovoltaics or solar collectors are required high costs. However, solar technologies have low energy conversion efficiencies. Green plants have great potential to store a large amount of energy in the form of biomass (Friedland et al. 2019). Many agricultural and forest plant species are recognized to directly mineralize the atmospheric CO_2. Therefore, the cultivation of such plants is use cost-effective storage of atmospheric carbon in both prospects of food and fuel. Economic profits are feasible only if the value of biomass products provides a long period of social and environmental gains.

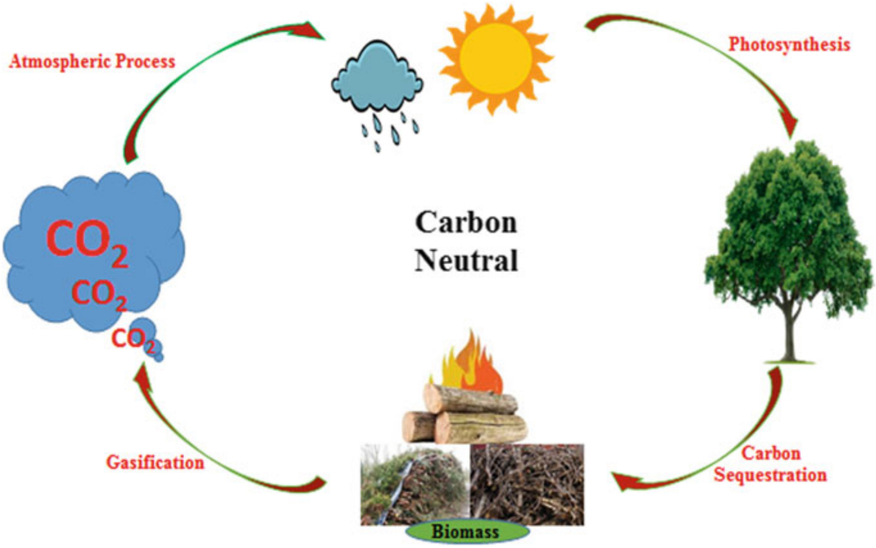

Fig. 11.2 Carbon neutral cycle of bioenergy

11.2.1 Biomass

Biomass stores energy in chemical form and it is the most valuable and dynamic asset on the planet. It includes plantation that produces energy crops by natural growing vegetation and carbon-based waste in the form of residues and organic waste. Residues from agriculture and forests, herbaceous as well as energy crops, aquatic flora and waste from municipalities in the form of municipal solid waste, animal waste are major waste types. Table 11.1 elaborates on various types of biomass feedstock and their prospective energy generation technologies.

11.3 Bioenergy Technologies

There are various types of bioenergy energy conversion routes developed and bioenergy use categorized traditional and modern technologies. Traditional use is mostly based on solid combustion of biomass such as wood, animal waste whereas modern bioenergy technologies are based on solid as well as liquid combustion such as biogas (anaerobic digestion), gasification, torrefaction, hydrothermal processes, fermentation and many more. Table 11.2 describes the advantages and limitations of bioenergy production technologies.

Table 11.1 Different types of biomass feedstock and prospective technologies for energy production

Supply sector	Types	Examples	Prospective technology
Agricultural residues	Lignocellulosic agricultural residual wastes	Rice straw, wheat straw, rice husk, corn stover, cotton residue.	Gasification, combustion, liquefaction and biogas
	Livestock waste	Urine, dung, wash water, residual milk, poultry litter	Biogas
Dedicated energy crop	Lignocellulosic woody and herbaceous energy crops	Corn cobs, poplar, eucalyptus, acacia sp., sorghum stalks, miscanthus, switchgrass	Gasification, combustion, liquefaction and biogas
	Oil crops	Cane beet, sugar beet, sweet sorghum	Biogas and bioethanol
	Starchy crops	Sugarcane-bagasse, wheat, maize, barley, potatoes, amaranth	Bioethanol
Forestry	Forest residue waste products	Wood chips, branches, leaves, bark, grasses	Gasification
Industry	Residual waste of wood industry	Plywood, pieces of wood, poles, sawdust, fibres, vegetable waste, pulp, off-cuts, bark	Gasification, biogas
Others (garden waste/ wastewater)	Roadside plants and grasses	Grasses and plant parts, sludge	Gasification, combustion, liquefaction and biogas

11.3.1 Biogas

Biogas production from biomass appears to have a large potential as a renewable source of energy as biomass is abundantly available throughout the country. The anaerobic digestion of biomass needs low capital investment as compared to solar, wind and hydro. Production of energy from biogas is widely spread and well-known technology in rural parts of the country. The major feedstock is locally abundant in the form of agriculture and forest wastes (Morero et al. 2015). Biogas is free from price fluctuation in world energy market and uncertain transportation cost of petroleum energy sources is also absent. With the population expansion, the growth rate of different energy consumption areas (such as heating and transport) is increased significantly, this has resulted in a big gap between energy demand and supply. Domestic energy demands as cooking, dairy and lightning are the main important sectors in villages (US, Department of Commerce, International Trade Administration 2008), which can easily complete by biogas.

11.3.1.1 Principle of Anaerobic Digestion

Anaerobic digestion or methanization is a biological process in which organic compounds are converted into methane (CH_4) and carbon dioxide (CO_2) through

Table 11.2 Advantages and limitations of bioenergy production technologies

Technology		Advantages	Limitations	References
Anaerobic Digestion	Fixed dome	Low-cost, long plant life, low maintenance, space saving	Risk of gas leakage in case of crack, underground tanks are hard to repair, high labour cost, gas pressure is not constant	Cheng et al. (2014)
	Floating drum	Easy operation, constant gas pressure, visualization of gas content due to floating storage drum	High installation cost of steel drum, short lifespan, regular painting of drum required to avoid corrosion	
	Bag/ balloon type	Low-cost, easy to install and maintain,	Short lifespan, structure can be easily damaged, low gas pressure	
Gasification	Updraft	Can process feedstock with high moisture, high tar content adds to the heating value of syngas	High tar content, low heating value of syngas, limited feeding rate, scale limitations	Beohar et al. (2012), Sikarwar et al. (2017)
	Downdraft	Low concentration of tar and particulates in the syngas	Low heating value of syngas, cannot handle feedstock with high moisture content, small feed size	
	Entrained flow	Scalable as per need, produces low tar, high-grade syngas, highly economical for large scale	High volume of carrier gas is required, higher particle loading, issues with raw syngas cooling	
	Fluidized bed	Low installation cost and easy to maintain, applicable for large scale, feedstock receives uniform temperature	Not suitable for small-scale operations, high load of particulate matter	
Combustion		Easy to operate, well-developed.	Low calorific value and thermal efficiency, high emission of pollutants	Awasthi and Bhaskar (2019)
Pyrolysis		Capable of processing different feedstocks, fast processing speed, requires less space for installation, low emission	Production of residual ash that may be rich in heavy metals and toxic inorganic salts, processing of plastic waste produces harmful emissions such as dioxins and furans	Caruso et al. (2019)

(continued)

Table 11.2 (continued)

Technology	Advantages	Limitations	References
Torrefaction	Increases energy density, reduces transportation and storage cost of char	Briquettes formation requires additives, susceptible to auto-ignition at high temperatures, not suitable for feedstocks with high moisture content	Eseyin et al. (2015)
Hydrothermal Processes	Can process wet biomass, use multiple feedstock	Blockage and corrosion of reactor, recycling of catalysts is not easy, high installation cost	Zanon Costa et al. (2020)
Fermentation	Bioethanol is a renewable fuel, less emissions on burning, high octane fuel	Hydrolysis of lignocellulosic biomass is a complex process, requires large land for feedstock cultivation	Segovia-Hernández et al. (2022)
Transesterification	Produces clean fuel having low sulphur content, high cetane number, low toxicity	Produced fuel has a high viscosity	Amirthavalli et al. (2022)

the action of microorganisms. This technology transforms solid and liquid waste into valuable gas and prevents global warming emissions. Anaerobic digestion can be categorized into a minimum of two steps. In the first stage that is also called as acid phase, complex organic compounds are converted into simple organic compounds which are then digested by acid-forming bacteria to produce acetic acid. This acetic acid is further transformed into methane through the process of methanogenesis (Singh et al. 2020). The by-products of anaerobic digestion are methane (55–75%) and carbon dioxide. A small fraction of hydrogen sulphide is also generated that marks the odour characteristic of digester gas.

11.3.1.2 Utilization of Biogas

India is implementing different renewable energy programme that is among the biggest on the global level. India ranks second in biogas production. Biogas can be easily generated and supplied at remote locations. Biogas provides sustainable solutions for fuel production, management of organic waste and the generation of organic manures. Biogas composition and their fuel properties make it sure for utilization in various areas as their requirement Fig. 11.3. Bottling of biogas is also one of the emerging technological aspects to prevent the black carbon emission from the chulha (traditional cook stove) in the rural part of the country. The purified biogas can be compressed in the bottle and are easy to transport. Biogas has many

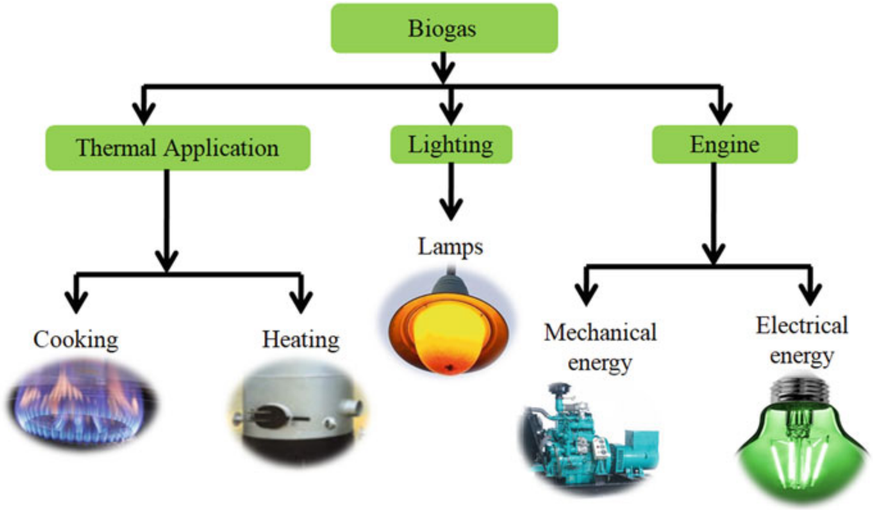

Fig. 11.3 Biogas utilizations

combustion and compositional features to compare with natural gas (Kapros 2009). Indian Institute of Technology—Delhi (IIT-Delhi) has successfully developed a technologically advanced yet simple and low-cost biogas up-gradation system through which biogas can be upgraded to automobile fuel-oil having up to 95% methane purity level (Vijay 2013; Jain et al. 2015). Rural lighting, cooking, thermal applications of biogas are traditionally adopted in various parts of the world. Apart from this, combined heat and power (CHP), Bio-CNG are emerging applications of biogas.

