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# Biomass Valorization to Bioenergy

Springer

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Springer

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# Preface

Energy demand has been rising remarkably due to increasing population and urbanization. Global economy and society are significantly dependent on the energy availability because it touches every facet of human life and activities. Transportation and power generation are two major examples. Without the transportation by millions of personalized and mass transport vehicles and availability of 24×7 power, human civilization would not have reached contemporary living standards.

The International Society for Energy, Environment and Sustainability (ISEES) was founded at Indian Institute of Technology Kanpur (IIT Kanpur), India, in January 2014 with an aim to spread knowledge/awareness and catalyze research activities in the fields of energy, environment, sustainability, and combustion. The Society's goal is to contribute to the development of clean, affordable, and secure energy resources and a sustainable environment for the society and to spread knowledge in the above-mentioned areas and create awareness about the environmental challenges, which the world is facing today. The unique way adopted by the society was to break the conventional silos of specializations (engineering, science, environment, agriculture, biotechnology, materials, fuels, etc.) to tackle the problems related to energy, environment, and sustainability in a holistic manner. This is quite evident by the participation of experts from all fields to resolve these issues. The ISEES is involved in various activities such as conducting workshops, seminars, and conferences in the domains of its interests. The society also recognizes the outstanding works done by the young scientists and engineers for their contributions in these fields by conferring them awards under various categories.

Third International Conference on "Sustainable Energy and Environmental Challenges" (III-SEEC) was organized under the auspices of ISEES from December 18–21, 2018, at Indian Institute of Technology Roorkee. This conference provided a platform for discussions between eminent scientists and engineers from various countries including India, USA, Norway, Finland, Sweden, Malaysia, Austria, Hong Kong, Bangladesh, and Australia. In this conference, eminent speakers from all over the world presented their views related to different aspects of energy, combustion, emissions, and alternative energy resource for sustainable development and cleaner environment. The conference presented five high-voltage plenary talks from globally renowned experts on topical themes namely “The Evolution of Laser Ignition Over more than Four Decades” by Prof. Ernst Wintner, Technical University of Vienna, Austria; “Transition to Low Carbon Energy Mix for India,” by Dr. Bharat Bhargava, ONGC Energy Center; “Energy Future of India,” by Dr. Vijay Kumar Saraswat, Honorable Member (S&T) NITI Aayog, Government of India; “Air Quality Monitoring and Assessment in India,” by Dr. Gurfan Beig, SAFAR, and “Managing Large Technical Institutions and Assessment Criterion for Talent Recruitment and Retention” by Prof. Ajit Chaturvedi, Director, IIT Roorkee.

The conference included 24 technical sessions on topics related to energy and environmental sustainability including 5 plenary talks, 27 keynote talks, and 15 invited talks from prominent scientists, in addition to 84 contributed talks, and 50 poster presentations by students and researchers. The technical sessions in the conference included advances in IC engines, solar energy, environmental biotechnology, combustion, environmental sustainability, coal and biomass combustion/gasification, air and water pollution, biomass to fuels/chemicals, combustion/gas turbines/fluid flow/sprays, energy and environmental sustainability, atomization and sprays, sustainable transportation and environmental issues, new concepts in energy conservation, waste to wealth. One of the highlights of the conference was the rapid-fire poster sessions in (i) engine/fuels/emissions, (ii) renewable and sustainable energy, and (iii) biotechnology, where 50 students participated with great enthusiasm and won many prizes in a fiercely competitive environment. More than 200 participants and speakers attended this four days’ conference, which also hosted Dr. Vijay Kumar Saraswat, Honorable Member (S&T) NITI Aayog, Government of India, as the chief guest for the book release ceremony, where 14 ISEES books published by Springer, Singapore, under a special dedicated series “Energy, environment and sustainability” were released. This was second time in a row that such significant and high-quality outcome has been achieved by any society in India. The conference concluded with a panel discussion on “Challenges, Opportunities and Directions for National Energy Security,” where the panelists were Prof. Ernst Wintner, Technical University of Vienna, Prof. Vinod Garg, Central University of Punjab, Batinda; Prof. Avinash Kumar Agarwal, IIT Kanpur; and Dr. Michael Sauer, Boku University of Natural Resources, Austria. The panel discussion was moderated by Prof. Ashok Pandey, Chairman, ISEES. This conference laid out the roadmap for technology development, opportunities and challenges in energy, environment and sustainability domain. All these topics are very relevant for the country and the world in present context. We acknowledge the support received from various funding agencies and organizations for the successful conduct of the Third ISEES conference III-SEEC, where these books germinated. We would therefore like to acknowledge NIT Srinagar, Uttarakhand (TEQIP) (special thanks to Prof. S. Soni, Director, NIT, UK), SERB, Government of India (special thanks to Dr. Rajeev Sharma, Secretary); UP Bioenergy Development Board, Lucknow (special thanks to Sh. P. S. Ojha), CSIR, and our publishing partner Springer (special thanks to Swati Meherishi).

The editors would like to express their sincere gratitude to large number of authors from all over the world for submitting their high-quality work in a timely manner and revising it appropriately at a short notice. We would like express our special thanks to reviewers, who reviewed various chapters of this monograph and provided their valuable suggestions to improve the manuscripts.

Renewable energy resources play a vital role in fulfilling the increasing energy demands. This monograph is aimed to explore the possibilities of using biomass as resource for bioenergy production.

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| Tiruvannamalai, India | R. Praveen Kumar |
| Chennai, India | B. Bharathiraja |
| Tezpur, India | Rupam Kataki |
| Guwahati, India | V. S. Moholkar |

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## About the Editors

**Prof. R. Praveen Kumar** is working as Head of the Department in Department of Biotechnology, Arunai Engineering College. His area of research includes biorefineries, renewable energy from biomass and municipal waste. He is having more than 50 research publications, 6 book chapters, co-author of 3 books and provisional registration for 4 patents. He had organized various National and International Conferences and served as Scientific Advisory Committee member in several National and International events. He has chaired sessions and delivered invited talks in various National and International conferences. He is a life member in various professional societies which includes BRSI, IICHE, ISEES, IFIBiop, BigFin, ISTE, EWBIndia. He is serving as Management council member in Biotech Research Society of India (BRSI) and as Vice-President in “Engineers Without Borders – India (EWB-India)” Chennai chapter. He is a recipient of “ISTE-Syed Sajid Ali National Award for Outstanding Research work in the field of Renewable Energy” for the year 2017.

**Dr. B. Bharathiraja** an Undergraduate in Chemical Engineering and post graduate in Industrial Biotechnology and Ph.D in Biochemical Engineering from Anna University Chennai, totally 14 years of experience in teaching. His area of research includes Biofuels from biomass and municipal waste. He had published more than 70 publications in peer reviewed journals, 2 books and 7 book chapters. Served as Chief Editor of International journal of Bioprocess Technology and polymer sciences and editorial board member in various journals. International Scientific Advisory Committee member in “The 2012 Asian Biohydrogen and Bioproducts Symposium (ABBS)” conducted by Chongqing University, on November 9-12, 2012 in Chongqing, China. He has visited various countries including USA, China & Bangladesh, Hong Kong to attend international conferences. He has chaired sessions and delivered invited talks in various International conferences which include "BEST -2013, 2015 and 2017 Tiruvannamalai India". He is a life member in various professional societies which includes BRSI, IICHE, BigFin, ISTE, EFB.

**Dr. Rupam Kataki** is currently serving as a Professor, Department of Energy, Tezpur University, and a former Head of the Department. He received his BSc and MSc from Assam Agricultural University, Jorhat and PhD from Tezpur University. Dr. Kataki has research interests in the areas, viz. thermochemical conversion of biomass to biofuel and biochar, utilization of agricultural, agro-industrial, and waste biomass for recovery of fuels and chemicals, C-sequestration and soil amendment through biochar application, production of biodiesel, biooil, and value-added products through a biorefinery approach from indigenous tree-borne oil yielding species of NE India, Water remediation and heavy metal removal through use of engineered biochar, industrial uses of biochar, and Ecological and economical aspects of charcoal production in traditional kilns in NE India. He has to his credit about 86 publications including edited books, book chapters, journals publication and full length papers in conference proceedings. He has been in the editorial board of a number of journals including SCOPUS indexed, International Journal of Renewable Energy Development. He has reviewed for as many as 33 different journals and received Top Reviewer Award from Bioresource Technology in 2017. He is a regular reviewer of research proposals of Government funding agencies like DST, DSIR and CSIR-NISTADS. Dr Kataki is an examiner of PhD thesis of several Universities including AcSIR. He has successfully completed a number of nationally funded research projects including an Indo-European Union collaborative research project with several European and Indian PIs, and a couple of research projects are currently undergoing. He has so far supervised three doctoral students and about 33 MTech thesis. He has been a member of a number of scientific societies, and of committees of Government at district and state level. He is also a member of the Board of Studies of Assam Science and Technology University.

**Dr. V. S. Moholkar** (b. 1972) is a Full Professor of Chemical Engineering and Head of Center for Energy at Indian Institute of Technology (IIT) Guwahati. He received Bachelors (1993) and Masters (1996) degree in chemical engineering from Institute of Chemical Technology (ICT) Mumbai, followed by Ph.D. from University of Twente in 2002. He has been Head of the Chemical Engineering Department at IIT Guwahati between 2012-2015. His main research interests are sonochemistry, cavitation assisted physical, chemical and biological processing, and thermo- and biochemical routes to biofuels. As of November 2018, he has published more than 140 papers in renowned international journals that have received more than 5000 citations (with h-index of 43). He has also filed 3 US patents (in collaboration with CTI Nanotech, CA, USA) on application of hydrodynamic cavitation reactors for biomass pretreatment and bioalcohol synthesis. He has graduated 15 Ph.D. and 26 M.Tech. students. He has been elected as Fellow of Royal Society of Chemistry (FRSC) in July 2016. He has also been elected as

Fellow of Institution of Chemical Engineers, UK. He is a Chartered Engineer (CEng) registered with Engineering Council of UK. He was admitted as Senior Member of American Institute of Chemical Engineers (MAIChE (Sr.)) in August 2016.

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## Chapter 1
# Agro-Industrial Waste Valorization to Energy and Value Added Products for Environmental Sustainability

**K. Senthilkumar, M. Naveen Kumar, V. Chitra Devi, K. Saravanan and S. Easwaramoorthi**

**Abstract** Agro-industries produce large amounts of various forms of waste, which come out from processing activities and waste management processes. The wastes generated may be multi-phase and may consist of multi-component. The amount, characterization and composition of this waste depend on the raw material sources, product types, and processes. Agro-industries, more specifically food industrial wastes, consist of great amount of organic matters which are rich in nutrient content, with higher values of BOD, COD and TSS. If agro-industrial wastes are not correctly treated, they may cause severe pollution problems. Besides, they represent a loss of valuable biomass and nutrients. The present book chapter reviews the various characteristics of pollution management problems of different agro-industries. In many agro-industries, water pollution is a serious threat as compared to solid wastes which have the possibilities for recovery of value added products. Various possible sources and impacts of different agro-industrial wastes on the environment are extensively reviewed. The possible ways of meting out of biomass and inhibition of micro-organism using Biorefinery principles and its challenges are also explored. The bio-refineries can reproduce an oil refinery by means of a bio-refinery using renewable biomass for the manufacturing different products. The possible future of technological developments in order to improve the quality of people's life and sustaining our environment by using clean bioprocess technologies and its future

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aspects are also explained. The present book chapter elaborately describes about the key activity of clean technology ‘recycling’ of agro-industrial waste that is deliberately important as it utilizes the integrated approach of waste minimization which guides to biological industrial complex where a group of industries share possible resources and recycling of wastes. This book chapter review highlights the application of bio-refinery concept on wastes obtained from the agro-industries.

**Keywords** Biomass · Bioenergy · Clean technology · Recovery · Recycling · Agro-industrial waste · Sustainability

## 1.1 Introduction

In recent times, revolt of industries is one of the important factors for the introduction of technological developments in enhancing the life style of a community. Due to this, the end results are utilization of land, modification in utilization, global trade, more expectancy, improved housing and sanitation, enhanced employability, etc. The very first occasion of using bio-fertilizer from forest for farming of fertility land by human being. The biomass recycling in a forest resulted nutrient–rich soil of a forest (Yusuf 2017). Fallen parts of trees and plants like leaves and branches decomposed by decomposers to provide organic waste from agriculture to nature. Similarly in addition to the firewood and wood clubs, huts’ roofs were made using agriculture residues like rice straw. People from agricultural background producing products from agricultural residue for their own consumption. The launch of Green Revolution in the 1950s was done with the aim to provide help to fast-growing people through yields of agricultural products. To attain this higher production, introduction of large-scale mechanized mono-crop culture systems has been done which intern causes capturing of agricultural lands and forest areas, evacuation of farmers from lands and moving into urban areas, etc. (Venglovsky et al. 2006). A variety of new chemicals such as chemical pesticides, and herbicides, fertilizers, were introduced to maximize crop production. The usage of these new chemicals made a significant impact like eradication of bacteria, microscopic algae and fungi present in the soil, diminishing natural fertility of soil, water pollution, resulting in severe eutrophication and harmful results on marine environment.

## 1.2 Sources and Impact of Agro-Industrial Wastes

Agricultural wastes are defined as the residue produced during the growing and processing of agricultural products such as fruits, vegetables, dairy products, crops, etc. Generally, the agro-industry can be classified into in two types. The primary type requires some activities like treating and manipulating crops like converting wheat into flour, preservating fruit and vegetables in refrigerants, etc.). The subsequent type involves direct industrial transformations of food products like preservative products from animals and vegetables.

In food processing industry, especially in the processing phases, separation of edible parts from non edible parts forms more amount of waste. At industry level trimming process can be more efficient in terms of potential loss of edible product, compared to the conventional methods. Efficiencies in transformation may change with respect to the type of products. Some of the unavoidable activities like excess production, packaging, damages and technical break down can also other causes for losses (Sarkar et al. 2012). Agro-industries mostly producing organic wastes include the by-products produced during agricultural-food processing like bagasse, dregs, degummed fruits, cellulose, etc. Agro-wastes are largely consisted of carbohydrates, multifaceted polysaccharide, polyphenolic components, etc.

The agro-industrial wastes are classified into agriculture residues and industrial residues, as shown in Fig. 1.1. Agriculture residues can be further categorized as field residues which are available in field at the final stage of harvesting process

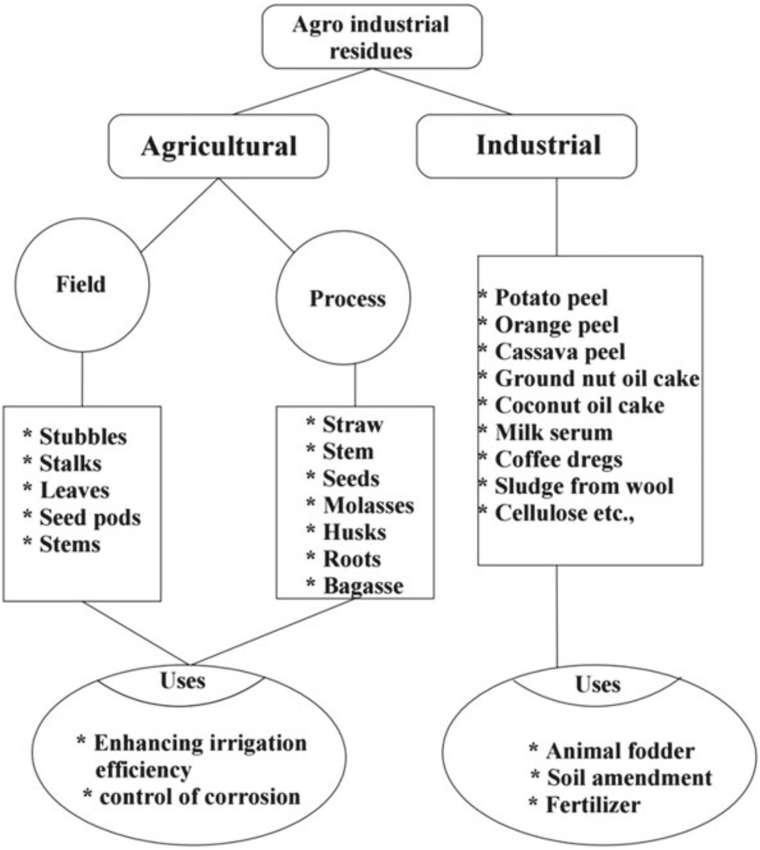

**Fig. 1.1** Classification of agro-industrial residues and its uses

(Kim and Dale 2004). The field residues contain of leaves, crop remains, stalks, seed pods, stems, livestock slurry, pruning waste and waste released from maintenance of woodlands etc. The process residues exist even after the crop is processed for example bagasse, molasses, husks, seeds, leaves, stem, straw, roots, etc. These residues are used to manufacture animal feed, soil fertility enhancement, organic fertilizers, manufacturing sectors, etc. Enormous volumes of field residues are generated and the majority of them are underutilized. Based on the availability and characteristics of Agricultural residues, it can be differentiating from other solid fuels.

Agro-industries like food industries produce huge amounts of multi-phase and multi-component wastes which may be in liquid, solid and gaseous form. These wastes are discharged from processing operations, their treatment and disposal process (Bharathiraja et al. 2017). The quantity and constituents of agro-industrial wastes mostly depends on the raw materials characteristics, nature of the products, types of operations and processing steps. Food processing wastes consist of large quantity of organic material such as carbohydrate, protein, fat, oil, etc. with higher values of environmental characteristics like BOD, COD, and suspended solids. Since agro-industrial wastes have rich in nutrient value, there is a huge chance for causing severe pollution problems, if not properly treated. The agro-industries may cause various kind of pollution such as waste effluent, solid waste, air pollution, with significant amount of noise pollution occurring in a very few industries (Jecu 2000).

Every year, an enormous amount of organic wastes and related wastewaters are generated by the various food industries. These organic residues can be used as the energy sources for different sectors. The continuous increase in populace increases the demand of food and its uses, which in turn enhances growth of food and beverage industries in order to fulfill the requirement of food. Generally fruit industrial wastes contain compositions of cellulose, lignin, moisture, ash, carbon, nitrogen, etc. (Salim et al. 2017). These are digested to produce products like biogas, bio-ethanol, and other commercially useful products. In India due to the enormous amount of production of fruits and vegetables, every year almost 20% of yield of fruits and vegetables are going as waste. So the percentage of waste generated from food related industries is highly depended on its production. Similarly, the waste generated from food related industries having high BOD, COD, etc. Mostly these untreated wastes caused undesirable effect on atmosphere, environment, human beings and animal health. Since these wastes contains different organic compounds which can be used to produce a variety of value-added products, which in turn reduce the production cost (Yusuf et al. 2017).

From the literature it is observed that conventional agriculture is the most important polluter of an environment, more particularly the uncontrolled usage of chemicals. For any nation, agricultural development is very much depended on the development of fertilizers, pesticides and herbicides. These fertilizers and herbicides can contaminate the water and soil because of its chemical composition. Besides, the knowledge about soil fertility and soil characteristics are more important. Lack of these knowledge may induce the farmers to use fertilizers and pesticides in uncontrolled manner, which in turn increases the risks of soil and water pollution. Water and soil contamination with heavy metals, micro and macronutrients, herbicides, pesticides and polycyclic aromatic hydrocarbons have become more significant (Yusuf et al. 2015, 2016).

## 1.3 Prioritization of Waste Management

In most of the agro-industries, if better and proper waste management techniques are employed problems related to environmental degradation could be minimized considerably. The execution of these good quality techniques may avoid all kind of pollution and minimize other environmental problems. These techniques are also used to promote socio-economic advantages like production of by-products from wastes, recovery of value added products and reduction of waste treatment costs. Prioritization of agro-industrial waste management can be implemented as mentioned below.

### *1.3.1 Industrial Waste Reduction*

By the implementation of in-plant modification steps, agro-industrial waste generation may be reduced. However, local conditions of the industry may play an important role in its applicability (Panesar et al. 2015).

### *1.3.2 Waste Protection*

Waste protection or waste conservation is a proficient precautionary action to be taken in order to reduce the waste generation. Possible usage of various resources in efficient manner for the maximum economic profit as well as environmental protection. A few of the potential agro-industrial waste management techniques are energy conservation, keeping bulk solid wastes and dispose as concentrated sludge, minimizing water usage and minimizing waste at source itself, etc.

### *1.3.3 Solid Waste Separation*

The various processes like isolation of solid wastes, eliminating suspended solids may be applied to diminish removable solids from agro-industrial effluent and to minimize the waste loading and treatment expenses. Another important operation of analyzing the characteristics of agro-industrial wastewater released from different process operations should be separated according to the characteristics of the wastewater (Kumar et al. 2017). This method is most useful when an agro-industry wanted to achieve effective by–product recovery, recycling, and reuse. By using various clean technologies such as waste utilization, returning to the place of their origin and soil, organic matters present in agro-industrial wastes can be recycled.

### *1.3.4 Three R Principles*

Even though waste minimization techniques are used in the agro-industries, it is unavoidable that solid and liquid wastes are still produced. The 3R principle i.e. recovery, reuse, or recycling of agro-industrial wastes for may be required. The products obtained using 3R principles might be used as raw materials for the manufacture of some other products. In most of the agro-industries more specifically from food processing effluent the recovery of solid, oil, protein from is in practice (Galanakis 2012).

## 1.4 The Concept of Bio-refinery and Historical Development

In the present scenario of the increasing population, to live a sustainable life, it is much important to develop a sustainable farming along with maximum utilization of available resources. So first priority may be given to set up bio-refineries whose raw materials are exclusively based on biomass, wastes discharged by human being and animals. The success of any bio-refinery concerned with food, energy and organic chemical production mostly depends on local people and some government organization. The biomass composition in chemical form is able to produce a similar kind of end products. Each region may have established bio-refinery which helps to have sustainability of land and environment, peoples and animals life. In the process of photosynthesis plants are producing the energy in the form of biomass and it will be stored as chemical energy (Gonzalez-Garci et al. 2017). Therefore, biomass is solar energy stored in a chemical form. The major goal of each bio-refinery is to utilize this stored energy for a sustainable development on this planet. Due to the growth of rapid industrialization and green revolutions the environmental problems are increased. Almost 90% of most of the communicable diseases occur in developing countries lead to invite call for strategies to sustain and improve environment and agriculture (Panesar et al. 2015; Tonini et al. 2016; Gonzalez-Garci et al. 2016).

## 1.5 Bio-refinery Management

The most important main concern of management is to ensure self-efficiency in food, energy and fertilizer manufacture for the region with a socio-economic marketing approach. This requires a good knowledge about availability and accessibility of biomass, Biodiversity in agricultural food products production, variety of animal production, nature of soil and Soil fertility, agricultural yields, land availability, Population growth, etc. The management of bio-refinery committee may consist of representatives from local communities, business, government and financial institutions, with expert advisers having knowledge on availability of biomass from local agricultural research institutions (Esteban and Ladero 2018; Aruldass et al. 2016). Once the fundamental requirements for the bio-refinery operation have been established, crop and process development be able to begin.

The schematic representation of concept of bio-refinery is shown in Fig. 1.2. There are a few basic sectors are involved in bio-refineries, as mentioned below:

1. The Farming sector mostly fretful with soil fertility, land utilization, biomass production, crop yield and pest control.
2. The bioprocessing division mainly concentrated on utilization of excess crop and agricultural waste to produce value-added products.

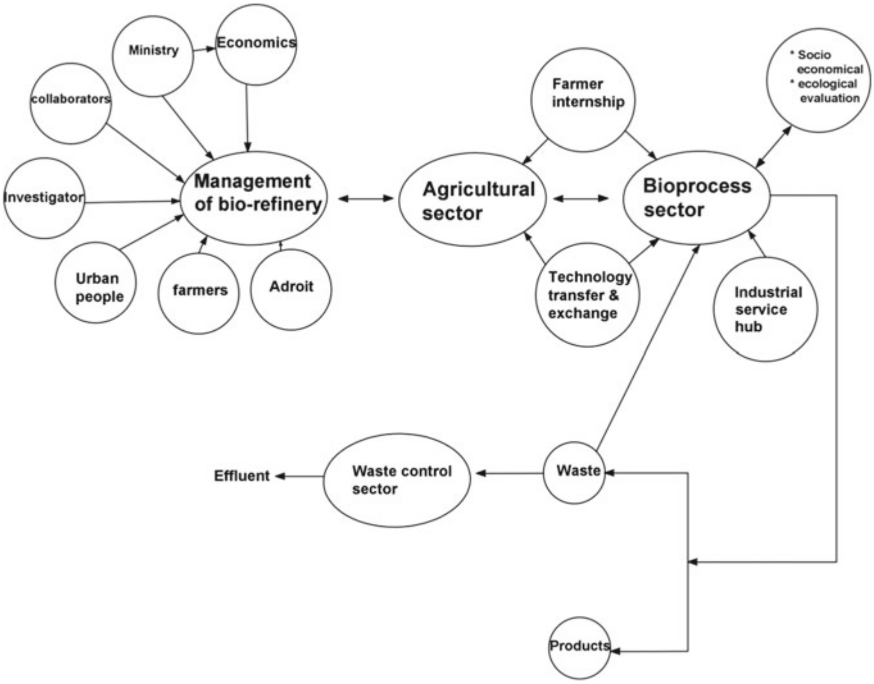

**Fig. 1.2** Schematic representation of concept of bio-refinery

3. The wastewater monitoring section, which controls and monitors all effluent discharged into the environment.

Any of these sections may or may not consist of various sub-units and may or may not be associated with everyone. It is important that management is kept to a minimum in favour of production. Besides, it is more significant to pressure that these units concerned with clean technologies, helping to live sustainable healthiness of human beings and the living environment, which in turn will enhance the life style of all people (Luchese et al. 2017; Govindaraj et al. 2017).

## 1.6 Conclusions and Future Prospects of Bio-refinery Techniques

The most important objective of each of the agro-industries is socio-economic, eco-efficiency and environmental sustainability. Such industries would honestly benefit the farmers as the generation of biomass would be maximized and the socio-economy, availability of jobs for rural people, in turn stabilizing the rural people life style, social structure of the rural communities and minimizing relocation into cities. Each and every agro-industry have an imperative demand toward the safe operation of agro-materials through proper reusing of wastes generated during the different steps in manufacturing processes. Agro-industry releases a huge volume waste material which could be utilized in many of the fields such as energy recovery, composting, fertilizer, etc. In the present scenario, energy requirement and cost-effective pressure on industries requires sustainability in the utilization of resources and to get optimum usage. The usage of agro-industrial wastes can be a good option to meet the needs of the present generation without compromising the future generations, so there is a heavy need for more attention into the utilization of agro-industrial waste and various recycling techniques. Unquestionably, utilization of wastes for the recovery and reuse of value added products eliminates the waste disposal problems and solves the problems related to pollution. Due to the environmental sustainability and conservation, universal awareness about agro-industrial waste is changing swiftly. In the current scenario, agro-industrial wastes have been used in a number of ways including the recovery and reuse of different value-added products. The most important applications of recovered/recycled wastes are production of biofuel and enzyme, extraction of pigment, extraction of food flavoring, agricultural composting, etc. Hence, additional authoritarian approval and capital investments are needed to expose these recovered products in the commercial market. The recovery and production of value-added products from agro-industrial wastes may not only provide future dimension to the current researchers but it diminish the present threats related to environment.

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# Chapter 2
# Role of Energy Crops to Meet the Rural Energy Needs: An Overview

**Pratyush Kumar Das, Bidyut Prava Das and Patitapaban Dash**

**Abstract** The dwindling energy resources are essential for our daily activities and socio-economic development. The excessive use of energy resources at national and international levels creates a burning problem of energy crisis. In rural sectors, multiple constraints limit the generation and availability of energy. To remove the rural sector energy crisis, it is essential to reduce the burden on the use of conventional sources of energy and to find out new avenues for the generation of non-conventional, renewable sources of energy. The people of the rural area have a feeble economic condition and many of them are from the marginal sections of the society, lying below the poverty line. The generation of renewable sources of energy like biofuel using biomass of energy crops as feedstock is possibly a viable concept in this context. The perennial, non-edible plants having high cellulose contents and requiring least pre-treatment are possibly the best option to be selected as energy crops under rural energy generation system. The biofuels like bioethanol and biodiesel produced from the biomass of energy crops have the potential to provide environmental security as these are low emitter of greenhouse gases (GHGs) like $CO_2$. The low cost bioenergy produced from the energy crops could be affordable for the rural people to use it as a source of energy input. The most supportive measure in this context is the expansion of research and development activities on production and consumption of biofuels at the global level. The success of this rural energy generation programme depends upon the acceptance and interest developed among the rural people to consume this energy to meet their requirements. This could further help in stabilizing the economic conditions of the people residing in the rural sectors. The current chapter mainly deals with utilization of energy crops as an alternative renewable resource to fossil fuels. Energy production processes from energy crops have been discussed along with

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their role to meet energy needs at the rural level. Current global statistics on energy production from the energy crops have been extensively reviewed. Further work on this aspect is essential to improve the energy demanding scenario of the rural sector and to strengthen the global economy.

**Keywords** Biofuel · Bioenergy · Energy crops · Renewable resource · Rural

## 2.1 Introduction

The energy is the backbone of an economy and essential for development at national and international levels. The development depends upon industrialization and urbanization at the global front. It has the possibility of increasing the energy demand by two to three times. The socio-economic development and increase in the demand for energy consumption are the factors responsible for energy crisis. It is an upsurge problem that affects the welfare of the living resources and their environment. Insufficiency of energy in the rural sector is of prime concern as it affects the livelihood of the marginal section of the society.

To achieve self-sufficiency in rural energy sector, it is essential to increase the production of energy from non-conventional sources like biomass. The conventional use of biomass as a source of heat energy in the rural sector is open burning (Singh et al. 2008; Roy and Kaur 2016). It leads to the release of solid and gaseous pollutants in the components of our environment like atmosphere, hydrosphere and lithosphere, ultimately leading to environmental pollution. The contamination of the environmental components like soil is a complex phenomenon that needs decontamination to restore the environmental quality (Das et al. 2018). The open burning of biomass has negative impacts on organisms and their environment through primary or secondary exposure.

In rural sector many people are pre-occupied with agriculture as their profession. It provides impetus for biosphere production. Amidst it, they are facing challenges like inadequate amount of available energy due to limited access to energy sources and poor energy distribution system in the local condition. The rural energy system commonly faces problems like inadequate infrastructural support, lack of skilled technical manpower and feeble financial condition of the local people. The available energy in the rural sector may be treated as a scarce resource for the marginal sections of the society.

Many people have no scope to get access to the modern conventional and non-conventional forms of energy. It leads to a precarious condition of increase in the demand for energy in rural areas. The environmental pollution is intimately connected to such a rural energy demanding scenario. Under such a condition, it is imperative to reduce the gap between the demand and supply of energy in rural sectors to make the system a self-sufficient one. A possible option in this context is to harness the energy present in the biomass of energy crops. Energy is essential for social transformation and technological development. To make the rural energy system self-sufficient, it is preferable to boost up generation of energy from nonconventional sources. Use of energy crop biomass as feedstock for the generation of bioenergy is advantageous as it is indigenous, available in the local condition, cheap and affordable by the marginal section of the society.

## 2.2 Energy Crops

The biomass from energy crops, due to their abundance, represents as one of the most vital sources of renewable energy. It can be used for the production of biofuels and substantially, to make up the declining global fossil fuel reserves.

### *2.2.1 Needs for Harnessing Energy from Energy Crops*

In last few years there has been an increased concern over energy security and higher oil prices. These concerns can be attributed to increase in demand for fuel and dwindling non-renewable sources of energy. Besides, the problem has been highlighted further with inputs from organizations and panels like IPCC (Intergovernmental Panel on Climate Change 2006). It highlights on the cost factor, the people have to pay for their fossil fuel requirements in days to come. The emission of greenhouse gases (GHGs) is another concern. The increased emission of GHGs is mainly responsible for climate change. One of the major GHGs is carbon dioxide ($CO_2$) (Rutz and Janssen 2007). The earth's atmosphere is receiving around 15 billion ton of $CO_2$ per year. It shows the direct consequence of combustion of large amount of fossil fuels (Kamm et al. 2006). People have misconception that global warming and climate change is mainly caused by emissions from road transport; however, the reality is different. According to OICA (International Organization of Motor Vehicle Manufacturers 2019a), many other sources are also responsible for carbon dioxide emission (Table 2.1).

**Table 2.1** Carbon dioxide emissions from various sources

| Sources | % emission of $CO_2$ |
|---|---|
| Electricity generation and heating | 43.9 |
| Manufacturing and construction | 18.2 |
| Road transport | 15.9 |
| Fuel consumption for other uses | 12.2 |
| Non-road transport | 5.8 |
| Other non-transport | 4 |

*Source* OICA (2019a): Climate change and $CO_2$

**Table 2.2** World motor vehicle production since year 2000

| Production year | No. of cars (in 1000s) | No. of commercial vehicles (in 1000s) | Total (in 1000s) |
|---|---|---|---|
| 2000 | 41,215,653 | 17,158,509 | 58,374,162 |
| 2005 | 47,046,368 | 19,673,151 | 66,719,519 |
| 2010 | 58,239,494 | 19,344,025 | 77,583,519 |
| 2015 | 68,539,516 | 22,241,067 | 90,780,583 |
| 2018 | 70,498,388 | 25,136,912 | 95,634,593 |

*Source* OICA (2019b): Production statistics

The energy like solar, wind, geo-thermal and hydroelectricity can act as an alternative option for fossil fuels during generation of heat and power. However, there are few alternatives for the transport fuels. The year wise increase in the number of vehicles has led to an upsurge in the demand for liquid transport fuels. It may be a possible factor for scarcity of non-renewable fuels and an increase in carbon dioxide concentration in the atmosphere. The global statistics of world motor vehicle production since the year 2000 has been presented in Table 2.2.

A substantial increase in the production of motor vehicles, during the last two decades, point towards a possible increase in the consumption of liquid fuels. This trend is possibly going to increase in the coming days. This would eventually magnify the ever increasing demand for non-renewable fuel stocks and thereby causing further depletion of these natural resources. Taking the current scenario into consideration, it is presumed that an energy crisis is inevitable at the global front. In order to avoid it, the need of the time is to search for an alternative sources of energy, which should be renewable in nature and can save carbon as is being prioritized in global agenda (Karp and Halford 2010).

The global primary energy supply is increasing over time. As per the statistics (WBAGBS 2018), renewables only account for 14% of the total energy supply and have just increased by 1% since the year 2000 (Table 2.3).

Renewables form approximately 18% of the gross final energy consumed from various energy sources during 2016. At the same time, oils hold a share of 38%

**Table 2.3** Global energy supply and percentage share of renewables

| Year | Total energy supply in EJ | % of renewables |
|---|---|---|
| 2000 | 420 | 13.0 |
| 2005 | 481 | 12.3 |
| 2010 | 539 | 12.6 |
| 2015 | 571 | 13.6 |
| 2016 | 576 | 14.0 |

*Source* WBAGBS (2018)

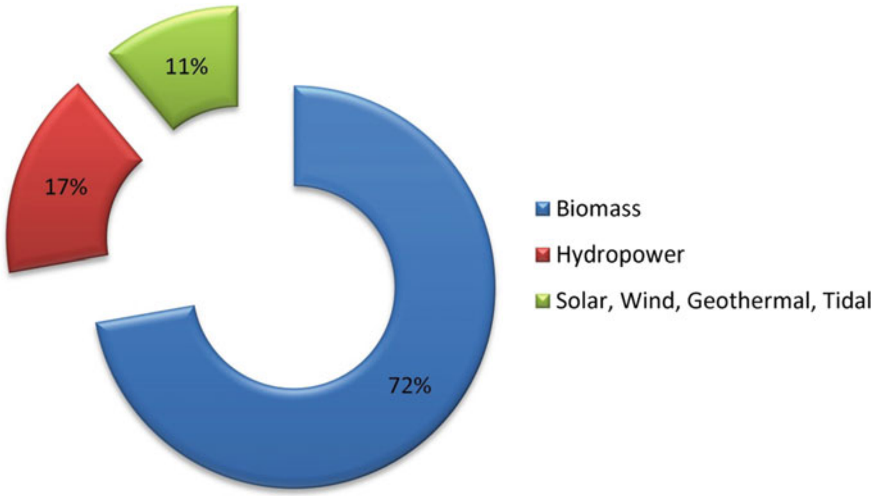

**Fig. 2.1** Share breakup of energy consumed from various renewables in 2016. *Source* WBAGBS (2018)

followed by natural gas and coal, each accounting for 21% of the total energy consumption. Among the renewables, energy sources derived from biomass holds the maximum share followed by hydropower and others (Fig. 2.1).

### 2.2.2 *Advantages of Energy Crops as a Source of Energy*

The biomass from energy crops tends to be a low emitter of $CO_2$. More often, it may be a possible low cost energy option to fulfil the rural energy demands. The lignocellulosic biomass are widely available, economical, eco-friendly and suitable as a feedstock for generation of bioenergy (Demirbas 2009). These plants acting as a source of renewable energy, generally termed as ‘Energy crops’. These are viable option for the farmers’ to provide stability to their income and to protect the environment. Hence, energy crops could be able to make the environment sustainable along with the society (Zhao et al. 2009).

Energy crops have several advantages over the traditional as well as the other renewable sources of energy (Fig. 2.2) (COM 2005). Annual energy crops like *Beta vulgaris*, *Brassica napus* and cereals provide feedstock for production of biofuels to be used in transport sector. Similarly, generation of electricity and heat relies often on perennial herbaceous and woody plants like *Miscanthus* spp., *Panicum* spp., *Salix* spp. and *Populus* spp. (COM 2005).

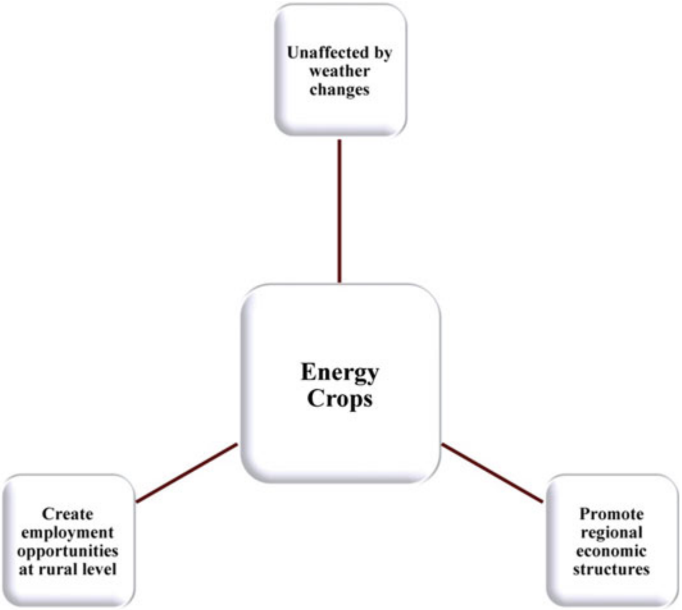

**Fig. 2.2** Basic advantages of energy crops over conventional and other sources of renewable energy. *Source* COM (2005)

### *2.2.3 Characteristics of Energy Crops*

Any crop plant cannot be selected randomly for the purpose of energy production, but to be considered as an energy crop, a plant must satisfy certain conditions. Energy crops have certain characteristic features that make them different from other crops. Plant species with faster growth rate, high tolerance to various stress conditions, high biomass content, high energy yield capacity, requiring less pre-treatments, preferably perennial plants with high cellulose and low lignin content per unit dry weight of the biomass can be suitable as an energy crop (Bhattacharya and Kumar 2010). Most importantly, energy crops should be able to adapt to any land types and climatic variations. Very low inputs are required for their establishment.

## 2.3 Use of Energy Crops as Resources for Energy Generation

The concept of energy crops has been in operation for years. Various products from agricultural and forest crops along with their residues formed a major part of energy source until oil was discovered in 1859. The decline in the fossil reserves and an increase in emissions of carbon dioxide as a direct result of combustion of these fossil fuels have instigated a rise in interest for promoting bioenergy and biofuels as a renewable source of energy. The biomass resources are theoretically the world's largest source of renewable energy with a capacity of around 4,500 EJ of energy production per year. It is anticipated that 273–1,381 EJ/year of energy may be provided by the bioenergy crops in 2050 (Smeets et al. 2007).

### *2.3.1 Classification of Energy Crops*

Energy crops include various grain and oil seed crops along with their residues. Besides, it also includes other types of crops. These crops are referred to as 'candidate bioenergy crops' and are expected to combat global emission challenges (Eisenbies et al. 2009). The bioenergy crops basing upon their biomass production and their use have been classified into traditional energy crops, first generation energy crops, second generation energy crops, third generation energy crops and dedicated energy crops.

Traditional energy crops (TECs) are the natural vegetation and crops residues that produce traditional biofuels like wood and are still in use in several countries like Bhutan and Nepal. The problem with these types of crops is that they are not sustainable. The exploitation of these plants as sources of energy could bring about degradation and desertification of land area in which they are present.

The first generation energy crops (FGECs) are the source for production of majority of current liquid biofuels. These crops can also be used for food and therefore these crops compete with other food crops for fertile land and other requirements like fertilizers and water. The FGECs are used to produce ethanol by fermentation of sugars obtained from their biomass. Trans-esterification of oils present in the biomass of such types of crop produces biodiesel.

Second generation energy crops (SGECs) produce non-oxygenated, pure hydrocarbon fuels from cellulose and lignocellulosic content of their biomass through biochemical or thermochemical approach. These crops carry high energy content as compared to the FGECs. These plants are better as compared to the previous group of energy crops as these are environmental friendly and cost-effective. They include perennial crops like *Panicum virgatum*, *Medicago* spp. and *Cynodon* spp. (Oliver et al. 2009).

The third generation energy crops (TGECs) include boreal plants, *Eucalyptus* spp. and microalgae. The boreal plants can be used as a potential feedstock for production of ethanol by direct fermentation of cellulose. Thermal conversion of biomass from *Eucalyptus* spp. can be used for production of bioenergy and algal biomass can be a promising source of biodiesel. Several oleaginous crops belonging to this category are being tested for their efficiency to produce biodiesel. Table 2.4 provides information on few of the oil yielding plants along with the oil content in their parts, studied for biodiesel production. The TGECs help in the reduction of the GHGs emission from the atmosphere by capturing $CO_2$.