11.3.2 Thermo-Chemical Conversion

The term implies thermo-chemical conversion the use of heat to change biomass into other forms. Thermo-chemical conversions are the group of methods employed in the production of different biofuels from lignocellulosic biomass. It includes combustion, liquefaction, gasification and pyrolysis. Different potential energy types are heat, liquid fuel, steam, electricity. Thermo-chemical processes have several advantages, including feedstock flexibility, conversion of both carbohydrates and lignin into valuable products, easy and faster transportation and reaction rates. Sewage sludge is also possible to convert into energy by thermo-chemical conversion. The treatment of sewage by thermo-chemical conversion is also providing a good opportunity for mineral recovery like phosphorous including soil conditioners.

11.3.2.1 Combustion

Combustion is the most commonly used method for biomass conversion into energy. It comprises the largest share of biomass energy generation that is about 97% of the world. Perhaps, it is the oldest method of biomass utilization from prehistoric times, burning of biomass for heat. In developing countries such as India, the combustion of biomass is used daily for heating and cooking food (Demirbas 2007). Combustion involves high-temperature burning of biomass in excess air (oxygen); heat is generated along with carbon dioxide and steam. In this process, volatile gases contribute more than 70% of the total heat generation. These volatile gases appear as yellow flame over the fuel bed. Fouling and corrosion are major concerns associated with the combustion of biomass. The combustion of dry feedstock on an industrial scale (i.e. large scale) is a complex process because there are various technical challenges in the biomass characteristics, co-firing process, combustors design, etc.

11.3.2.2 Gasification

Gasification is a promising approach to convert biomass into useful combustible gaseous products and gasification of biomass produces gas, syngas and other useful products. It offers a clean and highly efficient conversion process and converts various types of biomass feedstock into a wide variety of applications. Biomass gasification is a procedure involving the conversion of carbonaceous dry biomass into different combustible gases having specific heating values in limited oxysious (35%) conditions. In general, gasification is to create valuable gaseous products and combustion focused only on heat generation. Biomass gasification has double the potential for electricity generation than conventional boilers. With great efficiency, heat coming out of the gas turbine exhaust can be utilized for additional power production with a steam cycle. Gasification is an eco-friendly process as compared to combustion because gasification produces low emission of toxic fumes into the air and the more dynamic usage of the solid residues (Rezaiyan and Cheremisinoff 2005; Marsh et al. 2007). At present, gasification systems are being adopted in developed as well as in developing countries for heat and electricity generation. As the advancement in the technology of modern biomass gasifiers are widely accepted in place of coal gasifiers for small-scale industries such as bakery because of the abundance of biomass feedstock. Gasification technology has already been employed commercially in different regions of the country. In India since 1999, gasification continues for electricity generation. The sugar industry is a well-known example of gasification technology at the industrial level in which heat and power both are produced for captive use (Arora et al. 2010).

Gasifiers

The generation of gas from coal-based systems was started at the end of the eighteenth to the middle of the nineteenth century's story. Gasification was a prominent source for domestic and industrial use in the twentieth century. During World War second gasification was re-emerged by the effect of shortage of petroleum. It is estimated that nine million vehicles were running on producer gas in

World War second. Later on, domestic and industrial utilization of gasification decreased as economically viable technologies of fossil fuel came into existence (Breag and Chittenden 1979). Gasification takes place in specialized reactors known as gasifiers. Generally, gasifiers convert solid fuels into gaseous fuels. The gasification process also involves oxygen removal from the fuel to enhance the energy content. Due to this, the useful fuel gas holds only a little fraction of oxygen. Gasifiers can be divided into four zones that are based on different reaction types: dry zone where biomass moisture is evaporated; the pyrolysis zone, in this zone biomass is pyrolysed to produce char and volatiles materials with moderate calorific energy, the combustion zone where combustion reactions take place and the fourth zone is the reduction zone involving the production of hydrogen and carbon (Rajvanshi 1986). There are various types of gasifiers available as their requirement and various technological improvements are continuously making more accepted by current needs.

Fixed-Bed Gasifier

The fixed-bed gasifiers consist of cooling and cleaning systems. The fixed-bed reactor consists of a bed of solid fuel particles allowing movement of gasifying media and gas in either up or down direction. Fixed-bed gasifier is simple in construction having cylindrical fuel space, fuel feeding unit, as ash removing compartment and gas exhaust. The construction matter may be fire bricks, steel or concrete. It is used for long biomass solids conversion low gas yield and high ash content. It requires mechanically stable feedstock in the form of briquettes with particle sizes 1–3 cm (Riva 2006). Presently, the research focused on the catalytic conversion of tar for thermal performance. The cleaning and cooling system of gas usually consist of a multi-filter approach through cyclones and dry or wet gas scrubber filters.

Downdraft Gasifier

The downdraft gasifier is presently one of the most extensively used fixed-bed gasifiers. In the downdraft, air enters at the combustion zone and the product gas leaves near the bottom of the reactor. In this system, the air is injected into the reactor from the middle part. The hearth zone reverts the air in the reduction zone. The drying and distillation zone is pre-heated by the heat of the hearth zone. Most of the char is burned in this zone and, carbon dioxide and H_2O are eventually converted into carbon monoxide (CO) and hydrogen gas. The major benefit of this type of gasifier is that the thermal cracking of the tar is possible which is produced during pyrolysis. The design of this type of gasifier is a little bit complex to the updraft, but this construction makes sure complete burning of tar and also the exhaustible gases are comparatively cleaned that is not possible in the updraft gasifier (Fig. 11.4). The gas leaves at a higher temperature hence the efficiency of the gasifier is low (Vladimir and Tim 2015). This type of gasifier is most commonly used for engine application because of its ability to produce a comparatively clean gas. Downdraft gasification is simple, reliable and the most accepted technology for agro-waste. In this gasifier relatively dry (30 wt% moisture) with a maximum of 30 cm long coarse

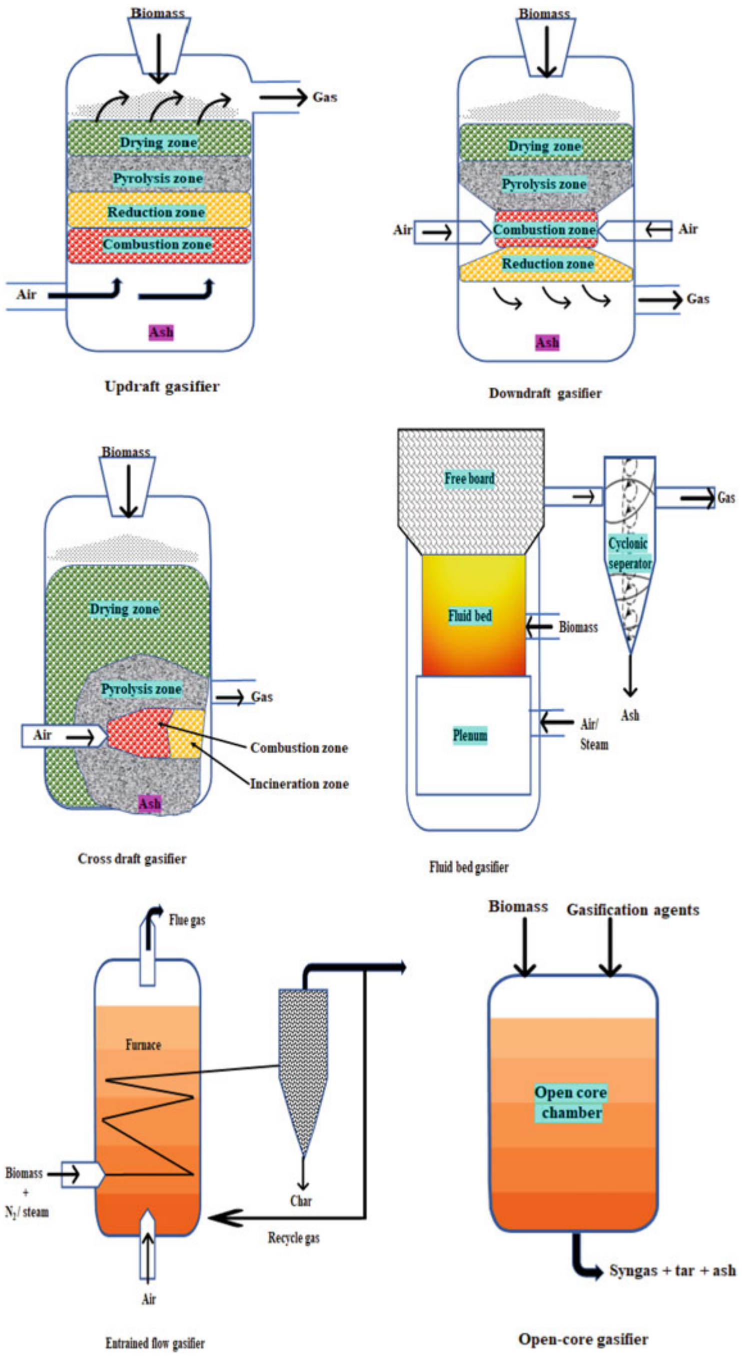

Fig. 11.4 Different types of gasifiers

biomass are allowed and this quality makes sure to small-scale electricity production through an internal combustion engine and it has an ideal production limit in the range of 0.05–1 MWth.

Updraft Gasifier

The updraft gasifier is also one of the oldest and simplest systems. The biomass feedstock is fed at the top, and oxygen or air passes upwards via a hot reactivate zone near the bottom of the reactor having an opposite direction to the flow of solid material. Feedstock material is pre-dried through a 'drying zone', then it is moved further to the distillation or pyrolization zone. During the pyrolization, feedstock undergoes decomposition stage and is converted into different volatile gases and solid residue as char. The reduction zone converts the gases and char into CO and H_2 gas. Some amount of char settles at the bottom of the gasifier, and an exothermic reaction takes place through the process of combustion in the 'heart zone'. Most of the small-scale gasifiers are based on the fixed-bed updraft (Fig. 11.4). It accepts biomass with high moisture content (about 60%) and produces high ash content (about 25%). The overall energy efficiency through this method is high because the produced gas escaping the gasifier at a low temperature does not take away much heat (Vladimir and Tim 2015; Ding et al. 2018). Updraft gasifier has been commercialized for small-scale application, for example cooking stoves developed for use in rural areas.

Cross-Flow Gasifiers

In cross-flow gasifiers, the feedstock material down-flows while air is introduced from either side of the reactor and the product gas is released from the opposite side of the reactor at the same horizontal level. The hot combustion zone forms around the air and a pyrolysis and drying zone are formed at the upper portion of the vessel. Ash formed due to high temperature (800–900 °C) fall on the bottom and does not hinder operation. The high exit temperature of the gases and low CO_2 reduction causes a reduction in the efficiency of the reactor. The fuel in the vessel behaves like a shield against radiant heat. The cross-flow design of the reactor is less suitable for the high-ash and the high tar fuels. If the top of the reactor is open then it can handle high moisture content because radiated heat can evaporate most of the water vapour into the atmosphere (Fig. 11.4). The reaction zone is relatively small with a low thermal capacity that makes a fast response, i.e., take a short start-up time (5–10 min). The particle size of the biomass should be controlled as unscreened feedstock can create clotting into the reactor. Therefore, this type of gasifier works more efficiently with charcoal or pyrolysed fuel and is commonly used in light and small (<10 kWe) applications (Motta et al. 2018; McKendry 2002; Vladimir and Tim 2015).