**Table 2.4** Third generation energy crops for biodiesel production with percentage of oil content

| Plant | Plant part | Oil content in % |
|---|---|---|
| *Elaeis guineensis* (African Palm) | Seed | 22 |
| *Cocos nucifera* (Coconut palm) | Fruit | 55–60 |
| *Ricinus communis* (Castor bean) | Grain | 45–48 |
| *Arachis hypogaea* (Peanut plant) | Nut | 40–43 |

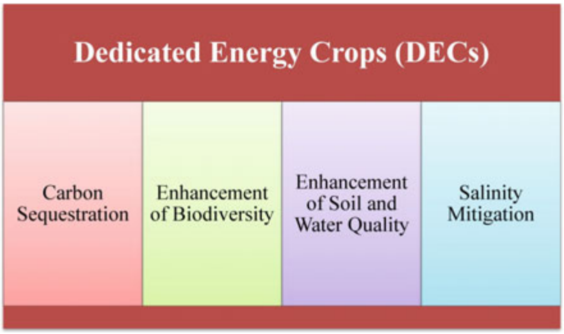

**Fig. 2.3** Environmental benefits of dedicated energy crops (DECs)

**Table 2.5** Different categories of dedicated energy crops

| | |
|---|---|
| Cellulosic crops (including short rotation trees and shrubs) | *Eucalyptus* spp., *Salix* spp., *Populus* spp., *Betula* spp. |
| Perennial grasses | *Panicum virgatum, Sorghum bicolor, Miscanthus* × *giganteus, Arundo donax* |
| Non-edible oil crops | *Raphanus sativus, Ricinus communis, Jatropha curcas* and *Pongamia pinnata* |

The most important and efficient class of energy crops are the dedicated energy crops (DECs). They help in the production of energy without threatening the security of food and environment. The DECs are highly beneficial for the environment (Fig. 2.3) and include crops as categorized in Table 2.5.

## 2.4 Production of Energy from Energy Crops

Production of energy from energy crops can be achieved employing basically any of the four different strategies. These include direct conversion, thermal conversion, biochemical conversion and chemical conversion.

### 2.4.1 Direct Conversion

Direct conversion or combustion is a traditional and most common strategy employed for the conversion of biomass obtained from energy crops into heat and power or a combination of both. In this process power is generated ranging from a small scale of 1–10 KW (Kilo Watt) to a large scale of even more than 5 MW. Types of biomass like wood pieces, straws and dried leaves can be used in the process. Higher combustion efficiency can be achieved inside a biomass boiler. Large power plants and industries could bring about a reduction in their carbon footprint by mixing these solid biomass particles along with coal during the process of co-firing. In this method a mixture of biomass particles along with coal is fed into a modified coal burning power plant to generate energy. Prior to the process, the biomass feedstock need to be processed so as to adjust their shape, size and moisture content to meet certain specifications. The system of co-firing can be broadly classified into blended delivery system and separate feed systems (National Renewable Energy Laboratory 2004). Utilization of biomass in coal-fired power plants has seen a rapid progress in recent years. Commercially efficient coals have been co-fired with biomass from energy crops up to 15% by energy content (Sims et al. 2006).

### 2.4.2 Thermal Conversion

In the process of thermal conversion, high temperatures are used to convert biomass from energy crops into energy carriers like methanol, synthetic gases and oils. These energy carriers have higher energy densities, low costs of transportation and efficient combustion characteristics (Wright and Brown 2008). The process of thermal conversion can be broadly categorized into two different processes—pyrolysis and gasification.

Pyrolysis occurs at temperature range of 400–800 °C in complete absence of oxygen. During this process the lignocellulosic part of the biomass subjected to pyrolysis are disintegrated to form gases and on cooling get condensed to form oil. The charcoal is formed from the residual biomass comprises of lignin.

The process of gasification occurs by partial oxidation of the biomass at approximately 800 °C. The partial oxidation or burning of the biomass yields producer gas and charcoal. The $CO_2$ and water ($H_2O$) present in the producer gas are converted to carbon monoxide (CO) and hydrogen ($H_2$) by the action of charcoal. The partial oxidation during gasification can be done using air, steam, oxygen or a mixture of these. Gasification with air produces a gas with low energy density. Gasification using either oxygen or steam produces ‘syngas’ which can be further utilized to produce wide range of liquid biofuels (Sims et al. 2006). Thus, a substantially large amount of fuel can be produced per ton of biomass by this technique (Darmouth College and Natural Resources Defense Council (NRDC) 2009).

### *2.4.3 Biochemical Conversion*

The process of biochemical conversion employs the use of microorganisms for synthesis of energy from biomass of energy crops. The conversion can be carried out by two methods like anaerobic digestion and fermentation.

**Anaerobic digestion**: It takes place in the absence of oxygen. In this process microorganisms like bacteria are used to breakdown organic materials present in the energy crops inside a closed chamber supplied with adequate moisture. The process of anaerobic digestion occurs via 4 different steps like hydrolysis, acidogenesis, acetogenesis and methanogenesis (Themelis and Ulloa 2007).

*Hydrolysis*: The biomass obtained from energy crops are made up of large chains of organic polymers like carbohydrates, proteins and fats. In this stage, the complex organic molecules are broken down into simpler molecules like simple sugars, amino acids and lipids by the action of certain fermentative bacteria. The molecules still being larger, enters the acidogenic phase.

*Acidogenesis:* This step employs the use of acidogenic microorganisms that further able to break the hydrolysed products. These bacteria create an acidic environment by production of acids like acetic acid, butyric acid, propionic acid and others. Gases like ammonia, hydrogen, carbon dioxide and hydrogen sulphide are produced during the process.

*Acetogenesis:* In this step of anaerobic digestion, a group of bacteria, acetogens produce acetate from various carbon and energy sources. Most of the products created in the acidogenesis stage are converted into acetic acid, carbon dioxide and hydrogen. The acetogens degrade the biomass to make it ready for utilization by the methanogenic bacteria in the succeeding step.

*Methanogenesis:* This forms the last step of anaerobic digestion process wherein a group of bacteria called as methanogens (Weiland 2010) create methane from the final products of acetogenesis. The methanogens produce methane, carbon dioxide (the main products of anaerobic digestion) along with water.

**Fermentation**: Fermentation is a biological process that involves microorganisms to convert simple sugars obtained from biomass into ethanol or other alcohols. Pure products are often obtained by distillation of the fermentation products. The energy crops contain polymeric carbohydrates in their cell walls which are a major source for production of bioenergy and biofuel. However, the biomass of most of the energy crops contain large amount of fibres and other polysaccharides like cellulose, hemicellulose and lignin rather than only the simple sugar. These polysaccharides are required to be broken down into simple sugars for the fermentation to take place and therefore require steps like pre-treatment (Chen et al. 2007; Zeng et al. 2011) and hydrolysis to release the sugars.

### *2.4.4 Chemical Conversion*

The chemical conversion of biomass from energy crops to biodiesel occurs through a process called transesterification (Karp and Halford 2010). The biomass from the crops is pressed to produce a liquid oil fraction. The large, branched chain structure of the liquid oil fraction obtained is broken down to simple linear chain molecular structure via transesterification. The base-catalyzed method of transesterification is widely used, because of its low operating temperature (50–66 °C), pressure of approximately 1.4 bar along with a very high yield of 98%. Moreover, the process directly produces biodiesel and glycerol (a byproduct) with no intermediates.

## 2.5 Energy Needs Scenario at the Rural Level

Like in many other countries, in India the rural energy requirements are from the domestic, agricultural and small scale industrial sectors. Conventionally, they are meeting these requirements by consuming energy from hydroelectricity, fossil fuels, sun, wind and biomass. The energy obtained from hydroelectricity is restricted in quantity and availability to meet the energy requirements. To meet their energy demand, the people are mostly depending upon fossil fuel as the source of energy. Fossil fuels are limited resource and mostly confined to countries like Algeria, Angola, Ecuador, Iran, Iraq, Kuwait, Libya, Nigeria, Qatar, Saudi Arabia, United Arab Emirates, and Venezuela. The reserve of fossil fuels is limited in extent. To reduce the pressure on fossil fuel load, the alternate possibility is to increase the use of renewable sources of energy like solar, geothermal, hydropower, wind, tides and biomass. For the use of renewable energy sources like solar and wind, infrastructural set up and technical skills are required. It may be impossible on the part of the people of the rural area.

Despite the availability of conventional and non-conventional energy resources, energy scarcity is a common problem in the rural scenario. To improvise the situation, emphasis should be laid on the use of renewable sources of energy. The basic requirements of energy in the rural sectors are for cooking, heating and lighting purposes. To achieve these objectives, it is preferable to set up self-reliant energy production systems in the rural areas. Harnessing energy from renewable energy sources like biomass is preferable in this context (World Resources Institute 1994).

The benefits of the use of biomass as an energy source is to get energy from the local resources at an affordable price and operating eco-friendly technique to meet the energy demand of the rural people. The generation of energy from biomass creates opportunity for the unemployed youth to get a livelihood amidst rural socio-economic condition. The quality of the environment is of prime concern for the healthy living of the rural people. Greenhouse conditions and global warming are deteriorating the global environmental conditions day by day. It also adversely affects the quality and health of the environmental components. Upon successful production and application, the renewable energy could be a potential source to replace fossil fuels to some extent in the global energy demanding scenario (Kaplan and San 2011).

Many people in the rural area are representing the marginal sections of the society and maintaining their livelihood on the basis of agriculture with feeble economy. Easily they could utilise the fallow period in between two successive crops or the marginal agricultural lands with proper agricultural panning for the plantation of agricultural crops. On the basis of these socio-economic aspects, bioenergy obtained from the biomass of energy crops is preferable as compared to the other available forms of renewable energy sources (Ravindranath and Hall 1995).

The use of biomass in energy consuming process of rural areas is being in practice since long. Available renewable resources like wood, forest products, cattle dung and crop residues have been consumed in rural sectors using indigenous technologies (Pachuri 1993). The serious adverse effects of these conventional practices lead to deforestation, loss of species diversity, loss of fertility of the soil, harmful emission of carbon monoxide, carbon dioxide, nitrogen oxides, hydrocarbons and suspended particulate matters (De Koning et al. 1985). The release of toxic gases into the components of the environment has hazardous effects on the health of the living organisms. The quantity of the toxic elements should be limited in the environmental components like air, water and soil so as to protect the human health from the adverse effects of these elements (Das et al. 2017). On a prolonged exposure, it may be responsible for types of pulmonary and cardio-thoracic diseases (Mittal et al. 2009; Long et al. 1998; Singh and Panigrahy 2011). The children are among the sensitive group of people and in severity it may leads to increased infant mortality (World Health Organization and the United Nations Environment Programme 1992). The release of these heat trapping gases are possibly the factors responsible for increase in global warming and greenhouse effects.

The time is inevitable for finding out the solution to these problems on a sustainable basis. The condition looks complex with the high population load and high dependency on biomass based fuels to meet these adequacies (Jackson 1992). Another similar study accepts the dominance of biomass as a rural energy source and presumes that it will be emerged as a leading energy source in the days to come (United States Department of Energy 1993).

## 2.6 Role of Bio-energy from Energy Crops to Meet Rural Energy Needs

Renewable feedstock gains importance as a substitute for the replacement of conventional sources of fuels. Biomass is a renewable resource of common uses, consisting of materials of plants and animals origin. The major advantage of the biomass based energy generation unit is the ability to establish the units at any location feasible for the growth of the specific organisms (World Energy Council 1993). The success of the pilot scale and field scale projects on biomass based rural energy system depends on the efficiency of the implementation of the projects. It is also not impossible to develop an ideal village system, to be completely supported by bioenergy technology (Ravindranath 1993). On getting success, it may be a step towards the development of sustainable rural areas at national and international levels (Cherail 1993). The constraints behind such a development may take the shape of local issues like social, economic or geographical (Hall 1991). One of the common questions comes to the mind regarding feasibility of the generation of bioenergy from the energy crops biomass. The best possible explanation comes from the study made by Ravindranath and Chanakya (1986). As per their observation, the biomass from a fraction of the degraded lands has the potential to meet the electrical energy requirements for half a million villages for lighting purposes. Mapako (1997) opined that bioenergy technology option uses locally available resources and it leads to observance of self-reliance in rural energy generation. It is also helpful in creating opportunity for local employment and initiating step towards reclamation of degraded and wastelands of the rural area. The enhancement of biodiversity of the rural area and the substitution of fossil fuels by energy from energy crops are possible positive outcomes of this process along with reduction of carbon emissions to the environment. Sustainable rural bioenergy programme needs generation of adequate amount of clean energy from the locally available renewable resources without disturbing the productivity of the agricultural land system and the environmental health. The selection and cropping pattern of energy crops used for generation of bioenergy are different from one location to other on the basis of the agro-climatic regions of their growth. The types of emissions taking place during the application of bioenergy technology as compared to the conventional fossil fuels are clean because of reduction of carbon release (Mapako 1997).

### *2.6.1 Bioenergy Markets and Global Initiatives*

The bioenergy market is steadily increasing and is highly influenced by the respective policies of different countries and regions. To support the production and use of bioenergy, countries including Brazil have implemented specific policies (US Department of Energy 2016). Although the use of biomass in case of traditional applications has been increasing slowly over the years, but the global share of traditional biomass in energy consumption has been on a declining trend.

**Biomass to Biofuel: Current Global Scenario**

The research and development efforts along with the production and use of biofuels in different regions of the world have been noticed. The possible reason behind this may be the desire by many nations to become self-sufficient in energy sector. Reduction of dependence on fuel imports may be supportive on this occasion. The overall development of domestic agricultural scenario may be the other driving factor behind this move (Araújo 2017; Kovarik 2013). The 2017 global biofuels production saw a rise of about 2.5% as compared to that of 2016, to reach 143 billion L. The top 5 biofuel producing countries were the United States, Brazil, Germany, Argentina and China (Xinhua 2017). As per the 2017 statistics, ethanol leads the global biofuel

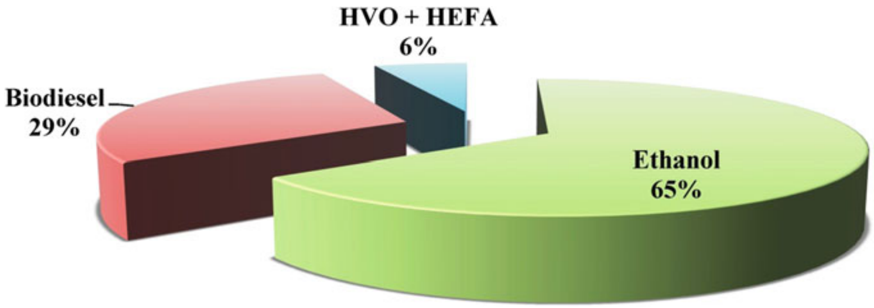

**Fig. 2.4** Production percentage of various biofuels during the year 2017. *Source* REN21 (2018). Global status report

production in the fuel sector. It is followed by the contributions from biodiesel, hydrotreated vegetable oils (HVO) and hydrotreated esters and fatty acids (HEFA). The contribution from biomethane is negligible in this regard (Fig. 2.4) (REN21 2018).

*Global Ethanol Production*: The ethanol production rose from 101 billion L in 2016 to 105.5 billion L in 2017 (Gagliano and Xiong 2017). The United States and Brazil continue to lead the global ethanol production scenario in 2017, collectively accounting for 84% (EC 2019). They are followed by China, Canada and Thailand, respectively (Table 2.6).

*Global Biodiesel Production*: The global biodiesel production for the year 2017 was 36.6 billion L (IEA 2018). The United States is the leading producer of biodiesel followed by Brazil, Germany, Argentina and Indonesia. The contributions from these five nations are 52% (Fig. 2.5) of the global production (EIA 2018).

*Production of Bioelectricity*: Countries have taken keen interest in producing electricity from biomass. China is at the top in terms of maximum amount of electricity generation followed by US, Brazil, Japan and India. Figure 2.6 shows the generation of bioelectricity by leading countries in Tera Watt Hour (TWh) during the year 2017. While China goes for the utilization of agricultural wastes, Brazil makes use of bagasse obtained during sugar production for the generation of electricity (REN21 2018).

**Table 2.6** Major ethanol producing countries in the year 2017

| Country | Production in billion litres | Reference |
|---|---|---|
| United States | 60 | REN21 (2018) |
| Brazil | 28.5 | Agencia Nacional do Petroleo (2018) |
| China | 3.3 | RFA (2019) |
| Canada | 1.7 | RFA (2019) |
| Thailand | 1.5 | RFA (2019) |

**Fig. 2.5** Leading biodiesel producing countries and their respective share in 2017. *Source* EIA (2018). Monthly energy review

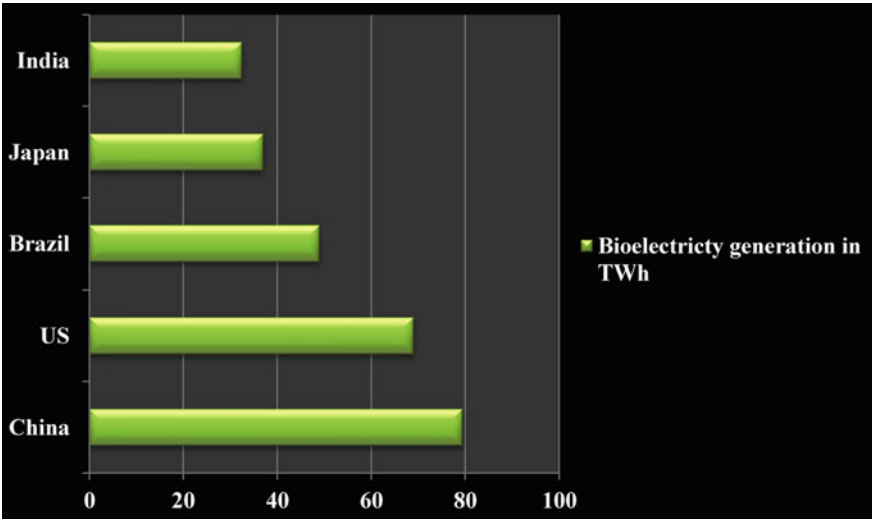

**Fig. 2.6** Top 5 leading countries in the sector of bioelectricity generation during the year 2017. *Source* REN21 (2018). Global status report

## 2.7 Challenges

Keeping the year 2040 in view, the global energy demand is estimated to rise by 37%. Researchers all over the world are making their best effort to find out alternative sources of renewable energy which would not only fulfil the energy demands but also limit the emission of GHGs (Schiermeier et al. 2008). In such a scenario, energy crops hold the key to all answers because of their vast energy producing potential. However, the production of bioenergy from energy crops poses certain challenges. Growing energy crops may impose a threat to the society in terms of scarcity of water (FAO 2011; Holland et al. 2015; Milner et al. 2015). There is a possibility that expansion of area under energy cropping may affect the normal agricultural productivity due to land constraint. An energy crop like the palm tree is a rapidly expanding crop in the region of south-east Asian rain forests. Increased production of palm oil for energy purposes have led to clearing of huge areas of rain forests and ultimately disturbing the biodiversity to a greater extent. Increased production of palm oil for energy purposes have led to clearing of huge areas of rain forests, disturbing the biodiversity to a greater extent (Fitzherbert et al. 2008; Koh and Wilcove 2008). Plantation and growth of energy crops require large scale application of insecticides, pesticides, herbicides and fertilizers. The input of these chemicals, not only affect the soil quality but also the water bodies along with its biodiversity (Jayed et al. 2009).

### *2.7.1 Recommendations to Mitigate the Challenges*

The challenges posed towards the cultivation of energy crops needs to be solved in an environmental sustainable manner. Availability of land for growing energy crops is a major challenge. However, it has been estimated that around 2.052 Gha will remain in the form of meadows and pastures in developing countries. These types of land masses are neither agricultural land nor under forest cover. As such the meadows and pastures could be used for production of energy crops. This will neither raise conflict with food production nor have any threat towards forest conservation (Eisentraut 2010). Figure 2.7 provides the percentage of permanent meadows and pasture lands

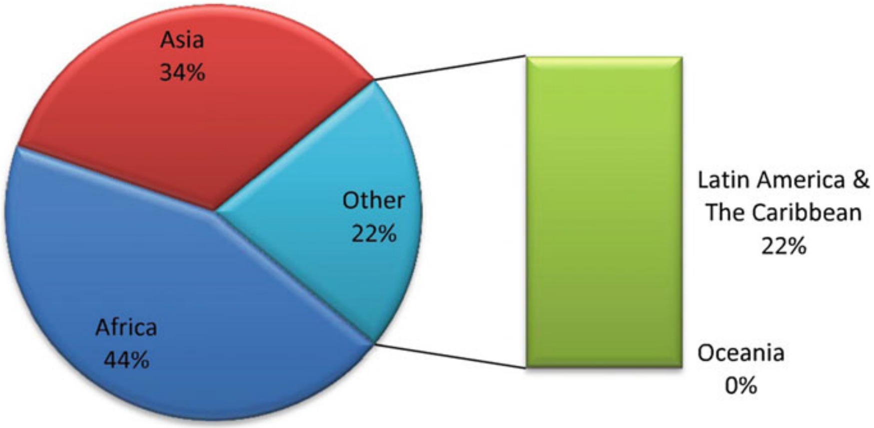

**Fig. 2.7** Percentage of non-agricultural land available in different regions of the world. *Source* Eisentraut (2010)

available in different regions of the world. Sustainable land management practices which collectively take into account land, water and other resources will ensure efficient usage of the resources (Deininger and Binswanger 1999). Use of short rotation energy crops may be given priority. This will result in making the carbon cycle a lot more balanced as the short rotation crops renew themselves on an annual basis (IRENA 2014).

Selection of energy crops must be judicious and those crops to be cultivated which require less water supply and nutrient requirements. This will help overcome the issues related to water scarcity and pollution arising out of excessive dependence on chemical soil fertilizers. Scientific evidences favour the use of second generation lignocellulosic plants like *Panicum virgatum* L., *Miscanthus* × *giganteus*, *Cynara cardunculus* L., *Arundo donax* L. as one of the most promising candidates that can be grown on marginal lands (Cosentino et al. 2014; Fernando et al. 2017; Pulighe et al. 2016).

## 2.8 Summary

The growing world population and their socio-economic development are magnifying the problem of energy crisis. The problem intensifies further in rural energy sectors. The situation demands production of more energy in the rural area to reduce the energy deficits. Under the prevailing situation, the feasible option is to use biomass from energy crops as feedstock for generation of renewable biofuel like ethanol and biodiesel. In order to protect the productivity of the agricultural system and food security, it is advisable to use non-food crops as energy crops. In addition to the optimal agricultural production, the use of marginal lands, wastelands and fallow period of agricultural production for the plantation of energy crops is quite helpful. It helps in the production of sizable amounts of feedstock for the production of adequate amount of bioenergy in the rural area without compromising with the primary agricultural production. The use of energy crops as renewable sources of energy reduces the environmental pollution like emission of greenhouse gases to a certain extent.

The people of rural area are in the search of an energy source which is technically simple, cost effective and retains the ability to be used by unskilled people with ease. The energy crops based bioenergy system, fulfilling the above criteria may be able to increase the interest of the people for its use in the rural area. The acceptability of this energy generation programme depends upon the success of the pilot scale and field scale trials. Further research and developmental activities on this aspect is essential to simplify the energy production technology and making it economical. Supplementing the energy needs of the rural area with the nonconventional energy sources like energy crops will strengthen the energy security in the rural sectors.

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# Chapter 3
# Coconut Shell as a Promising Resource for Future Biofuel Production

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**Abstract** Production of biofuel is an upcoming and crucial field in environmental biotechnology, due to the rising energy crisis and increase in the cost of the commercially available fossil fuel across the world. This has attracted many researchers to take a series of steps to find a resolution and to develop economically feasible source to produce as an alternative fuel. Many local communities who own small scale industries are not aware of how potential the coconut shell is, used as a biofuel. As the cost of petroleum price is increasing, simultaneously with the increase in demand of the same with depleting energy sources and supply, there arises an urge to go for eco-friendly and sustainable process for the production of biofuel. Coconut shell is being used by farmers as organic fertilizer as it has the capacity to conserve the moisture in the farm land and also it helps in the reduction in the nutrient loss during farming. In the course of time, the coconut shell is modified into compost by which it exhibits the property of fertilizer. So, if the coconut shell is being taken up as a source to produce biofuel, with low cost, it reduces the pollution due to carbon dioxide emission and it's by product can be used as fertilizer.

**Keywords** Coconut shell · Biofuel · Energy · Fertilizer

## 3.1 Introduction

Energy is an essential aspect for human being to retain development growth and sustain standard of living. Through worldwide, the transport sector is the second highest energy consuming one next to other fast growing industries and found to account for 30% of the world's total energy. The energy sector has faced a stable development in the past years. It has been estimated that the energy used for transportation is anticipated to rise by 1.8% average per year during the period from 2005 to 2035. Almost all energy consumption in the transport is from fossil fuel in the form of oil i.e. 97.6%.

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Nevertheless, the likely depletion of fossil fuels and the environmental issues related with firing them has made many researchers to involve in research to find alternative fuels (Atabani et al. 2012). To meet the future energy crisis globally energy crops which could be used for the production of biofuels, play a significant role. On the other hand, Energy farming in general refers to the use of agricultural lands for the production of energy instead of agriculture. Production of biofuels from energy crops are ecofriendly, economically feasible and easier to maintain energy production in a sustainable manner. Thus, investigation of substrates for biofuels from energy crops at present and in the past is very much required currently (Kocar and Civa 2013). Due to over consciousness of public towards pollution, rapid degradation of fuel sources, demand for petroleum products pave a way for the generation of biodiesel (Chozhavendhan et al. 2018). Identification of energy crops for production of biofuels is selected mainly on their characteristics as well as the environmental conditions adapted for their growth and development (Tian et al. 2009). Biofuel is a fuel obtained from biologically degradable materials, either from plants or animals. There are three types of biofuel when processed and has three forms such as solid, liquid or gas. The biofuel obtained from farmland biomass directly like rice hull, coconut shell or corn stalk and fuel wood takes solid form (Yerima and Grema 2018). Biofuel can be used in different forms of fuels for transportation. Although all fuels are produced mainly by utilizing plants as the major source, but the method involved in development of biofuels vary from one another. The method of breaking the sugar compounds into ethanol through fermentation process is used for bioethanol production. Similarly, energy dense fuels are obtained from plant biomass which is rich in lignin content by pyrolysis method is adapted for the production of biooil (Sorek et al. 2014). Dumping and removal of organic waste is a threatening issue met by the humans across world wide as there is increasing existence of normal human beings leads to the decrease in mortality. As a result, the population of human is rising quickly and their day to day activities and habitat are the major cause for the enormous production of waste (Jansirani et al. 2012). With respect to the versatile Coconut (*Cocos nucifera*), it is often used in traditional cosmetics (Madakson et al. 2012; Tan et al. 2008).[1] Because of sudden change in the cost of power resources such as fuel oil, natural gas and electricity, in some african countries, the waste from coconut are burnt and has been used as fuel (Madakson et al. 2012).[1] Abundant use of Coconut husk and shell for various purposes, these agro wastes are generated in large amount globally, thus creating pollution to the environment, coconut based biofuels can be used as an swap for the production of fuel and can be utilized in power plants for generation of energy. Because of low ash content, formation of high volatile substance and can be bought at cheap price, pyrolysis method is employed for fuel production from coconut shell (Yerima and Grema 2018). As lignin and cellulose is present in large amount, coconut husk has a high calorific value, lower ash content and moderate moisture content (Yong et al. 2009). The husk of mature coconut is made up of more fibers surrounded by a soft tissue called pith. Usually the fibers are about 15–35 cm

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[1] http://www.worldwatch.org/biofuels-make-comeback-despite-tough-economy. Retrieved on 31 Aug 2011.

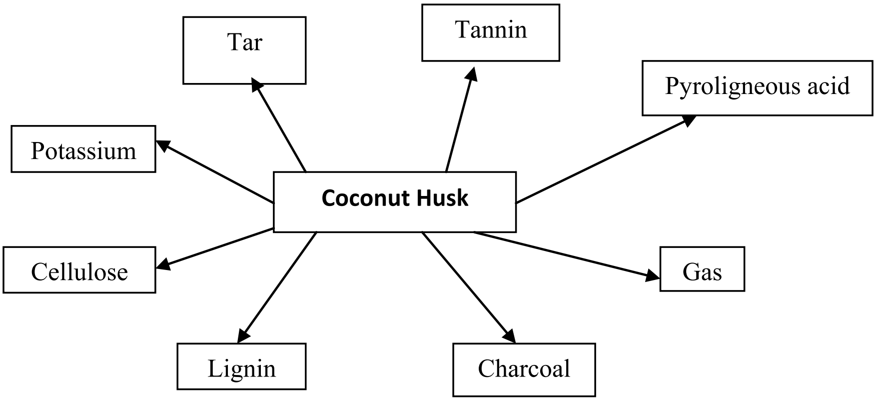


**Fig. 3.1** Components of coconut husk

large has large tensile strength, made up of lignin and cellulose. Coconut shell found in the mature coconut is dense material which is in uniform and made up of lignin and cellulose. Nearly 16.7 and 18.2 GJ/Tonne is produced in coconut husk and shell respectively. In general, both the coconut shell and husk are used as fuel for domestic use and for copra drying (Krishna 2010). Major part of the coconut is husk. Till date these husks are used as source of fuels for coconut processing, alternate household fuel and as fiber in the production of ropes and mats (Tan et al. 2008). Coconut is being planted in many countries around the world mainly Indonesia, Philippiness and India that produce nearly 75% of world coconut production nearly. In coconut fruit the fiber content is about 30%, of 40% coconut husk and remaining is of dust (Fig. 3.1).

Among the chemical components listed above, Coconut husk has more lignin and cellulose content when compared to other chemicals. Bacteria and fungi are more resistant in the materials that are obtained during the coconut fibers and husk casting process. Coconut husk and shells, an eye-catching feedstock for biofuels and charcoal, which is a byproduct obtained during processing. Agricultural waste generated from burning of coconut shell, contributes to the emission of $CO_2$ and $CH_4$ in many countries. Coconut shells and coconut husks can be classified as with many pros and cons. Coconut shells are processed by using pyrolysis method as it has less percentage of ash content and higher percentage of volatile substances. The most important use of coconut husks through burning in order to produce charcoal; if husks are discarded and it can be harmful but can be transformed into a improvised source which can replace fuel wood and other sources (Yerima and Grema 2018). Energy created from biomass and impact agricultural wastes is considered as cheaper sources for continuously power generate, and these are potential sources of energy which is renewable and ecofriendly (Appels et al. 2011). Though many researchers works for the production of biofuels from coconut husk, this review intends to give focuses on different methods for the same coconut husk as the potential feedstock for biofuels production which enables the enhancement of the sustainable development of local community (Bolivar-Telleria et al. 2018).

## 3.2 Transportation Biofuels

Nowadays biofuels are classified into three generations such as first, second and third. Traditional or Conventional chains come under the category of First generation. Second generation involves multifaceted and costly process when compared to first generation. Third generation biofuels are the follow-up of Second generation (Lang 2001).[1]

### 3.2.1 *Biofuels Versus Fossil Fuels*

Use of biofuels over fossil fuels seems to be advantageous based on the effects influenced by environment are taken into consideration. If more priority is given to preservation resources from greenhouse gases and fossil fuels, all biofuels favourably plays an effective role when compared with fossil fuels. Impacts brought out by environmental events like acidification, eutrophication or ozone depletion results in opposite effect. In fact, these disadvantages are connected to aggressive agricultural productions that results in emission of nitrogen compounds which creates bad impacts on the environment. Advantages of biofuels vary with one another based on the feedstock (Quirin et al. 2004). Apart from the known sources utilized for biofuel production, waste plastics accumulated in local areas could be used in biofuel production as it has high heat of combustion (Mohana Jeya Valli et al. 2012).

### 3.2.2 *Bioethanol*

Energy crops such as sugar beet, maize and Sugarcane are commonly used as substrates for bioethanol production (Kocar and Civa 2013). In 2013, production of Bioethanol from coconut oil accounts for 5.4% coconut oil consumption around worldwide (Moss et al. 2010). At present, sugar crops are paying more attention in the manufacturing of Bioethanol (Kocar and Civa 2013). Pure ethanol can be used as a fuel for transport system, but it is frequently used as a preservative of gasoline to enhance octane and develop automobile emissions. USA and Brazil are the major users of Bioethanol nowadays.[1] The US produces more ethanol than any other country; Brazil is the second most country next to US in ethanol production (Biomass energy data book 2011).

### 3.2.3 Biodiesel

Biodiesel is an emerging fuel around worldwide. In 2010, European Union, the world′s largest biodiesel producer accounts for 53% of all biodiesel production.[1] The tremendous growth of biofuels industries creates a larger amount of glycerol as the by-product which turn out to be a serious threat to the environment (Chozhavendhan et al. 2016). Raw materials such as canola, corn, soy, palm and rape seed is the most used substrate for the production of biodiesel. Other than these substrates, cotton seed, mustard seed, sunflower and peanut are considered as a raw material for biodiesel production. India accounts for only 4% of soybean production when compared to other countries such as US, Argentina, Brazil and china. Based on the availability of raw materials, different oils have been used as substrates in different countries. US utilize soybean oil and European countries employ rapeseed oil, whereas in Malaysia and Indonesia, coconut oil and palm oils are used for biodiesel production (Demirbas 2009). In India and southeast Asia, the feedstocks that are predominantly used for the production of biodiesel are *Pongamia pinnata*, *M. indica* and *Jatropha cursas* (USDA–FAS 2012).

### 3.2.4 Biogas

Biogas refers to the method of converting organic waste into an fertilizer, the effective method of disposal of aquatic weeds, agricultural residues, animal, human excreta and other organic materials under anaerobic conditions (Weiland 2003). Biogas, one of the alternative energy source used as a potential fuel in rural areas. The method involved in production process is technology is uncomplicated and become a thriving one across globally in the energy markets. Biodegradable waste materials such as straw, manure, sugarcane, agricultural and industrial processes byproducts and particularly full-grown energy crops can also be used for the energy production (Long et al. 2015). Farmers focus more attention in the biogas production since it is used as a source for generating money. Similarly the environmental and climate condition is well adapted for the production process. Germany, the leading biogas producer introduced new technologies in the biogas production process for the conversion of energy crops (Weiland 2003). Biogas market in many countries is inspired by the use of maize making extra expenses due to methanisation (Eurobserv’ER 2010).

## 3.3 Biomass Resources

Biomass is defined as the residues that are left over by the biological substances from different wastes such as forest, food, agro and other organic materials. Different forms of substrates that can be used as biomass are available in many types in india.

These resources can be categorized into different types that ranges from grasses to aquatic plants. Among them, algae and jatropha is used in the production of biodiesel. Industrial waste, agricultural crops, municipal waste are the major sources for energy production (Williams et al. 1997). Different components that are used as biomass are carbohydrates such as Monosaccharides, Disaccharides and polysaccharides, Lignin, fat, Crude proteins and crude fibres. Fat has higher percentage of carbon and energy composition of 75 and 39.8% among the various components (Encyclopedia of Energy and Environment 1997). The biomass available in our country is being classified into Energy crops, Agro, Industrial waste, Agricultural waste, Municipal solid waste and forest waste (Kumar et al. 2015).

### *3.3.1 Bio-Fuels from Biomass*

Biomass usually refers to any biodegradable waste material from plant sources such as corn, perennial grasses and sugarcane that can be used as fuel or substrates as a product for industrial production and not including any organic material. It can be measured in terms of dry weight. These fuels can be used as a fuel in different transport systems. Most commonly used biofuel today are ethanol and biodiesel (Encyclopedia of Energy and Environment 1997). Different crops can be used as feedstock for biofuels but the environmental factors restrict the use of such crops and development of novel crops is needed. Predominant feed stocks that are used for fuel production are woody species and crop residues. Currently, the substrates that are used for fuel production are food crops and development of non food crops is still in progress (Long et al. 2015). There is no significant method adapted for the complete utilization of feedstock into sugars in fermented form (Carrijo et al. 2002).

### *3.3.2 Biomass Use in the Developing World*

Biomass which is a part of the carbon cycle, is a renewable fuel source, and is frequently called as "carbon neutral" fuel. The carbon that prevails in the atmospheric environment is converted into organic substance through photosynthesis, emitted back to the same or soil through decomposition or burning. This takes place over a shorter duration and results in zero "net" carbon emissions. It is noted that the percentage of carbon present in biomass is 50 times by its weight (Smith et al. 2003).

The production of bioenergy and bio-based products is an emerging trend. Integrated processes and equipments used in the conversion of biomass into biofuels, power, and chemicals are referred to as biorefineries. Such refineries focus specially on processing biomass feedstock into valuable products like chemicals, fuels, pressboards, biocomposites, and so on. The biorefining from agricultural and plant resources is fast approaching due to the advancements in hydrolysis of the cellulose available in feedstock (Jarvis 2015).

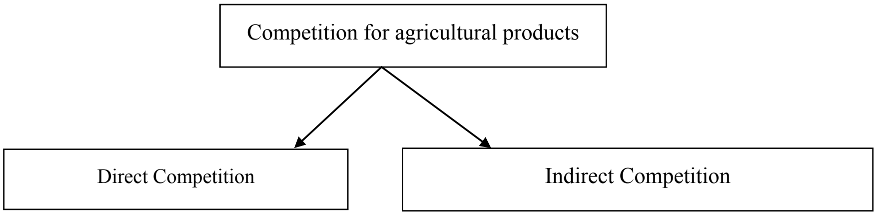


**Fig. 3.2** Competition among agricultural products

Recent studies on the process of obtaining energy crops based biofuels shows that there are numerous chances of finding novel potential energy crops that can be used as substrates upon the development of new techniques for conversion and for pretreatment methods with future perspective respectively (Kocar and Civa 2013). In the current situation, many countries are taking significant steps towards a biobased economy. Newer bio-based products have started to act as good replacements for fossil based products. Due to this drastic change, the emission of greenhouse gas are decreasing (de Jong and Jungmeier 2015).

## 3.4 Biofuel Impact on Agricultural Markets and Food Security

The increase in biofuel demand in turn increases the demand for feedstock. The main feedstock commonly opted for biofuels throughout the universe is crop residues. The more biofuel demand increases, there arises a competition with respect to the use of agricultural products for food, feed, value added food products, and industrial uses. This can have a great impact on human food consumption in domestic areas as well as international level. It also results in greater hit on agricultural and livestock markets (USDA–FAS 2014) (Fig. 3.2).

Production of Bioethanol and Biodiesel may root to indirect land-use change as a result of expanding production (Goldemberg 2008).

## 3.5 Biofuel Production from Coconut

Coconut (*Cocos nucifera*), a palm tree comes under the group *Arecaceae*, grows well in the atmosphere which is rich in moisture. This fruit can be used as a source to obtain oil and its juice is used in drinks (Egneus and Ellegard 1984). Two important commercial products such as copra and fiber are obtained from the nut present in coconut. Oil and oil cake is extracted from copra. The coconut shell is mainly used as a furnace for firing in large amounts like lime kilns, etc. Using destructive distillation, chemicals such as wood spirit, phenol, etc., gas and charcoal are obtained during processing of coconut shell. Activated carbon is produced by utilizing the charcoal obtained during the coconut shell processing, which can be used as gas masks alongside its usage in oil refinery and its application in decolorizing sugars. The energy calorie value of shell and shell charcoal are 4794 and 7222 kcal/kg, respectively (Vimal and Tyagi 1984). The mature coconuts are dried for its use in meat, milk and oil (Martins et al. 2016).

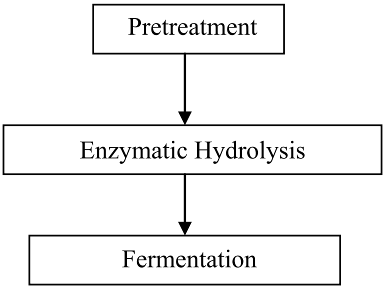
During the coconut processing, a lot of residues are left behind such as husk, fiber and shell and as well as pulp residue after extraction of coconut milk, which can be used as feedstock for biofuel production (Mariano et al. 2018). Most seed oils contain the major fatty acids such as lauric acid, palmitic acid, oleic acid, linoeic acid, linolenic acid and stearic acid. In coconut lauric acid is present in the seed of coconut kernel. The lengths of carbon chain present in palmitic, oleic, stearic, linoeic and linolenic acids were found to be 16 and 18 carbons, whereas 12 carbon chain is present in lauric acid (Gunstone et al. 2007; Metzger and Bornscheuer 2006). Good quality oil is produced by coconut and oil palm kernel (Gunstone et al. 2007). On the other hand, while the oil from both the sources together comprises of about 7% of the plant oil used annually worldwide, remaining sources all together represents <1%. This variation is due to high production costs, which leads to limitation in the number of applications (Carlsson 2009).

## 3.6 Biofuel Production Technology

The production of biofuels comprises of three fundamental stages (Fig. 3.3).

In order to reduce the uprising of the lignocellulosic material so that the accessibility to all polymers in the biomass increases, to reduce the cellulose crystallinity, porosity and surface area of the material, the crucial step of pretreatment should be performed (Cardona et al. 2018). In enzymatic hydrolysis, the enzyme further reduces the cellulose and converts it into fermentable sugars (Aguilar et al. 2018). The previous two stages come in combination to produce increased sugar concentration before fermentation (Su et al. 2015).

**Fig. 3.3** Stages of biofuel production



### 3.6.1 Pretreatment of Biomass

Conversion of biomass into ethanol as a substrate is a tricky one since the removal of lignin, cellulose and hemicellulose is at risk in hydrolyzing the chemical and biological substances (Sarkar et al. 2012). Pretreatment methods for biomass are classified into three types such as physical, chemical, biological and physicochemical (Park 2010; Wyman 1996).

**Physical pretreatment**: It involves the disruption of cell wall components that are present in lignocellulosic substances with the help of mechanical process. Commonly used methods for physical treatment are milling, irradiation, heat or steam treatment (Taherzzdeh and Karimi 2008).