Open-Core Gasifier

Open-core gasifiers are used for low-density fuels. This is best suited gasifies employing widely to gasify agro-biomass. It has a wide throat and mouth that is sophistically used for injection of feedstock without bridging. The rotatory grates and water basin at the bottom end of the gasifier are specially developed for the removal of ash during the gasification process (Rowland 2010). Particularly rice husk gasifiers require continuous ash removal systems because rice husk, results a large volume of ash about 55% (Fig. 11.4).

Fluidized-Bed Gasifiers

It is the most accepted gasifier and provides excellent mixing characteristics with higher reaction rates of the gas-solid mixture and uniform distribution of temperature within the reactor. A simple fluidized-bed gasifier comprises a chamber having a bed of inert particles. The bed temperature is maintained at 700–900 °C. Pressurized air is circulated through the distributor plate and the velocity of injected air is gradually increased so as to support the entries weight of the bed by the fluid drag on the bed particles by the effect of up-warding airflow (Fig. 11.4). Due to this, a moving mass of solid fluidized particles is produced on the bed. The same phenomena occurred in the bubbling fluidized gasifier (Hanchate et al. 2021; Motta et al. 2018). The size of fluidized-bed gasifiers can be designed easily as per requirement.

Entrained Flow Gasifiers

Entrained flow gasifier is characterized by the feed and co-current movement of air. This generally means that the gasifier has a short residence time (about 1 s), a higher temperature range (1300–1500 °C) and a small particle size of fuel. Due to high operating temperature and pressure (20–50 bar), repeated cooling of gas is required and this leads to the lower thermal efficiency of the gasifier. The heat recovered during cooling can be re-used. The pulverized feedstock is used in this system (Ku et al. 2014; Kong et al. 2021). These are megawatt grade gasifiers. Entrained flow gasifiers can be classified into two types: slagging and non-slagging (Fig. 11.4).

11.3.2.3 Pyrolysis

Pyrolysis refers to the thermal degradation of material types in the absence of oxygen (air). The final product of the process of biomass pyrolysis is liquid fuel (bio-oil), gases, solid char and tar. Pyrolysis is generally used at the industrial level for the conversion of biomass into energy. It is categorized into three stages on the basis of a thermal range of biomass conversion. The first stage of pyrolysis is observed that slight weight loss due to rearrangement, bond breakage, dehydration (water removal), formation of free radicals, carbon monoxide and CO_2 at the temperature range 120–200 °C. After this, solid decomposition is marked by a significant weight reduction from the initial feedstock. At the end of the stage, char devolatilization is occurred by the further breaking of C-H and C-O bonds. Fast pyrolysis is a thermo-chemical conversion process that aims to maximize the liquid yield of products in the low concentration or absence of oxygen. The temperature in this process is moderate (about 500 °C) and the vapour residence time is very less, so it needs quick cooling of volatiles. The main benefits of generating liquid fuel from biomass are increased energy density and storability and easy transportability of products (Suopajärvi et al. 2013; Roy and Dias 2017).

11.3.2.4 Torrefaction

Production of solid fuel from biomass is the prime objective of torrefaction. It is a thermo-chemical technique that is similar to pyrolysis but operates at relatively low temperatures (200–300 °C) in which hemicellulose is almost degraded to produce torrefied-biomass and energy. The energy density of raw biomass could be increased by torrefaction as the yield of the end product is up to 70% of the original feedstock. Moreover, the energy loss of the compressed fuel is just 10% thereby giving an approximated 90% energy yield. Torrefaction at the ideal temperature (200–300 °C) is an exothermic process, however, a small amount of external heat should be supplied to the medium to compensate for heat loss from the reactor (Basu 2018). The presence of oxygen at low concentrations could facilitate the rate of reactions. Thermo-chemical conversion of biomass through torrefaction is mainly studied under five regimes (Bergman et al. 2005). During 50–120 °C, there is the subsequent loss of moisture from the feedstock, next phase (120–150 °C) will dissolve lignin. During 150–200 °C, carbon and hydrogen bonds start breaking, synthesis of new short-chain polymers and their fusion with solid biomass is also observed in this stage. During the temperature range of 200–250 °C, there is a breakdown of carbon-carbon as well as carbon-oxygen bonds; this will result in the synthesis of liquids and few gases. Ultimately at the 250–300 °C operational range, a substantial breakdown of hemicellulose is observed producing solid as well as gaseous end products. Cellulose and lignin components of the biomass will observe an insufficient amount of devolatilization and carbonization reactions. End products of torrefaction include liquids (water, organics and lipids), solids (various sugars, modified polymers and ash) and various gases (CO_2, CO, H_2, CH_4, toluene, benzene, etc.)

11.3.2.5 Hydrothermal Processes

In hydrothermal processing, aqueous slurries of biomass are heated at high pressure for the production of biofuels. Biofuels produced through this method have a higher concentration of energy than the initial feedstock. In general, biomass having a higher percentage of moisture and ash such as manures, food waste, municipal waste, sewage sludge are preferred for hydrothermal processing. Furthermore, hydrothermal processing can be sub-divided into three different types; hydrothermal carbonization (HTC) is operated at pressures between 20 and 40 bar and temperature of 180–250 °C to produce pellets in the form of hydro-char, hydrothermal liquefaction (HTL) takes place at an elevated pressure which can reach up to 180 bar and temperature range of 250–375 °C, while in hydrothermal gasification (HTG) temperature and pressure are kept above 375 °C and 200 bar, respectively. Syngas is produced through hydrothermal gasification (Adams et al. 2018).

11.3.2.6 Fermentation

Fermentation can be described as a biochemical method that involves the conversion of organic feedstock into various types of valuable products; this feedstock in the form of biomass is anaerobically digested by certain kinds of microbes to yield biofuels such as bioethanol. In this process, simple molecules like amino acids, glycerol, monosaccharides are fed to suitable microbial cultures, which in turn ferment these molecules in a limited concentration of inorganic electron acceptors like sulphate, oxygen and nitrates (Patinvoh and Taherzadeh 2019; Madigan et al. 2015). It is expected that shifting to non-food crops for the preparation of biofuels can curtail greenhouse gases emissions approximately by 30–85% (Saini et al. 2015). Fermentation of lignocellulosic (biomass) feedstock needs to be hydrolysed first to release simple fermentable molecules. Hydrolysis of lignocellulosic biomass is the prime factor that decides the efficiency of the fermentation process. Since techniques like hydrolysis are in the developing stage (Kumar et al. 2015), special focus is being laid down for their continuous advancement. Fermentation of lignocellulosic feedstock for the preparation of second-generation biofuels expects the highly advanced techniques as break down of lignocellulosic biomass into simple sugars is a challenging step. Municipal solid waste could be regarded as a potent source of lignocellulosic biomass. Forest-based biomass could also be utilized for the generation of biofuels; however, higher bark content of the forest-based feedstock will pose more challenges to the conversion efficiency of the bioreactor.

Mode of operation of fermentation is usually carried out through batch, fed-batch or continuous manner. Various factors that influence the operational mode are the kind of substrate, operational liability, control over external environmental conditions of the production chamber, the likelihood of microbial contamination, the cost-effectiveness of the method. The procedure of batch fermentation is simple, yet providing all the substrates at the initial stage to cultured microorganisms is not manageable as it can resist the fermentation. Chances of contamination in batch fermentation are very rare; on the commercial scale, this method is employed by running parallel bioreactors to meet demand and supply (Patinvoh and Taherzadeh 2019). Continuous mode facilitates the supply of substrate to the reaction compartment and also enables the removal of the same volume of spent reactants or products. The supply of reactants is increased gradually to achieve equilibrium between substrates and spent (Brethauer and Wyman 2010). The fed-batch method is a combination of batch and continuous mode; supply of substrates at regular intervals is ensured without removing the spent (Zabed et al. 2017).

11.3.2.7 Transesterification

In transesterification, triglycerides are chemically reacted with short-chain alcohols in the presence of suitable catalysts to yield alkyl esters and glycerol. Usually, short-chained alcohols such as ethanol and methanol are used for transesterification to yield ethyl and methyl esters, respectively. This technique can be easily used for the production of biodiesel using various types of plant and animal-based oils and fats (Quader and Ahmed 2017). This is an eco-friendly method that is processed under mild operational settings.

$$\text{Triglycerides} + \text{R-OH} \underset{\text{(Biodiesel)}}{\overset{\text{Catalyst}}{\rightarrow}} \text{Alkyl esters} + \text{Glycerol}$$

11.4 Progress of Bioenergy in India

India has been building continuous growth in conventional as well renewable energy generation. Alternate energy in the country effectively started as a setting up a commission for additional energy sources in the Department of Science and Technology in 1981. After 1 year, this commission is changed into the Department of Non-conventional Energy source. The trajectory of growth of installed capacity started 1990s decade with the establishment of specially dedicated ministry, in 5-year plans. This is the first kind of specially dedicated ministry in the renewable energy sector in the world i.e., Ministry of New and Renewable Energy (MNRE). It is a key functioning body in the country and it helps to establish a wide range of research, development and demonstration activities. The renewable energy business in India has now grown into a vast industry as a result of the great effort of MNRE (Bhattacharya and Jana 2009). Consumption practices of bioenergy are found in ancient Indian manuscripts and it is mentioned in most of the natural modes of applications like firewood, cow dung cake, husk and many other agricultural and forestry resources (Liu et al. 2015). Bioenergy is the key initiative in starting the development of renewable energy in India. Biogas, biomass cook stove and biodiesel-based programmes are the main functional area of MNRE. National Biofuel Mission, Ethanol Blended Petrol Programme, Biodiesel Blended Programme, National Biogas and Manure Management Programme are some major initiatives of MNRE (Sinha et al. 2019). Thus, the development of bioenergy in India is continuously growing condition. Bioenergy energy resources have less attraction in society, due to high initial cost and lack of proper awareness. There are social obligations that also hindered the use of production of biogas by human excreta for cooking. Apart from these misleading things, the trend of bioenergy development is successively increasing in the biogas and biodiesel sectors. However, the direct combustion of solid biomass produces a huge amount of ash and smoke. These by-products cause many adverse effects on ecological systems. Therefore, people move towards the comparative less harmful side of biomass energy. Govt. of India promoted many technologies of biomass energy generation such as biogas, biomass gasification, bagasse cogeneration and many more. Bioenergy sources have the potential to meet the domestic energy requirements and can provide optimum energy with low emissions rats of greenhouse gases. Bioenergy harvesting technologies will make it possible to resolve most of the essential requirements like a reliable supply of energy and organic fuel economy. For the effective implementation and establishment of these technologies, many subsidies are given by the Govt.

11.4.1 Policy for Bioenergy Production

The total primary energy supply of India increased up to 55% from 2007 to 2017 and it is estimated that it will rise further up to two- to threefold in the next few decades. The economy of a country can be reflected in its energy consumption, however, using non-renewable resources including coal and oil for energy production has serious environmental challenges such as greenhouse gases emissions and air pollution. To curtail energy dependency on traditional fossil-based fuels and to meet the Paris Agreement targets, the Government of India (GOI) is determined to increase energy production from renewable energy resources such as wind, sunlight, geothermal and biomass (Tyagi et al. 2016; NITI 2020).

India is committed to achieving 175 GW of energy from renewable resources by the end of the year 2022, it comprises 60 GW from wind, 100 GW from solar, 10 GW from bioenergy and 5 GW through small hydropower projects (Kothari et al. 2020). India also aims for producing 450 GW of energy from renewable resources up to the year 2030 (NITI 2020). There is huge potential in biomass-based waste to energy projects in India. However, there is very little advancement made in this field. As energy obtained from biomass as heat and electricity is an eco-friendly and carbon neutral process, therefore investment to improve waste to energy conversion technology will ensure energy security and provide easy energy access in the form of electricity to remote parts of the country. The generation of bioenergy from waste such as bagasse from sugar mills has increased in recent years. Using biomass-based feedstock for biofuels is a more sustainable and energy-efficient approach than their traditional burning. At present, only a minor proportion of electricity is generated using wastes originating from urban, industrial and agricultural sectors (Sinha et al. 2019; NITI 2020). A huge amount of energy is present in this waste; however, its efficient tapping needs technological advancements that are still in the developmental stage.

11.4.1.1 Renewable Energy Institutions

MNRE is responsible for the formation of policies regarding renewable energy resources including solar, wind, geothermal, tidal, hydro energy and biomass in India. The MNRE also holds utilization of bioenergy for electricity from resources in the form of waste and biogas. Advancements in the field of biofuel generation and their policy implementation are regulated by the Ministry of Petroleum and Natural Gas. The Department of Biotechnology (DBT) and the Department of Science and Technology (DST) are under the Ministry of Science and Technology and are in charge of innovations in the field of bioenergy (NITI 2020). Apart from this, various local self-reliance groups and non-government organizations are involved in the development of bioenergy and utilization in villages and remote areas.

11.4.2 Policy for Gasification

Ministry of New and Renewable Energy (MNRE) issued updated guidelines for the "Waste to Energy Programme" on February 28, 2020. The programme set up its goals for the exploitation of various types of wastes for the generation of energy on large scale. Under this programme, encouragement will be given through financial support for the installation of various plants including gasifiers intended to utilize municipal solid waste (MSW) for the generation of energy and its utilization at the

Table 11.3 Summary of financial assistance given under Central Financial Assistance (CFA) scheme for various types of waste to energy projects (MNRE 2018a)

Type of plant	Central financial assistance	
	Parameters for CFA	Maximum CFA
Biogas	₹1 Crore/12,000 m^3/day	₹10 Crore
Bio-CNG	₹4 Crore/48 quintal of Bio-CNG/day (12,000 m^3 biogas reactor)	₹10 Crore
Power	₹ 0.5 Crore to 5 Crore/MW (minimum for boiler and steam-based turbines and maximum for MSW and RDF energy plants)	₹10 Crore for Gas/Boiler and Steam turbine and ₹50 Crore for MSW and RDF based plants
Bio-gasifiers	₹ 2500–15,000/kW for electricity producing gasifiers and ₹2 lakh/300 kW for thermal gasifiers	–

production site, and supply of surplus energy to the electric grid system. The energy thus produced will be utilized for compensation to the growing energy demand in various industries and the transport sector. The production of energy in the form of Biogas and Bio-CNG (Compact Natural Gas) and the installation of gasifiers in the different types of industrial units is kept under primary focus. Under this scheme, Central Financial Assistance (CFA) will be given in the form of various monetary subsidies and grants for the installation of different waste to energy units including biogas and Bio-CNG plants, bio-gasifiers (to compensate for energy requirement in rice mills and other industrial units) and MSW to energy plants (Table 11.3) (MNRE 2018a; Kothari et al. 2020).

11.4.3 National Policy on Biofuel-2018

National policy on biofuel-2018 primarily targets the use of second-generation lignocellulosic biomass. The policy aims at 20% blending of ethanol with traditional fossil-based petrol by the year 2030. Bioethanol is a cleaner fuel which when blended with conventional petrol will curtail emission levels and production costs by using crop residue as feedstock. Policy furthermore emphasizes reducing the import of petroleum by the production of biofuels. The production of biofuels in India will possibly decrease dependency on imports, thereby boosting the economy of the nation by reducing foreign exchange up to ₹4000 Crore. Moreover, the production of biofuels is a promising initiative for cleaner energy as it can help in curtailing CO_2 emissions up to 2×10^7 kg. Production of biofuels from the second-generation feedstock is a sustainable and eco-friendly approach as it will also not compromise food security. Moreover, it will also focus on additional goals including a boost in the employment sector, improving the earnings of farmers, using used cooking oil for the synthesis of biodiesel, and also utilizing MSW for biofuel production. This policy also aims at providing financial assistance for the setting up of second-generation biorefineries, for this ₹5000 Crore is set to be spent in the next 6 years (Ministry of Petroleum and Natural Gas 2018; Kothari et al. 2020).

11.4.4 New National Biogas and Organic Manure Programme-2018

MNRE issued a set of rules and guidelines for the "New National Biogas and Organic Manure Programme" (NNBOMP) on May 30, 2018. This programme mainly focuses on exploring various eco-friendly technologies for meeting present-day energy needs in the agricultural sector. This programme will be implemented in all states including union territories. Different objectives have been framed including prevention of further climate change and environmental degradation by keeping a check on the release of various greenhouse gases like CO_2 and CH_4 into the atmosphere, improvement of sanitary conditions of people living in villages and sub-urban areas, linking of conventional sanitary toilets with animal dung-fed biogas plants and to reduce the load on forestry for firewood and to deliver clean fuels for cooking in rural areas. Further hybridizing traditional biogas plants through linking with vermicomposting units and phosphate-rich organic manure (PROM) units. Encouraging the use of organic manures instead of chemical-based fertilizers and meeting small energy needs of farmers for lighting and thermal purpose by effective utilization of bioenergy resources. NNBOMP aimed at setting up more than 65,000 and up to 1 lakh biogas plants for the year 2017–2018 and 2018–2019, respectively. For this purpose, central financial assistance (CFA) will be given to the beneficiaries for the installation of biogas plants that will vary from ₹7500/m^3 to 35,000 for 20–25 m^3 sized biogas plants. For this purpose, the size limit of biogas plants has been increased from 6 to 25 m^3. Models of biogas plants that have been approved for setup include Fixed Dome Type, Floating Dome Type, Bag Type Flexi Model, etc. Installation of biogas plants will make cleaner fuel assessable among people living in remote locations across the county, spent slurry from the biogas plant could be used as bio-manure for crops. These plants could be fed using various types of wastes generated from kitchens, farms, kitchen gardens, cattle shelters, etc. Replacement of conventional LPG cylinders with biogas plants provides additional benefits such as less indoor air pollution from the fuel wood-burning and economic stability of the rural families (MNRE 2018a; Kothari et al. 2020).

11.4.5 Programme on Energy from Urban, Industrial and Agricultural Wastes

The programme on energy from urban, industrial and agricultural wastes is also initiated by the MNRE. This programme is initiated for encouraging the installation of waste to energy conversion units such as biogas/Bio-CNG and utilization of thermal energy from biomass gasifiers to exploit energy present in wastes generated from different sectors including agriculture, industries and urban localities. This programme will help in meeting growing energy demands especially in the sectors from where waste is initially generated. This initiative will be supported by monetary subsidies in the form of Central Financial Assistance (CFA). This programme has the potential to boost the economy of India through curtailing dependency on foreign fuel imports by focusing on green energy, therefore energy in the form of electricity could be fed to power grids, biofuels for transportation and thermal fuel to the industrial setups such as rice mills, small-scale industries. Till the year 2019, work for the establishment of around 200 waste-to-energy projects for the production of energy was completed across the country (MNRE 2018b; Kothari et al. 2020).

11.5 Conclusion

Bioenergy conversion technologies are widely distributed, matured and accepted in the country. The abundance of feedstock materials is also promoting the development of bioenergy. Plant wood, animal waste, forest residues and agricultural wastes are feedstock that are available at almost zero cost and abundantly. Anaerobic digestion, gasification, fermentation are established technologies that can supply sustainable energy. Biofuel policy, programs on biogas and organic manure, energy from urban, industrial and agricultural wastes are the main bioenergy policy outline that runs for the nationwide targets. The lucrative subsidies are ensuring the development of bioenergy in the country that can help to provide low cost, sustainable bioenergy.

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Bioeconomy: Scope Current Status and Challenges

12

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Abstract

The international government and agencies are working on smaller goals every year to achieve the reduction in global warming and helps in diminishing climate change. Sustainable Development Goals (SDGs) are framed to achieve three pillars (trio), i.e., social, economic, and ecological status which is achieved by taking different measures at every possible setup. One such concept which helps in achieving SDGs is bioeconomy. The initiation in the rise of the bioeconomy concept has occurred because of the advancement in the field of biotechnology and life sciences. Different industries across the world are dependent on bio-based products which could be used for rising economy, energy, food, and services by using biotechnological approaches. Bioeconomy could be future of countries in achieving the SDGs as it implies the microbial communities for conversion of substrates (crops, waste products, etc.) for energy, food, and services. To implement such technologies in any country an implementation laws are framed which is required to start new technology. So, here in this chapter we are focusing on the concept of bioeconomy, related issues, and its contribution in environmental and bioenergy security.

Keywords

Bioeconomy · Sustainable development goals · Bioenergy · Biomass · Environmental security

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12.1 Introduction

Expansion in farming as well as the utilization of natural resources has been seen since about 10,000 BC (Bocquet-Appel 2011). Considerable changes and evolution have occurred in science since then. The initiation of the rise of the bioeconomy concept has occurred because of the advancement in the field of biotechnology and life sciences (White House 2012). Economy of different industries are dependent on bio-based products and its gives way to different Sustainable Development Goals (SDGs), which helps in the improvement of social, economic, and ecological status in the current scenario of climate change risks. Even though, the development of agriculture has occurred in parallel to the progress of humans, it has been transformed into a major topic in policy agenda and scientific world by the global challenges. Bioeconomy does not have any universally accepted definition (OECD 2018). British biologist Hermann Reinheimer introduced the term "bioeconomics" in "Evolution by Co-operation: A Study in Bioeconomics" issued in 1913 (Reinheimer 1913). This requirement of development as well as collaboration has been stressed by the author. Sequentially, the issue of sustainability and climate change has been pointed out by one of the first economist Georgescu-Roegen. According to a comprehensive theory about biophysical constraints, economic development and institutional change has been introduced by him (Mayumi 2009). He stated that the "biological origin of the economic process which spotlight the problem of mankind's survival with a finite resources randomly distributed and unevenly appropriated" (Georgescu-Roegen 1977). An important point raised by Georgescu-Roegen while using the term bioeconomics was the incompatibility of the unlimited growth with the fundamental laws of nature (Bonaiuti 2014). However, the concept of bioeconomy became popular in the last decades of the twentieth century. There was a difference in the term from the earlier, which stated that "bioeconomics" is the biological knowledge for industrial and commercial purposes (Birner 2018). Strategic documents belongs to the European Commission as well as the 1993 White Paper included bioeconomy. The significance of advanced biotechnology and investments for development has been highlighted in the strategic agenda. One of the first definitions of the bioeconomy has been provided by Enriques and Martinez that liked by the policy makers. Authors defined bioeconomy as an economic activity based on scientific outcomes where its implementation is concentrated on understanding the tools and processes at the genetic level, to implement and its utilization in industrial product production (Martinez 1998). OECD report (OECD 2001) highlights the concept of bioeconomy in a strategy paper "The Bioeconomy to 2030: Designing a policy". OECD defined bioeconomy as the means of interchange of information resultant of the natural sciences to the noble, environmentally friendly, eco-efficient, and viable products (OECD 2009). Various documents have been presented by the European Commission in relation to this topic. In 2010, few production models on the basis of natural ecosystems as well as biological processes have been introduced in the paper "Bioeconomy for Europe" (European Commission 2010). The definition of bioeconomy has been refined in the use of infinite biological resources in variable fields of the economy (European