**Chemical pretreatment**: This method makes use of interaction of hemicellulose substances with chemical solutions to release the substances such as lignins, celluloses and hemicelluloses. Examples of this method are alkaline, acid and ozonolysis treatment and wet oxidation (Taherzzdeh and Karimi 2008).

**Biological pretreatment**: Microoorganisms that are used for the degradation of lignin and hemicelluloses, but this method is not efficient when related to physical and chemical methods (Taherzzdeh and Karimi 2008).

Pretreatment and hydrolysis methods are essential in order to extract fermentable sugars for production of Bioethanol. Investigation of best pretreatment method from coconut husks was studied (Ding et al. 2012). Use of alkali such as sodium hydroxide and calcium hydroxide for the removal of lignin and xylans in pretreatment will boost the saccharification of enzymes (Park 2010). Sodium hydroxide is the most commonly used alkali for the pretreatment of lignocellulosic substrates due to its unique characteristics (Kang et al. 2012). Due to over usage of coconut in brazil, there is an excess disposal of coconut husk. This coconut husk during decomposition release methane gases results in environmental pollution (Brito et al. 2004). Degradation of coconut husk using natural method took long time for the decomposition process.

As a part of enrichment of coconut husk, many optional methods are proposed to diminish the level of lignocellulosic biomass content in the environment (Carrijo et al. 2002). Bioethanol production from coconut husk was done by using alkaline and enzyme and the composition of chemicals was analyzed before and after the alkaline treatment. Based on the study, coconut husk is a good substrate for fuel production (Cabral et al. 2016). Fuels from coconut are less cost than other fuels used in transport which are used to generate revenue to the farmers (Krupa et al. 2018).

## 3.7 Properties of Coconut Husks and Shells

Calorific value of coconut husks and shells was measured in order to use this as a fuel by replacing the wood. To measure the calorific value, bomb colorimeter is used and the amount of heat generated was recorded. 17.40 and 10.01 MJ/kg calorific values was found in coconut shells and husks respectively. Hence coconut shell can be used as an alternative for the generation of energy and drying of crop (Amoako and Mensah-Amoah 2019). In order to use coconut shell as a source for fuel in Nigeria, different parameters like calorific value, Moisture content, Density, Ash content, Value Fuel Index, specific heat Capacity was studied. The results revealed that it has higher calorific value and lower ash content, moisture content, $CO_2$ as well as it does not produce any unpleasant odour when related to fuel generation from wood and rice hull. This will results in decreasing the utilization of natural resources (Yerima and Grema 2018). In Philippiness, coconut shell charcoal is comparatively high than wood due to high energy value and it is used for domestic and industrial use (Tc et al. 2002). Standard methods were used for the determination of physical properties such as Density, viscosity, flash point, GCV and pour point. Elemental analyzer was utilized for the analysis of elements like Carbon, Hydrogen, Nitrogen and Sulphur. From the analysis, it was found that the characteristics of oil is heavy, moderate heating value and viscosity (Joardder et al. 2011).

## 3.8 Byproducts from Coconut Husks and Shells

Coconut husk has the potential ability to generate silica, which can be used as a substitute for silica. In coconut fruit, the mesocarp is coconut husk which occupies the major percentage of about thirty to thirty five percentage. These husk are used as fuel source for coconut processing, domestic fuel as well as fiber sources in the manufacturing of ropes and mats (Tan et al. 2008). Similar to silica, extraction of $SiO_2$ was done, which can be a cheap method for production of silica since it is obtained in pure form an also best method for conversion of agricultural waste (Anuar et al. 2018). Coconut husk and shells can act as a good resource for fuel and charcoal. Coconut husk is mainly used for the production of charcoal. Activated carbon, which is produced from coconut shell is used in for eliminating the impurities present in waste water (Yerima and Grema 2018). Fixed bed fire tubing reactor used for the renovation of coconut shell into pyrolytic oil was performed and products like gases, oil and char was obtained (Joardder et al. 2011).

## 3.9 Conclusions

Biofuels are possible solutions for the present scenario with respect to energy security, reduction of Green house gas emissions and strengthening of agricultural development. The problem of disposal of agricultural and animal waste is overcome by their utilization as substrate for biofuels production, also the solid waste residues post biofuels production has the potential for effective biofertilizers. Among the agricultural products employed in the biofuels production, coconut shell possesses wider range of advantages over the other crop and animal residues due to its unique properties and its unchanging nature with respect to various environments. The composition and efficiency of biofuels is likely to change when crop and animal residues are employed. This problem is overcome by substituting coconut shell. Increasing the biofuels production will have direct impact on the energy crisis faced globally. It not only addresses the development of agricultural commodities, food security but also provides promising solution for the agricultural and household solid waste disposal. Biorefining this material for the production of biofuels and other end products with greater benefits will enable the countries globally to generate new jobs, income and resolve the present environmental crisis.

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# Chapter 4
# Thermochemical Conversion and Valorization of Woody Lignocellulosic Biomass in Hydrothermal Media

**V. Chitra Devi, S. Mothil, R. Sathish Raam and K. Senthilkumar**

**Abstract** Biomass conversion can provide the sustainable and promising alternative solution for the future energy demands and fuel supply. It can also be a major contributor to the chemical demand by acting as primary source for biofuel and value added chemicals. Thermochemical conversion can be a faster solution for this problem. Lignocellulosic biomass is the more preferred to other biomasses as it has uniform composition and well established models for degradation of its constituents such as Cellulose, Hemicellulose and Lignin. This process of thermochemical conversion of biomass is usually performed in the presence of hydrothermal media like water or acetone at high temperature and high pressure. The woody lignocellulosic biomass has a complex sterochemical structure compared to agricultural residues and energy crops. It is depolymerised into small compounds in sub critical and supercritical conditions to form three distinct phases such as: bio-oil, bio-gas and bio-carbon, which has their own significant role in the biorefinery. Based on the process conditions (temperature, pressure, media) the yield of the phases varies accordingly. According to the physicochemical properties of media, the process can be classified as hydrothermal carbonization, hydrothermal liquefaction and hydrothermal gasification. For the past two decades, significant researches is being reported for thermochemical conversion of various lignocellulosic biomass (hardwood/softwood), agricultural residues, fruit shells, cellulose wastes, industrial co-products, etc. in both wet and dry conditions. Also it was found that the wet biomass conversion results in high yield of various chemicals like alkanes, alkenes ketones, aldehydes, acids, alcohols, phenols, esters, ethers and other aromatic compounds with some amount of polymeric impurities. In this chapter more emphasis is given on the thermochemical conversion of woody biomass, its pre-treatment, hydro processing and refining of the products synthesised. It also focuses on the valorization of the end products obtained from the hydrothermal processing into value added chemicals in the presence of homogeneous and heterogeneous catalysts.

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## 4.1 Introduction

Biomass is carbon neutral and is the fourth major energy resource after petroleum, coal, and natural gas, delivering around 14% of the global energy demand. United Nations Conference on Environment and Development (UNCED) conducted an analysis on the future energy demand where this was projected to fulfill 50% by 2050 (Ramage and Scurlock 1996; Demirbas 2000). Biomass being renewable, sustainable and relatively environmentally friendly source is used to meet world's variety of energy requirements, including electric power, heat source for domestic and industrial needs, fuel and feedstock for chemicals (Balat 2006). Biomass is distinctive from all the renewable resources as it efficiently stores the solar energy from the sun in its cells through photosynthesis. This carbon stored in the plant cells can be transformed and used back as solid, liquid and gaseous fuels by various conversion methods (Demirbaş 2001; Saxena et al. 2009). The yield of biomass of one country varies from another due to the change in prevailing climatic conditions. Higher is the yield in sub tropics and tropics, and medium in temperate countries. From the 1992 statistics, the average carbon stored in tropical forests of Asia was calculated to be 255, 144 and 148 Mg $ha^{-1}$ as potential, actual and biomass stored under the soil; corresponding to total carbon evaluated as 74, 42, and 43 Pg ($1 \text{ Pg} = 10^{15}$ g), respectively (Brown et al. 1993). According to the 1993 calculations from species-wise volume records for all forest cover in various states of India, the mean above-ground biomass densities was 67.4 Mg $ha^{-1}$, equating to 34 Mg C $ha^{-1}$ (Haripriya 2000). Compared to other energy resources, biomass fuels have a very smaller amount of sulphur and, thus contributing very negligible $SO_2$ releases that causes acid rain. Biomass on combustion produces relatively a lesser amount of ash than coal; in return it also can be mixed with the soil to enrich its fertility. Biomass is a potential and sustainable source to mitigate climate change as its contribution in atmospheric $CO_2$ level can be controlled (Owusu and Asumadu-Sarkodie 2016). With the better utilization of biomass, the lifetime of non-renewable crude oil that is used for the manufacture of petrochemicals and other value added substances would be extended. Biomass as a domestic resource is not subjected to the supply uncertainties, unlike the imported fuels that change according to the world market price. Thus it secures the future generation with clean, safe, renewable energy source that could drive the country's economy and environment to high standards (Demirbas et al. 2009).

Table 4.1 Classification of biomass according to the source

| Supply sector | Type | Example |
|---|---|---|
| Forestry | Forest by-products | Wood blocks; logs and branches from thinning; wood chips; bark |
| Agricultural residue | Lignocellulosic agricultural residue | Straw and husk (rice, wheat, maize, barley, cereal, rye, sunflower, rapeseed); cobs (corn); shells (almond, olive, walnut, palm pit, hazelnut); stalk (flax, hemp, cotton, kenaf), leaves, seed pods and root |
| | Shrubs/herbaceous crop residue | Indian shrub, hay, switchgrass, Miscanthus, reed canary grass, and costal Bermuda grass |
| | Livestock waste | Manure from chicken, cattle, pigs, sheep |
| | Others | Weeds, aquatic plants, and algae |
| Industry | Wood/lumber industry residues | Waste wood residue from saw mills and timber mills (wood chips, off-cuts, bark, sawdust); |
| | Food industry residues | Bagasse (sugar cane); starch residue (potato, sugar beet, sweet sorghum, cassava, tapioka); fruit peels and residues |
| | Meat processing industry waste | Wastes from poultry houses, slaughterhouses, fisheries and dairies |
| | Others | Ethanol, paper pulp, black liquor, cellulosic sludge |
| Domestic | Organic waste | Waste food materials, kitchen vegetable waste; used cooking oil; municipal waste; sewage sludge |

## 4.2 Classification of Biomass

There are various classifications of biomass. But in crude point of view classification based on the source is given in Table 4.1.

## 4.3 Lignocellulosic Biomass

The plant cell walls are primary made of lignocellulose. A plant cell wall constitutes layers of cellulose microfibrils, hemicellulose, pectin, and lignin in a uniform arrangement (Koppejan and Van Loo 2012). It also contains proteins, extractives

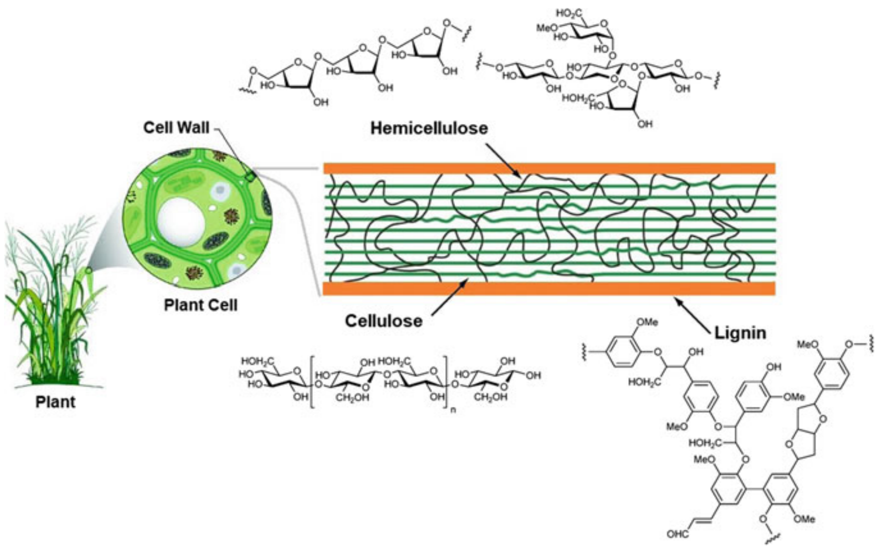

**Fig. 4.1** Structure of Lignocellulosic Biomass

in smaller amounts which are soluble and assimilates such as sugars, nitrogenous materials, waxes, chlorophyll and ash (Sticklen 2008). The lignocellulosic biomass structure of a plant is given in the Fig. 4.1.

Cellulose is a linear polymer made of D-glucose subunits connected to each other by α-(1,4)-glycosidic linkage which constitutes to its organized fibrous structure. Cellobiose is the repeating unit that is established throughout this linkage. These long polymeric chains are held together, packed into microfibrils by hydrogen bonding and van der Waals forces. Hemicelluloses and lignin cover the microfibrils, thereby adding additional strength for the plant. The cellulose in biomass is predominantly crystalline with a small proportion of amorphous cellulose due to unorganized chains forms. The main feature of hemicellulose is its short lateral chains and branches which are mostly different sugars. These sugars include xylose, rhamnose, arabinose, glucose, mannose, galactose, and uronic acids like 4-omethyl glucuronic, D-glucuronic, and D-galactouronic acids (Zhou et al. 2017). Hemicellulose consists of either a homo or heteropolymeric chain with short monosaccaride branches majorly by α-(1,4)-glycosidic linkage like cellulose and intermittently by α-(1,3)-glycosidic linkages. Lignin is a complex cross-linked polymer with large molecular structure containing three phenyl propionic alcohols namely: coniferyl alcohol, coumaryl alcohol, and sinapyl alcohol as monomers. These phenolic monomers are linked together by alkyl-aryl, alkyl-alkyl, and aryl-aryl ether bonds (Bajpai 2016). Extractives include a variety of organic compounds such as simple sugars, starches, proteins, and fats, simple to complex phenolics, alkaloids, glycosides, saponins, pectins, terpenes, mucilages, gums, waxes, resins and essential oils. Many of these are tree metabolites and intermediates act as energy alternatives, or used to defend the tree from insects and microbes. These compounds also contribute to wood's color, odor, durability and resistance to decay against moisture and other environmental conditions. Ash is the solid residue that remains after complete combustion composed of mostly metal carbonates and oxides. Wood from temperate zones have 1% ash and slightly higher in species from tropical climatic conditions (Pettersen 1984).

The chemical composition of one plant species varies from another. It is evident that woody species have higher amounts of cellulose, and hemicellulose, whereas grassy species like straw, husk and leaves have more extractives and ash (Table 4.2). In addition, these constituents vary from plant as a whole and within based on age, stage of growth, climatic conditions etc. *Eculalyptus globulus* species from Portugal is taken as an example to explain the above phenomena in Table 4.3.

This chapter covers mainly on woody biomass which has several advantages on the others. Also with little $CO_2$ emissions, less heavy metals and sulphur in the meager ash produced, the possibility of utilization of wood as low cost alternative fuel is studied. The energy intensification and thermal conversion of wood are also compared to other herbaceous and agricultural residues.

**Table 4.2** Chemical composition of various lignocellulosic biomass types

| | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Extractive (%) | Ash (%) | References |
|---|---|---|---|---|---|---|
| *Hard wood* | | | | | | |
| Alder | 45.5 | 20.6 | 23.2 | 9.8 | 0.7 | Taherzadeh et al. (1997) |
| Aspen | 52.7 | 21.7 | 19.5 | 5.7 | 0.3 | |
| Willow | 41.7 | 16.7 | 29.3 | 9.7 | 2.5 | |
| *Softwood* | | | | | | |
| Pine | 46.9 | 20.3 | 27.3 | 5.1 | 0.3 | Rabemanolontsoa and Saka (2013) |
| Spruce | 45.6 | 20.0 | 28.2 | 5.9 | 0.3 | |
| Japanese cedar | 45 | 22 | 30 | 2.6 | 0.5 | |
| *Agricultural/herbaceous crop residue* | | | | | | |
| Rice straw | 37 | 16.5 | 13.6 | 13.1 | 19.8 | Rabemanolontsoa and Saka (2013) |
| Rice husk | 37 | 23.4 | 24.8 | 3.2 | 17.3 | |
| Corn cob | 34.6 | 15.2 | 18.2 | 10.6 | 3.5 | |
| Corn leaves | 26.9 | 13.3 | 15.2 | 22 | 10.9 | |
| Miscanthus | 34.3 | 25.2 | 22.8 | 11.9 | 5.5 | |

**Table 4.3** Chemical composition of *Eculalyptus globulus* wood at different conditions

| | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Extractive (%) | Ash (%) | References |
|---|---|---|---|---|---|---|
| *Age* | | | | | | |
| 2 years | 50.0 | 18.6 | 26.9 | 4.2 | 0.8 | Miranda and Pereira (2007) |
| 3 years | 40.2 | 18.0 | 28.6 | 7.9 | 1.7 | |
| 6 years | 43.8 | 18.9 | 27.3 | 4.2 | 0.6 | |
| *Height/position of sampling* | | | | | | |
| Bole wood | 53.7 | 20.82 | 22.2 | 2.9 | 0.38 | Pereira (1988) |
| Bole bark | 51.5 | 19.89 | 20.2 | 6.3 | 2.11 | |
| Top wood | 52.3 | 19.34 | 24.8 | 2.8 | 0.76 | |
| Branches (<1 cm) | 41.2 | 18.77 | 21.8 | 16.7 | 1.53 | |
| *Climatic conditions (composition of Bole wood)* | | | | | | |
| Altitude (m): 500–550 rainfall (mm): 1273.0 Air Temp (°C): 13 | 53.7 | 20.82 | 22.2 | 2.9 | 0.38 | |
| Altitude (m): 300<br>Rainfall (mm): 710.7<br>Air Temp (°C): 15.6 | 50.1 | 19.25 | 22.3 | 8.0 | 0.35 | Pereira (1988) |
| Altitude (m): 150<br>Rainfall (mm): 882.9<br>Air Temp (°C): 15.2 | 58.2 | 10.81 | 24.9 | 5.6 | 0.49 | |

## 4.4 Biomass Conversion

Over 50% of all wood in the world is used as firewood especially. In developing countries, wood is the primary energy source and it makes up about 80% of the energy utilized for day to day purpose. Hence a fast, cost effective and economic energy intensification and conversion of biomass is needed. The two pathways by which biomass can be transformed into useful product are thermochemical and biochemical processes.

## 4.5 Thermochemical Conversion Techniques

### *4.5.1 Combustion*

Combustion is the chemical process by which biomass is burned directly in the presence of air to transform the stored chemical energy into heat, mechanical, or electric power with evolution of hot gases (CO, $CO_2$, $NO_x$, $SO_x$) at a temperature range 800–1000 °C. Combustion can be experienced in domestic stoves for cooking; furnaces for metallurgical applications; boilers, steam turbines, and turbo-generators for energy production. The moisture content plays a significant role during combustion of biomass and it must not exceed 50% for the process to be feasible (McKendry 2002). Normally biomass do not arise in an acceptable form of combustion; hence it requires some simple operations like chopping, drying, grinding, etc., that contribute to some additional costs increasing the total energy expenditure.

Inorganic constituents such as alkali chlorides, sulphates, carbonates and silicates in the biomass react among each other and contribute to most of the problems such as fouling and slagging. The exact chemistry and mechanism behind fouling and ash slagging is yet to be fully developed. Some combustion studies showed an increase in the fusion temperature of the ash by elimination of alkali and other elements in the biomass using pre-treatment techniques (Jenkins et al. 1998). There are many power plants that operate mixed biomass and coal feedstock, which tends to reduce net $CO_2$ emissions. Few studies have also been done successfully on using the oxygenated compounds from combustion of lignocellulosic biomass and use it to run a compression ignition engine (Baumgardner et al. 2015).

### *4.5.2 Gasification*

Gasification is the conversion of biomass into a mixture of low calorific value combustible gases of energy 4–6 $MJ/Nm^3$ by means of partial oxidation process at high temperatures from 800 to 900 °C. It is carried out at with limited oxygen supply and the gas produced can be burnt directly, or be used as a fuel for gas compression ignition engines and gas turbines. It is a most favorable route to generate producer gas with specified composition to produce fine chemicals like methanol.

There are four types of gas-solid gasifiers namely: Fixed bed, Moving bed, Fluidized bed and Entrained-flow bed. They were established primarily for coal gasification, but with advancement it is also used for gasification of lignocellulosic biomass with slight modifications (Zhou et al. 2009). The choice of gasifier is determined by various factors including the energy density, chemical composition, and other attributes of biomass feedstock, thus to attain desired form of the energy. The fixed and moving bed gasifiers generate huge volumes of tar and char, which is owing to the improper heat and mass transfer between solid biomass and the gasifying agent.

This is overcome in fluidized bed gasifier with enhanced reaction rate by using effective heat transfer medium and good quality catalysts (Alauddin et al. 2010). In the future, small gasifier plants may evolve into large scale units co-gasifying biomass with coal or with any other solid fuel to meet the growing energy demand.

### *4.5.3 Pyrolysis*

Biomass pyrolysis is well-defined phenomenon involving thermal decomposition of the biomass into liquid bio-oil, solid biochar, and non-condensable gas products in the absence of oxygen. It can be classified into three main subcategories namely: slow, fast and flash pyrolysis depending on the heating rate and residence time (Mohan et al. 2006). Slow pyrolysis involves heating of biomass relatively at low temperatures from 300 to 700 °C for long residence time that ranges from hours to days. This type of pyrolysis has been conventionally applied in production of low grade fuel like charcoal. Fast pyrolysis involves a higher heating rate of 140–200 °C/s with typically very short residence time of 0.5 to 10 s (Demirbas and Arin 2002). The flash pyrolysis is characterized by a higher heating rate of 103–104 °C/s but with short residence time of 0–0.5 s (Amutio et al. 2012). Fast pyrolysis results in biooil yield of 50–70 wt% while flash pyrolysis can achieve biooil yield as high as 75–80 wt%.

### *4.5.4 Carbonization*

The process of heating biomass under an inert or low-oxygen atmosphere to drive out the moisture and volatile matter present in it is called carbonization. This leads to a final product with increased relative carbon percentage and calorific value to that of the raw biomass. It is a very slow process which could take weeks for the whole carbonization process to end. Under these conditions with appropriate residence time, a normal dry wood would result in a charcoal with roughly double the calorific value with 75% weight loss (Meyer et al. 2011).

### *4.5.5 Hydrothermal Conversion*

Hydrothermal Conversion involves thermal depolymerisation of biomass in the presence of subcritical or supercritical water at high temperatures and pressures. Water breaks the macromolecules by acting as a catalyst and as an excellent reaction environment (hydrothermal media) with higher ionic products favoring reactions that are typically by acid catalyzed or base catalyzed in subcritical conditions (Kruse et al. 2013). In general, hydrothermal conversion processes are categorized into three distinct processes namely: (i) Hydrothermal Carbonization, (ii) Hydrothermal Liquefaction and (iii) Hydrothermal Gasification depending on the severity of the process conditions.

Hydrothermal carbonization of biomass takes place at temperatures below 247 °C in subcritical water. This process overtakes the natural coalification process, where peat is formed in several hundred years, coal in million years, while biochar that has properties equivalent to brown coal in maximum 12 h (Ramke et al. 2009). The main product is biochar which is also called hydro char and it has similar properties to that of a low rank coal. Hydrothermal liquefaction is characterized by hydrolysis followed by de-polymerization of macromolecules at an intermediate temperature ranges between 247 and 374 °C, resulting in smaller molecules. Dehydration or decarboxylation induced by subcritical water reduces a significant part of the oxygen as alcohols and esters. The produced liquid product (biocrude or biooil) consists of small unstable reactive molecules and in most of the cases they re-polymerize resulting in larger tar like compounds. The chemical composition and properties of biooil purely depend on the composition of the biomass substrate (Toor et al. 2011). By increasing the temperature above 374 °C induces gasification reactions and this result in the synthesis of a higher fuel gas mixtures and low biooil. Even wet biomass and organic wastes can be efficiently transformed into hydrogen rich fuel gas under suitable hydrothermal conditions (Schmieder et al. 2000).

## 4.6 Valorization of Woody Lignocellulosic Biomass in Hydrothermal Media

Woody lignocellulosic biomass has a large potential and acts a permanent source for the value added chemicals through hydrothermal conversion technique. Among the three, hydrothermal liquefaction produces comparatively large quantity of biooil, which is the starting point of the value addition chain. The process parameters that have a significant influence on conversion of biomass to biooil are feedstock composition, temperature, heating rate, pressure, solvent, residence time, and catalyst. This chapter enlightens the readers on the woody biomass conversion and all the major factors that affect the production of the biooil.

### *4.6.1 Effect of Feedstock*

Lignocellulosic biomasses are majorly composed of constituents such as cellulose, hemicellulose and lignin that influence the yield and quality of the oil formed during the hydrothermal conversion process. Due to different structure and properties each one acts different in the hydrothermal environment and depolymerizes in a specific manner.

**Conversion of Cellulose**. Hydrothermal conversion of cellulose happens along numerous reaction pathways during thermal depolymerisation process. It involved hydrolysis followed by Lorby de Bruyn-Alberda van Ekenstein transformation to break bulk molecules into small fractions. The interaction of molecules in the hydrothermal treatment were different during alkaline and acidic environments, where the alkaline environment led to further retro aldol transformation, rearrangement of aldehydes, hydration, dehydration to form simpler acid and alcohols, and acidic environment resulted in major portion of 5-(Hydroxy methyl) furfural (5-HMF) and its acid derivatives (Yin and Tan 2012). Baccile et al. (2009) study confirmed using $^{13}$C solid-state CP-MAS NMR, even when cellulose were taken from various sources like starch, sucrose, maltose and glucose, the 65% of the solid hydrothermal carbon materials resulted in formation of HMF ring structure. The yield of biooil in acidic environment was 3 times higher than in the alkaline environment. Under neutral conditions, some of the short chain acid and aldehyde components also decomposed into gases and HMF polymerized into residual solids reducing the bio-oil yields significantly (Chuntanapum et al. 2008).

**Conversion of hemicellulose**. Hemicelluloses constitute to 20–40% of plant biomass. Hemicellulose with its simple structure and abundant side-groups are easily soluble and hydrolyzed both in acidic and alkaline subcritical conditions at 180 °C (Delmer and Amor 1995; Bobleter 1994). Mok and Antal (1992) investigated on various woody and herbaceous biomass materials and found that the entire hemicellulose was hydrolyzed in 2 min at 230 °C and 34.5 MPa. During rapid heating of the biomass at these conditions, hemicellulose is selectively decomposed as saccharides, following similar pathway as cellulose in the same environment. Sasaki et al. (2003) experiments on subcritical and supercritical water extraction of D-xylose resulted in glycolaldehyde, glyceraldehyde and dihydroxyacetone thorough retro-aldol condensation and dehydration at 360–420 °C, 25–40 MPa and 0.02–1 s.

**Conversion of lignin**. Lignin has a complex structure constituting primary building blocks as p-hydroxy phenyl propanoids namely coumaryl alcohol, coniferyl alcohol and sinapyl alcohol that are held together by C–C or C–O–C bonds. Compared to cellulose and hemicellulose, it is relatively more resistant to both chemical and enzymatic degradation and yet, during hydrothermal degradation under alkaline conditions, hydrolysis of C–O–C bonds result in various phenols and methoxy phenols, leaving the benzene ring. During the lignin hydrolysis and degradation, there is a significant production of solid residue due to the condensation of the phenolic products. Thus the feedstock must be selected in such a way that the balanced lignin content is carefully maintained. The hydrothermal breakdown of pure lignin at temperatures more than 350 °C was examined by Kanetake et al. (2007) resulting in products: catechols, phenols, and cresols, confirming the occurrence of 2° hydrolysis of methoxy groups. Similar results were obtained for Kraft pine with major products: phenol, 4-ethylguaiacol and methyl dehydroabietate (Zhang et al. 2007). The hydrothermal degradation yielded 58–78% of liquid products not as an oil-phase, but in the water phase as dissolved organics. Karagöz et al. (Karagöz et al. 2005) investigated on commercial lignin at 280 °C and also obtained phenolic compounds 2-methoxy-phenol, 1,2-benzenediol, 4-methyl-1,2-benzenediol, 3-methyl-1,2-benzenediol and phenol.

Liu et al. (2006) studied on hydrothermal conversion of walnut shell that contains about 53.5% lignin at reaction temperatures of 200–300 °C in both acid and alkaline conditions. During hydrothermal degradation in alkaline conditions, several phenol derivatives were obtained which confirms the hydrolysis of both the lignin and the resulting methoxy groups. The biooil yield varies with respect to the percentage of these three constituents in the biomass as shown in Table 4.4.

### 4.6.2 Effect of Temperature

Temperature plays a key role in the operation of hydrothermal processing of all biomasses. The temperature that ranges between 250–320 °C generally supports the conversion depending on the type of feed stock (Table 4.4). Under such elevated temperatures, hydrothermal conversion shows symbiotic effect in the yield of value-added products from organic feedstock. The increased temperature depolymerizes complex organic molecule present in the feed stocks which intern produces the fine chemicals. Such conditions not only upsurge the reaction rate but also create variations in reaction mechanisms. From literatures it is understood that when operating temperature is elevated beyond the activation energy, depolymerization reaction occurs which results in dissociation of complex bonds (Kruse et al. 2013; Dimitriadis and Bezergianni 2017; Sudasinghe et al. 2014). C. Zhong et al. explained the effect of temperature and impact of lignin composition had placed a remarkable on the yield of bio-oil under non catalytic condition on wood varieties like *Cunnighamia lanceolate*, *F. mandshurica, P. tomentosa Carr*. and *P. massoniana Lamb* (Zhong and Wei 2004). Tar that is formed during the process is the impact of temperature under subcritical condition and it extremely stifled under supercritical condition. The two reasons are possible for the stifled change, (1) truncated dielectric constant which leads to free-radical reactions leaving away gaseous products, (2) under supercritical region tarry material behaves like a solvent (Promdej et al. 2010). The hydrothermal liquefaction performed on Spruce wood at temperatures from 250 to 300 °C, the yield of bio-oil increases slightly from 3.9 wt% to 6.6 wt%. But beyond 300–350 °C, the yield progressively decreases to 4.9 wt% because of bio-oil vaporization at these temperature ranges. Thus it is clear that high temperatures favors the radical formation that occurs generally in sub-critical water while the lower temperature induces the ionic reactions (Watanabe et al. 2004).

### 4.6.3 Effect of Hydrothermal Media

The hydrothermal media in general called as solvents enhance the stability and solubility of the depolymerized macromolecules. They enhance the fragmentation of the complex structures in the biomass. The mass ratio of solvent to feed has to be maintained in such a way that it should not promote gasification of all residual material in the reactor. Some studies show that when a portion of water replaced with compounds like ethanol, methanol, acetone, 2-propanol, they act as a tarry material enhancing the ionic product of the mixture yielding higher biooil as shown in Table 4.4.

**Table 4.4** Reaction parameters and their biooil yield of different wood species

| Feed stock | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Temperature range (°C) | Hydrothermal media | Yield without catalyst (%) | Catalyst | Yield in the presence of catalyst (%) | References |
|---|---|---|---|---|---|---|---|---|---|
| Oak wood | 38.1 | 23 | 32 | 260–320 | Water | 27% bio-oil yield at 320 °C | Fe | 29.35% bio-oil yield (water as solvent) at 280 °C | de Caprariis et al. (2019) |
| Common reed | 43.3 | 29.6 | 27.1 | 250–290 | EtOH, MeOH | 53.6 and 38.7% bio-liquid yield at 290 °C | 10 wt% NaOH | 57.6 and 44.2% bio-liquid yield at 290 °C | Küçük and Ağırtaş (1999) |
| Pine sawdust | 45.3 | 22.5 | 26.8 | 180–280 | Water | Maximum total oil yield of 8.5% at 280 °C | $K_2CO_3$ | Maximum total oil yield of 33.7% at 280 °C | Karagöz et al. (2006) |
| Pine sawdust | 45.3 | 22.5 | 26.8 | 200–350 | 50% aqueous EtOH, MeOH | 65% bio-oil yield | – | – | Cheng et al. (2010) |
| Rice straw | 41.1 | 23.8 | 19.5 | 260–300 | EtOH-water, 2-propanol-water | 38.35% and 39.7% bio-liquid yield at 300 °C | – | – | Yuan et al. (2007) |

(continued)

**Table 4.4** (continued)

| Feed stock | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Temperature range (°C) | Hydrothermal media | Yield without catalyst (%) | Catalyst | Yield in the presence of catalyst (%) | References |
|---|---|---|---|---|---|---|---|---|---|
| Beech wood | 47.7 | 21.4 | 25.5 | 300 | Water | 14% bio-oil yield | 6 wt% NaOH | 28% bio-oil yield | Haarlemmer et al. (2016) |
| Spruce wood | 45.6 | 20 | 28.2 | 250–300 | Water | 6.6% bio-oil yield at 300 °C (water) | KF/$Al_2O_3$ | 13.9% bio-oil yield at 300 °C | Alper et al. (2019) |
| Corncob | 38.8 | 33 | 13.1 | 300–360 | Water, EtOH | 38.6% and 38.8% bio-liquid yield at 340 °C | NaOH, KOH | 56.4% and 57.5% at 10% alkali to sample ratio at 340 °C respectively. | Khampuang et al. (2015) |
| Grape seeds | 32.7 | 37.6 | 24.9 | 300 | Water, supercritical EtOH | 18.7% and 46.33% bio-oil yield at 300 °C | $MgCl_2$, $TiCl_4$ | 17.47% and 50.69% bio-oil yield at 300 °C | Hao et al. (2019) |
| Cotton cocoon shell | 32.6 | 10.2 | 48.7 | 235–300 | Acetone, water | 35.6 and 69.1% bio-liquid yield at 235 °C | NaOH, $Na_2CO_3$, KOH, $K_2CO_3$ | 80.2, 66.5, 86.2, 68.7% at 100% alkali to sample ratio at 300 °C respectively | Çağlar and Demirbaş (2001) |

### *4.6.4 Effect of Catalyst*

Although water as a catalyst during the sub critical or super critical hydrothermal processes, the products formed are mostly oxygenated. Thus to reduce this it requires addition of one more catalyst into the system. In hydrothermal processes, addition of catalyst improvise the gasification efficiency, reduces tar and char by suppressing the repolymerization reactions of unstable molecules. Alkali hydroxides and salts have been frequently used as homogeneous catalysts, whereas Ni, Mn, Fe, Ti were used as heterogeneous catalysts but less frequently utilized in biomass liquefaction process. Heterogeneous catalysts are meant to promote low-temperature water gasification in biomass.

**Homogeneous catalysts**. Mostly alkali salts have a positive effect on deconstruction of macromolecules of woody biomass. Homogeneous catalyst improves gasification by speeding up the water gas shift reaction and also resulting in increases yield of liquid products. Addition of these catalysts raises the pH making the mixture more alkaline, thereby inhibiting dehydration of the cellulose, hemicellulose and lignin present in the biomass. Alkali has a high ability to suppress char and tar during the process. It also prevents a high degree oxidation of the biooil instead of decarboxylation that might be leading to the formation of unstable unsaturated compounds and in turn polymerize into char or tar.

Küçük and Ağırtaş (1999) conducted the hydrothermal liquefaction of common reed (Prangmites australis) with and without catalyst in sub critical water environment. It was concluded that with 10 wt% of NaOH the biooil yield by 4% at 290 °C. In another study, Haarlemmer et al. (2016) investigated the addition of 6 wt% of NaOH and the liquefaction of beech wood found to have increased the biooil yield from 14 to 28% at 300 °C. Similarly, hydrothermal treatment on pinewood biomass in the presence of alkali especially potassium as $K_2CO_3$ at 280 °C for 15 min showed a progressive effect on yield of biooil (Karagöz et al. 2006).

The percentage addition of alkali varies from one feedstock to other depending upon the constituents present in it. In another study, it was observed that hydroxides and carbonates of potassium were more effective than that of sodium. The catalytic effect according the chemical activity of alkaline homogeneous catalysts was ranked in the order as follows: $KOH > NaOH > K_2CO_3 > Na_2CO_3$ (Khampuang et al. 2015; Çağlar and Demirbaş 2001). The alkali catalysts have the tendency to promote water gas shift reaction during hydrothermal liquefaction, thus favoring $H_2$ and $CO_2$ formation from CO. The hydrogen gas produced during the process in turn acts as the reducing agent improving quality of the biooil and its heating value (HHV).

**Heterogeneous catalysts**. They have been typically used in hydrothermal gasification processes and low temperature applications in enhancing the quality of biooil obtained. There are few cases where it was used for hydrothermal liquefaction. Gasification is also crucial to a certain extent during liquefaction process for deoxygenation, when the biooil had higher percentages of oxygenated compounds. de Caprariis et al. (2019) investigated on addition of Fe as a catalyst for hydrothermal liquefaction of oak wood and revealed that it acted as a sacrificial catalyst by oxidation into $Fe_2O_3$, thereby reducing the acids and aldehydes from macromolecules and enhancing the quality and quantity of biooil. In another study, by doping oxides like $Al_2O_3$ with active substance KF and using it as a catalyst, the yield of the biooil increased from 6.6 to 13.9% at 300 °C (Alper et al. 2019). However, extensive gasification has a negative impact on the yield of bio-oil. Other heterogeneous catalysts that have been reported to be used hydrothermal processing include Ni and Ru doped over $Al_2O_3$, $TiO_2$ and $ZrO_2$ (Grilc et al. 2016).

## 4.7 Essential Chemicals Obtained from Hydrothermal Conversion

The prime objective of the hydrothermal processing of biomass is to derive value added chemicals out of cheap raw materials and residues. Many researchers, through Gas Chromatography and Mass spectrometry have confirmed the presence of various fine chemicals in the biooil obtained from hydrothermal processing. Some of the chemicals identified in biooil resulting from the hydrothermal liquefaction of cellulose, barley straw and walnut shell and their commercial significance are listed in the Table 4.5.

## 4.8 Conclusion

The hydrothermal processing of lignocellulosic biomass is simple compared to other biomass feedstock owing to their complexities in structure and absence of predefined reaction mechanisms. This chapter discussed briefly about the future technologies that need to be adapted for generation of fine chemicals. In the event of complete depletion of the fossil fuels, the hydrothermal technologies would be a promising alternate solution as it does not need large modification of industrial infrastructure. At present studies are being carried out and more emphasis is given in production of selective value added chemicals that have a high commercial significance. In energy sector, the biooil or the biocrude can be mixed with the natural crude, so that no need of retrofitting the entire refinery. Thus lignocellulosic biomass has a huge potential in the field of bio refinery and is yet to be tapped at a larger extent.

**Table 4.5** Essential Chemicals

| S. no. | Compounds | Significance |
|---|---|---|
| 1. | Phosphonic acid | Manufacturing of phosphate salts |
| 2. | L-Methyltartronic acid | Production of mesoialic acid and hydroxy dicarboxylic acid |
| 3. | 4-Penten-2-ol, 2-methyl | Paper industries as an additive |
| 4. | 2-Cyclopenten-1-one, 2,3-dimethyl | Anti-constipation agent and treating gastrointestinal disorder |
| 5. | 3-Pentanol; 1-Pentanone,1-(2-furanyl)- | Alternate to gasoline |
| 6. | 3,4-Dimethyl-5-hexen-3-ol | Curing agent for epoxy resin |
| 7. | 2-Cyclopenten-1-one, 2,3,4-trimethyl- | Drug delivery agent, cosmetics, treatment of ion Exchange resins |
| 8. | 3-Pentanol, 3-ethyl- | Solvent for coating CD's and DVD's |
| 9. | Phenol, 2-methoxy- | Household cleaners and mouthwashes |
| 10. | Benzene, 1,2-dimethoxy- | Making resins, rugs, rubber lubricants, etc. |
| 11. | 1,2-Benzenediol | Oxidant in electroplating bath |
| 12. | 4-Ethylcatechol | Antibiotics, manufacture of protein kinase inhibitors |
| 13. | Vanillin | Food flavoring, fragrances in beverages, ice-creams etc. |
| 14. | Acetophenone, 4'-hydroxy- | Perfumes |
| 15. | Ethanone, 1-(2,3-dihydroxy-4-methoxyphenyl)- | Odors reagents, enzyme modeling in inflammatory mediators produced by immune cells |
| 16. | Ethanone, 1-(4-dihydroxy-3,5-dimethoxyphenyl)- | Odors reagents |
| 17. | Eicosanoic acid | Hair care products |
| 18. | Octadecanoic acids | Soaps, softening plastics |
| 19. | Glycol | Antifreeze in automobile radiators |
| 20. | Lactic acid | Food preservations ingredients |
| 21. | Phenol | Disinfectant in cleaner liquids |
| 22. | o-Cresol | Produce pesticide, MCPA phenoxy herbicide, etc. |
| 23. | p-Cresol | Make phenol-formaldehyde resins |
| 24. | Butanoic acid, 2-hydroxy- | Food and perfume |
| 25. | Glycerol | Humectant, solvent and sweetener |
| 26. | Catechol | Precursor to fine chemicals |
| 27. | 3,5-dihydroxytolune | Production of dye, as reagent in chemical tests. |

(continued)

**Table 4.5** (continued)

| S. no. | Compounds | Significance |
|---|---|---|
| 28. | Dodecanoic acid | Medicinal field for treating HIV, yeast infection, chlamydia and ringworm |
| 29. | 2-heptadecanone | Flavouring agent |
| 30. | 11-cis-Octadecenoic acid | Drug delivery, vitamin formulations |
| 31. | 9-Oleic acid | Agent to damage lung artificially in animals for testing in laboratories |
| 32. | Fluorene | Dyes, pesticides, plastics, etc. |
| 33. | Acetic acid | Disinfectant, preservation of pickles, etc. |
| 34. | Homovanillyl alcohol | Treat diarrhoea |
| 35. | 1,2-Benzendiol, 3-methoxy- | Oxidant in electroplating bath and rubber lubricant |
| 36. | Pentenoic acid, 4-oxo- | Vaccine to inhibit fatty acid oxidation in rat heart mitochondria |

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# Chapter 5
# Prediction of Oil Yield from Oil Palm Mesocarp Using Thermally Assisted Mechanical Dewatering (TAMD)

**Hasmiera Hashim, Suzana Yusup and Patricia Arlabosse**

**Abstract** Thermally assisted mechanical dewatering (TAMD) is a new technology for the separation of solid/liquid. When applied to "nature-wet" biomass, the TAMD process significantly enhances the separation yield. In the present study, TAMD was used to extract the crude palm oil (CPO) from mesocarp. The CPO yield of 70.77 wt% was achieved at optimum parameters of 73.0 °C, 6.7 bar and 60 min of extraction time. This CPO yield was comparable with previous works on the enzymatic extraction and hot compressed water extraction (HCWE) with CPO yield of 71.0 and 70.50 wt% respectively. Apart from that, this value was higher for about 13.80% compared to commercial CPO extracted using screw press which obtained the oil yield of 61.0 wt%. Based on the literatures, the highest CPO yield was obtained from supercritical $CO_2$ extraction at 77.0 wt% whereas the lowest CPO yield was extracted using subcritical R134a which gave 66.0 wt% of oil yield. Nevertheless, the operational conditions of supercritical $CO_2$ were 300 bar and 80 °C which were higher than that of TAMD. In conclusion, TAMD extraction has a potential to be an alternative method to extract CPO by producing higher oil yield.

**Keywords** Crude palm oil · Oil yield · Thermally assisted mechanical dewatering · Response surface methodology

## 5.1 Introduction

Oil palm (Elaeis quineensis Jacq.) is known as the highest yielding crops for edible oil in the world. It made up 31.7% of global production followed by 25.3% of soybean,

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12.2% of rapeseed and 8.0% of sunflower oil (Hammond et al. 2005). Palm oil is an essential source of food and lipid that used in many consumer products such as cooking oil, cosmetic and dairy products. Palm trees are able to produce 4–10 times more oil per hectare than other oil crops (Barcelos et al. 2015). Comparing to soybean oil, palm oil only requires one-tenths of land, one-seventh of fertilizer, one-fourteenth of pesticide, and one-sixth of energy to produce the same amount of oil (de Vries et al. 2010). Cheap production of palm oil has increased the global demand significantly for last decades and it is expected to grow more in the future (Abdullah and Wahid 2010).

Despite of high global demand, the disadvantages come along with the production of palm oil. Palm oil is frequently associated with deforestation for the expansion of plantation to meet the global demand (Aikanathan 2013). The deforestation causes the loss of natural habitat for species such as tigers, elephants and orangutans (Sayer et al. 2012). However, this conflict can be prevented through another means such as enhancing the extraction process of palm oil to increase the oil yield. In typical palm mill in Malaysia, mechanical screw press is utilized to extract crude palm oil (CPO) production (Che Yunus 2015). The conventional process involves sterilization of fruit bunches, stripping, digestion of fruit and mechanical pressing. Various researches have been conducted to mitigate this drawback through alternative methods such as aqueous enzymatic, hot compressed, supercritical extraction using carbon dioxide ($CO_2$) and subcritical of 1,1,1,2-tetrafluoroethane (R134a) (Sarip et al. 2016). The use of these alternative methods showed significant improvement in the oil yield up to 0.77 g oil/g dried mesocarp (Berger 1983; George and Arumughan 1992). Nevertheless, most of these methods remained at research scale due to economic constraints, impracticality and environmental sustainability. Therefore, it is important to explore thermally assisted mechanical dewatering (TAMD) as a possible alternative method for the improvement of oil yield.

## 5.2 Methodology

The methodology involved sample preparation, extraction process using thermally assisted mechanical dewatering and oil yield calculation.

### *5.2.1 Sample Preparation*

Oil palm fresh fruits were collected from Felda Seroja Palm Mill in Jengka 18, Pahang, Malaysia. The feedstocks were treated using sterilization process. The fruitlets were sterilized at 130 °C for 1 h using a steam sterilizer. Mesocarps were obtained by shredding the softened pulp into 3–5 mm of particle sizes and sealed in the plastic container before being stored in a freezer at −5 °C for further experimental use.

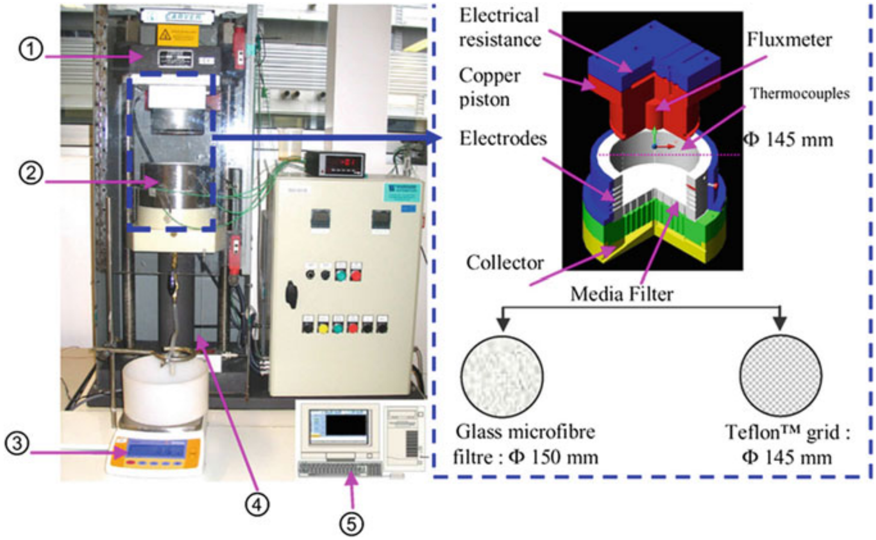

**Fig. 5.1** Detail of experimental set up. (1) CARVER hydraulic press; (2) filtration/compression cell; (3) electronic scale; (4) movement sensor; (5) computer and data acquisition

### 5.2.2 *Extraction Process*

The extraction process was conducted using thermally assisted mechanical dewatering (TAMD). The TAMD experimental set up was equipped with hydraulic press, filtration/compression cell, electronic scale, movement sensor and computer and data acquisition as shown in Fig. 5.1. The maximum capacity of temperature and pressure are 105 °C and 15 bar respectively in TAMD. Prior to the extraction process, the desired temperature (24–103 °C) was computed into the system to achieve the operating temperature for the sample. Three electrical resistances were inserted at the compressive piston to investigate the temperature impact and control the temperature with minimum error at ±0.1 °C. The sample was loaded into filtration/compression cell. The sample was weighed for 80.0 g using an electronic mass balance. The sample was pressed by the hydraulic press at desired temperatures (24–103 °C) and pressures (2.5–12 bar) for different extraction times (40–65 min). The sample was progressively separated into filtrate and pressed cake. The filtrate was filtered using the media filter to remove the impurities.

### 5.2.3 *Calculation on Oil Yield*

The wet weight and dry weight were 80 g of shredded pulp and de-oiled pressed cake respectively. The extracted CPO yield was calculated using Eq. (5.1):

$$Y_{oil} = \frac{W_W - W_d}{W_w} \times 100 \qquad (5.1)$$

where $Y_{oil}$ is the oil yield (g-oil/g-sample), $W_w$ is the wet weight (g) and $W_d$ is the dry weight (g).

## 5.3 Result and Discussions

TAMD extraction was conducted to extract CPO from mesocarp. The operating parameters used were temperature, pressure and extraction time. Total of 20 runs were conducted to determine the optimum parameters. Each run was conducted for three replicates and the average oil yield was taken.

### *5.3.1 Determination of Optimum Parameters*

The analysis of variance (ANOVA) was used to analyse the fitness of TAMD extraction, the adequacy of model, parameter studied, interaction between parameters as well as coefficient of variance (CV) and standard deviation (SD) by using Design Expert version 10.0 of Response Surface Methodology (RSM) model. The ANOVA for extraction of CPO was shown in Table 5.1.

**Table 5.1** Analysis of variance (ANOVA) for TAMD extraction of mesocarp

| Source | Sum of squares | DoF | Mean square | F value | *p*-value |
|---|---|---|---|---|---|
| Model | 828.78 | 9 | 92.09 | 84.24 | <0.0001 |
| A-temperature (°C) | 232.87 | 1 | 232.87 | 213.04 | <0.0001 |
| B-pressure (bar) | 4.44 | 1 | 4.44 | 0.86 | 0.3757 |
| C-time (min) | 70.76 | 1 | 70.76 | 64.73 | <0.0001 |
| AB | 30.92 | 1 | 30.92 | 28.29 | 0.0003 |
| AC | 0.081 | 1 | 0.081 | 0.074 | 0.7912 |
| BC | 0.38 | 1 | 0.38 | 0.35 | 0.5667 |
| $A^2$ | 419.68 | 1 | 419.68 | 383.94 | <0.0001 |
| $B^2$ | 111.52 | 1 | 111.52 | 102.02 | <0.0001 |
| $C^2$ | 4.49 | 1 | 4.49 | 4.10 | 0.0703 |
| Residual | 10.93 | 10 | 1.09 | | |
| Lack of fit | 5.14 | 5 | 1.03 | 0.89 | 0.6506 |
| Pure error | 5.79 | 5 | 1.16 | | |
| $R^2$ | 0.9870 | | Standard deviation | 1.05 | |
| Adequate precision | 33.084 | | C.V. (%) | 1.68 | |

The model f-value of 84.24 implied the model was significant. There was only a 0.01% chance that an f-value became large due to noise. The probability ($p$) value of the quadratic model was below 0.0001 which indicated that the model was well fitted to the actual values. The extraction of crude palm oil (CPO) from the mesocarp was accurately described by a quadratic polynomial model. The maximum oil yield (Y) as a function of independent factors was shown in Eq. (5.2). The coded factors of Y, A, B and C represented the oil yield, temperature, pressure and extraction time respectively.

$$\begin{aligned}\mathrm{Y(coded)} = {} & 68.28 + 4.13\mathrm{A} + 0.12\mathrm{B} + 2.28\mathrm{C} - 1.97\mathrm{AB} + 0.10\mathrm{AC} \\ & - 0.22\mathrm{BC} - 5.40\mathrm{A}^2 - 2.78\mathrm{B}^2 - 0.56\mathrm{C}^2 \end{aligned} \tag{5.2}$$

The accuracy of the model was evaluated using lack of fit to assess its significance. In this model, the insignificant lack of fit with $p$-value of 0.5506 was higher than 0.05 which concluded that second order polynomial equation provided good prediction of the CPO yield. According to Cameron and Windmeijer (Colin Cameron and Windmeijer 1997), R-squared should be at least 0.80 for good fit of the model. The R-squared of the model of 0.9870 indicated the regression model explained the experimental data well. The predicted R-Squared of 0.9414 was in reasonable agreement with the Adjusted R-Squared of 0.9753 where the difference was less than 0.2. Adequacy precision measures the signal to noise ratio and the ratio greater than 4 is desirable. The noise ratio was 33.084 which indicated a satisfactory signal. A low value of standard deviation of 1.05 demonstrated the closeness of data to the average value whereas the low coefficient of variation of 1.68 represented high precision to the estimated values. The predicted yield of CPO was 70.77 wt% at the optimum parameters of 73.0 °C, 6.7 bar and 60 min. The CPO yield extracted from TAMD was comparable with previous works on extraction of CPO using enzymatic extraction and hot compressed water extraction (HCWE) with CPO yield of 71.0 and 70.50 wt% respectively (Sarip et al. 2016; Berger 1983; George and Arumughan 1992; Mahmoud et al. 2008; Colin Cameron and Windmeijer 1997; Teixeira et al. 2013).

Although the obtained yield was comparable, TAMD was conducted at lower temperature of 73.0 °C compared to hot compressed water at 160 °C and enzymatic extraction at 90 °C. Apart from that, the CPO yield of 70.77 wt% was higher about 13.80% compared to commercial CPO extracted using screw press which obtained the oil yield of 61.0 wt% (Nagendran et al. 2000). Based on the literatures, the highest CPO yield of 77.0 wt% was extracted using supercritical $CO_2$ extraction followed by Soxhlet (Hexane) extraction with 75.7 wt% of oil yield (Lau et al. 2008). The lowest CPO yield was extracted using subcritical R134a which gave 66.0 wt% of oil yield (Mustapa et al. 2009). Nevertheless, the operational conditions of supercritical $CO_2$ were 300 bar and 80 °C which were higher than TAMD. Nevertheless, the alternative extraction methods produced higher oil yield compared to conventional method. The comparison between oil extracted using TAMD and other extraction methods was tabulated in Table 5.2.

**Table 5.2** Comparison of CPO extraction using TAMD and other extraction methods

| Extraction method | Operating condition | CPO yield (wt%) | Reference |
|---|---|---|---|
| Supercritical fluid $CO_2$ extraction | 80 °C, 300 bar | 77.0 | Lau et al. (2008) |
| Soxhlet (hexane) extraction | 65 °C | 75.7 ± 0.5 | Sarip et al. (2016) |
| Aqueous enzymatic extraction | 90 °C | 71.0 | Teixeira et al. (2013) |
| Hot compressed water (HCW) | 160 °C, 50 bar | 70.0 ± 0.5 | Sarip et al. (2016) |
| Subcritical R134a extraction | 80 °C, 100 bar | 66.0 | Mustapa et al. (2009) |
| Commercial CPO | 40 bar | 61.0 | Nagendran et al. (2000) |
| TAMD | 73 °C, 6.7 bar | 70.77 | This work |

### 5.3.2 *Effect of Independent Operating Parameters*

The effect of independent operating parameters on the CPO yield was shown in Fig. 5.3. Based on Fig. 5.3a, temperature demonstrated significant influence on crude palm oil (CPO) yield with $p$-value <0.0001. This positive result was in agreement with previous works related to the effect of temperature on the oil recovery from the oilseeds (Willems et al. 2008; Ebewele et al. 2010). CPO yield improved significantly with increasing temperature especially when the pressing temperature increased from 40 to 70 °C. In fresh mesocarp, the lipid and protein constituent were enclosed within the cell wall and intercellular voids (Silvamany and Jahim 2015). Introduction of temperature helped to rupture the cell wall and intercellular void which was subsequently increased the mass transfer rate (Burubai 2007). The broken cell wall led to protein denaturation and coagulation which reduced the oil viscosity. It facilitated the flow of oil from the cell into the inter matrix of mesocarp (Willems et al. 2008). Overall, the influence of pressing temperature caused change of solid structure and reduced the viscosity of the oil. However, further increasing temperature from 75 to 90 °C started to reduce the CPO yield moderately. At these temperatures, the colour of CPO became darker and the pressed cake was dried and hard compared to at low pressing temperature. The comparison of pressed cake condition at high temperature and low temperature was observed in Fig. 5.2. This phenomenon was contributed by the effect of water vaporization.

Water evaporated faster than oil at higher temperature which caused significant amount of moisture loss. The pressed cake became hard and dried thus reducing the oil flow through the cell matrices.

Applied pressure demonstrated the weak influence on the CPO yield. CPO yield increased slowly with increasing pressure from 4.5 to 7.00 bar. The CPO yield started to level off at pressure between 7.0 to 7.5 as shown in Fig. 5.3b. Beyond these applied pressure, the CPO yield reduced moderately as pressure was approaching 10 bar.

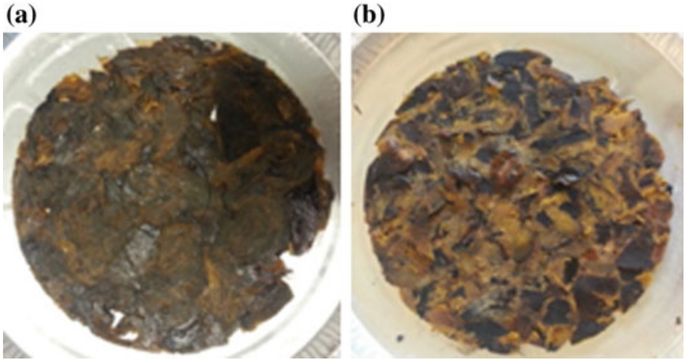

**Fig. 5.2** Pressed cake condition at temperature of **a** 87 °C and **b** 63 °C using TAMD

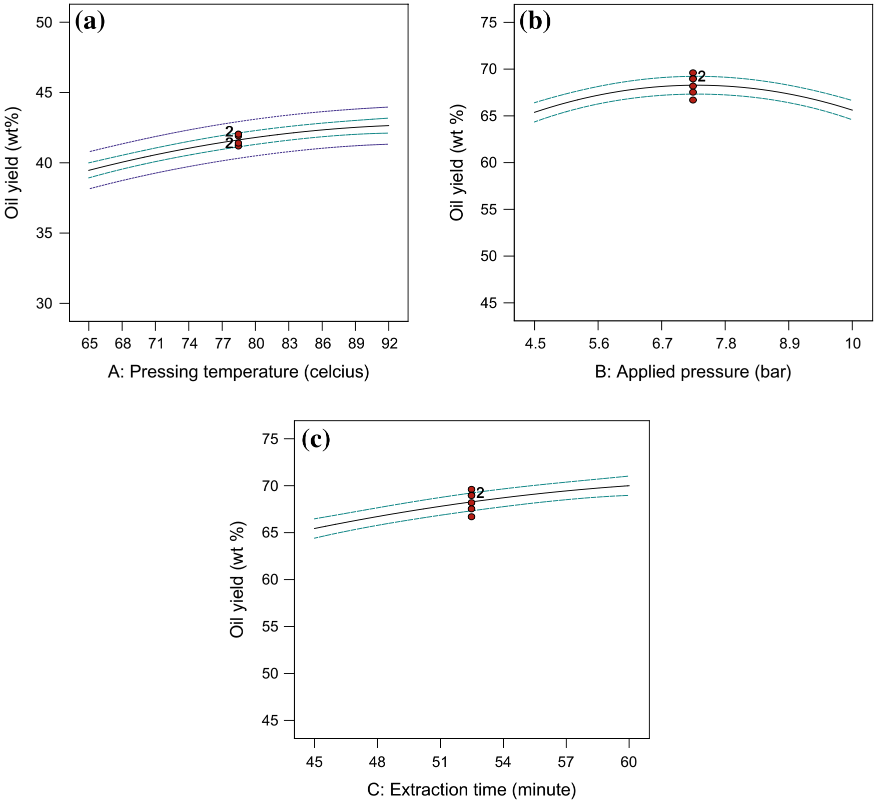

**Fig. 5.3** The effect of **a** temperature **b** pressure and **c** extraction time on the CPO extraction

This result was opposite with result in earlier work where a higher oil yield would be extracted at a higher applied pressure (Ebewele et al. 2010). At higher pressure, the cake slowly deformed and compacted. As the intercellular voids became smaller, the oil flow became restricted and subsequently reduced the oil yield. This condition indicated that the excessive pressure did not really give a positive impact on the oil yield. A similar result was observed in the extraction of oil from *Jatropha curcas L.* kernel. (Willems et al. 2008; Ebewele et al. 2010; Silvamany and Jahim 2015; Burubai 2007; Subroto 2015).

The effect of pressing time on the oil yields from mesocarp was shown in Fig. 5.3c. The oil yield was directly proportional to pressing time. The oil yield continued to increase as the pressing time increased. These results were in close agreement with the previous work reported by Acheheb et al. (2012) in the extraction of oil from *Pistacia atlantica* using hydraulic press machine. The pressing time showed moderate effect on the oil yield where the yield increments were approximately 5 wt%. It was concluded that the pressing time was within the optimum values. Longer extraction time than this range was not feasible as it added to operation cost for big scale production.

### 5.3.3 *Effect of Interactive Parameters*

The effect of interaction between the parameters was shown in Fig. 5.4. Based on Fig. 5.4a, the effect of pressing temperature was more significant at lower pressure compared to higher pressure to achieve maximum crude palm oil (CPO) yield. For instance, the temperature of 87 °C produced 68.15 wt% and 61.13 wt% of CPO at pressure of 7.25 bar and 10 bar respectively. The result indicated that lower pressure produced more CPO than higher pressure at constant pressing temperature and extraction time. A similar effect was also reported in previous works by Mpagalile and Clarke (2005) and Subroto et al. (2015). The oil yield started to be reduced at higher temperature and pressure. The interaction between these parameters became counteractive at higher values and this effect was explained by Bargale et al. (1999) in his previous work. Increasing temperature decreased the viscosity of oil thus facilitated the oil flow through the compressed cake. Conversely increasing pressure caused the cake to become harder and limited the oil flow from the intercellular voids (Bargale et al. 1999). In general, the oil yield increased with extraction time for all pressing temperature. Based on Fig. 5.4b, CPO yield increased progressively from 40 to 55 min when pressing temperature was conducted from 40 to 80 °C. This condition was contributed by coagulation of protein and reduction in oil viscosity which allowed the oil to flow easily.

A similar condition was observed by several researchers that the pressing temperature and extraction time showed significant effect on the oil yield (Pominski et al. 1970; Bongirwar et al. 1977). There was a significant reduction in oil yield at lower and higher range of temperature for longer extraction time. Extending the extraction time at high temperature led to substantial moisture loss and hardened the

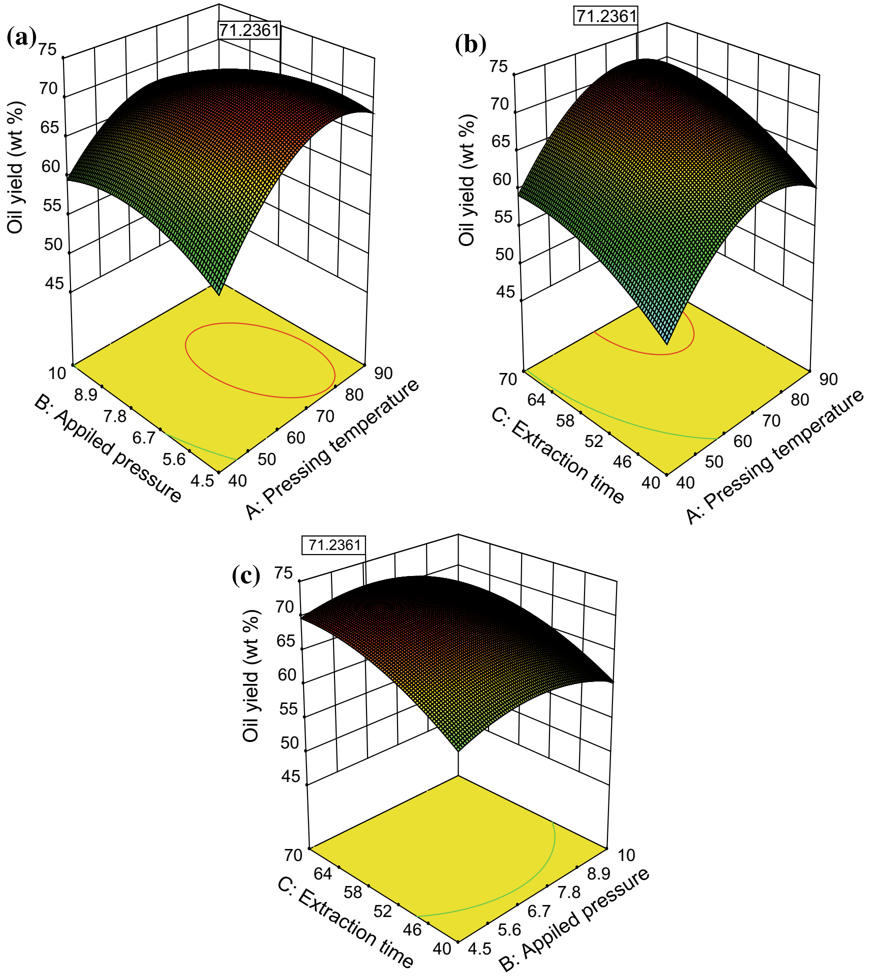

**Fig. 5.4** Oil yield as a function of interactive parameters

cake. This phenomenon was known as the effect of moisture content in the oil. Water acted as an interfacial agent between the protein-rich cake and oil. At higher pressing temperature, the adhesion became thicker and formed a paste-like plastized material (Subroto 2015). Furthermore, high temperature and long extraction time contributed negative influences on the quality of extracted oil and pressed cake (Anjou 1972; Ohlson 1976).

The applied pressure demonstrated minimal influences on the crude palm oil (CPO) yield for all pressing time. Based on Fig. 5.4c, the oil yield increased very slowly at pressure of 5.0 bar and started to level off at 7.0 bar. This condition was likely happened due to maximum consolidation point. Consolidation point is defined as a minimum pressure needed to flow oil out from the intercellular void (Ajibola et al. 2002; Herak 2013). Once the cake deformation reached maximum consolidation point, further increment in pressure and time showed no effect on the oil yield. The oil yield began to drop with pressure above 8.0 bar for longer extraction time. The adverse effect was affected by the closure of intercellular voids. Beyond the optimum pressure, the voids became smaller and restricted the oil flow.

## 5.4 Conclusion

The optimum parameters of CPO were at 73 °C and 6.7 bar for 60 min to obtain the maximum yield of 70.77 wt%. The obtained yield was in close agreement with the predicted value generated from RSM. Based on the ANOVA, the R-squared of the model and lack of fit were 0.9870 and 0.5506 which indicated that the model was significant. It was observed that the temperature and time were statically important in affecting the CPO yield compared to pressure. In terms of parameter interactions, temperature-pressure and temperature-time displayed significant influence on CPO yield based on their respective *p*-value. The oil yield extracted using TAMD was higher about 13.80% than conventional method, screw press which obtained 61.0 wt% of CPO yield. TAMD also produced comparable oil yield with other alternative methods at optimum parameters. As a conclusion, TAMD extraction has a potential to be an alternative method to extract CPO from mesocarp.

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# Chapter 6
# Optimization of Bio-ethanol Production from Whey and the Characterization of Bio-edible Films from the Fermentation Residue

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**Abstract** Dairy industries generate significant liquid waste, of which, cheese whey is the most abundant. Whey is the liquid resulting from the coagulation of milk and is generated from cheese manufacture. About 9 L of whey is generated for every kilogram of cheese manufactured. This study aims at optimizing the production of ethanol from whey. The fermentations were carried out using the yeast strain *Kluyveromyces marxianus*. A maximum of 6.4 ml ethanol per 250 ml whey was produced by the sole utilization of the inherent lactose concentration. Further the utilization of the fermentation residue to produce bio-edible films was done. Protein estimation of crude whey, crude casein and whey water was carried out which gave values of 45.6, 35.68 and 19.6 mg/ml respectively. The parameters that were checked and varied for the process of optimization were lactose concentration, urea concentration and time period of fermentation. The research analysis concluded that cheese whey which is currently being treated as a waste can be converted into highly beneficiary products.

**Keywords** Whey · Cheese waste · *Kluyveromyces marxianus* · Bio-ethanol · Edible wrapper · Fermentation

## 6.1 Introduction

Cheese whey, a liquid obtained from the coagulation of milk is a potent pollutant with a biological oxygen demand, (BOD) of 35–45 kg/m$^3$ and chemical oxygen demand (COD) of about 60–80 kg/m$^3$. About 9 L of whey is generated for every kilogram of cheese manufactured, with the world production of cheese whey estimated at over 10$^8$ tonnes per year yielding an important environmental pollution source (Anema 2008; Tsakali et al. 2010). The constituents of cheese whey include 7% solids comprising

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of about 10–12% proteins (*á*-lactalbumin, *â*-lactoglobulin, bovine serum albumin, and the heavy and light chain immunoglobulins, lactoferrin and lactoperoxidase.), the rest being lactose (74%), minerals (8%) and fat (3%).

Whey protein is used in many food applications because of its functionality and nutritive value. Several value-added products obtained from whey include single cell protein, ethanol, organic acids, biopolymers and biodegradable plastics (Siso 1996). Cheese whey has been used as an inexpensive and nutritionally rich raw material for ethanol production. The present study aims at using unconcentrated and concentrated cheese whey because, direct fermentation (Shahani and Friend 2010; Ghanadzadeh and Ghorbanpour 2012; Zhou et al. 2009) of cheese whey with low lactose content (3–5% w/v) leads to low ethanol concentrations (2–3% v/v). The parameters that were focused on for optimization were time and concentrations of lactose and urea. An optimum amount of yeast concentration, optimum amount of carbohydrate in the substrate and the presence of nitrogen source for the optimum growth of yeast cells are some factors which affect the process of ethanol formation. A high nitrogen concentration in the substrate will result in growth inhibition of the yeast. Yet a low concentration will lead to low overall effective growth of the yeast.

Food produces are exposed to a variety of physical, chemical and microbiological deterioration throughout their production, storage and distribution. Whey proteins have been successfully employed as raw material for biodegradable packaging (Campos et al. 2011) because they come from a renewable source and are a by-product of the cheese making industry. Whey protein isolates (WPI) represent the purer form of such whey proteins, and have shown promising mechanical features, as well as moderate moisture permeability and good oxygen barrier properties (Ramos et al. 2012)—comparable to those exhibited by the best synthetic polymer-based films available. In particular, addition of antimicrobial agents may enable extension of the shelf-life and safety of packaged foods, by reducing (or even preventing) growth of pathogenic and spoilage microorganisms. A secondary part of the research work aims at obtaining a simpler technique for the production of edible films rather than the more complex methods like blown extrusion used for the production of sodium caseinate edible films (Belyamani et al. 2014).

## 6.2 Materials and Methods

### *6.2.1 Cheese Collection*

Microbial strain required for the fermentation process was obtained from Microbial Type Culture Collection Bank, Chandigarh, India. Two strains were used for fermentation. The first strain, *Saccharomyces cerevisiae* (MTCC NO. 3157) was cultured in malt yeast agar. (malt extract 3.0 gm, yeast extract 3.0 gm, peptone 5.0 gm, glucose 10.0 gm, Agar 20.0 gm and distilled water 1.0 L) at pH 6.2 and temperature 30 °C in aerobic conditions for 48 h. The second strain, *Kluyveromyces marxianus* (MTCC

NO. 4139) was also cultured in malt yeast agar in aerobic condition at a pH of 6.2 and temperature of 30 °C for 48 h (Ghanadzadeh and Ghorbanpour 2012). The strain *K. marxianus* is known for its efficient conversion of whey to ethanol while *S. cerevisiae* is used because of being normally known as brewer's yeast. A nitrogen source is preferred by the microbial strain *K. marxianus*, for its efficient growth. For this purpose, rather than ammonium sulphate, urea was used. Cheese whey was collected from Kodai cheese dairy products Pvt. Ltd., Batlagundu, Tamil Nadu. 20 L cheese whey was collected and stored in normal refrigerator conditions.

### *6.2.2 Fermentation*

Fermentation was carried out in Erlenmeyer flasks. Both of the microbial strains were incubated on potato dextrose agar and were inoculated on nutrient media over night with continuous shaking, viz the seed culture (Ghanadzadeh and Ghorbanpour 2012). From the seed culture yeast cells were centrifuged out and 0.008 gm/ml yeast was used. During the usage of the strain *K.* marxianus 0.04 gm/ml of urea was added as a nitrogen source. Ammonium sulphate is not preferred because the sulphate ions left after nitrogen usage tend to be inhibitory for the microbial culture. Fermentation was carried out in aerobic as well as anaerobic conditions (Shahani and Friend 2010; Ghanadzadeh and Ghorbanpour 2012). Fermented liquor was centrifuged at 5000 rpm for 5 min so as to separate the yeast cells.

### *6.2.3 Bio-wrapper Formation*

To check the film forming properties, casein part from the whey was subjected to standard film forming procedures. To a specified amount of the bulk, glycerol and starch were added and was subjected to heating in a water bath with intermittent heating (Xiaomin 2004; Campos et al. 2011). The step is proposed necessary for the formation of inter-molecular bonds.

### *6.2.4 Characterization of Cheese Whey*

Prior to fermentation of cheese whey, it is essential to estimate the amount of protein present in the crude. The estimation of protein content was done by 'Biuret method'. Standard BSA and standard Casein was prepared as stock at a concentration of 10 mg/ml. From the stock 0.1–1.0 ml was pipetted out to test tubes S1–S5 respectively. 1 ml of crude whey, crude casein and whey-water were taken as test sample. The volumes were made up to 1 and 4 ml by adding of Biuret reagent to test tubes (Belitz et al. 2004; Berg et al. 2006). The solutions were incubated for 10 min and OD was taken at 540 nm in a UV-Visible spectrometer.

## *6.2.5 Fermentation*

### 6.2.5.1 Batch 1

The glassware used for fermentation were autoclaved at 120 °C for 20 min. 1000 ml whey was taken and pasteurized at 72 °C for 15 s. Fermentation was done in four Erlenmeyer flasks in which 250 ml whey were taken. Varying concentrations of lactose (0.04, 0.08, 0.12, 0.16 gm/ml) and 2 gm of yeast *S. cerevisiae* was added to the bulk. The reactor was aerated using an aquarium pump and magnetically Stirred. The batch was run for 48 and 120 h (2 and 5 days respectively). The yeast was removed by filtration. Fermented mass was subjected to distillation (Table 6.1).

### 6.2.5.2 Batch 2

The glassware used for fermentation were autoclaved at 120 °C for 20 min. 1000 ml whey was taken and pasteurized at 72 °C for 15 s. 50 gm lactose, 2 gm yeast, *S. cerevisiae* added into the bulk for fermentation process. The batch was run for 120 and 192 h (5 and 8 days respectively) under anaerobic conditions.

### 6.2.5.3 Batch 3

In the following batch, the yeast strain *K. marxianus* was used for the fermentation process. Varying concentrations of lactose and urea were used to evaluate the amount of ethanol produced. A very low air flow rate of 0.4 vvm was given for the effective growth of the strain. The presence of ethanol was confirmed by two methods, Iodoform test and Potassium dichromate test (Berg et al. 2006) (Tables 6.2 and 6.3).

**Table 6.1** Sample batch fermentation introducing *Saccharomyces cerevisiae*

| Strain *S. cerevisiae* Batch 1 and 2 | Lactose concentration (gm/ml) | Initial pH | Final pH | Time (hour) |
|---|---|---|---|---|
| Aerobic | 0.04 | 5.019 | 5.00 | 48 |
| Aerobic | 0.08 | 5.02 | 5.01 | 120 |
| Anaerobic | 0.12 | 5.018 | 4.98 | 120 |
| Anaerobic | 0.16 | 5.022 | 4.876 | 192 |

**Table 6.2** Sample batch fermentation using *Kluyveromyces marxianus*

| Strain *K. marxianus* Batch 3 | Lactose concentration (gm/ml) | Urea concentration (gm/ml) | Initial pH | Final pH | Time (hour) |
|---|---|---|---|---|---|
| Low aerobic condition (0.4 vvm) | 0.2 | 0.06 | 5.019 | 4.76 | 24 |
| | 0.14 | 0.1 | 5.02 | 4.71 | 48 |
| | 0.1 | 0.14 | 5.018 | 4.59 | 72 |
| | 0.06 | 0.2 | 5.022 | 4.34 | 96 |

**Table 6.3** Optimum ethanol production from each batch

| Strain *K. Marxianus* | Lactose concentration (gm/ml) | Urea concentration (gm/ml) | Initial pH | Final pH | Time (hour) | Ethanol produced (ml) |
|---|---|---|---|---|---|---|
| Batch 1 | 0.2 | – | 5.026 | 4.69 | 60 | 23.8 |
| Batch 2 | 0.14 | 0.06 | 5.018 | 4.59 | 72 | 19.8 |
| Batch 3 | 0.1 | 0.1 | 5.03 | 4.47 | 84 | 14 |
| Batch 4 | 0.06 | 0.14 | 5.012 | 4.48 | 48 | 8.6 |
| Batch 5 (Aerated) | – | 0.02 | 5.028 | 4.7 | 48 | 6.4 |

### *6.2.6 Film Formation*

Film formation is done for the effective utilization of the fermentation residue. To check film formation, crude whey was taken and mixed with glycerol. Magnetically stirred for 2 h. Then kept in boiling water bath for 20 min. Intermittent mixing provided using a glass rod. Further, allowed to cool under normal room temperature. It was then poured into gel rocker which was coated with aluminum foil. The film formed lacked structural stability and, upon exposure to the atmosphere for curing, fungal contamination was observed. To improve the formation of film, starch was added into the mixture (Fig. 6.1).

The second set of film formation procedures involved the usage of 6 gm starch mixed with 30 ml casein which was carefully pipetted out from whey water kept stagnant for 2 h. Standard procedure of film formation was carried out (Wang et al. 2010) and the mixture was poured onto petri plates. One plate was kept in incubator and other one in normal room conditions. Film formation was observed. Both the plates differed in color. The one kept at room conditions exhibited creamy white color while that which was kept in incubator exhibited brown color. For the optimization of the actual process, fermentation residue was taken after distillation of ethanol. 150 ml residue was obtained and it was mixed with 30 gm glycerol and 10 gm starch.

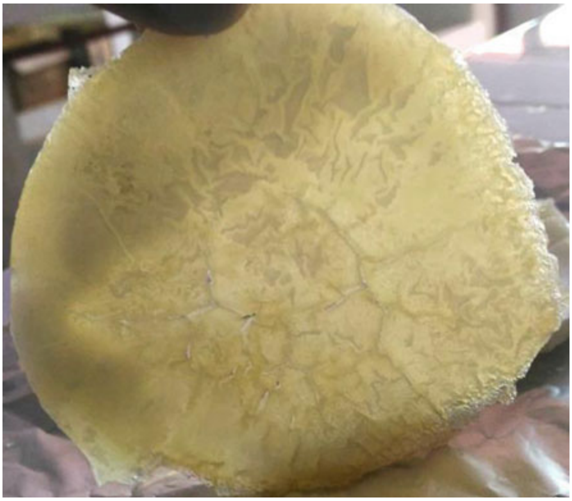

**Fig. 6.1** Bio-edible film formed from fermentation residue

The mixture was subjected to standard film forming techniques and was kept in an incubator for 72 h. Film formation was observed. Inferred that a better agent other than starch is to be used to improve the structural stability of the film.

## 6.3 Results and Discussion

Protein estimation of cheese whey was carried out as 3 tests. Initially the protein estimation of crude whey was done, followed by protein estimation of crude casein and finally the protein estimation of whey water was carried out. Protein estimation was done by biuret test taking a casein standard of 10 mg/ml. The optical density values were recorded and were calibrated to be 45.6, 35.68 and 19.6 mg/ml for crude whey, crude casein and whey water respectively.

The fermentation process yielded in comparable yields of ethanol. The results were comparable with the theoretical yield which shows that only 0.511 gm (w/w) ethanol can be produced from 1 gm of sugar.

From the results obtained, the optimum ethanol production was observed with adding only urea at a concentration of 0.002 gm/ml coupled with an aeration of 0.4 vvm. The result was obtained because of the inherent presence of lactose in cheese whey. The increase in the amount of ethanol in the initial batches is due to the utilization of the added lactose by the yeast strain. This doesn't necessarily mean that the whey is being used for ethanol production. Whey incorporates 5.4 gm lactose per 100 gm (Tsakali et al. 2010). Which in turn means 7.89 gm lactose was present in the 250 ml of whey taken for fermentation. The ethanol was quantified using Potassium-dichromate UV visible spectroscopy technique (Koushki et al. 2012). Potassium dichromate reacts with ethanol to oxidise it into aldehyde ethanol. The formation of chromium (III) ions change the colour from orange to green which can be spectroscopically read at 600 nm. The spectrometer used was a single beam type. The basic reaction involving is represented as;

$$3CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

The full reaction is rather complicated and can be worked out using electron-half-equations. The quantity of ethanol produced in the present work is better than the researches carried out in the same field. Little amount of work has been done with raw cheese whey. Although the species *K. marxianus* is previously used for the production of ethanol, the substrate utilized was whey protein isolate (WPI). The work was successful in producing maximum amount of ethanol in a lesser amount of time (48 h) than those of the previous researches (60 h).

Film formation was observed with the addition of glycerol (98% proof), corn starch and super refined wheat flour to the fermentation residue. Optimum values for the addition of binding agents are 20 gm glycerol, 20 gm corn starch and 10 gm of super-refined flour per 100 ml whey. The intermittent mixing which was provided while keeping in a hot water bath makes sure that inter molecular bonds are formed correctly. This ensures the stability of the biofilm that is produced. The curing procedure is done in gel rockers for the specific shape and uniform thickness. For enhanced stability the biofilm can be cured in a refrigerator after the initial curing in an incubator.

The biofilms were tested for light transparency in a UV-visible spectrophotometer (Ramos et al. 2012). 3 thin sheets of biofilm (4 × 1 cm) were cut and were attached on one side of the sample holder. It was then subjected to light transmission tests at wavelengths 200–280 and 35–800 nm. No values of transmission were detected in the UV light range. In the tests incorporating visible light (350–800 nm), transmittance was observed. The values of transmission ranged from 8.7 ± 0.5 to 61.2 ± 0.3%.

## 6.4 Conclusions

Cheese whey rather than being treated as a waste product, can be effectively and efficiently be used for the formation of many beneficiary products. Ethanol can be efficiently produced and the fermentation residue can be used for the production of bio edible wrappers that can be used to wrap food products. Ethanol yield was quantified to be 92.92% using the *K. marxianus* strain. A urea concentration of 0.02 gm/ml and aeration rate of 0.4vvm. Bio-edible films were produced using 0.2 gm/ml glycerol, 0.2 gm/ml corn starch and 0.1 gm/ml super-refined wheat flour.

The fermentation with *S. cerevisiae* did not give satisfying results. The fermentation process requires more time and the maximum ethanol yield of up to 48% was obtained.