Commission 2012). Accordingly, bioeconomy is defined as the sustainable production of renewable resources and their conversion into bioenergy, food products, feed and industrial goods (European Commission 2012). The definition of the EC and OECD are although similar, but the focus of the latter one is more on chemical industry, biorefineries, industrial biotechnology, biofuels, recycling, and transport. The discussion in USA also included bioeconomy. White house has defined bioeconomy as the economy which utilizes innovation as well as research in biological sciences to generate public profits and power economic activity (White House 2012). However, the definition by the European Commission is still under consideration. The concept of "from cradle to grave" has been introduced in a report (2016) entitled "European Bioeconomy Stakeholders Manifesto." Its focus was on the implementation of principle on biomass chain; creating and strengthening the concept of "product life cycle" and "value chains" within the scope of bioeconomy (The Fourth BioEconomy Stakeholders' Conference 2016). A new definition has been put forward with the update of the strategy of bioeconomy-"bioeconomy covers the almost areas and classifications that are based on biological resources such as animals, plants, micro-organisms, and biomass, including organic waste along with their roles and values" (European Commission 2018). Transformation of the bioeconomy concept has been occurring parallel with the global goals, challenges, and perspectives. These definitions vary on international, national as well as regional level. The aim of this chapter is to highlight the concept of bioeconomy, related issues and its contribution in environmental and bioenergy security.

12.2 The Bioeconomy to 2030: Designing a Policy Agenda

Integration of the concept of bioeconomy into strategy and policy is new. The process of policy strategies is fostered by bioeconomy strategies. The development as well as regulation of the comprehensive economic policy which is based on strategic sectors can be one by using bioeconomy as a strategic option. Political stability and sustainable economy is achieved by policy instruments to support the transition towards the bioeconomy. The Organization for Economic Cooperation and Development (OECD) document titled "The Bioeconomy to 2030: Designing a Policy Agenda" attributed to the initiation of publications on national bioeconomy strategies and policies.

A deep and broad concept of the BE and its probable development is produced by OECD in an extensive document—The Bioeconomy to 2030: Designing a Policy Agenda (OECD 2009). BE (bioeconomy) has been described in it as a "world where a considerable share of economic outcome is contributed by biotechnology." Three major elements make a BE for the OECD: renewable biomass, biotechnological knowledge, and integration across applications. Environmental sustainability is maintained by the economic growth in a bioeconomy, which involves disassociation of economic growth from environmental degradation. It aims to describe the situation of BE in 2009, its growth in 2015 and what it may be in 2030. According to

OECD a bioeconomy will be global, and OECD and non-OECD countries will encounter the challenges related to population, environment, social construction, and the economy. The novel business models, trans-sectoral associations, and efforts are required. The OECD pointed out that more than 80% of research venture from the private sources will go to health sector and 75% of future economic contributions to the bioeconomy will be the agriculture and industries. Hence, OECD suggests that research funding from the public sector; encouragement of public–private partnerships and reduced constraints in these sectors can be used to boost industrial and agriculture research. Use of biotechnology has been proposed to address the issues of global environment by supporting international agreements to generate and withstand markets for environmentally sustainable biotechnology products. OECD highlights the requirement of a foundation for long-term development of the bioeconomy, as well as the need for cross-sectoral work both in public and government. In 2030, an estimate of 2.7% is contributed by the BE to GDP in OECD countries, assuming a "business as usual" development of institutional factors, for example, regulations. Two fictional scenarios can be used to describe the development up to 2030: one in which rapid development is seen by encouraging innovations in health, industry, and agriculture and another where resistance from the general public hinders such development. Competition among different renewable energy sources such as algal fuels, biomass based energy, and electricity based transportation system is explored in these scenarios, which is quite advanced. OECD (2009) reports that development if bioeconomy, for example, economic competitiveness of biotechnological innovations and eminence of governance or regulations and policies can be influenced by few political events. A system for coordination relationships among the various institutions, such as economic and technological divisions are required where integration of government, business and society is found. Few developmental problems are being created in the current bio-economy agenda that could result in a failure, if the past lessons are not accepted and adopted, for example, the damage faced due to Jatropha crop failure as biodiesel source. The bioeconomy is an concept of cooperation among various sectors, as well as management between policies, stakeholders, academics, and civil society which is organized in The European Bio-economy Panel in 2013. Moreover, policy research is strengthened by multidimensional initiatives in data-based bioeconomy.

12.3 Policy Formulation for Bioeconomy

Effective bioeconomy innovation system based on circular economy requires developments, investments, and policy formulation. Growth of biosciences in bioeconomy activities is faster in some countries than others. Surplus feedstock has an economic potential for the bioeconomy together with industrial biotechnology and should be focused while making policy decisions for creating a high value bioeconomy. There is a variation of bio-economic policies from other spatial policies in terms of their performance and application. The outcome of this urban growth can be witnessed in urban communities. However, lack of city planning, public policies to regulate urban growth intensifies urban sprawl in the developing countries. Industrialization of most Latin-American cities has intensified the growth since 1950, and policies have been implemented since 2001, to avoid mismanagement in urban development. Policymakers, academic, stakeholders, etc., should make more integrated and more coordinated efforts in bioeconomy to make the bioeconomy web extra beneficial in the conversion of raw materials to the products. The European (ETPs) are technology platforms which provide backup structures of association policies to structure a system for bioeconomy organizations to improve the concepts. The World Bio-economics Summit is held in Berlin in November 2015 to discuss bioeconomics policies and generate globally (GBS 2015). Societal challenges can be addressed by raw materials and biological resources for bio production in collaboration with the stakeholders engaged in policy making for the application of bioeconomy as the chief purpose. Improvement of nutrition, reduction of GHG emissions, development of foods and threats to human health can be minimized by resources of bioeconomy. An important role is played by various stakeholders cooperating and participating in the bioeconomy on internet based portals for the collection, simulation and sharing of data and various communications on bioeconomy related issues. Bioeconomy have few communication and understanding related issues which has to resolve for various economic and industrial sectors and to increase the efficacy in scientific and technological responsiveness. Active participation in specific projects and policy making affects the success of bioeconomy. Under developed countries where the bioeconomy's development is in its initial stages have a limited impact of the agro energy policy (Paul 2013). The focus of bioeconomy on agro based fuels undesirable impacts on socio-enviro-economics. Impacts of gradual implementation of policy instruments on bioeconomy are higher in comparison to the rushed full introduction. The issue of consistency in bio-economy and related innovation can be addressed by policy coordination between regions. Collaboration as well as policy coherence can be maximized within and between nations at regional bioeconomy level. Reduction of waste and demand must be considered in bio-economic policy due to increased scarcity of resources. Lack of political support as well as pressure groups to establish new methods in the bioeconomy market may result due to the implementation of the policy implications to improve demand and supply of bioeconomy dependent on biomass based raw materials and products. The traditional markets and the peculiarity of bioeconomics display the lack of bio-economy policy (Pannicke et al. 2015). A valuation of policy based matters as well as prospects of bioeconomy and bio-based applications is required to address so that it can be applied to problems, policies and activities on bioeconomy development by the government.

12.4 Enabling Bioenergy Contributions to Environmental Security

Context specific properties of bioenergy production are observed with environment (Karp et al. 2015; Efroymson et al. 2013). Biofuels can lower reduce GHG emissions and mitigate human health toxicity in contrast to fossil fuels (Chum et al. 2015). Additionally, evapotranspiration is locally increased by biofuels and also enhance sequestration of soil carbon along with improvised soil organic carbon management and practices (Berndes et al. 2015). By-products of biofuel production like sugarcane vinasse save economic resources by providing nutrients such as potassium and water for irrigation. Usage of agricultural management techniques which are biodiversity-friendly additionally agro-ecological zoning lower the negative effects produced by agriculture intensification and land-use change. Conservation of biodiversity, adoption of location-specific management of production systems, making sure sufficient bio-connectivity across agro-systems to virgin areas at landscape levels and recognizing the context specific effects can lower the negative impacts of bioenergy, forestry or food production (Joly et al. 2015). Actually, the disparity between domesticated species production and biodiversity conservation should be regarded as interdependent. It is required to identify that the expansion of bioenergy in controlled multi-functional landscapes may be advantageous. Agricultural landscapes contain a substantial amount of biodiversity. Full biodiversity protection is impossible to be offered only in conservation entities like biological reserves and national parks even if they worked properly. Hence, complementary biodiversity conservation is provided by evolving agriculture within multifunctional landscapes in real world. Specialized managed environments are important for the survival of the most endangered world taxa such a wild varieties and domesticated species. It is important to them conserve them to get domesticated relatives for the continual adaptation of their to environmental changes like newly evolved parasites and pathogens and also the global challenges of climate change (Verdade et al. 2014) and also to become a part of the ecological process (Hicks et al. 2016). These multifunctional landscapes consist of sources of food, biodiversity, shelter, and conserve water cycles and nutrient (Joly et al. 2015). Effectiveness of the resource is vital all through the chain. Time and efforts are needed to develop the management strategies Indicators of sustainable environment that guide certification schemes consist of productivity, GHG emissions, biodiversity, soil quality, and water quality as well as quantity (Endres et al. 2015; McBride et al. 2011). Various empirical literatures on indicators are now present that can be included into best management practices to ensure resilience towards climate change in different agroecosystems (Cabell and Oelofse 2012).

12.5 Biomass and Bioenergy

Global biomass systems for food, forest products, fiber, fodder, and waste as well as residue management also involves bioenergy in complex ways. An important and critical part is played by bioenergy in the day-to-day livings of billions of people in developing countries. Substantial increase of bioenergy production involves refined management of the use of water and land; increase of international feedstock productivity for energy, food, fiber, fodder, and forest products; considerable improvements in conversion technology; as well as improved understanding of the multifaceted environmental, social, and energy interactions related with use and production of bioenergy.

12.5.1 Usage of Biomass Falls into Two Main Groups

- Low efficiency traditional biomass 7, for example, manure, dung, straws, and woods are utilized for space heating, lighting, and cooking in developing countries by the poorer populations. Serious negative impressions on health as well as living conditions are created by combusting this biomass. In rural areas, charcoal is increasingly becoming a secondary energy source to create productive chains.
- High-efficiency modern bioenergy generate transport fuels, combined heat and power (CHP), heat as well as electricity for several divisions by using extra suitable gases, liquids, and solids as secondary energy carriers. Global road transport and few industries utilize liquid biofuels, for example, biodiesel and ethanol.

Electricity, heat or both can be generated from the gases derived from biomass, such as, methane, from municipal solid waste (MSW) treatment as well as anerobic digestion of agricultural residues. Solids like pellets, recovered wood and previously used along with chips contribute mostly to these energy services. Heating comprises of hot water and space heating, for example, district heating systems. Modern bioenergy requires an estimate of 11.3 EJ/year total primary biomass supply and roughly 6.6 EJ/year is the secondary energy given to consumers of end-use. Approximately 7.7 EJ of biomass is consumed annually by the industrial sector, for example, pulp and paper, food and forestry industries, mainly as a source for industrial processing energy.