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# Chapter 7
# Captivating Technology for Generation of Bioenergy from Industrial Waste: Microbial Fuel Cell

**M. Naveen Kumar and K. Senthilkumar**

**Abstract** Due to the increasing human activities, the energy requirement gets increased which leads to the depletion of fossil fuel. Because of this precarious scenario, many research works are being carried out all over the globe to identify a source that is potentially cheap and renewable for energy production. This alternate fuel source should satisfy the energy requirement and also should be eco-friendly. The pollution is the major problem in developing countries which is caused by waste materials. Technically they are not waste because enormous amount of energy is hiding in those materials. A technology which taps out energy from waste materials can solve both problems. One of those promising technology is fuel from microbes. This is a method in which microbes are employed to both degrade the waste materials and synthesis energy from it in form of electricity. It is advantageous over other anaerobic digestion systems, because the end product is biogas which is mostly used for the production of electricity with some loss of energy. But by using Microbial Fuel System the problem can be eliminated. This is one of the emerging technologies for treating wastewater and generating electricity. In last few years, Microbial Fuel Cell has attained significance due to their ability to produce energy from renewable sources such as organic waste. This chapter reviews about the different aspects of MFC to treat industrial waste which has more organic waste in a batch and fed batch mode. Besides, the key components of the MFC are electrode materials and its performance is influenced by living biocatalyst and a electrochemically active biofilm developed at the anode. Carbon based electrodes derived from waste materials are commonly used as both anode and cathode and are employed in MFC's due to their biocompatible nature, durability, conductivity and lower cost. The present book chapter describes elaborately about the possibilities of bioenergy from industrial waste, effects of industrial waste on environment, traditional treatment methods

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and its demerits, MFC concepts, prospects, confront, applications, its design and configuration, challenges and next generation point of view.

**Keywords** Biomass · Biorefinery · Microbial fuel cell · Bioenergy · Waste to wealth · Waste management

## 7.1 Introduction

The industrial revolution fossil fuels are one of the mainstays for providing energy. Fossil fuels are deemed for supporting the population and growth of economy. Burning of fossil fuels namely coal, oil and natural gas, for producing energy and other industrial processes releases an enormous amount of carbon dioxide along with other greenhouse gases like CO, $SO_2$, $NO_x$ and $CH_4$, into the atmosphere. These adversely affect the human health and environment (Mukhopadhyay and Forssell 2005). Almost 85% of the total greenhouse gas emissions are energy related. These in turn require sustainable solutions. Energy production can be made more sustainable by using more renewable sources like biomass and lowering the dependency on fossil fuels (COMMISSION E 2010).

Biomass is one of the renewable energy resources that can be combusted directly as a solid fuel by thermal process in order to generate heat and electricity. It can also be converted to methane rich biogas, by a biological process under anaerobic conditions in a controlled environment. Waste management of biomass is possible using landfill method where the resulting landfill gas can be used as fuel for generating power. Microbial fuel cell is employed to produce electrical energy from these bio fuels. The gas obtained from such biological processes is known as bio alcohol (Jacques et al. 1999). Biofuels are thus prospective candidates to replace petroleum fuel. Production of biofuel from biomass is a sustainable solution to reduce both consumption of oil and environmental pollution. These gases could also be produced from food by processes like fermentation. Bioethanol is one among those which could be produced through the fermentation of corn, potato, beet and wheat.

## 7.2 Possible Effluent Sources of Bio-Energy

One of the important energy sources in organic industrial sectors is waste materials like dregs and by-products. Solid wastes from food industries such as peelings and scraps chopped from fruits and vegetables, poor quality food, filtered sludge, pulp, fibre from sugar and starch extraction wastes etc. are dumped on non-living region landfill (Smith 2008).

Food processing industries are generating a huge volume of effluent because of various processing operations like cleaning, washing, blanching, pre-cooking etc. (Kim et al. 2008). These effluent containing sugars, starches, dissolved and solid organic matters. These industrial wastes may be aerobically/anaerobically degraded to produce several commercial waste-to-energy conversion products such as biogas, ethanol etc.

One of the major polluting industries is pulp and paper industry because it consumes more amount of water for various unit operations. This industry discharged wastewater is heterogeneous in nature and it contains wood and other raw materials related compounds, processed chemicals etc. The effluent containing black liquor can be used for the generation of bio-energy by using UASB reactor (Rasi et al. 2007).

## 7.3 Industrial Waste Impacts on Environment Resources

Due to rapid industrialization, major part of pollution is coming from industries and factories. A range of pollutants are discharged into the environment including the water body, land filling and open to atmosphere. All industrial effects are liable for creating a non-conducive environment for living things because of discharge effluent having toxic and highly concentrated contaminants. Additionally, it generates problems for living and non-living things like habitats, sickness, loss of life, and ecosystem devastation. Due to industrial waste there are a some pollution effects along with their serious consequences.

The major effects of industrial pollution are follows:

### *7.3.1 Global Warming*

The major problem of industrial waste is Global warming. It is one of the most severe effects of industrial pollution, because of uncontrolled industrial activities. Most of the Industries release a mixture of greenhouse gases together with carbon dioxide ($CO_2$) and methane ($CH_4$) into the open environment. Released gases are absorbing thermal radiation from the sun so normal temperature of the earth will be increased and leads to global warming.

### *7.3.2 Water Pollution*

The untreated industrial Pollutants discharged from the industries and factories are having prevalent toxic concentration. Generally, these wastes are discharged into the water body and it affects the aqua cultures, flora and fauna lifecycles etc. Usage of unsuitable contaminated water and the discharge of untreated industrial wastewater into water bodies create water pollution mainly.

### *7.3.3 Air Pollution*

The main cause of air pollution is mainly due to the rapid increase in industries/factories. Emissions from various industries have contaminants like methane ($CH_4$), oxides of nitrogen (NO), carbon dioxide ($CO_2$). If these gases are highly present in the atmosphere, they repeatedly create several toxic illnesses and dangerous hazards to the environment. Some of the effects of these gases are formation of acid rains, the presence of smog, and heightened incidents of respiratory disorders among humans, etc.

### *7.3.4 Soil Pollution*

Soil pollution occurs due to untreated disposal of industrial wastes into soil, it is having high toxic contaminants, which leads to soil pollution. Industrial wastes are having different amount of toxic contents and hazardous chemicals such that when deposited in soil, they affect the soil layer strength in the top soil, thus reducing the soil fertility and biological activity of the soil. In addition to that a hazardous effect leads to ecological imbalances thus making troubles in crop production. Apart from that, it may cause severe health problem for those who are consuming such crops because soil and crops are contaminated by toxic chemicals and hazardous materials.

### *7.3.5 Effect on Human Health*

Untreated industrial wastes are having more amounts of toxic contents and hazardous chemical wastes that are disposed into water bodies or soils. It may cause illness, cancers and human cell poisoning etc., For example, inorganic arsenic causes tumors to form in human health. Therefore Untreated industrial wastes are liable for thousands of illnesses and early deaths across the earth.

## 7.4 Conventional Treatment Methods

Generally, industrial wastewater treatment includes primary, secondary and tertiary process which involves large amounts of energy, excessive sludge production, high operational cost and more bad odors in the treatment of industrial wastewater. A traditional treatment method requires more amount of energy for treating wastewater. For overcoming these drawbacks, it is important to develop alternate technology which can efficiently operate with minimum energy making the operation sustainable. In last three decades, rapid anaerobic treatment processes are finding increasing applications in the treatment of domestic and industrial wastewaters. Moreover, global environmental concerns and energy insecurity demands a sustainable and clean energy source. Traditional biodegradation processes focuses only on degrading organic pollutants and not the extraction of chemical energy from the pollutants which resulted in most of this chemical energy being converted into biomass. The excessive biomass produced can often cause clogging of bioreactors which in turn inhibits mass transfer and biodegradation. Thus, resource utilization of waste is unavoidable. The proposed chapter describes the principle and applications of MFC for treating the effluents and generating bio-energy from the same. It is one of the emerging and promising technologies for the treatment of wastewater.

## 7.5 Theory of Microbial Fuel Cell

Microbial fuel cell (MFC) is an emerging technology that treats wastewater by converting its chemical energy into electrical energy using microbes as catalysts. Microbial fuel cell (MFC) is the device which converts chemical energy into electrical energy during oxidation of organic and inorganic matters with the help of microbes. There are two categories of MFC's, of which one uses mediator and another one is mediator-less. The first MFC's demonstrated in the early 20th century used a chemical mediator that transferred electrons from the bacteria in the cell to the anode. Mediator-less MFC's are a more recent development dating to the 1970's; where MFC the bacteria typically have electrochemically active redox proteins such as cytochromes on their outer membrane. These transfer electrons directly to the anode. MFC's started to find a commercial use in the treatment of wastewater since 21st century. Microbial fuel cells (MFC's) are devices that use bacteria as the catalysts to generate energy as electricity utilizing organic and inorganic matter. Electrons generated by the microorganisms from these substrates are transferred to the anode (negative terminal) and flow towards the cathode (positive terminal) linked by a conductive material containing a resistor, or operated under a load. Positive current flows from the positive to the negative terminal. The direction of electron flow is opposite because of convention process. The fuel cell must however be able to oxidize the substrate present in the anode compartment, either continuously or intermittently; otherwise, the system is considered to be a bio-battery. Electrons can be transferred to the anode by electron mediators by direct membrane associated electron transfer, or by other possible means. For most of MFC's the electrons that reach the cathode chamber combine with protons that diffuse from the anode chamber through a membrane and under aerobic conditions; resulting in a water production as a by-product. Biomass originally is generated in the atmosphere due to photosynthesis. A component of the fuel cell is described in Table 7.1.

**Table 7.1** Compulsory elements of microbial fuel cells

| Items | Materials |
|---|---|
| Anode | Nickel electrode, fibre, mesh, graphite materials, carbon materials like paper, cloth, stainless steel etc. |
| Cathode | Nickel electrode, fibre, mesh, graphite materials, carbon materials like paper, cloth, stainless steel etc. |
| Anode chamber | Glass, acrylic |
| Cathode chamber | Glass, acrylic |
| Proton exchange membrane system (PEM) | Nafion membranes, salt bridge, PEM |
| Catalyst | Polyaniline, Pt, $MnO_2$, $Fe^{3+}$ |

### 7.5.1 MFC Configurations and Designs

Many researchers have been examined for increasing the power output of MFC, focusing areas like altering MFC designs, cost effective electrodes, electrode modification, membranes, etc., for enhancing electrode surface area and their actions in order to overcome the potential constraints in $e^-$ and $H^+$ transport system. The schematic of MFC is shown in Fig. 7.1. In anode chamber microorganisms act as electrochemically active bacteria to oxidize the substrates through proton exchange membrane. These $e^-$ and $H^+$ transfer through an external electrical device to cathode chamber, and it diffused through electrolyte and PEM. With platinum as a catalyst, protons and electrons are joined at the cathodic chamber with oxygen to form

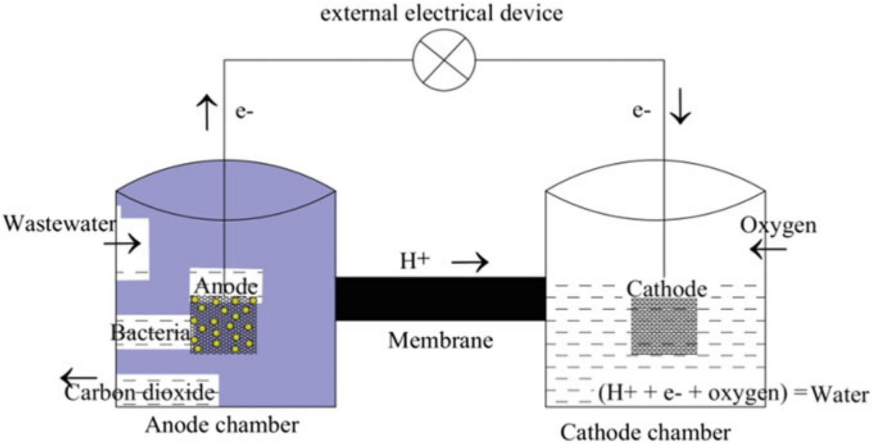
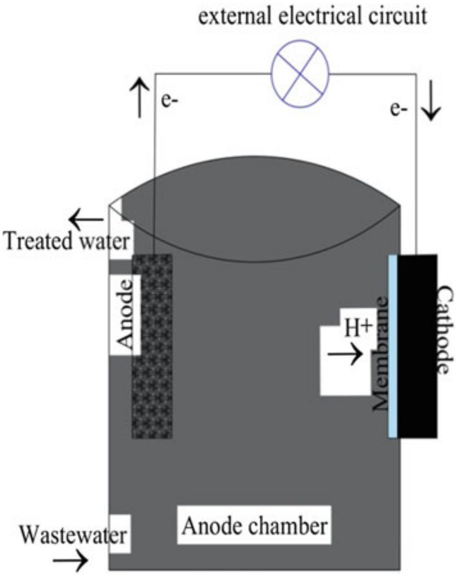


**Fig. 7.1** Experimental setup of dual chambered microbial fuel cell

**Fig. 7.2** Experimental setup of single chambered microbial fuel cell



$H_2O$. There are numerous configuration and shapes of MFC that have been developed to run in batch and fed-batch mode operation. A dual chambered microbial fuel cell setup consists of an anode compartment and a cathode compartment separated by a membrane that facilitates proton exchange like Nafion (Logan 2010). In recent times, Single-Chambered MFC (SC-MFC) has gained considerable attention, because cathode is direct contact with atmosphere shown in Fig. 7.2. Since open air cathode systems can be used in single chambered MFC, which are quite attractive for its increasing power production efficiency. Nevertheless, a lot of single-chambered MFC still use Nafion or PEM membrane for separating the electrons and protons (Ren et al. 2014).

A considerable increase in transfer of oxygen in anodic section in absence of a PEM was reported. Whereas, two-chambered MFC can have a wide range of applications even with a relatively low power output. Cathodic denitrification is such a good example. This design is having outstanding applications in industrial effluent treatment due to its effortless scale-up, proton transfer problems, etc. Nevertheless, oxygen back diffusion is a dangerous disadvantage which is comparatively higher than in membrane-based used MFC. It demonstrated successful generation of electricity using an open air bio-cathode system with biocatalysts (microorganisms).

## 7.6 Research Opportunities in Microbial Fuel Cell Technology

### *7.6.1 Electrodes in MFC*

The performance and cost of MFC highly depended on electrode material. To make making MFC a cost-effective and ascendible technology. It is important to note that electrode design is the greatest challenge. Recently, area of motivation is increased in the electrode material and their configurations of MFC are studied. From the literature it is observed that during the earlier period, a number of electrodes have been widely used for MFC's. For electricity generation electrode and Surface area is an important parameter. In MFC, the electrode materials are having different characteristics and their support materials may have some important characteristics such as good conduction, high mechanical stability, cost effective and fine chemical strength. Carbon based materials are most-widely used base materials in microbial fuel cell. However, there are some specific requirements such as high bio-catalytic activity, rough surface, biocompatible and surface area of electrode are necessary (Shakunthala and Manoj 2017). Electrodes part of research is one of the recent topics of interest in the explore of microbial fuel cell.

### *7.6.2 Effect of Spacing Between Anode and Cathode on Power Production*

An important parameter which has a high influence on total power production is spacing between the electrodes (Karuppiah et al. 2018). The total power production increased when the spacing between the anodic chamber and cathodic chamber are at less distance. Maximum power density was found at observed electrode spacing in their investigations. It is also observed that highest power density output was observed at larger spacing. However, increasing and decreasing the electrode surface area and distance between the both anodic and cathodic chamber will give the better electricity production.

### *7.6.3 Effect of Electrode Surface Area on Power Production*

Electrode surface area has a significant influence on power production in MFC. To increasing the electrode surface area will increasing the electricity production. Cathode area influence on MFC outputs depends on microorganisms and hydrogen whereas anode area did not make such impact. In most of the Microbial fuel cell investigations using proton exchange membrane, air cathode and rate-limiting reactions (Prakash 2016). MFC performance may purely depend on cathode reaction.

### *7.6.4 Influence of Microorganisms in MFC*

The literature evidenced that numerous microorganisms have the capacity to producing protons and electrons from the substrate and transfer electron through their metabolic activity. Microorganisms' sources are river embankments, soil sediments, all type of wastewater which contains more organic matter and sludge. To increasing the power generation in microbial fuel cell microorganisms are optimized. The theory of Microbial fuel cell process is based on the anodic electron transfer mechanism. In dissimilarity metal reducing microorganisms, the chemical compounds are involved in the electron transportation. The microorganisms such as S. putrefactions, G. sulferreducens and G. metallireducens transfer electrons to anode by similar method (Naveen Kumar 2017).

## 7.7 Dispute in Microbial Fuel Cell

The MFC technology has attained and seen wide commercial applications because it can use all kind of biomass for producing electricity. However, present scenario the microbial fuel cell was in initial stage because of their low energy production. To improve the power generation in microbial fuel cell, microorganisms which enormously improve electron transfer process in anode chamber to cathode chamber are important one. Components of microbial fuel cell are one of the limitations for application in the small household consumers because of expensive components will restrict the utilization of MFC for electricity generation (Du et al. 2007).

The conventional type of MFC consists of anode and cathode chamber, which are connected by PEM. This typical two-chamber design of MFCs is frequently operated in batch mode and fed-batch mode. The purposes of proton exchange membrane (PEM), such as Nafion 117, are to separate the protons from anode to cathode chamber. PEM can be more expensive and stronger. Due to the very high internal resistance the power output was very low. Cathodes used for MFCs are Platinum; it is a well-known oxygen reduction catalyst. But platinum is expensive so it needs to be substituted by cheaper. A number of factors such cost of the electrode materials, requirement of precious metal catalysts, low performance, low power densities and costly PEM are limiting MFC technology in commercial applications. Even though these issues can be addressed at lab scale, ultimately pilot scale studies are necessary for analyzing the performance and longevity of materials at large scale especially when dealing with wastewater which doesn't possess constant conditions (composition, temperature etc.) with time.

## 7.8 Use of Microbial Fuel Cell

### *7.8.1 Electricity Generation*

MFC is conversion of chemical energy into electrical energy through the action of catalytic microorganisms. In MFC's the substrates oxidization is directly converted into electricity, experimental results shows electricity generation with an yield of electron 75% and upper yield up to 85% (Tharali et al. 2016). The present scenario microbial fuel cell processes were used in small scale appliances because of low electricity generation. To overcome this issue, one sensible method is to make storage of the produced energy in the form of electricity in electrical storage devices and deal out it to the consumers.

### *7.8.2 Bio Hydrogen*

Another application of microbial fuel cell is bio hydrogen production. Microbial fuel cell is one of the biological process depends on microorganisms present in the substrate. Microbes are generating the protons ($H^+$) and electrons ($e^-$) by their metabolism activity. Through the anolyte reaction generated protons ($H^+$) and electrons ($e^-$) are combined at to form hydrogen (Tamboli and Eswari 2019). In the cathode compartment there is no need of more oxygen for bio hydrogen production. The major benefits of the microbial fuel cell process are produced energy can be stored for future prospects and utilizations (Sevda et al. 2017).

### *7.8.3 Wastewater Treatment*

Microbial fuel cell application is treating all type of wastewaters which contains only more organic matter present in it. Microbial Fuel Cell process is one the unique process because it treats wastewater and produce electricity simultaneously. Microorganisms can play an important role for an effluent treatment as well as bio-energy generation. Microbes can act as electrochemically active bacteria during wastewater treatment for their growth and influencing the performance of microbial fuel cell. Important parameters for producing electricity in microbial fuel cell is wastewater because source of energy in the form of organic matters. Moreover, investigated report shows reduction level of COD was 85% and efficiency as high as 90% were revealed.

### *7.8.4 Biosensor*

Microbial Fuel Cell type of BOD sensors has good significances such as accurateness, reproducibility and operational strength is valuable over other types of BOD sensor. For control and monitoring of industrial process sensor has attained more significant. Microbial fuel cell is able to serve BOD with wastewater strength and yield of microbial fuel cell makes it.

### *7.8.5 Artificial Wastewater*

The wastewater which is artificially produced for research works is called artificial wastewater. It is also called as synthetic wastewater. While using the natural wastewater; it should be stored in the cold condition; it shows different characteristics while testing it. So, artificial wastewater is employed for avoid the change in characteristics of the wastewater and to maintain the same characteristics throughout the research work.

## 7.9 Conclusion and Future Prospects of MFC

Without incorporating any expensive materials into the microbial fuel cell such as electrodes and nafion membranes for electricity generation. The existence of microbial fuel cell technology has surfeit of applications in the day today lives as it is environmental friendly, eco-friendly and more importantly green technology. There are more challenges left over for the complete utilization of MFC, to find ways to make it cost effective, and to fabricate the innovative MFC bioreactors for industrial effluent treatment. Identification of new microorganisms can be treating contaminated effluent in microbial fuel cell through the mechanism of direct electron transfer (DET) along with generation of electricity. There is a broad scope for design and development of these reactors as the power density is too low for consumption in various industrial applications. Besides, the organism may be genetically altered in order to form high reducing microbial strains with wide range of MFC applications. Future researches are necessary to minimize the internal resistance and corrosion related problems in MFC. MFC can also have utilization in army applications in order to power up remote surveillance and communication gears for use in unmanned applications. Further, potential researches on optimization of the electricity production from the two chambered MFC are also necessary. Development and components optimization will enhance the electricity generation and researchers are working to enhance it for the scale up and commercial applications. Also MFC as a continuous reactor may also be studied. Further research towards the conditions to be maintained in the reactor, aerated condition in order to produce more electricity may be needed.

Thus, both the process will reduce the cost of wastewater treatment. On the other hand, Microbial Fuel Cell is one of the captivating technologies for both wastewater treatment and bioelectricity production but it is in early step and it needs more and unique interest in upcoming investigation.

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# Chapter 8
# Production of Biodiesel from Municipal Sewage Sludge by Transesterification Process

**P. Bharathi and M. Pennarasi**

**Abstract** In this work, the biodiesel was produced from municipal sewage sludge contains high free fatty acids (FFA) act as a feedstock. The main sources are primary sludge (P.S) and secondary sludge (S.S) was used as lipid source to compare high yield percentage for the transesterification reaction. Through the base transesterification process, the yield percentage of biodiesel 90.3% was obtained at the optimum conditions of 2% NaOH, chloroform–ethanol (2:1) ratio, 600 rpm and 60 °C temperature for 90 min. The produced biodiesel was analyzed and confirmed by GC-MS. The properties of biodiesel were analyzed and it was found on the inside of ASTM standard limits. Hence, municipal sewage sludge serves as a valuable renewable raw material for biodiesel production.

**Keywords** Biodiesel · Municipal waste · Sewage sludge · Transesterification · Lipid extraction

## 8.1 Introduction

Biodiesel is a clean-burning diesel fuel and its chemical structure is that of Fatty acid alkyl esters (FAAE) (Bojan and Duraira 2012). Biodiesel is environmental-friendly and renewable, whose raw materials are from plants and animals. Sewage sludge is the waste formed during treatment of waste water. These waste water treatment plant produces primary and secondary sludge. This sludge consists of a variety organic matter and microorganisms. The primary sludge contains the floating grease and solids, it has been collected at the bottom of the primary settler during screening and grit removal process. The activated (secondary) sludge contains the collection of microbial cells and variety of suspended solids. It may be produced in the time of aerobic treatment and settled in at the bottom of secondary settler. A part of the activated sludge is recycled back to the aeration tank to keep up a

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sufficient density of microorganisms. Be comparable, the proper study have not been completed for frequently used animal oils. Oil from algae, bacteria and fungi also has been investigated (Deng et al. 2005). Many researchers were agreed with the statement of biodiesel is an alternative fuel for the substitution of conventional diesel due to it possess of fatty acid methyl esters (FAME) and it can be produced from the source of triglycerides through transesterification process (Dube et al. 2007). Generally, the primary sludge contains low-quality fats and grease. The biodiesel produced from primary sludge is low quality while the produced from secondary sludge is high quality (Dufreche et al. 2007). Sulphuric acid and ferrous sulphate are used as catalysts and the yield of FAMEs from FFA is ~86% for both catalysts under suitable condition (Ma and Hannab 1999). Municipal solid waste has biofuel potential in the form of cellulosic ethanol which can replace 5.36% of gasoline consumption (Guana and Kusakabe 2012). Potassium hydroxide and sodium hydroxide are the mostly used among alkaline catalysts which are inexpensive. The other advantages are they are easy to handle in transportation and storage and are preferred by small producers (Meher et al. 2004). A two-step acid pretreatment esterification and base catalyzed transesterification process was selected to improve the yield (Olkiewicz et al. 2012). The main objective of this work is to produce biodiesel using as a sludge waste. As a result, utilization of municipal sewage sludge for biodiesel production, provides dual benefits, it serves as an alternative fuel and also save our environment from solid waste.

## 8.2 Materials and Methods

### *8.2.1 Materials*

Chloroform (99% purity), *n*-hexane (99% purity), diethyl ether (99% purity), ethanol (99.9% purity), methanol (99.9% purity), sodium hydroxide (99% purity), sulphuric acid (95–97% purity), hydrochloric acid (99% purity), acetone (99% purity), isopropyl alcohol (99% purity), phenolphthalein, bromophenol blue, silica gel were purchased from Southern India Chemicals, Chennai, Tamil Nadu, India.

### *8.2.2 Collection and Preparation of Sewage Sludge Sample*

The municipal sewage sludge was collected from the Municipal Waste Water Treatment Plant located in Koyambedu, Chennai, Tamil Nadu, India. The primary sludge was taken from primary clarifier and the secondary sludge was collected from secondary clarifier. Mainly the secondary sludge consists of variety of microbial cells (protozoa, rotifers and aerobic bacteria) and suspended solids. The sludge and water contents were separated through gravity settling process. The sludge was filtered and dried. The dried sample was taken and then powdered using mortar and pestle.

### 8.2.3 Extraction of Lipids

Lipids were extracted from the dried sludge using solvents. The extraction was done in the mode of single and two stage process using different solvents such as chloroform, methanol, diethyl ether, *n*-hexane and ethanol.

**Two Stage Extraction Process: Primary and Secondary Sludge**

A thermostatic glass reactor at atmospheric pressure was used for two stage extraction process. Three trials were carried out for each solvents and process conditions. Dried sludge (10 g in each) was loaded for effective extraction using four different solvents. The extraction was executed for 6 h with solvent system as 50 mL of chloroform methanol mixture (2:1 ratio), 50 mL diethyl ether, 50 mL of *n*-hexane and 50 mL of ethanol. These samples were heated at 50 °C for 30 min and transferred to a separating funnel and allowed for overnight for phase separation. The solvent was removed under vacuum at 400 mbar in a rotary evaporator.

The solvent removed from the first stage was used in second stage extraction process to increase a high yield of lipid content. This procedure was also done for extract of lipid from secondary sludge. The samples were withdrawn from the two-stage extraction process during the preestimated time periods to determine the yield of lipid content; the assortment was allowed to separate into two layers. The upper phase consists of lipids and the lower layer contains sludge waste with other impurities. The lower layers were taken into further extraction process. The lipid was collected from upper layer and washing with distilled water thrice. Residual water was then removed by evaporation at 100 °C. The final purified lipid was taken for TLC analysis and lipid properties examination.

The yield of lipid was calculated using the following formula

$$\begin{aligned}&\text{Yield of lipid } (\%)\\&= \left[\text{Grams of lipid obtained/Grams of dried sludge taken}\right] \times 100\end{aligned}$$

The various solvents were used to investigate their effects on lipid yield.

**Confirmation of Lipids by Thin Layer Chromatography**

The glass slide was cleaned with ethanol and coated with aqueous slurry of silica gel. The slide was heated at 110 °C for 1 h. Allowed it to cool for sometimes and then lipid was spotted over it. The slides were kept in solvents and allowed it to move through the gel. Allowed it to air dry for some time and then spray 50% sulfuric acid, then heated for 10 min. The formations of colored spots were observed.

### 8.2.4 Experimental Set Up for Biodiesel Production

A stirrer glass rector at atmospheric pressure was used for acid–base transesterification process. Three trails were carried out for each combination of reactants and process conditions.

*Acid Transesterification*: The lipids sample extracted from sludge was taken in a glass reactor. The lipid was supplemented with 1% sulphuric acid in methanol and it was heated at 50 °C. The vigorous stirring was applied to the reaction mixture to complete the esterification.
*Base Transesterification*: The lipids sample extracted from sludge was taken and added 1% sodium hydroxide in methanol to lipids and the mixture was heated at 50 °C. The vigorous stirring was applied to the reaction mixture to complete the esterification.

### 8.2.5 Recovery of Fame (Biodiesel)

The FAME was recovered with the added of 5% sodium chloride in water and the FAME was extracted two times with the provision of efficient mixing using vortex with supplementary of 5 mL of hexane in the vial. After sometimes the hexane phase was washed and biodiesel was recovered (Kargbo 2010).

### 8.2.6 Biodiesel Washing

The biodiesel needs to be washed after the transesterification process to remove remaining catalyst, methanol, glycerol, soaps and gums. Water should be sprinkled on top of the tank; the water droplets are collected at the bottom of the tank. Separation of wash water from biodiesel may be helped by added neutralize the catalyst such as vinegar and hydrochloric acid. The washing process was repeated until clear biodiesel was obtained. After washing, the biodiesel was heated to 120 °C for approximately one hour to evaporate any remaining water and methanol. The final biodiesel was taken for GC-MS analysis and fuel properties examination. In this process, the reaction parameters such as type of catalyst, reaction temperature and type of sludge were used to find their effects on biodiesel yield.

The yield of biodiesel was estimated using the following formula (Singh et al. 2006).

$$\text{Yield of biodiesel } (\%) = \frac{\text{Weight of biodiesel produced} \times 100}{\text{Weight of sample oil}}$$

### 8.2.7 Biodiesel Characterization

Biodiesel produced from sewage sludge was analyzed by gas chromatography mass spectrometry (GC-MS). The following parameters also measured to check the properties of biodiesel.

**Iodine Value**: It is used to measure the total amount of unsaturation fatty acids present in the mixture. It means how much of iodine required to iodize the double bonds present in the biodiesel. It is used to express in grams of iodine per 100 g. This value is limited to 120 g for every 100 g as per the guidelines of European biodiesel standard (UNE-EN 14214, 2003).
**Saponification Value**: It is used to measure the average molecular weight of all the fatty acids present in the sample.
**Cetane Number**: The sufficient cetane number is needed for the good engine performance. It assures the good starting performance of engine and avoiding the white smoke formation. It is estimated by the comparison of fuel value with the reference fuel value mostly the *n*-cetane.
**Heating Value**: It governs the fuel consumption rate. If it is greater means lesser the fuel consumption. As per the European standard (EN 14213), the minimum heating value is 35 MJ/kg.
**Ester Content**: This is also one of the important parameters for analyzing the biodiesel properties.

### 8.2.8 Tests for Biodiesel

Some of the test was conducted for the confirmation of biodiesel such as pH test, complete conversion test, emulsification test, clarity test, density test, soap titration test, acid number, and test for cloud point.

### 8.2.9 Optimization of Transesterification Process

Optimization study was conducted with temperature effect, catalyst concentration and reaction time.

**Table 8.1** Test for biodiesel

| Solvents | Lipids extracted from primary sludge (g) | | Total (g) | Lipids extracted from secondary sludge (g) | | Total lipids extracted from sludge (g) |
|---|---|---|---|---|---|---|
| | Stage 1 | Stage 2 | | Stage 1 | Stage 2 | |
| Chloroform:methanol | 5.50 | 1.0 | 6.50 | 3.80 | 1.10 | 4.90 |
| *n*-hexane | 2.66 | 1.24 | 3.90 | 3.30 | 0.90 | 4.20 |
| Diethyl ether | 3.44 | 1.20 | 4.64 | 2.40 | 0.90 | 3.30 |
| Ethanol | 2.20 | 0.80 | 3.00 | 2.52 | 1.0 | 3.52 |

## 8.3 Results

### *8.3.1 Quantification of Lipids by Extraction Process*

Lipids were obtained through extraction process from primary and secondary sludge. Chloroform:methanol (2:1), *n*-hexane, diethyl ether and ethanol solvents are used. The lipids were extracted in the laboratory in a separating funnel. Therefore, the above 4 combination of solvents with 2 types of sludge, totally eight lipid samples were obtained. The yield of lipids was calculated by weighing the lipids after evaporating the solvents. The quantity of lipids obtained from sewage sludge was given (Table 8.1). In single stage extraction of Chloroform and methanol mixture, 5.5 g of lipid was extracted and it was increased to 6.5 g in second stage extraction when compared with secondary sludge the yield was 3.8 g and 1.1 g in first and second stage of extraction. The amounts of lipids extracted from primary sludge with other solvents were comparatively lower than the mixture of solvents. In case of *n*-hexane the yield of lipids in single stage was 2.66 and 1.24 g in further increase of stages of extraction from primary sludge. On extracting lipids by two stage extraction with diethyl ether, the yield was 4.64 g and 3.3 g respectively. The amount of lipids extracted with ethanol from primary sludge was 11% in first stage and increased to 16% in second stage. In case of ethanol, the quantity of lipids in single stage was 2.2 and 0.8 g in further increase of stages of extraction from primary sludge and secondary sludge yields a quantity of 2.52 and 1 g.

### *8.3.2 Selection of Solvent System for Production of Biodiesel from Sludge*

The percentage yield of lipids from sludge indicates that chloroform:methanol in the ratio of 2:1 yields a high quantity of lipids. The single stage extraction system was 27.5% and it was increased to 32.5%, when two stage extractions were performed with primary sludge. On comparing the yield of lipids from secondary sludge with

**Table 8.2** Test for free fatty acids

| Type of sludge | % of residual NaOH |
|---|---|
| Primary sludge | 5.01 |
| Secondary sludge | 5.02 |

single and two stage extraction system chloroform and methanol (2:1) shows high yield with 25.5%.

### 8.3.3 *Transesterification*

Transesterification process was performed using acid (ACT) and base catalyst (BCT) for the production of biodiesel from municipal sewage sludge to resolve the problems of saponification phenomenon and biodiesel stability. Transesterification was performed with lipids extracted from primary and secondary sludge by chloroform:methanol. The equal amount of lipids used for all transesterification process.

**Test for Free Fatty Acids**

This test determines the amount of NaOH lye catalyst that must be added to neutralize free fatty acids produced when lipid is heated. 1 g of NaOH was dissolved in 1000 mL of water. This was used as burette solution. 1 mL of lipid sample in 10 mL of isopropyl alcohol was used is oil solution. The dilute NaOH was dropped into the 1 mL of oil solution at a time. The drops are counted. After each ml, the pH level of the oil solution was measured with standard pH paper. This procedure was repeated until it reaches a pH of 8–9. The number of drops used plus 5 equals the number of grams of NaOH required for the processing of 1000 mL. Table 8.2 shows the efficiency of solvents in lipid extraction process. It is understood that mixture of solvents (chloroform:ethanol; 2:1) only provided high amounts lipids from sewage sludge, Hence 1% sulphuric acid can be used for the process of base catalyzed transesterification. This test was also used as a measure to predict the end point for the conversion of free fatty acids.

The transesterified product samples from primary and secondary sludge were labeled as 1, 2, 3 and 4.

1—Biodiesel from P.S by ACT, 2—Biodiesel from S.S by ACT
3—Biodiesel from P.S by BCT, 4—Biodiesel from S.S by BCT.

### 8.3.4 *Biodiesel Properties Analysis*

Produced biodiesel properties were analyzed such as iodine value, saponification value, cetane number, high heating value and ester content and compared with commercially available diesel (Table 8.3).

**Table 8.3** Properties comparison of sewage biodiesel with commercial diesel (D-commercial diesel)

| Sample no. | Properties | | | | |
|---|---|---|---|---|---|
| | Iodine value (mg of $I_2$/g) | Saponification value (mg of NaOH) | Cetane number | High heating value (MJ/kg) | Ester content (%) |
| 1 | 61.63 | 135.87 | 72.6 | 42.93 | 89.22 |
| 2 | 73.31 | 131.20 | 71.4 | 40.61 | 91.2 |
| 3 | 66.52 | 162.41 | 64.9 | 41.77 | 90.64 |
| 4 | 57.7 | 141.50 | 71.8 | 42.76 | 90.26 |
| D | 82.2 | 121.40 | 72.6 | 43.08 | 0 |

### *8.3.5 Tests for Biodiesel*

Some of the tests are conducted for biodiesel produced from sewage sludge and were tabulated (Table 8.4).

### *8.3.6 Optimization of Transesterification*

**Effect of Temperature**: Temperature plays a major role in the production of biodiesel (Fig. 8.1). The transesterification process of triglycerides with solvents using catalysts are done at different temperature ranges such as 50, 60, 70 and 80 °C and the end point was analysed by test for free fatty acids. The results show that the process of BCT and ACT the conversion was done at short time at 80 °C.

**Effect of Catalyst Concentration**: The catalyst concentration also plays a major role in the production of biodiesel. The increased amount of catalyst will not result good quality of FAME. The effect of catalyst concentration was monitored by two different concentrations 1 and 2% of NaOH and Sulphuric acid. The results clearly indicated that both alkali and acid catalysed reaction done at 2% catalysts could yield biodiesel at short time. The further increase in concentration burnt the lipids in the source (Fig. 8.2).

### *8.3.7 Gas Chromatography-Mass Spectrometry of Sample*

The FAME produced by transesterification was analyzed by using an Agilent Gas Chromatograph JEOL—GCMATEII with a flame ionization detector. The separation was achieved in a HP-MS capillary column with Helium as carrier gas and injector temperature of 220 °C. The injection volume of sample was 1 μL and the oven temperature was 50–250 °C at a rate of 10 °C/min. The four samples were analyzed by

**Table 8.4** Test for biodiesel

| Sample no. | Test for biodiesel | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | pH test | Complete conversion test | Emulsification test | Clarity test | Density test | Soap titration test NaOH (ppm) | Acid Number test (mg of NaOH/g) | Cloud point |
| 1 | 9 | Completely converted | Emulsion formed | Clear solution | 0.86 | 18.2 | 0.08 | 1 |
| 2 | 9 | Completely converted | Completely converted | Clear solution | 0.87 | 11.4 | 0.15 | 7 |
| 3 | 9 | Completely converted | Completely converted | Clear solution | 0.85 | 4.5 | 0.11 | 0 |
| 4 | 9 | Completely converted | Completely converted | Clear solution | 0.86 | 2.2 | 0.15 | −1 |
| D | 9 | – | – | – | 0.85 | 3.4 | 0.31 | 10 |

**Table 8.5** Fatty acid composition of extracted biodiesel from municipal sewage sludge

| Name of the fatty acid | Relative % |
|---|---|
| Octadecanoic acid methyl ester | 3.23 |
| Myristic acid methyl ester | 3.25 |
| Oleic acid methyl ester | 2.25 |
| Palmitoleic acid methyl ester | 75.23 |
| Stearic acid methyl ester | 2.57 |
| Elaidic acid methyl ester | 10.56 |

GC-MS (Figs. 8.3, 8.4, 8.5, 8.6 and 8.7). The compounds in the sample were analyzed by NIST library search. The compounds and their relative% are listed in Table 8.5. From this, it was understood that most (70%) of the fatty acids are saturated and remaining (30%) are unsaturated present in extracted lipids from municipal sewage sludge.

The FAME yield was calculated using the below formula (Phan and Phan 2008)

$$\text{Yield }\% = \frac{\text{Weight of methyl esters}}{3 \times \frac{\text{weight of oil}}{\text{mol. wt of oil}} \times \text{mol. wt of ester}} \times 100$$

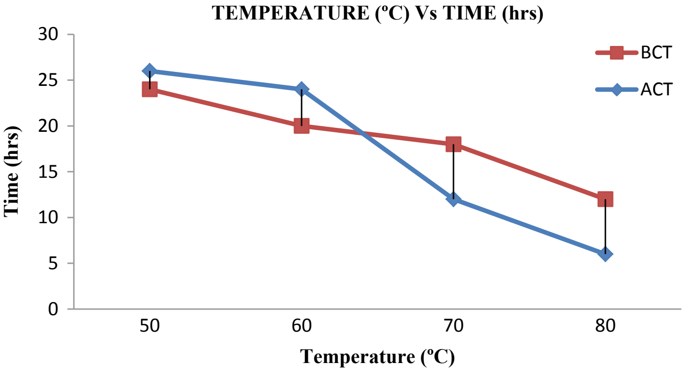
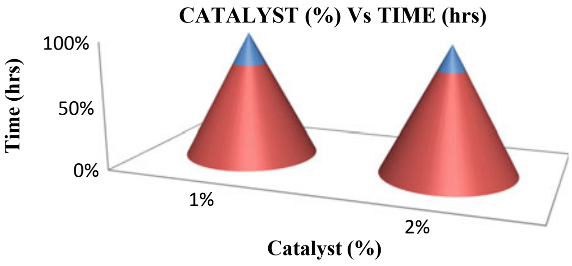


**Fig. 8.1** Effect of temperature

**Fig. 8.2** Effect of catalyst



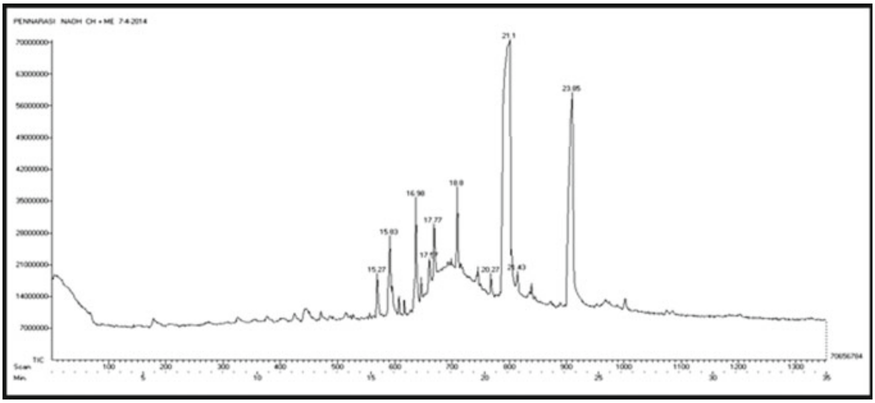


Fig. 8.3 GC-MS chromatogram of biodiesel 1

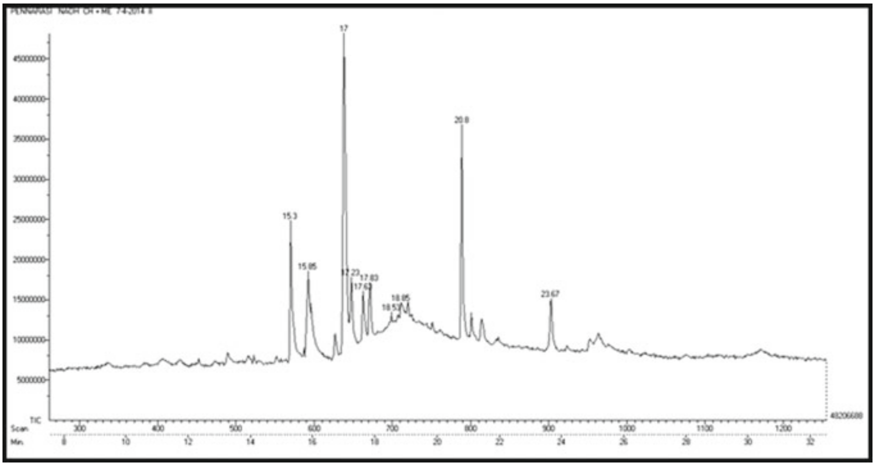


Fig. 8.4 GC-MS chromatogram of biodiesel 2

The yield can be calculated by weighing the biodiesel produced from sludge. The comparison was based on the percentage of biodiesel produced from the weight of lipids undergone transesterification. From the graph, it is clear that the biodiesel produced by transesterification of lipids from primary sludge was higher than that of secondary sludge. The ACT provides 87% of FAME production from primary sludge and 65% from secondary sludge. The BCT provides 78% from primary and 60% from secondary sludges (Fig. 8.8). On comparing both acid and base catalyzed transesterification, the acid catalysed reactions were most consistent on both the sludges. The above yield% are calculated base on three trails.