12.5.2 Resource Potential of Bioenergy

It is difficult to characterize and assess the combined technical potential controversial because of the inherent complexity of biomass resources. Research estimates from global modelling efforts range from zero technical potential (zero biomass available for bioenergy) to a maximum theoretical potential. Technical potential of biomass for energy is as follows, nearly 50 EJ/year biomass is used globally for energy at the present time and harvested biomass consumed for food, fodder, and fiber, when expressed in terms of caloric equivalent, gives around 219 EJ/year; about 150 EJ/year deployment level of bioenergy is achieved by the entire current global biomass harvest by 2050. The modelling studies assesses the technical potential and arrives at the decision that the upper limit of this technical potential is about 500 EJ in 2050. The research accepts policy frameworks that insures better management of land use as well as main developments in agricultural management and takes into account water scarcity, biodiversity protection, soil quality degradation, and competition for food. Nearly, 40–170 EJ/year is estimated by residues originating from organic waste (comprising of the organic fraction of MSW, process residues, dung, etc.), agriculture, and forestry, with a mean estimation of nearly 100 EJ/year. There is a relative certainty of this part of the technical potential, however, the net available energy for applications may be lowered to the end of the range due to competing applications. Extra technical potential of nearly 60–100 EJ/years contributed by numerous forestry products other than forestry residues. A lower estimate for energy crop production is 120 EJ/year for pasture lands, surplus, and good quality agriculture. An additional amount of 70 EJ/year is contributed by degraded and marginal lands and water-scarcity. It would consist of a large area where there is a severe soil degradation and limitations are imposed by water scarcity. Improvements in livestock and agriculture management by assuming strong learning in agricultural technology would amount to 140 EJ/year. An analysis of the three groups put together results in a technical potential of nearly 500 EJ/year. Major policy efforts are required to develop this technical potential, and hence there will be a lowering of actual development and the biomass resource that is reserved in organic wastes and agricultural and forest residues, cultivation of bioenergy crops on wasteland and degraded lands, and other regions where biomass is a common and cheaper energy source as compared to the main reference crops such as sugarcane sugar-based ethanol production.

12.5.3 Significance of Bioenergy

Patterns of energy consumption in OECD as well as non-OECD countries reveals that utilization of energy will mostly occur in the developing countries. Economic activity directly affects consumption of energy which results in better opportunities for improved educational level, better public health, and human development. Since the last 15 years, it was in practice to use the lower cost products for the economic benefits without forecasting the danger to the environment this would be, however with the arrival of global trade extra critical studies are investigating the sustainable consumption as well as production patterns that are valuable all around and that reflect the relative improvement of nations. Such as, in the case of bioenergy as well as biomass, biomass is more suitably produced by the developing countries that have sufficient water and land. Furthermore, it is critical to provide the non-OECD countries an access to the sustainable energy sources due to increased energy demand for development. Or else, they will be forced to expend fossil energy and hence reduce the international effort to lower greenhouse gases (GHG) emissions. Fortuitously, various substitutes that enhance the portion of renewables in the energy matrix consists of numerous bioenergy options (Foust et al. 2015), additionally, in 2015, the investment of the developing countries in renewables outdid those of developed countries (REN21 2016) demonstrating that the portion of international final energy consumption is 19.2%. Various countries of the world invest in the bioenergy initiatives that add to a considerable segment of their matrix supplying heat, biogas, biofuels, and bioelectricity. Bioenergy can have various added benefits in addition to sustainable development, climate change as well as food security provided that efficient systems are used and good management practices are followed (Nogueira et al. 2015; Osseweijer et al. 2015; It is also known that even the international targets of 2 °C decrease of GHG cannot be achieved without bioenergy on the basis of 2016 INDCs (Rogelj et al. 2016). Sustainable biomass production can significantly contribute to climate change mitigation along with diversification of energy resources. Most important global GHG mitigation set-ups demonstrate that it is possible that bioenergy may contribute 25% of the primary energy use. A major role is played by bioenergy integrated with carbon capture and storage (CCS) (Rogelj et al. 2016). Other carbon dioxide lowering technologies required for unrestricted emissions include large emissions from commodity-scale bioenergy and CCS.

The UN Sustainable Development Goals and its 17 global aspirational goals (United Nations Global Sustainable Development Report 2015), suggests climate change related measures to secure livelihoods of people in future. It also suggests that every human should feel the moral duty so that the development of supply at large-scale for bioenergy can be achieved (Nuffield Council on Bioethics 2011; European Group on Ethics in Science and New Technologies to the European Commission 2009) and further significant sequestration of fossil fuel related carbon emissions. Production of liquid renewable fuels is the first issue that must be addressed to aid the reduction of change in climate and biofuels is vital for two motives. First, nearly 27% of the world transport fuels (mainly long distance road sectors, aviation and shipping) (Meier et al. 2015) can be provided by this renewable energy source which currently is acquired from fossil fuels. Lowering of 2.1 Gton of CO_2 can be achieved per year in the atmosphere by the use of such biofuels (OECD/IEA 2011, b). Second, renewable energy services are provided by biofuels which can substantially improve the well-being of human and generate wealth at the present and also in the future which cannot be achieved by other options of renewable energy. Substantial evidence exits that show various benefits of bioenergy besides GHG reduction, which includes urbanization, intensive food production as well as solving problems associated with fossil fuels (Leal et al. 2015). Examples that profit from better energy access as well as lessening of poverty include improved agricultural efficiency in rural areas to lowering of pollution in urban centers (Souza et al. 2015). Even though at commodity scale various feedstock options are already available yet constant efforts are required to improve and/or develop forestry as well as crop systems that can efficiently produce bioenergy (Long et al. 2015).

Environmental benefits and higher productivity can be achieved by second generation biofuels (lignocellulosic biofuels). Important contributions to meet the GHG reduction targets are being made by modern biofuels that supply high yields per hectare and are technologically advanced, for instance, sugarcane ethanol (Youngs et al. 2015). Few biofuels of first generation demonstrate features that level them with the biofuels of second generation in terms of emissions, positive social impact, and sustainability. Hence "advanced biofuels" refer to the resulting characteristics of the fuels in terms of emissions mitigation and sustainability instead of the feedstock utilized or the technological path followed (Brito Cruz et al. 2014). Biofuel production technology does not matter, however, the sustainable outcome does. Regional development is affected by bioenergy efficiency. Infrastructural problems can result in bioenergy inefficiency in developing countries where technological training and education are facilitated, positive effects can occur (Moraes et al. 2015). Developed countries have infrastructure and technology and competition becomes the main problem as the commodities are unsteady and dependent on market (Foust et al. 2015). Recently, bioenergy produced from conventional technologies such as agricultural and urban waste as well as traditional feedstocks like sugarcane can be used in various areas by taking the benefit of knowledge from experience, for instance, the Brazilian Ethanol program or examples of production of biogas from all over the world with positive results (Leal et al. 2015). Anaerobic digestion of crop residues as well as animal manure with double cropping is a conventional technology which when combined with improved practices of farm management can produce much more energy (Biogas Consortium, http://www.consorziobiogas.it). A second or "double crop" is produced by the farmers in an Italian Biogas program during the era when land is not cultivated but the usual food crops were allowed to grow in respective seasons. The biomass produced was harvested and then feeded to the animals and dung was added to these anaerobic digester along with various wastes to produce biogas. Electricity is produced by burning the biogas. The fields are drip irrigated by the liquid fraction of the digester effluent to recycle the nutrients and incorporate solid fraction of the effluent into the soils, hence enhancing soil fertility by sequestering carbon. Farm economics is improved by depending less on purchased fertilizer, as does the existence of a second "crop"—revenues from the generated electricity that is sold to the main grid. The presence of double crops reduces surface water pollution, soil erosion, and ground water contamination through leaching. Hence, several characteristics of sustainability are met: improvement of water quality, promotion of rural development, sequestration of carbon, and production of large amounts of renewable energy. This example where wastes do not exist shows the power of circular economy.

12.6 Linkage of Sustainable Human Development to Biomass Energy Systems

Efforts towards the achievement of the Millennium Development Goals (MDGs) measure the progress of any nation today. Convergence of many factors makes bioenergy a viable opportunity and a key component in the great effort towards the achievement of the Millennium Development Goals (MDGs). Even though MDGs do not treat the sustainable access to energy as the main concern, yet most of them have a direct energy implication, mainly Goal 1 (Eradicate extreme poverty and hunger) as well as Goal 7 (Ensure environmental sustainability) (FAO 2005). Energy must be considered a human need like the other basic human needs (biodiversity, food security, shelter, clean water, sanitation, and health care) according to the WSSD Johannesburg Declaration.

Sustainable energy supply from firewood and other plant biomass has greatly changed since the issues of a strong dependency on fossil energy carriers have been highlighted. Planners and operators of development programs in forestry, agriculture, and energy domains consider the socio-economic as well as environmental benefits of bioenergy projects (http://www.spatial.baltic.net/_files/Planning_indicators.pdf). Additionally, bioenergy is now being recognized as a method to improve livelihoods and lower poverty in rural areas removing the negative perception of bioenergy as a key symptom of under-development or an environmental hazard.

12.6.1 Sustainability Concerns

Sustainability criteria as well as certification systems are needed to control biomass trade because of potent harmful consequences of large-scale production and export of biomass, such as competition between food and biomass production and deforestation. Incorporation of few sustainability criteria into the relevant policy instruments have to be done to make sure that biomass renewable and sustainable energy source will be produced and processed in a reliable way. Particularly, countries at the national and international levels moreover international governmental and non-governmental organizations at the international level are requested to improve the idea of indicators of sustainable development.

The following aspects are foreseen as the minimum criteria for bioenergy sustainability:

- Act in accordance with current international obligations as well as local jurisdiction, along with other specific indicators.
- Abide by the specific indicators and active conservation.

A set of internationally agreed criteria is given by Otto (2007) which includes:

- Wide acceptability
- Ease of orientation

- Capital
- International economy
- Regional/national protocols
- Account specificities

Sustainability addresses both conversion of biomass to energy as well as cultivation. It aims to lower the emission of greenhouse gases and also emphasize on the concerns like economic development, energy efficiency principles, biodiversity aspects, soil carbon, and social well-being and hence is a multidimensional concept. Principles of sustainable utilization of biomass for energy proposed are more concrete, as observed in various initiatives focusing at the certification of biomass, bioenergy, and biofuels are:

- Sustainable production: legal sources should be used for raw materials instead of the land that has been diverted (e.g. highly biodiverse grassland, primary forest, peatlands, protected area or areas with high stocks of carbon).
- High greenhouse gas (GHG) performance in comparison to fossil fuels: the lifecycle GHG emissions of the fossil fuel should be replaced with bioenergy chains with lower GHG emissions.
- Efficient energy conversion: maximum energy efficiency should be struggled.
- Biodiversity production: biodiversity should not be negatively affected by the production of biomass.
- Contribute to local welfare and prosperity: social well-being of local population and employees should be taken into account by bioenergy chains.