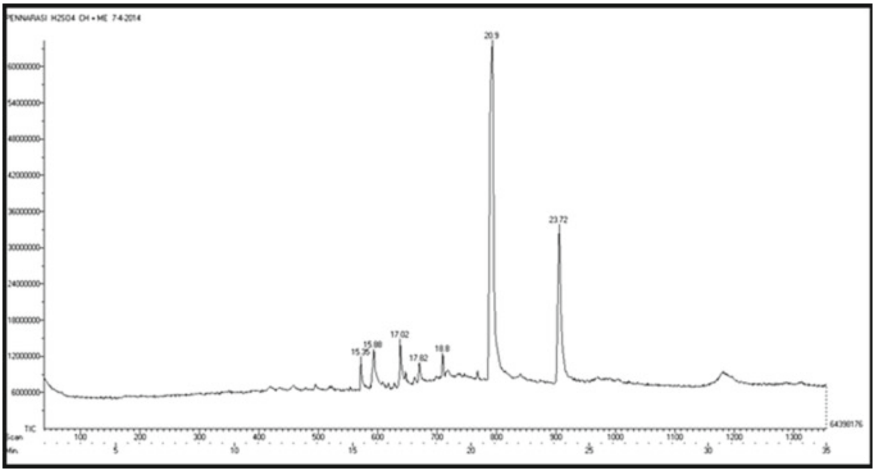


**Fig. 8.5** GC-MS chromatogram of biodiesel 3

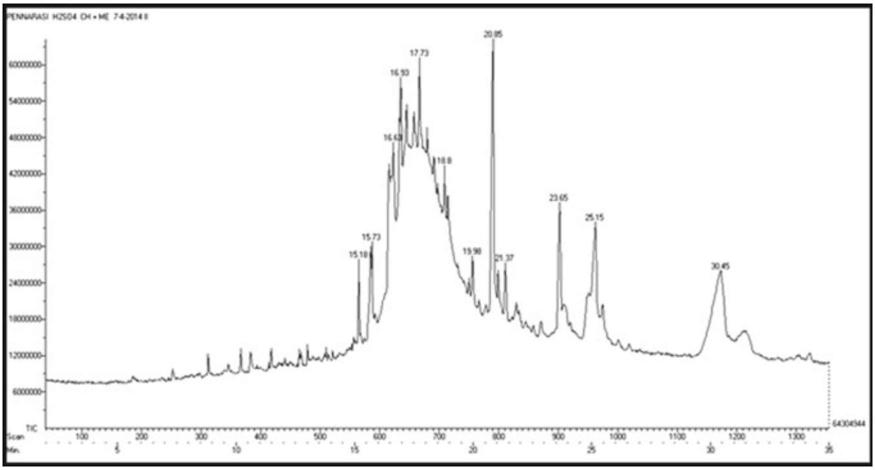


**Fig. 8.6** GC-MS chromatogram of biodiesel 4

## 8.4 Discussion

The extraction with a polar solvent help in destroying the cellular membrane and when it is followed by a non-polar solvent, it will favor the lipids extraction within the cell (Singh et al. 2006). The yield of lipids from primary sludge by using chloroform and methanol as co-solvent was higher when compared to use of single solvents. The lipids extracted from dried form of primary sludge were 32.5% by using this mixture of solvents. On comparing the amount of lipids extracted from secondary sludge the

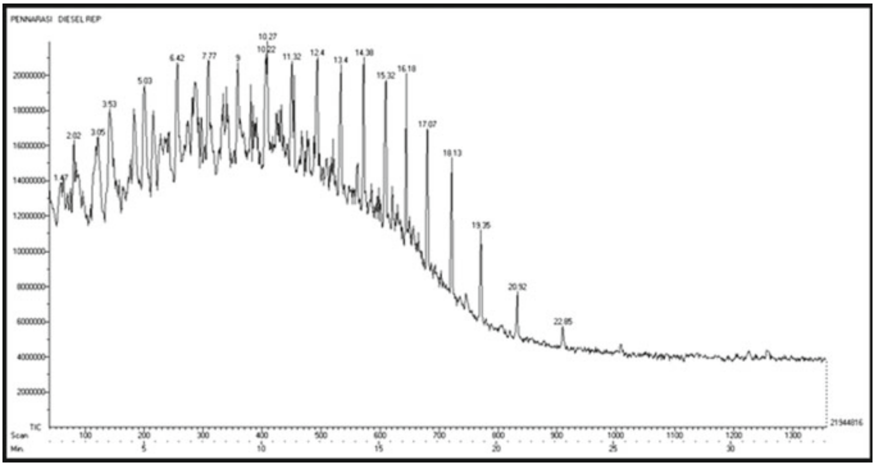


Fig. 8.7 GC-MS chromatogram of diesel

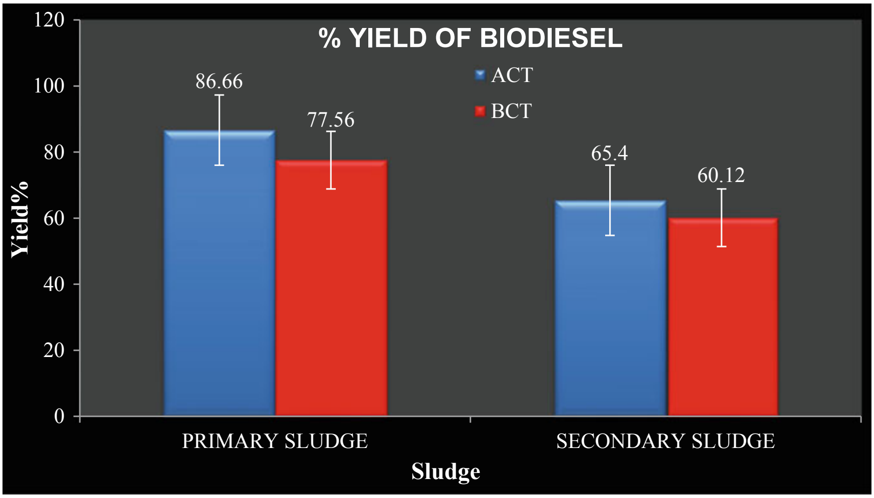


Fig. 8.8 Yield% of biodiesel

solvent mixture provides high quantity of 24.5%. The amount of lipids were obtained from primary sludge with hexane was 25.3% and from blended sludge was 21.9% (Kargbo 2010). The use of single solvent ethanol for the extraction of lipids from primary sludge and secondary sludge yields lower when compared to other solvents. The yield was only 15% and 17.6% respectively. The mixed solvent double stage extraction has higher efficiency when compared to single solvent extraction in two stages. The results have showed that the solvents diethyl ether and *n*-hexane has moderate efficiency. The extraction tests yielded different lipid quantities depending on the extracting solvent. 4 wt% of the starting sludge mass was recovered as lipids when diethyl ether was used, whereas the recovered amount greatly increased when using *n*-hexane (8 wt%) and methanol (14 wt%) (Sokoto et al. 2013). They stated that methanol was the most effective solvent to maximize the recovering of the lipid fraction in the starting sewage sludge. On comparing the results of yield of lipids from municipal sewage sludge, the use of chloroform with a co-solvent methanol in the ratio of (2:1) was found to be effective and extract high quantity of lipids. The lipids produced by extracted from primary sludge and secondary sludge were undergone transesterification with acid and base catalyst. The FAME was recovered from the transesterified products with the help of biodiesel washing and the byproducts were separated. The esters present in the compounds were analysed with the help of GC-MS and it shows the occurrence of esters in it. The esters were tabulated and the content were analysed. The ester content was ~90%. The high heating value favors the performance of engine. The results shown that the high heating values of the biodiesel produced were correlating with the HHV of commercially available diesel. The standard limit of 120 g I2/100 g given by the European biodiesel standards. The previous reported that biodiesel produced from *Cucurbita pepo* seeds oil has iodine value within the standard limits. It is revealed that the composition of FAME has a predominant effect on the cetane number (CN) of the biodiesel. The heat of combustion value is not given in the biodiesel standards (ASTM D6751 and EN14214). However, a European standard (EN 14213) given a minimum heating value of 35 MJ/kg (Sivaramakrishnan and Ravikumar 2012). The cetane number of the biodiesel samples were high and it favours its usage in vehicle. Cetane number was predicted from the iodine value and saponification value by using the equation. The cetane number of samples produced by BCT was high when compared to the biodiesel produced by ACT. The density of the biodiesel produced was found to be within the limitations. The acid numbers of the samples were found to correlate with the ASTM standards and it was found to be safe for using in vehicles. The energy stored in lipids depends on the various factors like place where grown, weather and concentration. Generally, the calorific value of vegetable oil was lower than the biodiesel (Sokoto et al. 2013). The cloud point and soap number were found to be within the international standards for biodiesel and correlate with the values of diesel. The test for emulsification, complete conversion and clarity were done and the results indicated the presence of biodiesel. The parameters such as temperature and catalyst were optimized and the simple lab scale production of biodiesel was designed and it includes the solvent recovery.

## 8.5 Summary and Conclusion

The FFA rich lipid extracted from municipal sewage sludge. The lipids were obtained from primary sludge is 32.5% by using mixture of chloroform:methanol (2:1) solvents. From the secondary sludge the maximum amount of 24.5% of lipids only extracted. The above percentages are high than the using of single solvents and these results were obtained through two stage extraction process. The acid and base transesterification processes were done for the conversion of lipids into biodiesel. The sulphuric acid used as an acid catalyst and NaOH is a base catalyst. The FAME yield (87%) was high with primary sludge through base transesterification process than the secondary sludge.

Therefore, it is concluded that municipal sewage sludge is a best and suitable source of lipid production. The FAME yield reaches approximately 87% for base transesterification process under optimized conditions. To develop an efficient production rate for biodiesel production, the analyze of various catalyst will be studied in the future.

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# Chapter 9
# Enhancement of Feedstock Composition and Fuel Properties for Biogas Production

**S. Chozhavendhan, G. Gnanavel, G. Karthiga Devi, R. Subbaiya, R. Praveen Kumar and B. Bharathiraja**

**Abstract** Biogas production has materialized as an auspicious technology for the conversion of renewable energy sources such as agricultural, animal, industrial and municipal wastes into a beneficial form of energy. Biogas production is a very attractive and changeling task because of its slower degradation and requires higher retention time via anaerobic digestion (AD) process. Additionally, there is a chance of toxic intermediates in some of these feedstock may result in the decline of the biogas production process. This Biogas technology can be integrated with various strategies to mitigate the environmental pollution. high availability and low cost of these feedstocks promote new strategies for the minimization of waste. Considerable efforts in chic research are undertaken in order to upgrade the composition of the feedstock, efficiency in terms of fuel property and flexibility of biogas production to enhance the economic viability of biogas plants. Along with the methane, biogas consists of various compounds like $CO_2$, $H_2S$, water vapor, nitrogen, hydrogen and oxygen which tend to pull down the calorific value when compared with natural gas. Absorption, adsorption, cryogenic method and membrane-based gas permeation are several technologies employed to increase the fuel property of biogas.

**Keywords** Biogas · Anaerobic digestion · Absorption · Adsorption · Cryogenic method

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## 9.1 Introduction

On one hand, energy sector at present is focused on the generation of energy for industrial and domestic uses from traditional resources such as fossil fuels (Alexis 2016). However, these fossil fuels are not renewable hence it will lead to depletion of fossil fuels and emits greenhouse gases like carbon dioxide and carbon monoxide which contributes the global warming issues (Ganzoury and Allam 2015). In other hands, since from the industrial revolution, there is a constant increase in the $CO_2$ concentration in the atmosphere and is likely to go above 750 ppm by this century (Zhang et al. 2014). Because of this the $CO_2$ traps the infrared radiations thereby raising the atmospheric temperature of the earth, resulted in greenhouse effect. This effect has many shattering consequences, and therefore it becomes mandatory to search for alternative energy sources (Ganzoury and Allam 2015; Alexis 2016).

Biowastes are considered as one of the prevailing next generation renewable energy sources for providing continuous power generation, and these energies are renewable and environmental friendly (Appels et al. 2011). The quest for new forms of renewable energy in many countries has enthused worldwide research in the development of AD process during recent years. Biogas is a clean and accessible futuristic source of energy produced from AD sort out the solution for world's unquenchable energy demands (Shivali et al. 2018; Weiland 2010). At the same time, it helps in reducing the carbon footprints and protect environments which have paved the way for additional importance of anaerobic treatment processes (Kocar and Civas 2013).

Biogas can be considered as alternative green energy carrier for harnessing electricity, heat, and as a transport fuel (Shivali et al. 2018). The development of substrate for the biogas production was supported by a numerous basic research, consequent with a better understanding of microbiology and biochemistry of the process (Zhang et al. 2016). Production of biogas involves a series of four complex biochemical processes (hydrolysis, acidogenesis, acetogenesis and methanogenesis) depending upon different factors like type of substrates, temperature range, pH and inoculum concentration (Kadam and Panwar 2017; Chen et al. 2015; Van Stephan et al. 2016).

### *9.1.1 Feedstock Composition and Properties*

The most and common benefitting substrate used for the biogas production is agricultural biomass residue, animal manure, human excreta, waste water from industries, livestock residue and organic fraction of municipal waste reside. The added advantage of this feedstock as a substrate is its availability, sustainability, energy and economic value.

## 9.2 Characteristics and Pretreatment of Feedstocks

The cheapest and abundant primary source for biogas production is agricultural residue which comprises crop-straws, sugarcane molasses, fruit- and nutshell, plant stovers, leaves etc. Lignocellulosic biomass can be employed as an effective source for the biogas production which replaces the limitations imposed by crude oil. All the agro-based residues are mainly comprised cellulose (polymer of glucose), hemicellulose (polymer of xylose, mannose and galactose) and lignin (complex chains of phenol molecules). The composition of lingo cellulose varies for each crop based on their origin (Bertero et al. 2012; Iqbal et al. 2013). Cellulose is most abundant on earth and makes up over 25% of plant biomass (Klemm et al. 2005). Hemicellulose is always associated with cellulose as a carbohydrate polymer and makes the interface more firmness (Laureano-Perez et al. 2005). Their structure comprises of sugar molecules arranged as polysaccharides of 100–200 sugar units. Lignin is one of the major cell wall components which act as a barrier to the enzymatic degradation f lignin has a complicated arrangement due to different linkages between the monomers of phenylpropane (Iqbal et al. 2011; Ladisch et al. 2010). This random structure arises from an enzymatically initiated free radical polymerization of lignin precursors in the form of p-hydroxycinnamyl alcohols. The composition of cellulose, hemicellulose, and lignin of various agro-based product (Bahaa et al. 2011; Ye and Jiayang 2002) are shown in Table 9.1.

Rice straw, wheat straw, and corn stalks are the major agricultural waste in the World (Bharathiraja et al. 2016). Wheat straw possess a high C/N ratio and lignocellulose content which causes slower biodegradability in AD process and results in the lower efficiency of biogas production (Wang et al. 2012; Nkemka and Murto 2013). Biogas production was effectively observed in the co-digestion of cow manure

**Table 9.1** Shows the composition of cellulose, hemicellulose and lignin of various agro based product

| Lignocellulosic materials | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|
| Hardwoods stems | 40–55 | 24–40 | 18–25 |
| Softwood stems | 45–50 | 25–35 | 25–35 |
| Nut shells | 25–30 | 25–30 | 30–40 |
| Grasses | 25–40 | 35–50 | 10–30 |
| Paper | 85–99 | 0 | 0–15 |
| Wheat straw | 30 | 50 | 15 |
| Leaves | 15–20 | 80–85 | 0 |
| Cotton seed hairs | 80–95 | 5–20 | 0 |
| Rice straw | 32.15 | 28 | 19.64 |

and rice straw when compared with that of mono-digestion of cow manure (Li et al. 2015). Whereas in wheat straw along with cow manure does not show any significant improvement in biogas production.

The pretreatment of feedstock is a necessary step during the biogas production in order to avoid the process failures as well as to increase the degradation process quickly thereby increasing the yield of biogas (Mshandete et al. 2006). This practice has beeb followed since long time for the purpose of increasing the porosity of the material by reducing the cellulose crystallite structure and removing lignin and hemicellulose content for the effective utilization of the substrate by the microorganism (Ye and Jiayang 2002).

Pretreatment of lignocellulose material helps to avoid the formation of byproducts which acts as an inhibitory material for the fermentation process and it also prevents the degradation or loss of carbohydrate. It also helps to improve the formation of sugar or the ability to subsequently form the sugar by an enzyme or other hydrolysis processes. Physical physicochemical, chemical methods and biological processes have been played second hand for pretreatment of lignocellulosic materials (Sivers and Zacchi 1995). Based on the need, the combination of pretreatment can be done.

### *9.2.1 Animal Manures*

Animal manure includes cattle, poultry, pig manure and considered a major carbon source for biogas. Animal manures comprises 90% moisture content and volatile solids of the total solids present. It acts as an ideal substrate due to its good buffering capacity (Fujino et al. 2005; Muller et al. 2004). The presence of diverse microbial flora in animal manure is added advantage because of elimination of inoculation digester. The nutrient content of the animal manure has not reduced significantly and hence it can be used as fertilizer (Risberg et al. 2013; Neshat et al. 2017).

The high nitrogen content of animal manures drags down its usage in anaerobic digestion for biogas production due to its C/N ratio (Tufaner and Avşar 2016). To address this issue, carbohydrate-rich source or nitrogen free the raw material is added to increase the carbon content in the animal manure before the anaerobic digestion process proceedings.

### *9.2.2 Municipal Solid Waste*

The decomposition of organic matter in the municipal wastes has been done globally which resulted in $CH_4$ emissions over years (Cheng et al. 2016). Composition of OFMSW could vary from high-income countries to low-income countries which includes food and garden waste (Weiland 2010; He et al. 2012). Municipal Solid Waste (MSW) is chiefly comprised of organic matter which accounts for about 55% of organic solid waste. MSW as a substrate possess minimal carbon content which makes delay in fermentation and also deficient in N and P. However, when MSW are digested properly it has the potential of high biogas production (Del et al. 1999). Municipal solid wastes are comprised of kitchen wastes which include residues of food from households, restaurants, hotels, etc. Kitchen waste is good in carbon source and co-digestion with animal manure significantly increases the biogas production of about 44% as compared to sole digestion of kitchen waste (Zhai et al. 2015).

To increase the biogas production pretreatment of MSW is processed to reduce the particle size reduction and co-digestion with municipal or animal sludge to increase the biogas production (Gomez-Lahoz et al. 2007). Another important thing is to ensure the efficient operation of anaerobic digester and prevention of equipment failure it is recommended to remove the inorganic compounds like metals and glass in material handling (Bernal et al. 1992).

### *9.2.3 Industrial Waste*

The hasty increase in the industrialization provides a aggressive impact on the environment due to their incompetence in effluent treatment processes. Paper and pulp mills, coal manufacturing, pharmaceutical, textile, and petrochemical are the major sectors which releases the copious amount of impurities and known to cause negative impacts on the environment. A wide range of pretreatment methods are employed to lower the level of toxicity to comply with environmental standards (Ruben et al. 2016).

In which, paper has been used in many forms in our day to day activities and comprises more lignocellulose materials. Paper and pulp industrial waste creates an undesirable effect on environment due to its ion balance, disruption of carbohydrates and failure of enzyme activity (Desika et al. 2018; Kinnarinen et al. 2016; Kong et al. 2016). Paper wastes has been used majorly in biomethane production. Baba et al. (2013) reported that, when pretreated paper waste added with rumen fluid the methane yield was increased about 2.6 folds. The methane yield was increased promisingly on microwave pretreatment process in pulp mill sludge waste when compared with ultra-sonication and chemo-mechanical treatment on (Saha et al. 2011). In recent years, several studies have focused on new techniques by means integrated existing pretreatment approaches with the combination of UV pretreatment techniques (Jaafarzadeh et al. 2017). Ferrer et al. (2008) experiments resulted with 30% rise in biogas production on medium—temperature pretreatment process at 70 °C on both primary and secondary clarified wastewater. Thus pretreatment of substrate is mandatory to overcome the negative impacts of waste discharge and to increase the biogas production within a stipulated period of time (Sivagurunathan et al. 2017).

## 9.3 Influential Parameters of Biogas Production

Along with the biochemical process, pretreatment of feedstock for AD processes must be examined to ensure successful operation (Tiehm et al. 2001). The presence of inorganic and organic toxic material and variation in temperature causes the sudden upsets and failure of anaerobic reactors. The various performance parameters which enhance the biogas production are seeding, volatile fatty acid, pH, particle size reduction, thermal pretreatment, an addition of metals, etc., (Carlsson et al. 2012).

### *9.3.1 Seeding*

Seeding is the most common process of initiating the microbial growth of a in new plant by inoculating the material from already existing plant to the newly established setup. The ultimate aim of this method is to introduce set inoculant into the system. This method will help to reduce the time of digestion of animal manure or municipal waste for the newly commissioned biogas digester as the digested material is already loaded with sufficient quantity microorganisms (Ward et al. 2008).

### *9.3.2 Volatile Fatty Acid*

The most common parameter which governs the AD is Volatile Fatty Acid (VFA) composition and concentration. AD of organic wastes produces series of VFAs include acetic acid, propionic acid, butyric acid, and valeric acid, (Zhang et al. 2014; Pham et al. 2012). Generally, syntrophic acetogens and methanogenic bacteria convert the VFAs produced during anaerobic process are transformed into $CH_4$ and $CO_2$. However, VFAs releases large mount of organic components which ultimately decreases the pH and even causes the failure of AD process (Zhang et al. 2013) VFA accumulation reflects a kinetic uncoupling between acid formers and consumers. This typical condition was caused by the presence of toxic or inhibitory compounds, by hydraulic or organic overloading and sudden variation in temperature etc.

### *9.3.3 pH*

pH is an important parameter and has to be monitored and controlled during anaerobic digestion process of biogas production processes because of its activity on the microorganism. Ammonia toxicity is caused due to an increase in free ammonia concentration and controlling the pH levels helps to attain optimum microorganism's growth on the feedstock. The optimum pH value for AD is in the range of about 6–7.8. The pH values less than 6.2 considerably results in decrease of methanogenic activity and causes several side effects in terms of permeability of microorganisms (Jiang et al. 2013; Mao et al. 2015).

### *9.3.4 Acid/Alkali Pretreatment*

Acid/Alkali pretreatment solubilize hemicellulose, the presence of methanogens has the ability to adapt to inhibiting compounds. But due to the high acid cost, a menace of accumulation of inhibiting compounds and the problems of corrosion are considered to be the downsides of this process (Xiao and Clarkson 1997; Sumphanwanich et al. 2008). The alkali treatment in AD substrate was found to enhance biogas yield when plant material as feedstock (p1-190). The alkali solution often leads to saponification reactions in continuous plants. The bio toxicity phenomenon is less pronounced in alkali treatment since the substrate degradation process were in the range of 60–80% for acetate and glucose respectively (Mouneimne et al. 2003).

### *9.3.5 C/N Ratio*

Carbon to nitrogen ratio gives a better idea in the nutrient composition of the substrate. C/N ratio has a great influence on AD process. The waste material used as a substrate may have unbalanced C/N ratio. The optimal C/N ratio for biogas production is between in the ratio of 20 to −30 or 20 to 30. Lower the ratio increases the risk of ammonia inhibition and higher the ratio results in nitrogen degradation by microbes which leads to insufficient nitrogen to maintain cell biomass (Hassan et al. 2016; Mao et al. 2015).

### *9.3.6 Particle Size Reduction*

The particle size of the substrate mainly influences the digestion of the substrate by indicating the available surface area for hydrolyzing enzyme, especially with the plant fiber. Fiber degradation and methane yield are found to be improved when there is a decrease in feedstock particle size from 100 nm to 2 mm (Mshandete et al. 2006).

### *9.3.7 Temperature*

Temperature is one of the influential parameters affecting the physiochemical properties of liquid phase in AD, because it directly influences the activity of enzyme and co-enzyme which indirectly influence the methane yield and digestate quality (Appels et al. 2011). Generally, anaerobic bacteria has the ability to grow at psychrophilic mesophilic and thermophilic conditions (Sanchez et al. 2001). The performance of AD, however, increases with increasing temperature. The temperature has a potent effect on the partial pressure of $H_2$. Even preheating of the substrate before AD has found effectively improve the methane production which leads to reduction of volatile solid content (Carrere et al. 2009). Thermodynamics shows that higher temperature is the most favorable condition for endergonic reactions and less favourable for exergonic reactions (Appels et al. 2011).

### *9.3.8 Addition of Metals*

The cations of heavy metals like Cr, Co, Cu, Zn, Ni, etc. play an important role in AD for synthesizing of enzymes and their maintenance apart from normal nutrients like C, H, O, N and light metal like Na, K, Mg, Ca, Al (Schattauer et al. 2011; Facchin et al. 2013). Heavy metals are not biodegradable and cause inhibition by disruption of enzyme function and a structure on its accumulation. Many literatures stated that cd and Ni addition had an impact in increasing yield of biogas on anaerobic co-digestion of combination of cattle manure with potato waste (Kumar et al. 2006), sodium and potassium presence could have also found to increase the performance of mesophilic and thermophilic organism on biogas production.

## 9.4 Ultrasonic Treatment

Generally, this method involves the anerobic digestion of sewage sudge as feedstocks in order to which effectively results in increase in biogas production. This technique introduces ultrasonic cavitation into the system by building up the mechanical shear forces for sludge disintegration to improve the physical properties of feedstocks.

### *9.4.1 Basic Principles Involved in Biogas Production*

Anaerobic conversion of organic waste into biogas consists of a chain of interrelated biochemical process and which comprises a consortium of microorganisms (Merlin Christy et al. 2014). The overall process of biogas production includes Hydrolysis, Acidogenesis, Acetogenesis, Methanogenesis.

Hydrolysis is the first step in biogas production in which the larger organic compound is converted into smaller compounds by the aid of anaerobic hydrolytic bacteria (Ganzoury and Allam 2015; Jain et al. 2015). The fastest step in the anaerobic

**Table 9.2** Chemical composition of biogas

| Compound | Yield (%) |
|---|---|
| Methane | 50–75 |
| Carbon dioxide | 25–45 |
| Water vapor | 2–7 |
| Nitrogen | <2 |
| Oxygen | <2 |
| Hydrogen sulfide | <1 |
| Hydrogen | <1 |
| Ammonia | <1 |

digestion process is acidogenesis, in which the hydrolytic products are converted into small and volatile organic acids like butanoic, propionoic (acetic), ethanoic and lactic acid. The third stage of the AD process is the acetogenesis, is the third phase of AD process, in which acetogenic bacteria undergoes acidogenesis resulted in the acetic acid, hydrogen and carbon dioxide. This process is very important for methanogenesis process, as it converts the acidogenesis product into methanogenesis substrate by the microorganisms belong to various genera, including *Clostridium, Acetobacterium, Syntrophospora, Ruminococcus, Syntrophomonas, Sporomusa, Thermosyntropha, and Eubacterium* (Jain et al. 2015). Methanogenesis is the final phase in the biogas production, in which the methanogenic bacteria produces the end product methane from acetic acid, hydrogen and carbon dioxide obtained from the acetogenesis process. Methanogenesis is accomplished by the acetoclastic methanogenesis and hydrogenotrophic methanogenesis process (Chaudhary et al. 2013). 70% of the methane production was done by methanosaeta group of microorganisms in AD. The hydrogenotrophic process, the genus *Methanosarcina* accounts for the 30% conversion of hydrogen and carbon dioxide into methane in anaerobic digestion process (Kothari et al. 2014). The usual chemical composition of biogas composition is represented in Table 9.2.

### *9.4.2 Biogas Utilization*

Biogas is an excellent fuel with a numerous application. The biogas is mainly used as a combined heat and power (CHP) application in worldwide and apart from it can be utilized in three aspects such as production of steam, electricity and fuels for vehicles. Biogas produced from renewable organic waste is considered an alternative energy for fossil fuels for its application in fuel and transportation sector (Appels et al. 2011; Ward et al. 2008). By changing the air ratio, the conventional gas burner technology has been utilized to produce biogas. CHP find its application in internal combustion engine as dual engine or spark-ignition. In future biogas is centered as a fuel cell with high efficiency and low emissions.

### 9.4.3 Need of Biogas Upgradation

The future potential of bioenergy is evident because of high demand on the dependence of bio-energy production from natural resources (Verdonk et al. 2007). Along with methane gas, biogas contains gases such as $CO_2$, $H_2S$, water vapor, nitrogen, hydrogen and oxygen. The efficiency of biogas fuel is determined by its calorific value generally, the calorific value of natural gas is 35.8 $MJ/m^3$ whereas for biogas is 21.5 $MJ/m^3$. The incombustible $CO_2$ value not only reduces the calorific value but also limits economic feasibility of biogas production in generating the power. The contaminants released during biogas production corrodes the downstream equipment. For the high quality of methane and wider application either as heat and electricity or fuel vehicles the impurities need to be removed (Shivali et al. 2018). The purified biogas emits fewer greenhouse gases when compared with fossil fuels and has numerous environmental benefits.

The improved quality of biogas is achieved by improving the feedstock quality or choosing the proper feedstock or eliminates the influencing the parameters of the production process or implementing the upgraded technologies for purification of produced biogas.

### 9.4.4 Biogas Upgradation and Purification Technologies

Technological development plays an important role in biogas upgradation and purification processes in large-scale commercialization of biogas. The improvement in biogas production is done by either conventional method or implementation of new technologies. The conventional method includes physical absorption chemical absorption, membrane infiltration and biological methods (Eze and Agbo 2010; Bharathiraja et al. 2018) and new technologies include cryogenic upgradation, membrane enrichment, multistage and high pressurized AD.

### 9.4.5 Physical Absorption

Absorption is a chemical or physical phenomenon in which the components of gas phases diffuse into liquid phase by passing through an interfacial area. The unwanted components of biogas are absorbed with the help of non-reactive fluids in physical absorption process. Either by depressurizing or by heating the spent absorbents are regenerated. In general, either we use water scrubbing or physical scrubbing processes (Cozma et al. 2013).

### *9.4.6 Pressurized Water Scrubbing*

The absorbed gas components are physically bound to the scrubbing liquid. Water scrubbing based absorption technology is most commonly used in the world in recent years. This method is achieved by scrubbing the liquid with a higher solubility of $CO_2$ and $H_2S$ at lower vapor pressure and usually, polyethylene glycol is employed (Kapoor et al. 2017). The pressurized raw biogas stream is introduced to an absorption vessel from the bottom of the tower and whilst water is flushed from the top. Usually, pre-treated $H_2S$ is used to avoid the problem of corrosion. Raw biogas and water flow in a countercurrent flow in a scrubbing unit and due to the difference in mass transfer coefficient, high concentrated methane gas is collected in the stripper region and whereas the water and other observed heavier compounds are collected at rectifier section. Upgraded biogas is collected, dried and stored for further uses (Cozma et al. 2013). The water used in the scrubbing either by single pass system or it can be recirculated again for the upgradation process. The compression of biogas and recirculation of water through pumps leads to high energy consumption in pressurized water scrubbing process (Patterson et al. 2011).

### *9.4.7 Pressure Swing Adsorption*

Pressure swing adsorption (PSA) is an interesting technology for biogas upgrading, due to compactness of the equipment, low energy requirements, low capital cost, and safety and simplicity of operation (Augelletti et al. 2017). At present, PSA is most commonly used when compared with other types of adsorption and for biogas upgradation. Zeolite, activated carbon, carbon molecular sieves (CMS), silicate, metal-organic framework, silico aluminophosphate sorbents are some of the most common adsorbents employed. PSA work on the principle on physisorption process in which the gas molecules are selectively adsorbed on the surface of the solids based their molecular size.

The design of PSA comprises four columns one is engaged in adsorption while the remaining columns are in regeneration of different phases. In PSA process the $H_2S$ removal step is added since $H_2S$ are absorbed by adsorbents irreversibly. After $H_2S$ removal, is allowed to pass through the column at a given pressure, at which the given amount of $CO_2$ is absorbed by adsorbents. The equilibrium is attained when the loading of $CO_2$ also decreases as the pressure is decreased. The cycle is usually completed in approximately 3–5 min. A major drawback with PSA is 15–18% methane losses are observed and also proper treatment of vent is also required as it is directly released into the atmosphere (Sun et al. 2015).

### 9.4.8 Chemical Absorption

Chemical absorption works on the principle of reversible reaction between absorbed substances and solvent. In general, amines are most commonly used solvent in chemical adsorption process, which chemically interacts by removing acidic gases ($CO_2$ and $H_2S$) from methane are diethanolamine (DEA), monoethanolamine (MEA), and methyl diethanolamine (MDEA) (Ryckebosch et al. 2011). Nowadays, a mixture of MDEA and piperazine (PZ), called as activated MDEA (AMDEA), is commonly used in this process. By this process, the high purity methane of more than 99% is achieved due to high selectivity of the chemical solvent towards $CO_2$ and secondarily to $H_2S$. In these techniques, high energy input is required for the regeneration of solvents and significantly lower operating pressure is needed but for breaking of bonds (Kapdi et al. 2005). The operating pressure in amine scrubbing plants will be slightly above atmospheric pressure when compared with all other upgrading technologies. The raw biogas and amine solution is get contacted in countercurrent manner in the column in which $CO_2$ present in the biogas is absorbed by the amine solution by the exothermic reaction and hence the temperature is raised in the column. In this cases increase in temperature increases the absorption of $CO_2$ in amine solution and pure methane is obtained as exit gas at the top (Deng and Hägg 2010). The major drawbacks with these techniques are massive investment, high operation cost and high energy input and increased chemical consumption have the risk of releasing potentially hazardous degradation products (Voice et al. 2013).

### 9.4.9 Membrane Separation

In solution-diffusion model is a method in which concentration difference exists through which permeates are dissolved in a membrane and then diffuse by means of convection through small pores (Rongwong et al. 2012). Some considerations are taken into account for upgrading the biogas plant as well as their production. In such separation, the carbon dioxide content will be high and it flows through the membrane while the methane remains as retentate (Baker and Lokhandwala 2008). The process operates at low capital cost and also it requires very less energy. For the purification purposes, mainly polymeric and inorganic membranes are employed as they offer high mechanical as well as thermal stability.

Membrane-based technology has many advantages over other systems as it requires low labor maintenance. The process of separation is based on the concentration of volatile organic compounds (Scholz et al. 2013). It has some limitations such as high cost and the sensitive to damage by the vibrations caused by colloidal solids.

### 9.4.10 Emerging Technologies

Removal of $CO_2$ from biogas is easy from the above-mentioned process. However, removal of trace elements like $H_2S$ and other volatile organic compounds (VOCs) is a task for a search of new technologies. These trace elements are needed to be removed before utilization or else it creates a serious problem by corroding the pipelines. Thus an emerging technologies came into existence.

### 9.4.11 Cryogenic Upgradation

The continuous modification of biogas process leads to the development of cryogenic upgradation process to purify and bottling of biogas. Cryogenic separation of biogas is based on the principle that various gases liquefy under different operating conditions. This whole process operated at a very low temperature and high pressure conditions which are usually maintained by a number of compressor and heat exchanger (Zanganeh et al. 2009). This cryogenic technology is 4 stage process. In stage 1 all trace elements were removed before entering stage 2. Whereas in stage 2 the biogas is compressed and cooled subsequently. In stage 3 the biogas is further cooled to $-50$ °C and liquid $CO_2$ is removed before entering in stage 4 and in final stage finally, the remaining gas stream is further cooled to collect purified methane gas and $CO_2$ is removed in solid form (Imran et al. 2017). Cryogenic technology is demanding technique but it has limitations I high methane content ($<99\%$) and low methane losses ($<1\%$). Another advantage of this is an environmentally friendly technique and pure $CO_2$ is received as a byproduct. The main drawback of this process is the use of variety of process equipment and which raise its capital and operational costs.

### 9.4.12 In Situ Methane Enrichment

The major task involved in scaling up the biogas process involves the separation of methane-rich biogas from $CO_2$ which is highly expensive. In situ methane enrichment based biogas upgradation technology was done using desorption process When is flow is in counter flow direction, $CO_2$ dissolved in the sludge was desorbed with $O_2$ and $N_2$ in the desorption column from the digestion chamber. The circulated sludge is then sent back to digester from desorption column for absorption of an additional $CO_2$ present (Kadam and Panwar 2017). A simple in situ technique was developed to separation of $CO_2$ and $CH_4$ from biogas was done using in situ techniques based on solubility differences. The purity of methane gas was found at a greater percentage 98% (Richards et al. 1994).

### 9.4.13 Multistage and High Pressurized AD

A number of researches and ideas are proposed to evaluate different configurations in order to improve the efficiency of anaerobic digestion. The biogas production was carried out in four stages in two different reactors which increase the rate of bioconversion of organic material to methane. The major application of multiple bioreactor systems is to improve the process stability and higher efficiency with the drawback of cost of installation.

### 9.4.14 Cost Economics and Environmental Sustainability

Cost is one of the most crucial and determining factor involved in optimizing the particular production process. The production process largely depends on the capital and operating costs of biogas upgrading technologies involved in biogas production, quality of raw biogas produced, product quality, importantly the size of the plant (Yang et al. 2014). Maintenance cost is one of the key factors which biogas production as it increases the operation cost of the upgrading technologies (Campanaro and Treu 2016; Bassani et al. 2015). Utilization of biogas as a vehicular fuel requires a highly concentrated methane purity which can be ensured by several technologies. Chemical absorption technologies provide higher efficiency with higher investments where as the technologies like water scrubbing and in situ are economically viable (Bauer et al. 2013). However, cryogenic technology produces high pressurized liquid fuel and cost-effective in terms of maintenance cost in larger scale applications (Collet et al. 2017). For, membrane separation processes the operational cost is very low but the investment cost is apparently high, (Vrbová and Karel 2017).

## 9.5 Conclusion

Biomethane is a promising renewable technology as well as an effective substitute for natural gas for grid and vehicular applications. Utilization of agricultural waste, industrial and municipal waste as a source of biogas production will make an economic feasibility. Methane gas and carbon dioxide are the major compounds produced along during biogas production along with various compounds in traces. The impurities present in trace level affects the commercial application of biogas in large scale and hence it has to be removed before utilization. For the past two decades, numerous different technologies have been employed for upgradation of biogas production and have an impact on reducing greenhouse gas emissions and ensuring a more sustainable environment. The proposed technologies like physical and chemical absorption, adsorption, membrane separation, cryogenic separation and in situ upgrading can help to improve stability and reliability of the biomethane production chain.

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# Chapter 10
# Impact of Bioenergy on Environmental Sustainability

**Kankan Kishore Pathak and Sangeeta Das**

**Abstract** Energy and environments are vital elements to our daily life and a way forward for our viable development. The fossil fuels are widely used as primary energy sources that threaten its depletion along with the formation of various harmful greenhouse gases. This necessitates for efficient utilization of energy and the access to the alternative energy resources like bioenergy. It is always being a major concerned for bioenergy deployment while referring to availability of the biomass, competition between the various uses of biomass and the sustainability issues. In spite of its wide applications, there is less study on the environmental effects of bioenergy. This enthuse the challenges that calls for multidisciplinary researches related to environmental sustainability. Production of bioenergy conveys significant prospects to provide a series of environmental, social, economic benefits in addition to the energy and climate goals. In order to open up better chances for agricultural souk and to endorse sustainable growth in rural community, bioenergy plays a vital role. Proper planning and management might yield multiple benefits using bioenergy synergies with the production of food, water, ecosystems and health. This chapter addresses a survey on pertinent literature related to the environmental sustainability arising from the production of bioenergy. In this context, the chapter also deals with the bioconversion technologies and its impact on environment and applications, greenhouse gases and biodiversity, etc.

**Keywords** Bioenergy · Bioenergy production · Environmental sustainability · Economic benefits

## 10.1 Introduction

Bioenergy as a main source of renewable energy plays a vital role in the modern energy systems. It is always been a concern about the availability of biomass, contest

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between the various biomass uses, as well as the sustainability anxiety to the bioenergy growth. Regardless of immense qualms, the majority approximations indicate that biomass is likely to be adequate to play a important role in the comprehensive energy delivery system. Severe use of carbon based fossil energy results various environmental impact that have made many nations to start short, medium and long term plans aiming to efficient employment of renewable energy. Bioenergy may be considered as the enormous source of the renewable energy which may contribute to the half of the world's total renewables consumption, i.e., as much as hydro, wind, solar and all other renewables combined (International Energy Agency 2018). Bioenergy can have a certain influence on decarbonizing some sectors like cargo road transport, aviation, nautical transport, etc. Growth of bioenergy depends on the ability to accumulate huge amount of biomass. The direct and indirect trade of biomass might play a leading role in the bioenergy development in near future.

Biomass includes a broad range of feedstock from different parts like lignocellulosic biomass, agricultural food biomass, waste of biomass which includes several conversion ways: biochemical, chemical, thermochemical, etc. These conversion processes generally rely on the nature of the accessibility of biomass and the energy needs. Therefore, the resultant efficiency of the energy not only depends on the resources of biomass, but on the technology also which is engaged for the energy conversion.