12.6.2 Challenges

There is still no global/common definition in relation to consistency and transparency which describes that how the sustainability concept should be adopted into practice, i.e. how to measure sustainability and criteria/indicators. A common language which uses the same terminology on "what is sustainable and how it has to be verified/documented" is hence very important. A cross-sector approach is necessary to ensure implementation and uniform application of sustainability criteria which covers harmonized global sustainability principles and certification systems. A more effective and efficient global approach can be developed by exploiting the similarities and interactions among the different existing schemes. A key driver for the disposition of biomass for energy as well as the acceptance of biomass as a cost efficient substitute for fossil fuels/resource is the establishment of a common approach and coordination of the various standards and schemes. Establishment of a meta-standard is a potential solution, which includes overall criteria and principles of sustainability for all regions which can be transparently as well as equitably applied to form and efficient and effective certification system depending on the social and ecological context on national/regional or local levels. The structure and operation of the certification systems requires strict guidelines to avoid weak verification and implementation practices besides effective and enforceable sustainability criteria. A detailed set of processes for verification and implementation are required to be formed and implemented as part of the sustainability standard. Developmental guidelines for these processes are already in place, e.g. ISEAL and ISO. A high level consensus is achieved by few initiatives, e.g. CEN and ISO:

- CEN (the European Standardization Institute) is presently expanding a European standard in line with the EU RED requirements for sustainable biomass for energy applications. Currently, there is a European pre-norm prEN 16214. This pre-norm is still in the commenting stage, but may result in as European norm in the short while.
- ISO is creating a global standard (ISO 13065) as well as harmonized criteria on sustainable production of bioenergy which also addresses economic, environmental or social aspects of production, supply and use. It might be a time taking process as it considers principles and criteria of voluntary development of legislation and standards of various countries, which describe the two key approaches of getting standards globally.

Sustainability of bioenergy/biofuels is defined by both processes. Still we need to overcome various challenges; e.g. how to tackle indirect effects or how to reach consensus on global definitions and methodologies. It can be solved by creating a common language concerning verification as well as implementation and working towards a global governance of land use principles as well as guidelines (e.g. a Multilateral Environmental Agreement). A framework of 24 sustainability indicators to measure and guide the policies and programs of government in the development of bioenergy as well as biomass is set up by South-Africa, Mexico, China, G8 + Brazil, and Mexico but can be used by all other countries is the Global Bioenergy Partnership (GBEP) which is forum for dialogue on bioenergy on a multilateral level. Credibility, market penetration, and acceptance can be gained by a uniform approach and might also avoid various impacts/effects. It would help to save costs due to better management practices, allow for more efficient structures, ease administration tasks involved, and create new standards. Greater market penetration can offset the costs derived of being part of a broader effort.

12.7 Future Perspectives

Various nations around the globe have published the strategies of national economy. Although there is a difference between the developmental stages of the many countries yet the specific needs and want to improve the transformation from a fossil-based economy towards an economy based on renewable resources is the same. Nevertheless, the maturing bioeconomy will prosper within the next 20 years in food and feed as well as agricultural sector. Also, various new products, like chemicals based on renewable materials, will reach the market. Further developments can be enhanced by new technologies like digitalization of the primary sector, metabolic engineering, and genome editing in plant breeding. Novel (bio-based) products should be developed to enhance the current agricultural status to feed the population of the world. Holistic strategies and better supply chain management can be developed by research to improve the future bioeconomy. Conflicting goals as well as their implication for future developments should be dealt with the updated economy at an early stage. It is important to consider the regional aspects as they lower the shortcomings while moving forward. Crucial assessment of knowledge as well as funding is required to improve the bioeconomy. National agendas, e.g., for basic and applied research requires sufficient funding and access to capital. It is also important to update the fossil fuel subsidy, export-promoting policies, and bio-based procurement policies.

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Algal Biofuel: Global Policies and Their Implication

13

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Abstract

As a promising alternative renewable energy source, biofuels offer a significant responsibility for environmental sustainability and energy security. Various strategies related to government policy for sustainable development and technological implementation of biofuels should be set by different countries. Thereby, factors include availability of feedstock, biofuel infrastructure in the country, compatibility with vehicular performance and emission behaviour, blending targets, supporting schemes for farmers and industries before an algae policy is recommended by the government. The objective of this chapter is to explore the biofuel policy, policy gaps, and policy mismatches with respect to biofuels and advocates some of the key factors, and amending biofuel policies can help in algal biofuel policy making.

Keywords

Biofuel · Policies · Energy · Investigation · Factor

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13.1 Introduction

The combustion of fossil fuels (Coal, Petroleum, and Liquid petroleum gases, etc.) triggers the global warming issue. This encourages the global minds to shift towards renewable energy sources that could be produced from more sustainable and environmental friendly feedstocks (ÓhAiseadha et al. 2020). The global warming problem could be solved to a greater extent by various sustainable means like adopting cleaner energy generation technologies through sun, wind, and biomass (Kang et al. 2020). These sustainable and cleaner energy generation ways require certain aspects to be fulfilled for effective generation like technology development, environment sustainability, economic feasibilities, and most importantly government aid in the form of policy making and general public awareness (Clauser et al. 2021). All the aforementioned factors could be tackled through proper research and development (R & D), nevertheless a good policy making can bring all these factors to reality (Zhao et al. 2021). Most of the private and commercial vehicles are equipped with liquid fuels compatible combustion engines. Therefore, if the consumers have to shift from conventional to other energy efficient alternative means like electric vehicles, then the financial and technological problem arises (İnci et al. 2021). Hence, the electric vehicles cannot be good and efficient alternatives for all such private and commercial automobiles. Biofuels are a remarkable alternative energy source and offers security as well as sustainability in the energy production area (Srivastava et al. 2020). The governmental involvement has helped a lot in augmenting the biofuel production from the past 20 years (Rai et al. 2021). Twenty percent of the over-all US corn stock was used for the production of ethanol in the year 2006 (Mai et al. 2021). Therefore, for the hike in the food prices during 2003 and 2008, biofuels were somewhat held responsible for this (Kaniapan et al. 2021). There was an increment of 70%, 69%, and 276% in the indexes of cereal grains, oils, and sugar prices, respectively, from the 2002 to 2004 average values to January 2010 (Dijkman and Benders 2010). Though significant progress has been made in understanding algal-based production since 2010, the algal-based bioenergy production situation is currently more difficult than it was in 2010 (Kumar et al. 2021). Despite tremendous advances in fundamental algal culture and upgrading technologies, algal-based biofuel still face tough competition in the commercial market from crude oil due to the crude oil's comparably low cost (Xing et al. 2021). Elevated cultivation and harvesting cost of the algal biomass feedstock is a greater challenge in bringing the algal biofuels to the market as compared to the terrestrial plant biomass. When compared with the terrestrial plants, algae are more biodiverse and exhibit metabolic plasticity (Yang et al. 2021). The algae acclimatize their biochemical metabolic pathways and the composition of cell wall under the influence of external stimulus. In some geographical environments, algae can also be grown on non-arable land; hence, in this way it does not face any competition with the land for providing the uninterrupted food supply (Shuba and Kifle 2018).

13.2 Global Biofuels Policy

On an international level, biofuel energy plays a fundamental responsibility to secure more competitive, secure, and sustainable energy system. Each country or region has its own approach for incorporating renewable energy into its national or regional fuel and energy infrastructure on a worldwide scale (Gielen et al. 2019). Without a considerable increase in renewable energy contributions to our current infrastructure, this shift will be unachievable. Government policies have largely encouraged the production and use of biofuels in order to minimize oil dependency and, as a result, increase the share of renewable energy contributing to CO_2 emissions reduction (Sarkodie et al. 2020), as shown in Fig. 13.1. The most common mechanisms for governments to support biofuel policies are blending mandates and tax exemptions; however, other policies, such as grants to support the installation of production facilities (Sandesh and Ujwal 2021), farmer premiums for the production of energy crops, and supporting research and development (R & D) funding, can also be used to help nascent industries develop.

The European Commission (EC) promotes the use of biofuels and bioenergy to assist the European Union (EU) in meeting various climate and energy targets by 2020 (often referred to as the 20-20-20 targets) (Širá et al. 2021). These objectives include: (1) 20% reduction in GHG emissions compared to 1990 levels; (2) a 20% final energy consumption derived from renewable sources, such as biofuels and bioenergy; and (3) a 20% reduction in primary energy use compared to projected levels, which will be achieved through energy efficiency improvements (Bórawski

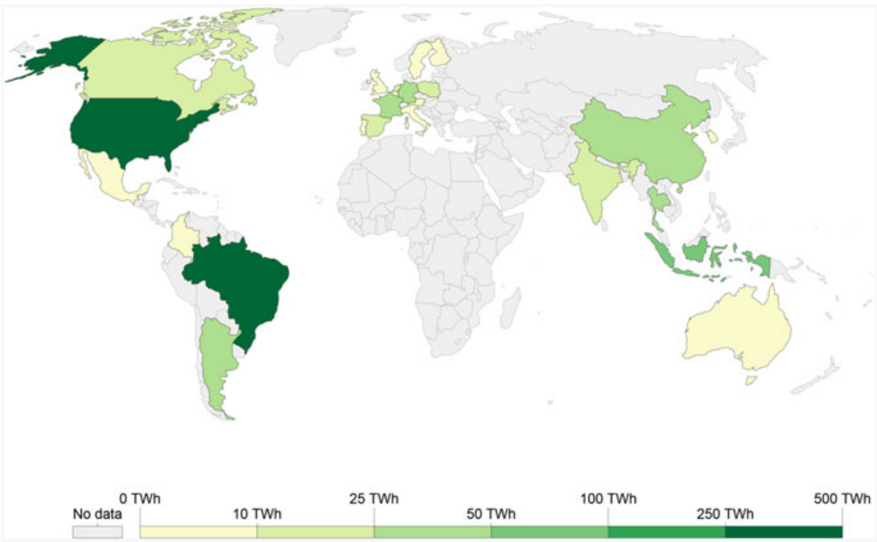

Fig. 13.1 Bioenergy production (2019) measured in Terawatt-hours (TW h) per year. European Union (EU) source, BP Statistical Review of World Energy

et al. 2019). The RED developed rigorous sustainability rules to ensure the long-term use of biofuels and bioenergy.

13.2.1 United State of America

The Energy Independence and Security Act of 2007 (EISA), formerly known as the Clean Energy Act of 2007, expands the Renewable Fuel Standard (RFS) by enhancing and diversifying alternative biofuel options as well as increasing biofuel use in the transportation sector (Skogstad 2020). EISA separate into four categories EISA, each with its own set of minimum Green House Gas (GHG) output requirements (Johansson et al. 2020). As part of the US-RFS implementation, the US Environmental Protection Agency (EPA) must estimate GHG emissions for renewable fuels pathways in order to determine their eligibility for the available RFS fuel categories (Yeh et al. 2016).

13.2.2 China

China implementing the 13th Five Year Plan in year 2016–2020 provide strengthen to tackle the environmental degradation of China by developing the country's clean and, green energy. In 13th five year plan ten policies are related to environment out of 25 (Hou et al. 2018). China mostly works on algal bioenergy and collaborates with the universities, commercial entities, and research institutes and provides financial assistance (Galanakis 2020). China National Basic Research Development Programme (BRDP) provides funding to government and nongovernmental organization to investigate and utilize the energy production from microalgae, and feedstock development for algae.

13.2.3 South Korea

South Korea government currently sponsors major research and development projects related to biofuel. The Marine Bioenergy Development Project (MBDP) and Algal Biomass project (ABP) of South Korea focus on clean and green energy production from marine algal biomass. The Global Frontier Project (GFP) and the Carbon Capture and Sequestration (CCS) 2020 projects, which explore methods for mass biomass cultivation and CO_2 capture and storage, both include algae technology (Lau et al. 2021).

13.2.4 Japan

Japan concentrated on second (rice straw, woody biomass) and third (microalgae) generation biofuels using feedstocks due to rising food demand and high pricing. For the Technological development *Pseudochoricystis algae* is used and the Ministry of Agriculture, Forestry, and Fisheries provide funding to joint research project with farms and universities to produce biofuel from algae (Koizumi 2013). The main goal of Ministry of Agriculture, Forestry, and Fisheries to produce and commercialize jet fuel from algae and commercialize by 2020.

13.2.5 Taiwan

Taiwan approved the Renewable Energy Development Act (REDA) in 2009, allocating money for renewable energy assistance through 2030 (Hung 2020). Funding distributed to government semi government universities, research laboratories, and industry. In dealing with policy, Taiwan government REDA Act mainly focus selection of microalgal species, technological development and cultivation of microalgae, and lipid extraction (Lu et al. 2020). National Taiwan Ocean University (NTOU) research on feedstock and seed stock of microalgae and industrial partner Easter Bio-Tec Co. of Taiwan collaborate with Taiwan's China Steel Co. will investigate decreasing GHG emissions by repairing flue gas with microalgae (Singh et al. 2019). Aside from that, the Industrial Technology Research Institute's Green Energy (ITRIGE) and Environment Research Laboratory (ERL) research the generation of physiochemical behaviour (cell disruption and nutrient starvation, for example) in algae for biofuel production.

13.2.6 India

India's National Policy on Biofuels (NPB) offers financial assistance for the development of first, second, and third generation biofuels. This policy support investigating topics related to algal treatment technology of wastewater and biofuel production from microalgae and diatoms (Prasad et al. 2021). NPB also support government and private organization such University of Madras, Chennai, for development of biogas and biodiesel production from microalgae (Elangovan et al. 2020). A National Algal Biofuels Network (NABN) was also established in 2008–2009 to encourage algal biofuels research, however, research progressed slowly, and the programme has since shrunk in size. Indian government will support financially and take action on budgetary measures from time to time as part of the National Policy on Biofuels, 2018, to guarantee that biofuels are effectively developed, promoted, and adopted throughout the country.

13.2.7 Brazil

The National Fund for Research Projects and National Research Council in Brazil collaborate with other federal organizations, state organizations, and private organization of Brazil give financial support, for bioenergy research (Brandão et al. 2021).

Most of the government fund allocate for research on algae growth and GHG emission. The Federal University of Rio Grande do Norte (FURG) has teamed up with the Petrobras Research Center (CENPES-Petrobras) to run a 100-m^2 pilot plant for microalgal culture (Viegas et al. 2020).

13.3 Global Implication of Algal Policy and Its Technological Implementation

Over the past two decades, huge amount of funding was infused for financial supporting for the Algae Research Community (ARC) under American Recovery and Reinvestment Act (ARRA) of 2009 approximate $44 M to the National Alliance for Algal Biofuels and Bio products (NAABB) in 2009. The Department of Energy (DOE) US, financially supported large part of this work and also provided a roadmap for developing economically viable technology for algal bio-refinery or algae biofuels. This large multi-year project had specific outcomes including basic advances in algal biology, i.e. genomic sequencing of the production strains, demonstration and use of low energy harvesting technology, development of a new open pond cultivation system (Lammers et al. 2017). In addition to numerous government-supported projects, a large number of commercial companies are sponsoring algae (both micro- and macro-algae) cultivation and research. The techniques employed range from open pond cultivation to photobioreactors in phototrophic cultivation to large-scale aerobic fermenters for heterotrophic algae production (Ananthi et al. 2021). Commercial facilities are used to produce either algal biomass feedstock (phototrophic and heterotrophic microalgae culture installations) or macroalgae (phototrophic and heterotrophic microalgae cultivation installations) (Brasil et al. 2017). Similarly, there are intermediate-scale research programmes underway to promote the development of a bioenergy economy based on algae production. In the field of algal biofuels, academic publishing is dominated by North America and Europe, whereas the bulk of patent applications are filed in the USA, the European Union, and China (Cruce et al. 2021). Currently, the bulk of algae-related businesses (in coastal areas) concentrate on either natural gathering or, in Asia, seaweed cultivation as a food or bioenergy crop (Mac Monagail and Morrison 2020). Seaweed has a long history in China's economy and aquaculture industries; nevertheless, as given in Table 13.1, a major part of the world's microalgae is farmed in this region as well.

13.4 Factor Affecting the Global Algal Policy and Implication

Extensive production of algal biomass for biofuel and other value added products (pharmaceutical and nutraceuticals) not a big deal but some policy mismatched and regulatory gaps are present in every nation biofuel policy related to algal fuels which are clear cause of local and global environmental governance.

Table 13.1 Global Implication Technological Implementation by different governmental and nongovernmental organization

Funding agencies	Funding utilization	Funding amount	Future outcome	References
National Alliance for Algal Biofuels and Bioproducts (NAABB)	Solazyme Inc.	\$22 M	This project aims to reduce GHG emissions by 90%, with a facility capable of producing 300,000 gal/year of pure algae oil per year.	Unkefer et al. (2017), Lammers et al. (2017)
	Algenol Biotech LLC	\$25 M	Integrating the photosynthesis driven algal conversion and CO_2 to ethanol that can be economically scaled to enable commercial production	
	Sapphire Energy Inc	\$50 M	Construct and operate a 300-acre algae culture farm and biocrudes oil conversion complex in Columbus, New Mexico	
Consortium for Algal Biofuels Commercialization (CAB-Comm)	University of California, San Diego	\$11 M	This project includes increasing biomass productivity, and creating advanced biotechnology tools for commercializing of microalgal bioproducts with industrial partners	Harmon et al. (2021)
	Arizona State University's Arizona Center for Algae Technology and Innovation (AzCATI)	\$6 M	Developing microalgal consortia based on growth/process conditions and develop technology for converting whole algal biomass, in to of algal biofuels as replacements for petroleum-based fuels	
Cornell Marine Algal Biofuels Consortium	Cornell University and Cellana	\$9 M	Develop an integrated design for the production of higher value products alongside biofuel production at Cellana's large-scale algae production facility in Kona, Hawaii.	Greene et al. (2017)
	Algae Test bed Public Private Partnership (ATP3)	\$15 M	The project's objectives are to develop collaborative open test beds that will increase stakeholder access to scale-up facilities and to gather and publish high-impact data from long-term outdoor cultivation operations.	
National Bioproducts Programme Algal Biofuels Initiative Canada's National Research Council (NRC)	Regional Algal Feedstock Test bed (RAFT) and Texas, New Mexico, Washington and Arizona	\$5 M N.A	Creating long-term cultivation information to identifying, derisk, and promoting the production of increased algal biomass	Pankratz et al. (2017)

(continued)

Table 13.1 (continued)

Funding agencies	Funding utilization	Funding amount	Future outcome	References
	NREL, Sandia National Laboratories, and PNNL	N.A	Deployment of algal Biorefineries with Canadian wastewater treatment plants	
Canadian federal government (CFG)	Solarvest (PEI), Inc.,	$0.377 M	Production of hydrogen through algae	Scaife et al. (2015)
Algal Carbon Conversion (ACC) Flagship Programme	N.A	N.A	Identify the most appropriate algal species for industrial deployment, and develop different routes to reduce algal processing cost and also developing various route for the conversion of biofuel and value added product	Dickinson et al. (2015)
Mexico's Secretariat of Energy and its National Council for Science and Technology	N.A	N.A	Funding for algae biofuels research	Rodríguez et al. (2019)
European Algae Biomass Association (EABA).	Algae Cluster Umbrella (ACU)	€20 million	This project include several small projects these are given below:	Araújo et al. (2021)
			InteSusAl: On an industrial scale, an integrated approach to the production of biofuels from algae in a sustainable manner.	
			BioFAT: Developing a 10hactarec microalgae-to-biofuel demonstration project	
			Algae BioGa: Aims to demonstrate algal treatment of biogas digestate	
			EnAlgae: Nine pilot facilities for micro and macroalgae growing are in operation.	
			Fuel-4-Me: Targets the pilot scale production of biofuels from algal lipids	
			MIRACLES: Overcoming the technological obstacles that hinder microalgae from being used in food, aquaculture, and other products	

13.4.1 Policy Mismatches in Algal Policy

Policy mismatch dilemma arise where political systems supporting contradiction in policy objectives. According to European energy (EU) renewable energy policy there is potential conflict between the production algal biofuel and driven factor. Policy mismatched driven factor directly affecting the production of sustainable biofuel. Every nation work on reducing the carbon emission foot print to tackle the phenomenon of global warming but in term of waste, water and biodiversity production of biofuel from algae produced more corban emission foot print than first generation feed. According to physiological behaviour of microalgae it not grow in land with high biodiversity value these organism only grow in peat land where resultant cultivation could increase the emission of carbon foot print. Removal of high carbon forests or wetlands, use of GMO microalgal species and technological feasibility for high yield of biofuels boosts emissions of carbon footprint in the environment. (Trentacoste et al. 2015). But according to Cartagena protocol of biosafty use of GMO species is strictly prohibited which directly contradicting the aims of renewable energy policy.

13.4.2 Regulatory Gaps

With regard to regulatory gaps, environmental law currently plays an important role in working out environmental impacts, but there is a need to change environmental laws from time to time to work out the effects of environmental events. Making biofuel by algae is a good proof of renewable energy but biofuel if made from biomass. Therefore, the biomass is classified as municipal and industrial waste as biodegradable according to the regulations by the European Union. According to the UK government, biofuels generated from waste biomass are classified as waste products rather than biofuels. Classifcation in the waste product is potential gap in the environmental policy which affects the agenda of clean energy from the renewable source (Benson et al. 2014).

Another potential regulatory difference may exist with respect to onshore and offshore marine macroalgae production. Biofuel production by algae is a very promising future plan. If new species of algae or GMO introduced in these onshore and offshore sea areas, So what will be the effect on the biodiversity present in these areas, as well as what changes will occur in the ecological system of the ocean. Introducing new spices of microalgae in sea water which also affect the marine ecosystem services such as fisheries, shipping operators and tourism. According to Bosma and Verdegem (2011) if the production of algal in marine environment at large scale affecting the local aquaculture environment as well as communities who currently use these resources. Sustainability issues, including biodiversity, invasive species and eutrophication impacts, are supposed to be considered in marine plan objective-setting.

13.5 Conclusion

From the past decade fuel industry shifted towards biofuels industry which has been driven by government policies. Governments implementing the by supporting, granting capital, tax exemption on target end-products. More information and research are needed to improve the potential magnitude, gaps for policy makers and industry executives for expansion of the biofuel sector which ensuring the future ecological sustainability of algal biomass production. Very few research and policy related literature are available for understanding the algal biofuel policy.

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