In order to ensure a competitive, sustainable, and safe energy, supportive policies are always needed to obtain the energy and climate targets. The latest developments in renewables and technology help in reduction of the investment costs (mostly for solar photovoltaic and wind energy). It is interestingly noted that availability of relatively cheap or even negative cost of feedstock makes bioenergy study competitive in several cases.

Support requires are usually modified on the basis of the feedstock, technology and volume of the plant. An appropriate policy structure and stronger implementation procedures are required to prop up the bioenergy production, to benefit the energy system of low-carbon and to achieve the targets for reduction in emissions. Considering certain specific circumstances to gain growth in a balanced market, support should be distinguished among technologies, feedstock, and plant size at different level of development.

The bio-based economy is dependent on the sustainability of biomass. Studies revealed that use of biomass lowers greenhouse gases emissions in comparison to the use of fossil fuel if change in land use can be prevented. Biomass production, using low energy input or highly efficient residue streams or renewable energy, emits lower greenhouse gases as much as close to carbon neutrality. The noteworthy opportunities of biomass production include social, environmental and economic profits along with climate and energy goals. It also helps agricultural markets and helps in promoting stable development in rural communities. Bioenergy combined with the production of food, ecosystem, water, health and welfare might provide numerous benefits on proper planning and management.

The future role of bioenergy is highly challenged in European countries where use of clean energy is of utmost motive. The composition of advanced biofuels must be similar to drop-in biofuels to prevent the costs of new power train infrastructures. The future research of biomass will comprise of improvement of net process efficiency of biomass conversion and to develop cost-effective technologies for production of new biofuels.

Biomass is considered as a renewable resource but its use is limited due to the finite resources those necessary for production. Because of the rising interest on bio-economy, the biological assets are sustainably formed and transformed into final value added products. This chapter encompasses the basis of bioenergy/biomass production and the composition/characterization resulting from their productions that decide the different biomass types and classification. Moreover, a wide review of the various biological resources at global scale centering on their various environmental impacts is reported.

## 10.2 Overview of Bioenergy Research

Practically for the betterment of a society in the world it requires energy to be the basic condition for development and this is also vital for the existence of ecosystems along with the life and human civilizations (Jiang et al. 2014; Ozturk et al. 2017). Nevertheless, the utilization of conventional energy sources can raise various problems like the conventional energy resources like fossil fuels are not renewable, and its overuse will lead to major catastrophe of energy and thus becomes a big worry for the world. Another problem may be the environmental pollution because of the utilization of the traditional fossil fuels which accelerates the global warming, for example, increases of carbon dioxide and other greenhouse gases (Mallick et al. 2017, 2018). Again, it may be noted that the released nitrogen oxides due to the combustion of the fossil fuel compromise the quality of air and causes harms to the health of human beings (Hoekman et al. 2018). It is very much unfortunate that the consumption of energy highly depends on the fossil fuels and will increase in the coming years (Ozturk et al. 2017). Therefore, bioenergy may be considered as the strong renewable substitution of fossil fuels to achieve the safeguard of the energy security, mitigate the global warming and the rapid growth of the world population (Hoekman et al. 2018). Recent studies (Sang and Zhu 2011; Wu et al. 2015) unveil the fact of using different feedstocks for biofuel production. Thus, bioenergy draws attention to a great extent and engaged an active status in the energy consumption of earth with reference to the change of climate (Jiang et al. 2012). According to the world energy council and the report (Souza et al. 2017), 14% of global energy consumption is accounted by the bioenergy. However, it is expected that there might be an admirable potential of bioenergy in future. In the developing countries sustainable production of bioenergy can proficiently diminish the peril of energy poverty and subsidize to the economic growth (Schroder et al. 2018; Wicke et al. 2011).

Therefore, a government around the globe tries to promote the production of bioenergy and looking for suitable policies or regulations for its development. For example, EISA (The Energy Independence and Security Act, US Congress 2007) is instigated by the government of the United States to upsurge the accessibility of renewable energy through the production of biofuels. Similarly the eighth Malaysia plan (2001–2005, the fifth fuel policy) is fortified to promote the production of bioenergy (Tock et al. 2010). In the recent time, China shows genuine demand for the production of bioenergy in conjunction with the rapidly emergent economy that prevents the energy disaster, and achieving the goal of reduced emissions of greenhouse gases. In reality, it has possible bioenergy crop farming due to its better profit and ecological benefits. It may be noted that the extension of bioenergy raw material production might potentially cause some adverse ecological modifications yet it is considered to be an influential source for energy safety. Now-a-days, scientists from all over the world have paid enormous attention to the balance between the production of bioenergy and safeguard of the environment. This can be done by choosing multiple approaches, including the best management practices (BMPs) (Guo et al. 2018; McCalmont et al. 2017; Wu and Liu 2012). However, involvement of the complexity in the bioenergy production system and the deficit information make the knowledge of the overall environmental effects unclear. Therefore, an overview of the present situation regarding the production of bioenergy and its impacts on environment is required. Following the article (Wu et al. 2018) it has been observed that bioenergy production and its environmental effects were examined within the reference period of 17 years starting from the year 2000–2017. The research work relevant to bioenergy is observed to grow continuously from the year 2000. However, the pertinent studies of bioenergy involving environmental effects (e.g., water quality and quantity, Greenhouse Gas emissions, biodiversity and soil erosion, etc.) increased gradually with a diminutive growth rate since 2000. Furthermore, the continuous boom of publications associated to environmental impacts suggests that more and more attention is paid to the protection of environment while endorsing the development of bioenergy.

## 10.3 Production of Bioenergy/Biomass

Bioenergy may be the renewable energy that is obtainable from material derivative of biological sources. Biomass is kind of organic material which is capable of storing the sunlight in the form of chemical energy. The resources needed in the production of bioenergy are termed as feedstock. In order to know better of biomass, it is important to explore the several sources first. The production of biomass is based on the increase in the quantity of organic matter in a specified area. Biomass is chosen as the renewable energy because it is stocked up as animals and plants grow. There are generally two different ways of production: (i) primary and (ii) secondary production. Primary production is related to the production of energy by the plants in the course of photosynthesis. The gross amount of biomass in the environment is increased by storing and adding the extra energy generated. In this production system, production might be assessed from the total cover of the forest in a particular year. The other type of production i.e. secondary type involves assimilation of the organic substances as body tissues used by different organisms. In this production, animal's feeding on other animals or plants and decaying of the organic matters through micro level organism is involved. It might be also estimated based on the total meat production per year. Although biomass might be evaluated as much as organisms living and dead in a given circumstances, it is difficult to guesstimate the production. This may be reviewed as the raise in volume though part of the supplementary biomass may have been substituted through natural processes. Various methods of producing bioenergy are discussed next.

## *10.3.1 Direct Combustion (For Heat)*

From the earliest civilizations, it has been noticed that biomass conversion to energy through direct combustion is the oldest procedure exist in the present scenario. By varying feedstock in different ways, thermochemical conversion could be attained. The various ways of direct combustion are detailed as follows:

### 10.3.1.1 Standalone Combustion

The bio mass generators usually burn the organic fuel in order to produce electricity. There are varieties of ways to complete the combustion process by means of different feedstock, application range and the conversion ways.

(a) Bio-mass generators: Vegetable oils (for e.g., jatropha, nahar etc.), may be capable of replacing diesel in diesel generators to generate electricity suitable for off-grid applications or self-regulating mini-grids.

(b) Bio-mass power plants: The heat resulting from the direct combustion of biomass in a boiler might be utilized for producing electricity using a steam turbine or engine. Though the efficiency related to the electricity generation of the steam engines is not high enough as expected but it is presently the cheapest and most trustable way to generate power from biomass in standalone type of applications (IEA 2009).

(c) Biomass-based co-generation plants: The process of co-generation is used for producing two valuable forms of energy from the same fuel source, i.e., electricity and heat. The overall efficiency of a power plant may be significantly increases because of the co-generation which also results in competitiveness provided there may be an economic application for its waste heat (IEA 2009). The overall efficiencies of a combined heat and power (CHP) plants may be in a range from 80 to 90%. Some industries like, pulp and paper, palm oil mills, sugar mills use the heat from the biomass combustion.

(d) Municipal solid waste (MSW): Waste-to-energy plants is a very much different and heavily tainted feedstock, necessitates strong technologies, rigorous emission control systems, leading to the increase of the costs of waste-to-energy amenities, makes MSW a largely idle energy resource despite its noteworthy potential in many countries (IEA 2009).

#### 10.3.1.2 Biomass Co-combustion

In addition to the stand-alone combustion, biomass might be combined with other fossil fuels and burnt to generate energy. Biomass co-combustion (or co-firing) includes adding of existing fossil-based (mostly crushed coal) power plants with biomass feedstock (IEA 2009). Woody to grassy and straw-derived materials which include both residues and energy crops are considered as biomass fuels. Based on the different types of biomass, the properties of biomass change significantly and also differ from those of coal. The properties of the biomass having lower heating value and low bulk density might differ from those of coal having higher values of ash, moisture and chlorine content. The performance of co-firing/co-combustion systems highly depends on these properties (IEA Bioenergy, Task 32 2002). There are three basic types of biomass co-firing available and those are as follows:

(a) Direct co-combustion: Existing coal furnace is used to burn the biomass directly. This type of co-combustion maybe done either by pre-mixed the raw solid biomass (granular and dust form), with the coal in the coal handling system or by injecting directly to the crushed coal firing system.
(b) Indirect co-combustion: The resulting synthesis gas is burned in the coal furnace after the biomass gasification.
(c) Parallel co-combustion: With the steam produced within the main coal power station steam circuits are used to burn the biomass in separate boilers (IEA 2009). Indirect and parallel co-combustion options are considered to avoid biomass-related contamination problems. Parallel or indirect co-combustion are much more expensive than the direct co-firing approach as latter requires additional infrastructure. One of the applications of parallel co-combustion units are pulp and paper industrial power plants (IEA 2009).

One of the main advantages of biomass co-combustion is that it may reduce the greenhouse gas (GHG) emissions from the coal fired plants and enables effective power generation with a higher efficiency. The efficiency can be increased further if the co-combustion takes place in the combined heat and power (CHP) plants. The cost factor is also an advantage of biomass co-combustion as the rising investment for burning biomass in coal-fired plants is significantly lower than the cost of dedicated biomass power. In the present scenario, co-combustion projects in coal-fired plants are more than the biomass capacity of the biomass plants. Kijo-Kleczkowska et al. (2016) studied the processes and kinetics of combustion of sewage sludge, coal and biomass and their co-combustion in pellets having spherical shapes. The adding of sewage sludge to hard coal and lignite reduces combustion periods when matched with coal, and the adding of sewage sludge to willow *Salix viminalis* yields an increase in combustion period. Guo and Zhong (2018) studied the simultaneous combustion of biomass pellets and coal by means of thermo gravimetric analyzer and fluidized bed. The pellets mixing ratio of 30% is thought to have optimal ratio for coal and biomass pellets, accordingly having minimum activation energy and slagging problem. The addition of biomass pellets can lessen the production of polycyclic aromatic hydrocarbons (PAHs) and trace metals. Khanmohammadi et al. (2019)

developed a novel thermodynamic model to extract excess heat using thermoelectric waste heat recovery systems (WHRSs) in integration with biomass power generation. The investigation showed that the first law efficiency of the system was increased by 0.35% if all the heat coming out from the stack passed through the WHRSs. Whereas, on placing the WHRSs in such a way that the entire heat from the condenser passed through it, the first law efficiency was increased by 1.17%.

#### 10.3.1.3 Types of Combustion Systems

As discussed in the previous sections, combustion/burning are the oldest and conventional procedures to obtain high temperature from the biomass. The high temperature is obtained by converting the chemical energy contained in biomass through numerous chemical reactions during biomass burning. The good reaction between the oxygen in air and the biomass might influence the efficiency of the combustion. The major products result inefficient combustion of biomass are $CO_2$ and $H_2O$ vapor along with secondary production of smoke, tar, alkaline ash particles, etc. The classification of various types of combustion systems is shown in Fig. 10.1. Fixed bed and fluidized bed combustions, suspension burners, etc. are the most common type of combustion systems available in biomass based power plants.

When the solid biomass is first cut into small pieces and then burnt on a flat static surface, it is known as fixed bed combustion. The rise in temperature in fixed bed systems are in a range from 900 to 1400 °C. The combustion of biomass fuels with higher moisture and ash content takes place in grate furnaces. The grate system helps in providing uniform distribution of fuel and bed. Fixed grate systems are suitable for small scale applications. Managing the fuel transportation in such systems is

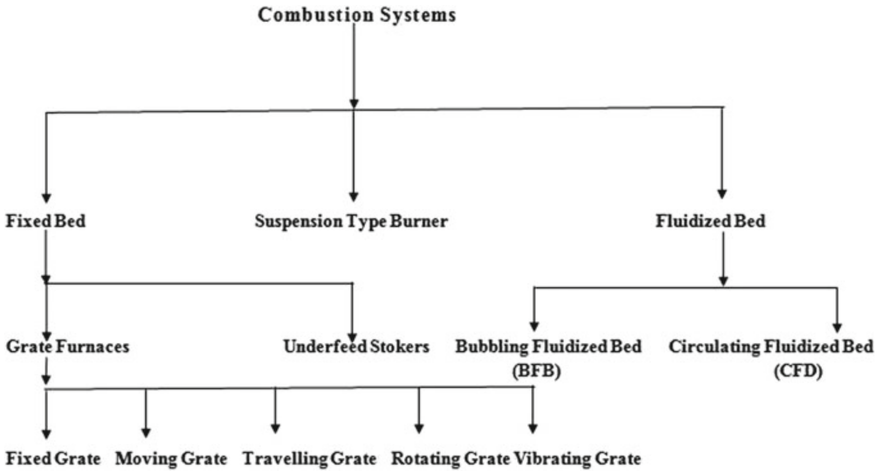

**Fig. 10.1** Classification of combustion systems

generally based on consuming of fuel and the gravity action produced due to the inclination of the grate. In moving bed combustion, a grate is set to constantly and evenly move leaving ash behind. The fuel burns in combustion levels. They may be inclined or horizontal in design. In case of travelling grate systems; the grate bars form an endless band through the combustion chamber. When biomass fuels having small amount of ash and tiny particles, underfeed stoker fixed bed combustion systems are more appropriate. These are flexible in case of the load changing behavior. In case of dry biomass (<15% moisture) with very fine particles, suspension burners are suitable. These types of burners are having higher specific capacity. It produces the flame very similar to oil fired burner. It is found that suspension burners are not up to the level whenever efficiency is concerned. This is attributed to the excess air needed to prevent the formation of slag in the combustion system and there is an enormous production of fly ash. Again when fuel is boiled under high pressure mixed with sand, the sand serves to distribute the heat evenly. This is known as fluid bed combustion. This type of combustor comprises of a cylinder attached to a perforated base plate filled with a suspension bed of granular materials. Dolomite, silica, and sand are the common materials for bed. Air is blown through the perforated bottom plate to fluidize the bed using a fan. It aids in rapid transmission of heat generating a large heat transfer surface. These combustors can handle easily different sizes and shapes of fuel particles, high moisture and ash content. Lee et al. (2019) analyzed the economic viability of a 600 MW ultra-supercritical (USC) circulating fluidized bed (CFB) boiler functioned with coal or a combination of coal and biomass as fuel. The economic viability was assessed in terms of collective cash flow, payback period, NPV, and IRR. In spite of high capital costs, low technology and high power use, the USC CFBC was highly developed to achieve clean environment and high energy conversion efficiency. In burner combustion, wood dust and fine dust are placed in a burner similar to that of liquid fuel. When a kiln furnace is used to burn organic matter with high moisture content, such waste as food residue or other moist farm waste is burnt this way is known as rotary furnace combustion.

## *10.3.2 Thermochemical Methods of Biomass Production*

### 10.3.2.1 Pyrolysis

Pyrolysis is another form of processing bio-fuels by burning under very high temperatures without oxygen, which might cause complete combustion. This is responsible for the irreversible physical and chemical variations. In the absence of oxidation and halogenation processes, it may result a very dense bio-fuel that could be used in combustion, co-combustion or changed to gas. The solid charcoal can be obtained through slow pyrolysis at about 400 °C. Fast pyrolysis occurs in a temperature range from 450 to 600 °C and it results in various organic gas, pyrolysis vapour and charcoal. The vapour is then condenses to liquid form as bio-oil. This conversion must be done within fraction of seconds to prevent further reaction. The liquid obtained through this process is dark brown and it is denser than wood biomass and has equal content in energy. The bio-oil is easier to transport, burn, and store. Several kinds of feedstock can be processed through pyrolysis to produce biooil. Figure 10.2 describes the conversion of energy into a usable form of bio-fuels through pyrolysis.

The main advantage of pyrolysis being an attractive option to attain bioenergy is due to its carbon negative property (Glaser et al. 2009; Lehmann 2007), increased biogas, biooil and biochar production (Zhang et al. 2010; Aysu and Küçük 2014). Following the report (Manara and Zabaniotou 2013), the pyrolysis process might be classified into four stages, i.e., (i) moisture evolution, (ii) hemicelluloses decomposition, (iii) cellulose decomposition and (iv) lignin decomposition. The chemical bonds usually break and form a new compound in the absence of oxygen. The organic matters present are converted into (i) gaseous (or major components are $CO_2$, $H_2$, and CO, syngas), (ii) liquid (i.e., biooil) and (iii) solid (biochar) fractions that are used for generation of electricity (Zabaniotou 2014; Akhtar and Amin 2012). It is reported in the articles (Xiu and Shahbazi 2012; Lehmann et al. 2006) that bio oil is having the potential of being applied as biofuels (renewable) for combined power stations or in generation of power and in a transport systems. The net reduction of $CO_2$ emissions could be achieved while biochar blending has been applied with the fertilizers in the cropland (Chan et al. 2007; Lehmann et al. 2003). There are generally three main categories of pyrolysis as shown in the Table 10.1 (Patwardhan 2010; Goyal et al. 2008). Detail study of these processes is discussed in (Ben and Ragauskas 2013; Lee et al. 2013; Kan et al. 2016).

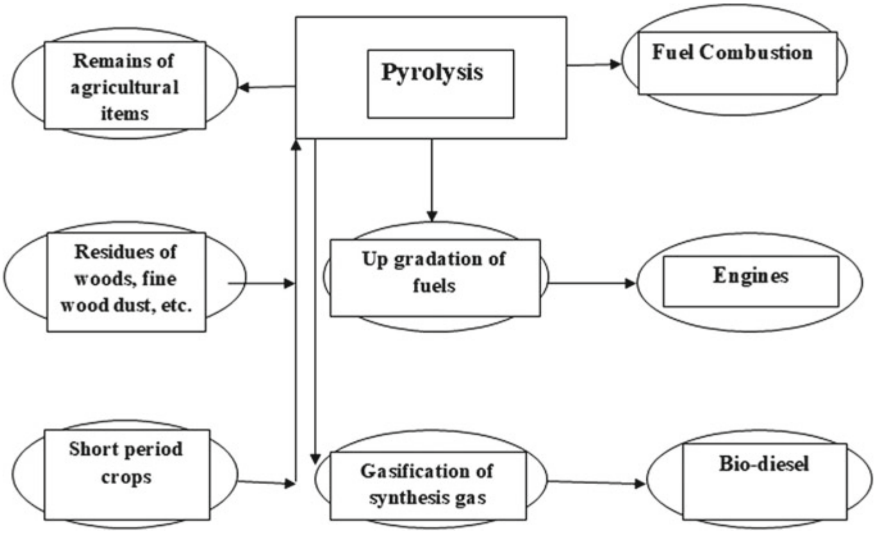

**Fig. 10.2** Conversion of energy through pyrolysis

**Table 10.1** Types of pyrolysis, related operating conditions and the final listing of products (Patwardhan 2010; Goyal et al. 2008)

| Types of pyrolysis | Operating conditions | | | Final products | | |
|---|---|---|---|---|---|---|
| | Operating temperature | Rate of heating | Retention time | Char | Bio-oil | Syngas |
| Slow pyrolysis | 400–600 °C | 5–7 °C/min | 5–30 min | Lesser than 35% | Lesser than 30% | Lesser than 40% |
| Fast pyrolysis | 400–600 °C | 300 °C/min | Lesser than 5 s | Lesser than 25% | Lesser than 75% | Lesser than 20% |
| Flash pyrolysis | 400–600 °C | 1000 °C/s | 30 ms–1.5 s | Lesser than 25% | Lesser than 70% | Lesser than 16% |

#### 10.3.2.2 Biomass Gasification

Biomass gasification or thermal gasification is the method of transforming solid fuel into the gaseous fuel through thermo-chemical means without leaving any carbon contain solid residue. This technology is now an established technology and its application of commercial use has been found since 1830. The equipment that transforms biomass into producer gas is known as gasifier. Gasification involves partial combustion and reduction operations of biomass. Partial combustion indicates oxidation in limited quantity of air or oxidant. In a classic combustion process usually there is an excess of oxygen, while in gasification fuel is in excess amount. The combustion products, mainly $CO_2$, water vapour, N, CO and H pass through the shining layer of charcoal to ensure the reduction process. In this stage both $CO_2$ and water vapour, oxidize the char to form carbon monoxide, hydrogen and methane. Major reactions involved during gasification are as follows (Khan 2017):

$$C + O_2 \rightarrow CO_2 \quad \text{(Combustion, 240 kJ/mole)}$$

The available moisture in the biomass is transformed into steam and generally there is not any requirement for extra moisture. Thus the product of combustion pyrolysis gases results in $CO_2$ and steam ($H_2O$), which later reacts with the char:

$$C + CO_2 \rightarrow 2CO \quad \text{(Boudouard reaction, } -164.9\text{ kJ/mole)}$$
$$C + H_2O \rightarrow CO + H_2 \quad \text{(Water gas reaction, } -122.6\text{ kJ/mole)}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{(Water shift reaction, 40.2 kJ/mole)}$$
$$C + 2H_2 \rightarrow CH_4 \quad \text{(Methane reaction, 83.3 kJ/mole)}$$

The degree of equilibrium attained among various reactions decides the composition of the gas produced. Gasification may be regarded as a suitable process for obtaining eco-friendly energy. In this process material is burnt in a temperature range from 800 to 1300 °C (Panwar et al. 2012). The syngas produced during gasification can be used for the energy generation by means of turbines or gas engines (Field et al. 2016). In the report of De Andrés et al. (2016), it emphasis the importance of transforming the syngas into the final value added products. For instance, production of synthetic natural gas and dimethyl ether from syngas is observed in this report. It also reports that two byproducts, viz., char and tars are also produced in addition to syngas. The biomass composition is an important parameter and it is being fed to the gasifier which usually decides the formation of these products. The char might be used as a domestic fuel or it can be moved into fertilizers and turned on carbon in other applications. However, in gasification, the tars are an unwanted byproduct. The presence of tars decreases the value of the syngas consequentially creating corrosion and blockage in the equipment (De Andrés et al. 2016). The gasifiers may be categorized as fixed bed gasifier and fluidized bed gasifier. Based on the direction of airflow, the fixed bed gasifiers are further classified as downdraft, updraft and cross draft types.

#### 10.3.2.3 Biomass Liquefaction

The method in which the macromolecules of biomass are hydrolyzed or degraded with water at average temperature and high pressures is commonly known as hydrothermal liquefaction. There are generally two paths through which liquefaction of biomass mainly takes place: (i) liquefaction through the process of pyrolysis without any gasification medium and (ii) liquefaction through methanol with gasification medium. The former process is a relatively low temperature (250–450 °C), high pressure (270 atm) thermochemical conversion of wet biomass, usually occurs by means of high hydrogen partial pressure and also need a catalyst to augment the rate of reaction and/or to improve the fussiness of the process. Liquefaction through gasification medium involves the production of methanol from mixture of $H_2$ and CO (producer gas). The temperature of this reaction takes place at 330 °C and 150 atm pressure.

$$2H_2 + CO \rightarrow CH_3OH$$

The $H_2$ and CO required for this process is produced by gasifying biomass fuel. Gasification often produces less $H_2$:CO ratio than 2:1 required for methanol synthesis. The gas mixture is often reacted with steam in presence of catalyst to promote a shift to increase hydrogen content.

$$CO + H_2O \rightarrow H_2 + CO_2$$

At the operating conditions, water being a liquid fluid having some great advantages like, having a low dielectric constant makes water act as a poor polar solvent resulting a better solubility with organic compounds rising from the biomass (Zhu et al. 2015). The article (Biller and Ross 2011) reports that molecules hydrolyzed by hydrothermal liquefaction are highly reactive and are repolymerized quickly to form bio-oils. Typically, hydro thermal liquefaction uses water as the reaction medium and catalyst. Thus, it becomes an ideal process for high moisture content biomass. It has been found that hydrothermal liquefaction is reported for a large number of raw materials including the marine and microalgae (Biller et al. 2012). The advantage of hydrothermal liquefaction over general thermochemical processes lies in procuring biooil directly in a single step without having pre drying (Gai et al. 2015). This results a reduction of the consumption in energy, and therefore greater economic benefits can be attained (Gai et al. 2015).

## *10.3.3 Biological Methods*

### 10.3.3.1 Fermentation

The process of fermentation is used by the early civilizations to make foods such as bread, yogurt, wine, beer, etc. However, the increasing needs of human desires make the researchers to think for complex products that might cope up with the challenges of humanity (Jiang et al. 2015). The recent development in the science and technology in conjunction with the population growth increases the energy consumption tremendously. In order to meet the energy demands, various industrial processes have been developed to focus on the production of fuels using large amount of nonrenewable resources which might cause serious environmental problems (Nualsri et al. 2016). In this note, a much higher attention is given to the technologies that utilize renewable raw materials for biofuel production. Different processing technologies are available for the production of renewable biofuels. The most demanding technology till date is fermentation. It is a biological process through which biomolecules required in the industries are achieved, such as biofuels (ethanol, butanol, biogas, hydrogen, etc.) (Nualsri et al. 2016), drugs, food and biopolymers (poly-3-hydroxybutyrate and polyols) (Kreyenschulte et al. 2016). The process of fermentation varies based on the type of microorganism and the raw material used. According to the article (Kwietniewska and Tys 2014), in cases where the raw materials cannot be incorporated directly by the microorganism, there must be some pretreatment procedures before the hydrolysis to get fermentable sugars for the microorganism. Again, depending on the requirement of oxygen of the microorganism fermentation can be categorized.

### 10.3.3.2 Aerobic Fermentation

In aerobic fermentation microorganisms require high accessibility of oxygen in the culture soup (Oliveira 2004). In order to meet the required growth of the microorganisms, the accessibility of oxygen must be put above a minimum level. The aforesaid article also reports that due to the low solubility of oxygen it is hard to access and supply of oxygen in spite of the large requirement by the microorganisms. The significant products obtained by aerobic fermentation are terpenes, antibiotics, organic acids, amino acids, etc. (Kwietniewska and Tys 2014).

#### 10.3.3.3 Anaerobic Fermentation

It is a biological process in which the microorganism does not need to access oxygen to adjust to the medium and to generate different products. The most significant fermentation for the generation of biofuels is dark fermentation such as production of hydrogen (Farhana Azman et al. 2016) and methane (Kwietniewska and Tys 2014). Methane production procedure is commonly known as anaerobic digestion.

(a) **Anaerobic digestion of biogas**

Anaerobic digestion (AD) is an auspicious technology that recuperates bioenergy from lignocellulosic biomass or wastes (Zhang et al. 2015). Anaerobic digestion is a biological process through which organic matter is broken to produce biogas in the absence of Oxygen. In this process microorganisms (like acidogenetic bacteria, acetogens, etc.) convert the biodegradable matter to biogas. This process may be considered as a waste deposition method and it serves as an environmental conservation technique. The basic equation for this conversion which results in carbon dioxide and methane may be written as follows:

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

Biogas is produced from wet biomass with about 90–95% water content by the action of anaerobic bacteria. Part of carbon is oxidized and another part reduced to produce $CO_2$ and $CH_4$. These bacteria live and grow without oxygen. They derive the needed oxygen by decomposing the biomass. This process is favored by wet, warm, and dark conditions. The airtight equipment used for conversion is known as biogas plant or digester, which is constructed and controlled to favor methane production. This conversion process is commonly termed as anaerobic fermentation (or biodigestion). Nutrients such as soluble nitrogen compounds remain available in solution and provide excellent fertilizer and humus, the energy available from the combustion of biogas is 60–90% of the input dry matter heat of combustion. Thus its energy conversion efficiency of the process is 60–90%. Following steps can be followed in this process: In the first step, for the smooth conversion, organic matters containing complex compounds e.g. carbohydrate, protein, fats, etc., are broken into sizable molecules. This process is commonly known as hydrolysis. This process takes about a day at 25 °C in an active digester. In the second step, acidogens act on the decomposed matter and converts into volatile fatty acids (VFAs), mainly producing acetic and propionic acids. This stage also takes about one day at 25 °C. Ammonia, $CO_2$ and hydrogen sulfide are also produced along with the VFAs. This process is commonly known as acidogenesis. In the third step, VFAs are additionally broken down into acetic acid, carbon dioxide and hydrogen. This process takes about two weeks' time to complete at 25 °C. The fourth and the final stage is the combination of emissions to produce water, methanol and carbon dioxide (Fig. 10.3). Biogas plants or digesters are broadly classified as batch type and continuous type. Further continuous type plants are further classified into constant pressure type or floating drum and constant volume type or fixed dome type. In case of the batch type plant, it is charged at 50–60 days interval. Once charged, it starts supplying the gas after 8–10 days and continues its service about 40–50 days till the digestion process is completed. Again in case of continuous type, the plant is fed daily (not intermittently) with certain quantity of biomass. The gas produced is stored in the plant or in a separate gasholder and remains available for use as required. The biomass while slowly passing through the digester is completely digested and the digested slurry is rejected through an outlet. The period during which the biomass remains in the digester is known as retention period, which depends mainly on the type of biomass and operating temperature. The plant operates continuously and stopped only for maintenance or for removal of sludge .

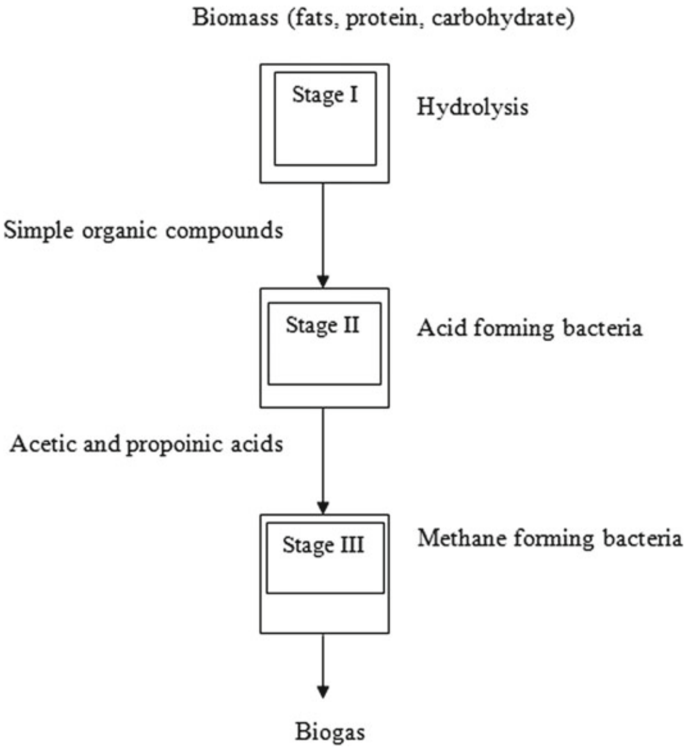

**Fig. 10.3** Various stages of anaerobic digestion process

### (b) Alcoholic fermentation

The process of conversion of sugars into cellulose is known as the alcoholic fermentation. It is a decomposition in absence of air of simple hexose sugars in aqueous solution by action of enzyme (a natural catalyst) present in yeast, in acidic conditions (pH value 4–5). It is considered as an anaerobic since it takes place in the absence of oxygen. The by-products obtained from this process are ethanol and carbon dioxide. In addition to the bread baking and manufacturing alcoholic brews, this process also produces alcoholic fuel. In dry situations sugarcane is the main feedstock for alcoholic fermentation process. Corn or sugar bits are also used in tepid climates. The hexose (i.e., glucose and/or fructose) needed for alcoholic fermentation is usually derived from (i) sucrose (ii) starch or (iii) cellulose. The preparation is explained below (Khan 2017):

(i) Sucrose: It is the most available disaccharide and is manufactured from sugar cane or beetroot. Generally commercially available sucrose is removed from the cane juice, and the remaining molasses, which has low commercial value, is used for ethanol production. The molasses itself has about 55% sugar content and serves as very good raw materials for ethanol production. On hydrolysis with dilute acids or enzyme it gives equal amounts of glucose and fructose.

$$C_{12}H_{22}O_{11}\ \text{(Sucrose)} \rightarrow C_6H_{12}O_6\ \text{(Glucose)} + C_6H_{12}O_6\ \text{(Fructose)}$$

(ii) Starch: On hydrolysis with dilute $H_2SO_4$ or enzyme, starch breaks down to maltose and finally to glucose.

$$\begin{aligned}2(C_6H_{10}O_5)_n\ \text{(Starch)} + nH_2O &\rightarrow nC_{12}H_{22}O_{11}\ \text{(Maltose)} + nH_2O\\ &\rightarrow 2nC_6H_{12}O_6\ \text{(Glucose)}\end{aligned}$$

(iii) Cellulose: It is not hydrolyzed so easily as starch, but on heating with dilute sulphuric acid under pressure yield glucose (393 K, 2–3 atm).

$$(C_6H_{10}O_5)_n\ \text{(Cellulose)} + nH_2O \rightarrow nC_6H_{12}O_6\ \text{(Glucose)}$$

Sucrose materials are readily available in fermentable form, require least expensive preparation, but are generally most expensive to obtain. Starch bearing materials are often cheaper, but require processing to solubilize and convert starch to sugars. Cellulosic materials are the most readily available raw materials, as cellulose is the most abundantly available organic compound in the world, but they require the most

**Table 10.2** Ethanol production from various hydrocarbon rich plants (Khan 2017)

| S. no. | Raw materials | Ethanol produced per ton of crop (L/ton) | Ethanol produce per hectare per year (L/ha) |
|---|---|---|---|
| 1. | Barley | 310–350 | 700–1300 |
| 2. | Cassava | 175–190 | 2200–2300 |
| 3. | *Hardwood hydrolytic agent* | | |
| | Dilute acid | 160–180 | 1500–2500 |
| | Conc. acids | 190–220 | 1800–3000 |
| 4. | Jerusalem artichoke | 80–100 | 2700–5400 |
| 5. | Maize | 360–400 | 1500–3000 |
| 6. | Potato | 100–120 | 2200–3300 |
| 7. | Sugarcane | 60–80 | 3500–7000 |
| 8. | Sugar beet | 90–100 | 3800–4800 |

extensive and costly preparation. Finally, ethanol is obtained from fermentation of hexose sugar

$$C_6H_{12}O_6 \text{ (hexose)} \rightarrow 2C_2H_5OH \text{ (Ethanol)} + 2CO_2$$

The ethanol produce from various types of raw materials is given in Table 10.2.

### 10.3.4 Application of Products

The applications of the product can be listed as follows: Acetone is a one such product which can be used for production of food additives, act as grease removers, glue dissolver, thinning of paint, and in the cosmetic products. Hydrogen can be used as a cooling agent in power industries also used in hydrogen cells for production of energy. Butanol can provide better fuel than ethanol. It may be used as an ingredient in polymer extractions, manufacture of synthetic fiber, cosmetic products, etc. Ethanol can be used as fuel, paint component, a preservative in antiseptics and in alcoholic beverages.

## 10.4 Environmental Issues Related to the Bioenergy Production

### 10.4.1 Water Quality and Quantity

The biomass production systems can influence the availability and quality of water. The different systems use different amounts of water from surface and groundwater, depending on, among others, the water-use efficiency of the crops and whether the system is irrigated or rain-fed. The various effects of bioenergy production on water quality and quantity depends mainly on the possible water consumption of bioenergy crops and land based conversion. For instance, in US, the extensive expansion in corn ethanol production, which may be considered as the first-generation biofuel, encouraged by EISA (Energy Independence and Security Act 2007) was projected to generate probable stress at local and regional scales (Hoekman et al. 2018; Gasparatos et al. 2011; Zhou et al. 2015). This is because of the corn needs more water relative to the other crops like wheat and soybean due to the consumption of additional water in almost every growing stage (Wu et al. 2018). In general, Bioenergy crops optimized for rapid growth usually devour more water than natural flora/many food crops. Some biomass crops, for example, sugarcane compete directly with food crops for irrigation water. According to a report (Sivan 2006) in some cases, like harvesting residues, cultivating tree crops without undergrowth, and planting species that do not produce satisfactory amounts or types of disorder, might reduce the ability of rainfall to infiltrate the soil and refill groundwater supplies, aggravating problems of water over consumption. The modeling results by Kim et al. (2013) exemplified that wide plantation of bioenergy crops will upsurge the amount of evapotranspiration (ET), decrease annual surface water and water harvest in the Yazoo river basin of Mississippi River becomes the main corn production region in US. Similar conclusions can be found in the literature of Wu and Liu (2012), Guo et al. (2018). These reports also forecast that the land conversion to bioenergy crops might cause reduction of water resources at the watershed scale.

### 10.4.2 Quality of the Soil and Its Fertility

Some of the bioenergy production systems use and restore tainted lands, while others may contribute to the degradation of the land. Thus, in many cases, production of bioenergy probably changes the quality of the soil in terms of carbon and nutrient content. It also effect the risk associated with the soil erosion. Consequently, biomass crops impose a particular challenge for better soil management since the material of the plant is habitually harvested completely, leaving little organic matter or plant nutrients for salvaging to the soil. It is noted that in many rural areas of the developing world where soil management relies on recycling crop wastes and manure rather than using the external inputs, biomass production might lead to intense reduction in soil fertility. Despite of the fact of adding more plant matter on the land may reduce the yielding capacity of the bioenergy crop material but it is always needed to maintain soil organic matter by adding sufficient amount of plant matter. In many situations, it is possible for the farmers to reduce the risk of nutrient depletion by allowing the twigs and leaves of the trees to decompose on the field. The nutrients available on the feedstock's can also be regained from the conversion facilities in terms of sludge or ash and it is converted into a suitable form which can be applied to the field rather than put in a landfill. This method is available in many bioenergy systems.

However, the nutritive value of the ash or sludge may be lower than the optimal. There are three main ways that can cause the soil erosion: (i) the corn acreage extension, (ii) residue removal, and (iii) land use change. Because of the rising demand for ethanol might have intense adverse consequences in the process of soil retention since the corn acreage extension is having the slacker planting space. The benefits of the various conservation measures on soil retention would be reduced more if the increased corn cropping ensued on these lands, and cultivating the existing corn crops with suitable cultivation practices may reduce the soil erosion (Hoekman et al. 2018). It is reported in the article (Blanco-Canqui and Wortmann 2017) that the crop residue leaving behind the soil surface may buffer wind and water erosive forces. Thus, harvesting the crop residue may upsurge the erosion risk due to the minimum physical shield of soil surface (Environmental Protection Authority Act 2011; Lal 2005), leading to nutrient and SOC losses. But, following (Cibin et al. 2016), soil erosion persuaded by higher residue removal rate may be alleviated by suitable management choices like direct input of organic matter and other security measures. Moreover, land use conversion might aggravate erosion or shelter soil from erosion. For example, conversion from forest to perennial bioenergy crops may surges the risk of losses related to the soil and water (Liu et al. 2012), while the conversion from the grain crops to perennial grasses could generate encouraging effects on the soil and water preservation because of the erect and ribbed stems with sods that are generated by perennials (Cooney et al. 2017). The perennial grass, particularly the switch grass, might decrease the residue yield in stream flow and soil erosion and increase the use of water and infiltration regardless the climate conditions in the Chinese loess plateau, representing the advantage in soil and water preservation of perennials compared to the outmoded crops in such regions (Cooney et al. 2017; Brown et al. 2000). So, growing perennial grasses particularly in erosion prone areas has a superior potential than that of the corn ethanol production.

### *10.4.3 Biodiversity*

The environments and biodiversity are greatly influenced by the production of bioenergy feedstocks. The environment for bioenergy crop production is alike to natural habitat relative to other agricultural options that improves biodiversity to seal the difference between the remnant fractions of natural habitat. For instance, the present environmental regulation in Brazil needs to leave 25% of the total plantation area for natural vegetation to maintain a balance in the ecosystem. The natural vegetation helps in controlling pests in surrounding plantation by using predators. The migrating wild lives are benefitted from the bioenergy crops that functions as corridors between the natural habitat areas. For instance, the production of *Pinus patula* and *Acacia melanoxylon* in South Africa, *Pinus pinaster* in Uruguay, and eucalyptus in various regions has increased rapidly that act as pests to the local vegetation. The evading of monoculture stops the spread of pests or disease into natural habitat. In India, there exists a circumstance of spreading of fungal disease from exotic pines on plantations to native pines. The food production and ecosystem services are greatly influenced by biodiversity (Qin et al. 2018). The initial condition of land, way of bioenergy production and landscape pattern effects the biofuel production (Correa et al. 2017; Immerzeel et al. 2014). Land use conversion is related to plant type and planting locations that disturbs the biological abundance. The biofuel crops maintain the ecosystem and increases the efficiency with the alteration of production system (Sang and Zhu 2011; Correa et al. 2017). Additionally, the Miscanthus has lesser negative impact on biodiversity than annual crops as regular cultivations offer stable habitats for maintaining wild life (Rowe et al. 2009; Werling et al. 2013). The landscape design improvement and reduction of biodiversity risk can be achieved by growing energy crops on low production lands (Sang and Zhu 2011; Manning et al. 2015). Soil organic carbon (SOC) signifies soil quality and crop productivity, soil biodiversity; soil water retention is increased with high amount of soil organic carbon. The soil organic carbon is influenced by bioenergy production in three ways, viz. elimination of deposits, tilth and modification of land use. The reaping of dead plant residuals can speed up the reduction of soil organic carbon due to less carbon input (Hoekman et al. 2018). The managing of residue by adding organic matter in the form of manure can control the reduction of soil organic carbon (Robertson et al. 2014; Sheehan et al. 2014). The biochar is mainly produced from crop residues using suitable techniques. The biochar improves the function of carbon sink in agricultural sector by aggregating soil organic carbon and absorbing $CO_2$ in air (Li et al. 2017) and improves the air quality by mitigating $NO_x$, methane and PM 2.5 (Pourhashem et al. 2017). The soil disturbance and ill management is the second cause of soil organic loss. The report (Drewniak et al. 2015) examined the impacts of tillage practices on soil organic carbon through simulated biogeochemical model and observed that tillage causes soil organic carbon loss. Also, several experiments suggested that the reduction soil organic carbon is possible through tillage practices (Cheng 2009; Ouyang et al. 2015; Warren Raffa et al. 2015). The land conversion is a vital factor for soil organic carbon change.

### *10.4.4 Greenhouse Gas Emissions*

The primary GHG emissions, viz. $CO_2$ and $N_2O$, must be reduced while producing bioenergy (Dunn et al. 2013; Qin et al. 2016). Many studies proved that the biofuels produce less $CO_2$ emissions than fossil fuels (Fu et al. 2014; Wang et al. 2012). Liu et al. (2017) replaced fossil fuels to reduce $CO_2$ emissions by 29 million ton eq/year by more switch grass production on marginal land. The model suggested that in US, the GHG emissions may be reduced by 40–85% using ethanol in comparison to gasoline on a per mega joule (MJ) energy basis. However, the amount of reduction of greenhouse gas emissions is different for different feed stocks and bioenergy production indirectly effects $CO_2$ emissions (Dunn et al. 2013; Searchinger et al. 2008). Harris et al. (2015) reviewed the impact of biofuel and confirmed a reduction of $CO_2$ emissions through land transitions from arable to second generation bioenergy crops. While, conversion of land from native grassland to first generation bioenergy crops and short rotation coppice (SRC) exhibited a noticeable rise in $CO_2$ emissions. Hence, categories of bioenergy crops and its management are important for mitigating $CO_2$ emissions. The $N_2O$ is the second important GHG that largely contributes to global warming and mainly produced from agriculture (Williams et al. 2010) and land transitions. Liu et al. (2011) replaced fossil fuel and stated that the biomass production on marginal land for energy consequences in good environmental impact on national greenhouse gas emissions. The $N_2O$ emissions may be stimulated by expanding corn cultivation that is driven by ethanol demand. The corn cultivation demands higher nitrogen fertilizer in comparison to other crops that leads to soil denitrification increasing $N_2O$ emission. Hence, the selection of bioenergy plant type and planting locations is of utmost necessity for controlling $N_2O$ emissions.

Wielgosinski et al. (2017) compared the pollutants [i.e. carbon monoxide (CO), nitrogen oxide (NO) and the total organic carbon (TOC)] emitted during the combustion of seven biomass samples, viz. rape straw, oak bark, firewood and wood pellets, shrub willow and rape cake, with pulverized hard coal samples. The study was carried out in laboratory chamber furnace at five different temperatures between 700 and 1100 °C and three different air flow rates with excess oxygen. The various pollutants, especially the TOC, were found to be higher in the biomass combustion than in hard coal combustion. Hence, biomass cannot be always considered as an eco-friendly fuel even though it is renewable. The emission levels are too high or comparable to that of combustion of coal, whereas the biomass emits higher hydrocarbon than coal.

### *10.4.5 Socio-economic Problems and Governance Implications*

Various issues related to the rights of the labours, land dealings, building capacity, gender neutrality, loss of traditional cultural practices and the conflicts arise from the land disputes might cause socio-economic problems arising from the production and consumption of bioenergy and biomaterials. Following the article (Müller et al. 2015), it may be argued that production and consumption of biomass could have negative and favorable impacts based on the conditions in which they occur. Moreover, these effects take place at different levels and scales covering from local to international standards. International policies, for example, European Union's Biofuel Directive, World Bank's scheme like RAIP (Responsible Agricultural Investment Principles), etc., have been implemented to influence the biomass production. These policies are important for finding what/where/how/by whom biomass production have been carried out.

According to the aforementioned report (Müller et al. 2015), as a part of the future development agenda (post-2015), the international community decides on global sustainable development goals (SDGs) in order to establish a comprehensive normalize framework that may be universally acceptable. The year 2015, thus, becomes a benchmark for sustainability governance worldwide. These SDGs are more complex and wider set of goals than the former Millennium Development Goals (MDGs). These governance schemes are vital to bridge the increasing and diverse demand of biomass and highlighting the achievement of social needs within the environmental boundaries which actually considers the socio-economic ambitions of SDGs with respect to equity, protection of natural resources required for biomass production and various impacts by these parameters. Again, inequalities in terms of opportunities, power, access to the resources needs to be taken care while implementing these governance schemes.

## 10.5 Conclusions

Last but not least it should be noted that sustainable bioenergy is not just a subject of suitable metrics (standards and indicators) and respective dimensions but also relies highly on how those are demarcated, and applied, and by whom (Müller et al. 2015; Stupak et al. 2016). Latest work of de Man and German (2017) direct that certification if sustainability for biofuels is an inadequate substitute for public directive. Certain frail systems are working which only consider fall of greenhouse gas targets and very few addresses for biodiversity. On the other side, even ambitious sustainability schemes might not able to overcome the problem of land-use leakage: It is seen that sectoral or commodity-related certifications illustrate that unsustainable practices could be shifted to the external biomass which is outside of the scheme. Hence, in a broader way, it may be said that sustainability governance of bioenergy is a vital part of a sustainable bioeconomy governance (El-Chichakli et al. 2016) which generally holds all land use to avoid cherry picking and leakage. Following (Müller et al. 2015), we need to incorporate reviewing business standards say WTO regulations, private governance scheme and national legislations to find where modifications are desired and how the sustainability aspects could be strengthened.

There are genuine advantages of the bioenergy relative to the traditional fossil fuel because of the huge quantity and its renewability. Thus bioenergy plays a vital role in protecting the energy safety of the earth. However, it is always desirable to consider the cost of resources and environment while employing the bioenergy production. The present study is made to summarize the environmental impacts of bioenergy production based on the previous studies. It is noted that in spite of the increasing trend, the attention is not given much on bioenergy focused on environmental effects. It may also be concluded that among all the factors of bioenergy production, water issues receives highest attention and least concern has been given to the soil erosion. In addition to the various negative effects on the surrounding by the bioenergy production, the hostile impacts on the environment varied greatly among plant types and land sources. Recognizing the suitable cultivation areas, types of proper bioenergy crops and optimum management practices may be useful to the both bioenergy production and environment. South-East Asia has a large potential of bioenergy production, but the production in this region has lagged behind and does not attain its growing energy consumption. It is always recommendable to do research on the leading countries in this field, accumulate better knowledge and identify the optimum solutions for the development of bioenergy in the developing nations. These types of study may give a lucid picture on designing the bioenergy development as well as environment safeguard.

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# Chapter 11
# Process Simulations of Chemical Looping Combustion for Mixtures of Coal and Biomass Using an Iron Based Oxygen Carrier—Part I

**Justin Lam, Ramesh K. Agarwal and Xiao Zhang**

**Abstract** Chemical-looping combustion (CLC) is a recent carbon capture technology that has shown great promise for almost pure $CO_2$ separation and capture in combustion of fossil fuels in power generation plants. In this paper, several process simulations of chemical-looping combustion are conducted using ASPEN Plus. The entire CLC process is modeled and validated against the experimental data using a mixture of biomass and coal and pure biomass as fuels. The effect of fuel reactor temperature on gas concentrations (namely $CO_2$, CO, $CH_4$ and $O_2$) in the fuel and air reactors, the conversion efficiency of carbonaceous gases, the char conversion efficiency, the carbon capture efficiency, and the energy output are investigated. It is found that increasing the fuel reactor temperature increases the $CO_2$ concentration in the fuel reactor for the biomass/coal mixture and decreases the $CO_2$ concentration for pure biomass in agreement with the experimental data. However, for the coal/biomass mixture and pure biomass, there is an increase in CO concentration in the fuel reactor. Poor oxygen transport capacity of the iron ore ($Fe_2O_3$) used as an oxygen carrier results in decrease in conversion efficiency for both types of fuels. However, both types of fuel showed an increase in carbon conversion efficiency since lesser amount of residual char made it past the fuel reactor as temperatures increased. Energy output for both fuels grew steadily with increase in fuel reactor temperature, but for pure biomass it stagnated between 760 and 800 °C and it peaked for biomass/coal mixture at 960 °C. Variations of gas concentrations in fuel and air reactors as well as energy output as a function of different mass fractions of coal and biomass are also obtained. The concentrations of $CO_2$, CO, and $CH_4$, and energy output all decrease with decreasing fraction of coal in the coal/biomass mixture.

**Keywords** Chemical looping combustion · Process simulation · Biomass · Coal · Carbon capture efficiency

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## 11.1 Introduction

Fossil fuels are increasingly burnt every day to sustain the energy needs of the modern society. The combustion of fossil fuels releases substantial amounts of $CO_2$ which is the primary greenhouse gas contributing to global warming. One technology that can capture $CO_2$ efficiently and economically is the Chemical-Looping Combustion (CLC). CLC captures almost pure, concentrated $CO_2$, in contrast to other means of $CO_2$ separation from flue gas such as the chemical absorption and physical adsorption (Cuadrat et al. 2012; Wang and Anthony 2008). CLC employs a dual fluidized bed system consisting of a fuel reactor and an air reactor with an oxygen carrier (OC) circulating between them which is used as a bed material in the fuel reactor to provide oxygen for combustion as shown in Fig. 11.1. The OC is used to transport oxygen from atmospheric air in the air reactor to the fuel reactor without direct contact between the air and the fuel. This is accomplished by means of a recycle redox reaction as given in Eq. (11.1) (Lyngfelt et al. 2001; Cuadrat et al. 2012).

$$2\mathrm{Me}_x\mathrm{O}_y \leftrightarrow 2\mathrm{Me}_x\mathrm{O}_{y-1} + \mathrm{O}_2 \tag{11.1}$$

The reduced OC from the fuel reactor is transferred to a second bed in the air reactor where it is oxidized by the atmospheric air before being returned to the fuel reactor to complete the loop (Cuadrat et al. 2012). Since there is no direct contact between the air and fuel, a high concentration of $CO_2$ and $H_2O$ is generated in the fuel reactor. $H_2O$ condenses easily, leaving pure $CO_2$ for geological sequestration or other applications. Thus CLC avoids costly air separation techniques needed for oxy-combustion or gas separation techniques required to purify $CO_2$ from the flue stream.

Biomass is a plentiful resource that can be used as fuel. A number of investigations have shown that biomass is a viable fuel that can be effectively used in CLC (Li et al. 2014, 2015; Khorshidi et al. 2013, 2014). Biomass co-firing can improve plant performance and lead to overall negative carbon emissions since more $CO_2$

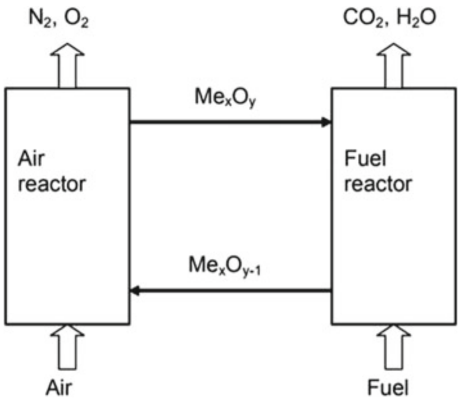


**Fig. 11.1** Schematic of chemical looping combustion

is consumed by the biomass during its creation and growth than released during its combustion (Basu et al. 2011). Additionally, it can decrease carbon capture costs and provide tax credits in many countries. Although coal/biomass co-combustion may be a near term solution for reducing $CO_2$ emissions; nevertheless it has great merit since fossil fuels such as coal and natural gas will remain the main source of power generation for next several decades before they are replaced by renewable energy sources. However, the survey of literature indicates that little has been published on using a mixture of biomass and coal for co-combustion in CLC fuel reactor.

Proper selection of the oxygen carrier can significantly affect the CLC performance. An ideal oxygen carrier should have properties such as high reactivity, high redox reaction rate, high conversion to $CO_2$ and $H_2O$, and high resistance to attrition and thermal sintering. Metals based oxides of Ni, Fe, Co, Cu, and Mn exhibit good properties as an oxygen carrier (Jerndal et al. 2011). Iron (Fe) based oxygen carriers are the cheapest, non-toxic and easily available among all others and therefore are widely used.

ASPEN Plus is a process simulation software code that simulates chemical processes at system level and has been very successful in modeling CLC (Sahir et al. 2014; Shen et al. 2007; Meng et al. 2015; Zhang et al. 2015). In this paper, a CLC process is modeled based on the published experimental data using different mixtures of coal and biomass as solid fuels including the pure biomass. The effect of fuel reactor temperature on gas concentrations, conversion efficiency of carbonaceous gases, carbon conversion efficiency, and energy output are obtained from ASPEN Plus. The effects of varying mass fractions of coal and biomass on gas concentration and energy output are also investigated.

## 11.2 Process Simulation and Its Validation with Experimental Data

The process simulations corresponding to the experiments of Gu et al. (2011) (Fig. 11.2) are conducted using ASPEN Plus. Some of the input information used in the present simulations is obtained from Kevat et al. (unpublished). The CLC process is simulated as shown in the flow sheet in Fig. 11.3. The air reactor is a high velocity circulating fluidized bed and the fuel reactor is a spouted fluidized bed.

The two fuels used in the simulations are bituminous coal and biomass (sawdust). The proximate and ultimate analysis of coal and biomass is given in Table 11.1.

Hematite ($Fe_2O_3$) is used as the oxygen carrier. The size ranges of the fuel and oxygen carrier particles are 200–450 $\mu$m and 100–300 $\mu$m respectively, and both are used at atmospheric conditions. The reactor temperature was varied from 900 to 980 °C when the biomass/coal mixture was used, and was varied from 720 to 930 °C when pure biomass was used. The various process models used in ASPEN Plus are shown in the flow sheet in Fig. 11.3 and are summarized in Table 11.2. The pyrolysis and devolatilization of coal and biomass takes place in RYIELD reactors,

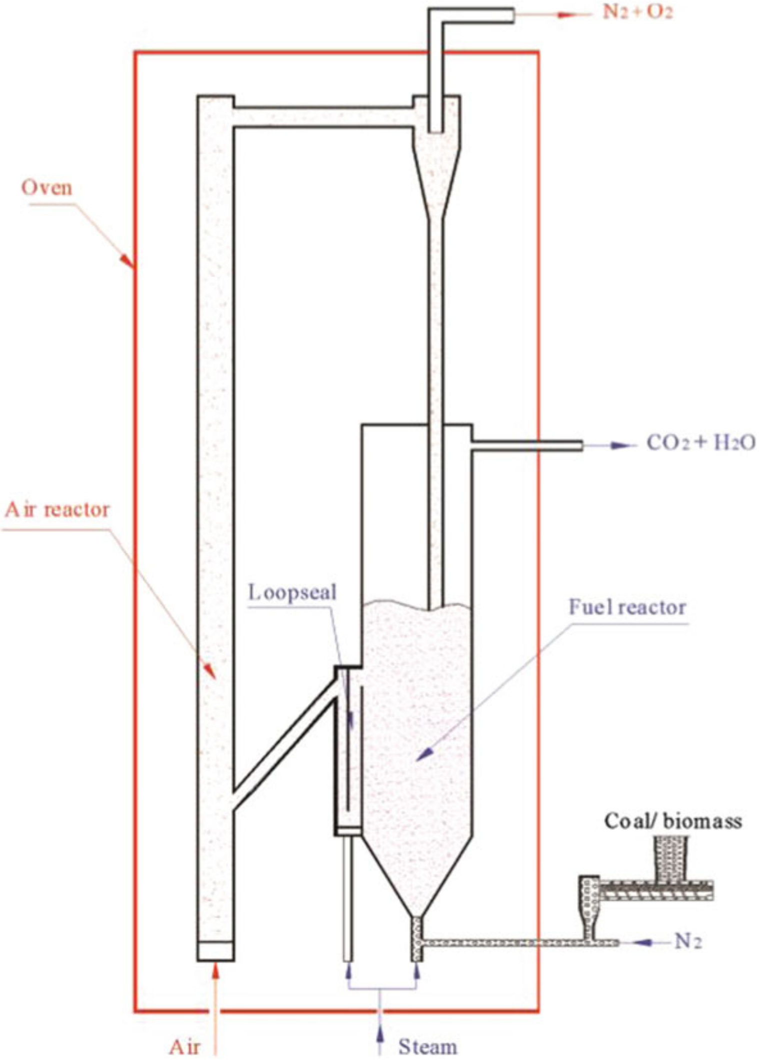


**Fig. 11.2** Schematic view of experimental setup (Gu et al. 2011)

DECOMP-1 and DECOMP-2, respectively. The products of the RYIELD reactors are moved to the RGIBBS reactor for residual char gasification by steam. The products from RGIBBS reactor are transferred to the first RSTOIC block, FUEL-R, where the combustion of generated flue gases with the oxygen carrier produces $CO_2$, $H_2O$, and $Fe_3O_4$. The four reactors mentioned above together constitute the fuel reactor of the experimental setup. This is because the ASPEN Plus does not have a single component that performs all the required functions. After combustion in the fuel reactor, reduced oxygen carrier particles ($Fe_3O_4$) proceed to the second RSTOIC

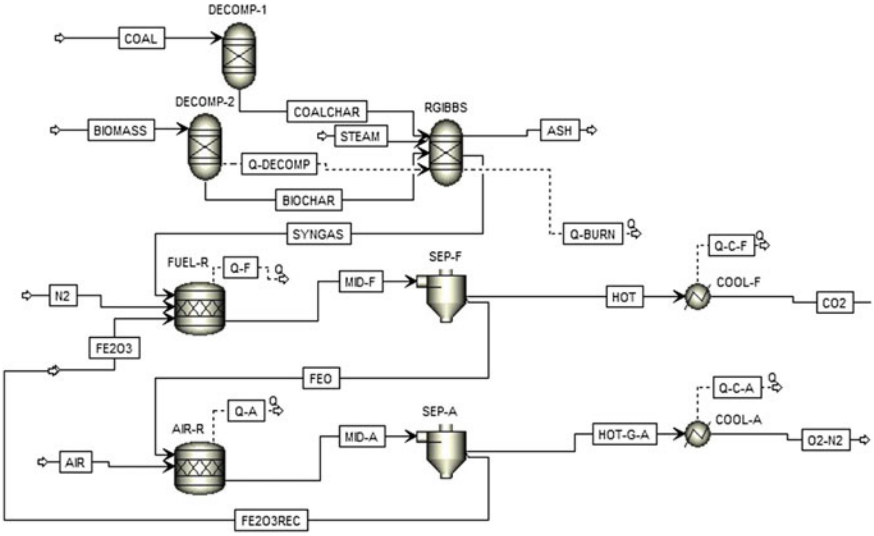


**Fig. 11.3** Flowsheet of CLC process in Aspen Plus

**Table 11.1** Proximate and ultimate analysis of coal and sawdust (Gu et al. 2011)

| | Sawdust | Coal |
|---|---|---|
| *Proximate analysis* (wt%) | | |
| Moisture | 14.28 | 6.01 |
| Volatile matter | 74.61 | 35.1 |
| Fixed carbon | 10.1 | 54.13 |
| Ash | 1.01 | 4.76 |
| *Ultimate analysis* (wt%) | | |
| Carbon | 37.43 | 69.57 |
| Hydrogen | 5.61 | 4.3 |
| Oxygen | 40.55 | 13.81 |
| Nitrogen | 1.02 | 1.03 |
| Sulfur | 0.1 | 0.52 |
| LHV (MJ/kg) | 14.5 | 27.1 |

block, AIR-R, for oxidation using air with a mass fraction of $O_2$ of 0.21. This makes up the air reactor of the experimental setup in ASPEN Plus.

Oxidized particles from air reactor move back to the fuel reactor to start a new cycle. In a CLC system with interconnected fluidized bed reactors, not all char particles are converted, and the remaining particles from the fuel reactor go through the air reactor. The exit flue gas steam of the air reactor, therefore, has unreacted $O_2$, $N_2$, and $CO_2$. Raising the fuel reactor temperature decreases the amount of unconverted char, causing a lower $CO_2$ concentration in the air reactor.

**Table 11.2** Process models used in various parts of the CLC process in ASPEN Plus

| Name | Model | Function | Reaction formula |
|---|---|---|---|
| DECOMP-1 | RYIELD | Coal devolatilization/pyrolysis | Coal → volatile matter + char |
| DECOMP-2 | RYIELD | Biomass devolatilization/pyrolysis | Biomass → volatile matter + char |
| RGIBBS | RGIBBS | Gasification | Char + volatile matter → $CO_2 + H_2O$ |
| FUEL-R | RSTOIC | OC reduction reactions | $H_2 + 3Fe_2O_3 \rightarrow H_2O + 2Fe_3O_4$<br>$CO + 3Fe_2O_3 \rightarrow CO_2 + 2Fe_3O_4$<br>$CH_4 + 12Fe_2O_3 \rightarrow 8Fe_3O_4 + H_2O + CO_2$ |
| AIR-R | RSTOIC | OC oxidation reaction | $2Fe_3O_4 + 0.5O_2 \rightarrow 3Fe_2O_3$ |

For the purpose of validation, the CLC process model was simulated using the input values from the simulation done by Kevat et al. (unpublished). The input values for various streams in ASPEN Plus are presented in Table 11.3.

**Table 11.3** Input values in ASPEN Plus corresponding to the simulation of Kevat et al. (unpublished), which are based on the experiment of Gu et al. (Gu et al. 2011)

| Component | Temperature (°C) | Pressure (atm) | Flowrate |
|---|---|---|---|
| *Mixture of biomass/coal* | | | |
| Coal | 25 | 1 | 60 gm/hr |
| Biomass | 25 | 1 | 60 gm/hr |
| Steam | 200 | 2 | 2.5 gm/min |
| $N_2$ | 200 | 2 | 0.27 $m^3$/hr |
| Air | 75 | 1/25 | 0.84 $m^3$/hr |
| $Fe_2O_3$ | Fuel reactor temp | 1 | 0.132 $m^3$/hr |
| *Pure biomass* | | | |
| Coal | 0 | 0 | 0 |
| Biomass | 25 | 1 | 70 gm/hr |
| Steam | 200 | 2 | 1.1 gm/min |
| $N_2$ | 200 | 2 | 0.66 $m^3$/hr |
| Air | 75 | 1.25 | 0.72 $m^3$/hr |
| $Fe_2O_3$ | Fuel reactor temp | 1 | 0.525 $m^3$/hr |

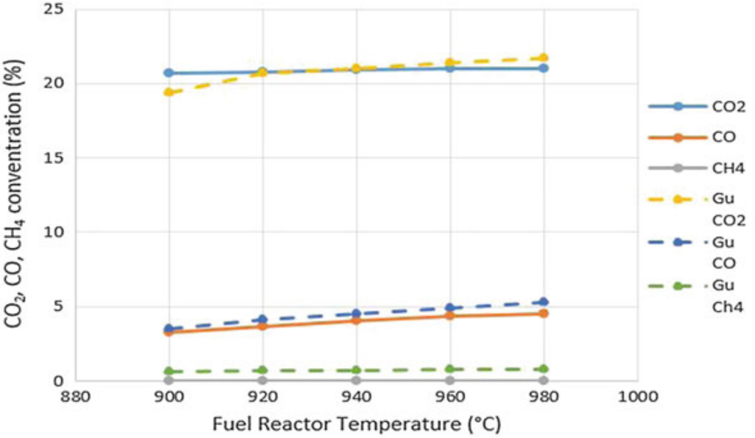
## 11.3 Results and Discussion

### *11.3.1 Gas Concentrations*

#### 11.3.1.1 Biomass/Coal Mixture (1/1 Ratio)

The effect of fuel reactor temperature on gas concentrations is presented in Fig. 11.4 and is compared to the experimental results of Gu et al. (2011) when a 1/1 ratio of biomass and coal mixture is used as fuel. The concentrations of $CO_2$ and CO

(a) Gas Concentrations in Fuel Reactor



(b) Gas Concentrations in Air Reactor

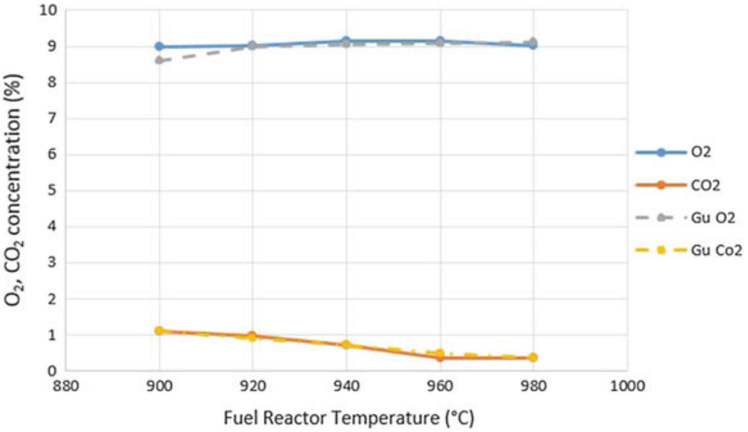


**Fig. 11.4** Effect of fuel reactor temperature on gas composition in **a** fuel reactor and **b** air reactor with biomass/coal mixture as fuel

in the fuel reactor increase when the fuel reactor temperature increases. The concentration of $CH_4$ is independent of the fuel reactor temperature. Biomass and coal both volatilize at a lower temperature, therefore increasing the fuel reactor temperature may accelerate syngas production consisting mostly of CO and $H_2$, leading to less time for oxidation of the fuel. This, in conjunction with low oxygen transport capacity of the OC, leads to an increase in CO concentration. The products of coal and biomass interact with OC more as the temperature increases causing improved oxidation and since there is more CO, there is a higher concentration of $CO_2$. In the air reactor, as fuel reactor temperature increases, $O_2$ concentration remains about the same and $CO_2$ concentration decreases. $CO_2$ is the product of residual char getting through the fuel reactor. At higher temperatures, more char is converted in the fuel reactor reducing the amount of $CO_2$.

#### 11.3.1.2 Pure Biomass

Figure 11.5 shows the effect of fuel reactor temperature on gas concentrations compared to the experimental results of Gu et al. (2011) when pure biomass is used as fuel. Fuel reactor temperature is varied from 720 to 930 °C. As the temperature increases, $CO_2$ concentration decreases, but the CO concentration increases. $CH_4$ concentration is not changed. The difference in the $CO_2$ concentration for biomass/coal mixture and pure biomass is due to the fuel reactivity (Gu et al. 2011). The biomass (sawdust) used contains a high percentage of volatile, as can be seen in Table 11.1, and is thoroughly gasified at a relatively low temperature, whereas the gasification of coal is harder even at a much higher temperature. Therefore, temperature does not have significant effect on the gasification of biomass within the considered temperature range of 720–930 °C. When CO concentration is low, the transformation of $Fe_2O_3$ to $Fe_3O_4$ tends to be favored, leading to a lower $CO_2$ concentration (Shen et al. 2009). For pure biomass, $CO_2$ concentration is based mostly on these thermodynamic factors while for the biomass/coal mixture, $CO_2$ concentration is primarily based on the gasification properties of coal to some extent.

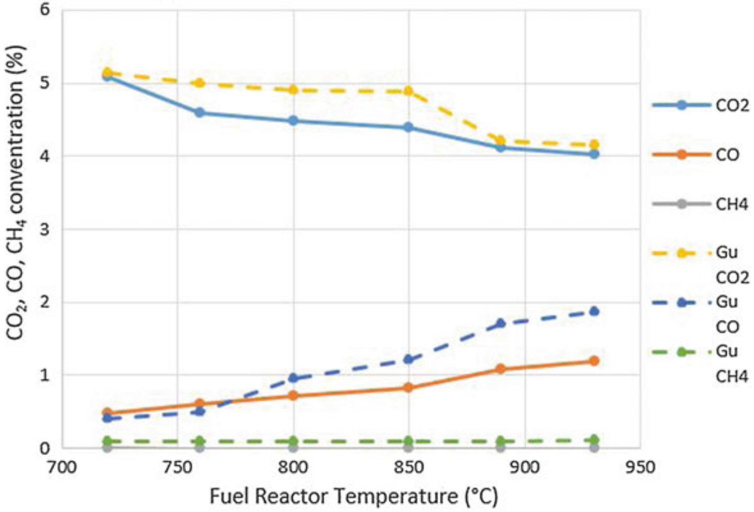
### *11.3.2 Conversion and Carbon Capture Efficiency*

The conversion efficiency is defined as the amount of carbonaceous gases converted to $CO_2$ in the fuel reactor given as (Gu et al. 2011):

$$\eta_{\text{conversion}} = \frac{W_{\text{CO}_2,\text{FR}}}{W_{\text{CO}_2,\text{FR}} + W_{\text{CO,FR}} + W_{\text{CH}_4,\text{FR}}} \tag{11.2}$$

where $W_{\text{CO}_2,FR}$, $W_{\text{CO},FR}$, and $W_{\text{CH}_4,FR}$ denote the volume percentages of $CO_2$, CO, and $CH_4$ in the fuel reactor, respectively. The definition in Eq. (11.2) assumes that only $CO_2$, CO, and $CH_4$ are carbonaceous gases. Figures 11.6a and 11.7a show the effects

(a) Gas Concentrations in Fuel Reactor



(b) Gas Concentrations in Air Reactor

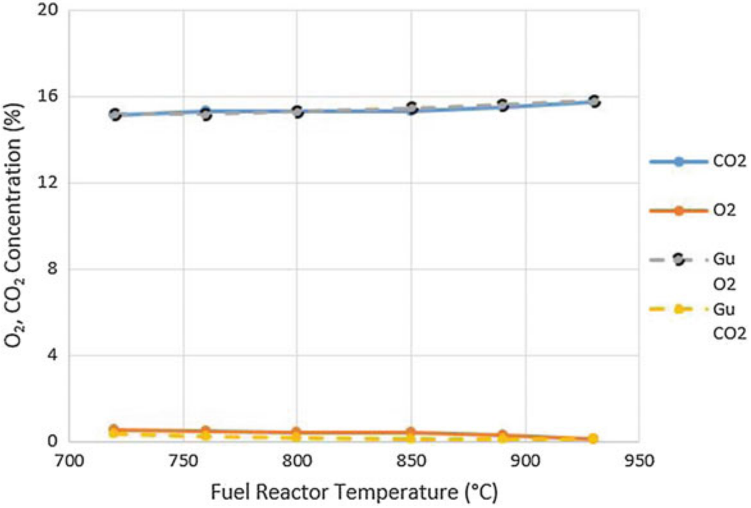
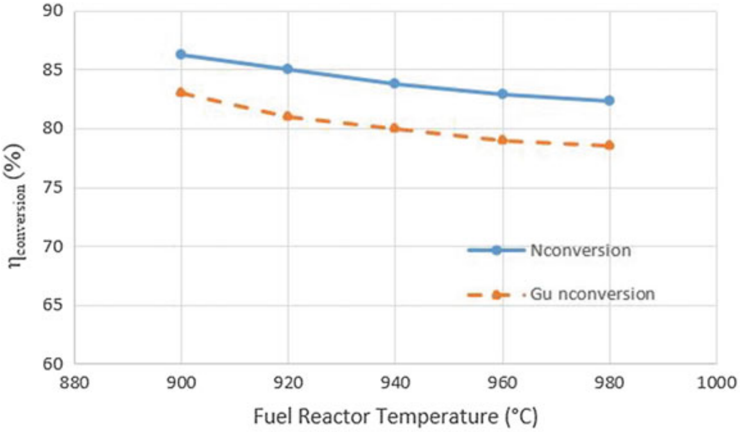


**Fig. 11.5** Effect of fuel reactor temperature on gas composition in **a** fuel reactor and **b** air reactor with pure biomass as fuel

(a) Conversion Efficiency of 1/1 Ratio of Coal/Biomass Mixture



(b) Carbon Capture Efficiency of 1/1 Ratio of Coal/Biomass Mixture

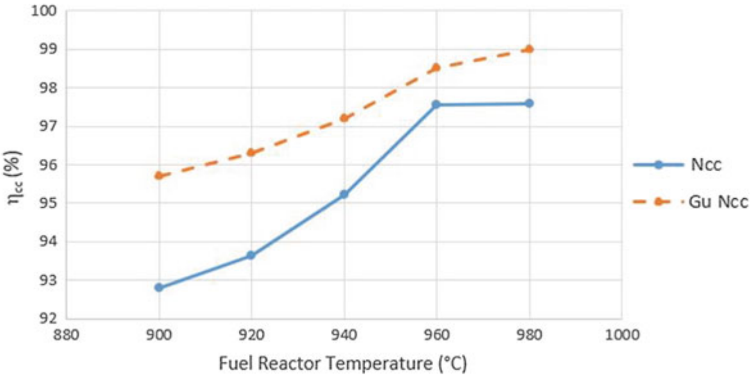


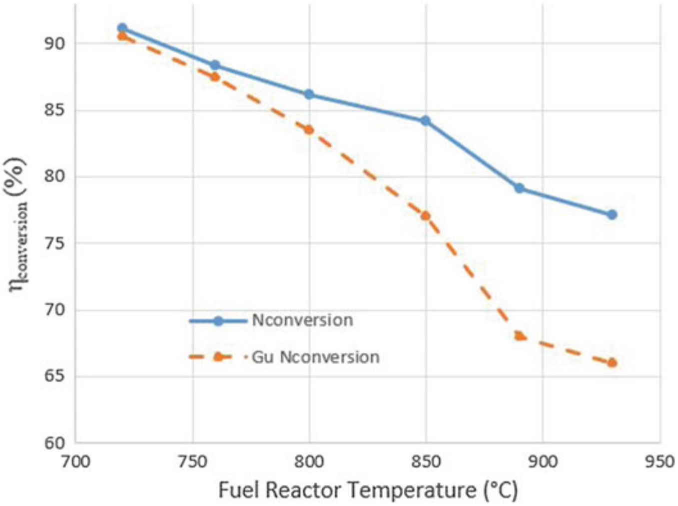
**Fig. 11.6** Effect of fuel reactor temperature on **a** conversion efficiency of carbonaceous gases and **b** carbon capture efficiency for 1/1 ratio of coal/biomass mixture

of fuel reactor temperature on conversion efficiency for the biomass/coal mixture and pure biomass respectively. For both biomass/coal mixture and pure biomass, $\eta_{\text{conversion}}$ decreases as fuel reactor temperature increases. Due to the endothermic nature of the char gasification reaction, at higher temperatures, production of carbonaceous gases increases. The OC has a poor oxygen transport capacity and as a result cannot keep on oxidizing an increasing amount of carbonaceous gases. This leads to lower conversion efficiency. $\eta_{\text{conversion}}$ decreases more rapidly for pure biomass due to thermodynamic factors discussed earlier.

The carbon capture efficiency is defined as (Mendiara et al. 2013):

$$\eta_{cc} = \frac{\left[F_{\text{CO}_2,FR} + F_{\text{CO},FR} + F_{\text{CH}_4,FR}\right]_{out}}{\left[F_{\text{CO}_2,FR} + F_{\text{CO},FR} + F_{\text{CH}_4,FR} + F_{\text{CO}_2,AR}\right]_{out}} \tag{3}$$

(a) Conversion Efficiency of Pure Biomass



(b) Carbon Capture Efficiency of Pure Biomass

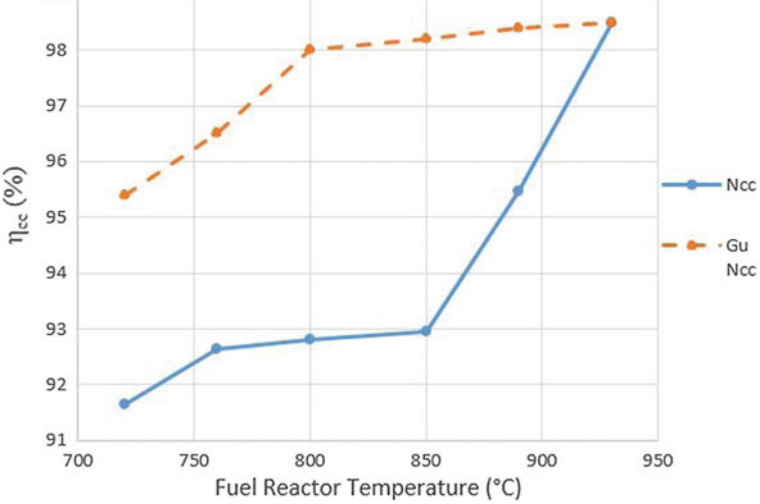


**Fig. 11.7** Effect of fuel reactor temperature on **a** conversion efficiency of carbonaceous gases and **b** carbon capture efficiency for pure biomass

where $F_{\mathrm{co}_2,AR}$ denotes the volume percentage of $CO_2$ in the air reactor. Figures 11.6b and 11.7b show the effect of fuel reactor temperature on carbon capture efficiency. As discussed before, higher fuel reactor temperature leads to increased char conversion, which means less char reaches the air reactor. Therefore, a decrease in $CO_2$ concentration in the air reactor would increase the carbon capture efficiency, for biomass, $\eta_{\mathrm{cc}}$ increases steadily until 850 °C, after which it increases rapidly. For the biomass/coal mixture, $\eta_{\mathrm{cc}}$ increases until 960 °C and then stagnates, suggesting a highest possible maximum efficiency. Carbon capture efficiency is dependent on the residual char combusted in the air reactor. Because the CLC system is made up of interconnected fluidized beds, some of the residual char is carried by the OC particles into the air reactor. As shown in Figs. 11.4 and 11.5, there was an increasing amount of $CO_2$ found in the fuel reactor, but a decreasing amount of $CO_2$ in the air reactor, resulting in an increase in $\eta_{\mathrm{cc}}$ for both types of fuels. The difference in the carbon capture efficiency of the two types of fuels is due to differences in the fuel reactivity of the two types of fuel explained earlier.

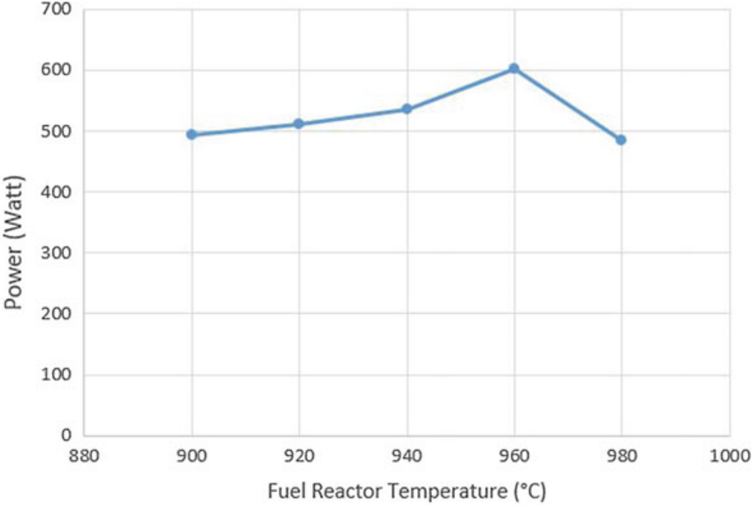
### *11.3.3 Energy Output*

Figure 11.8a and b show how the fuel reactor temperature affects the energy output. For 1/1 ratio of biomass/coal mixture, energy output peaks at 601.5 W. Higher temperatures seem to decrease the energy output. This could be explained by the fact that by raising the fuel reactor temperature beyond a certain threshold will just consume more energy by the fuel reactor, resulting in a lower total energy output. As shown in Fig. 11.6b, as the fuel reactor temperature increases from 960 to 980 °C, $\eta_{\mathrm{cc}}$ stagnates and at the same time energy output decreases as shown in Fig. 11.8a. For pure biomass, energy increases steadily except between 760 and 800 °C. In Fig. 11.7b, $\eta_{\mathrm{cc}}$ stagnates between 760 and 850 °C. These energy trends almost follow the same pattern as carbon capture efficiency indicating that they might be related.

### *11.3.4 Gas Concentrations and Energy Output for Various Mass Fractions of Coal and Biomass*

The previous sections studied in detail the gas concentrations, conversion and carbon capture efficiencies, and the total energy output for a 1/1 mixture of coal and biomass and pure biomass corresponding to the experimental conditions of Gu et al. (2011); the results were also validated against the experimental data. In this section, we consider different mass fractions of coal and biomass and evaluate their performance with respect to the above three outputs. In all simulations, fuel reactor temperature of 900 °C was used and 0.94 $m^3/h$ of $N_2$ flow was employed. Total mass flow of the

(a) Energy Output for 1/1 Ratio of Coal/Biomass Mixture



(b) Energy Output for Pure Biomass

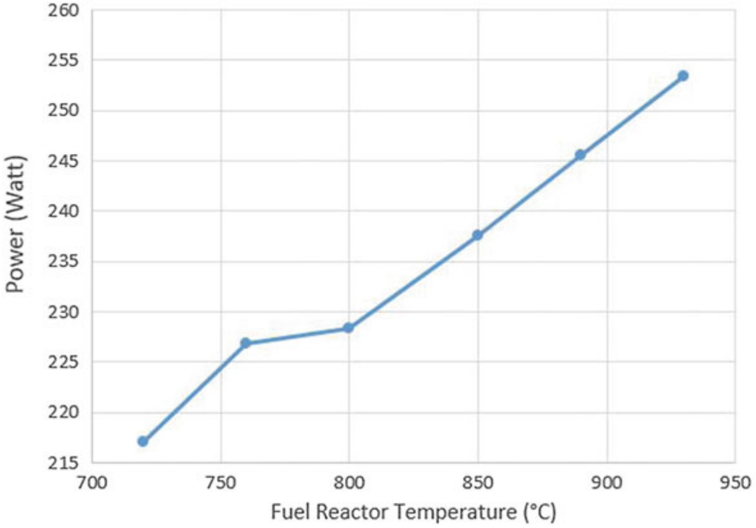
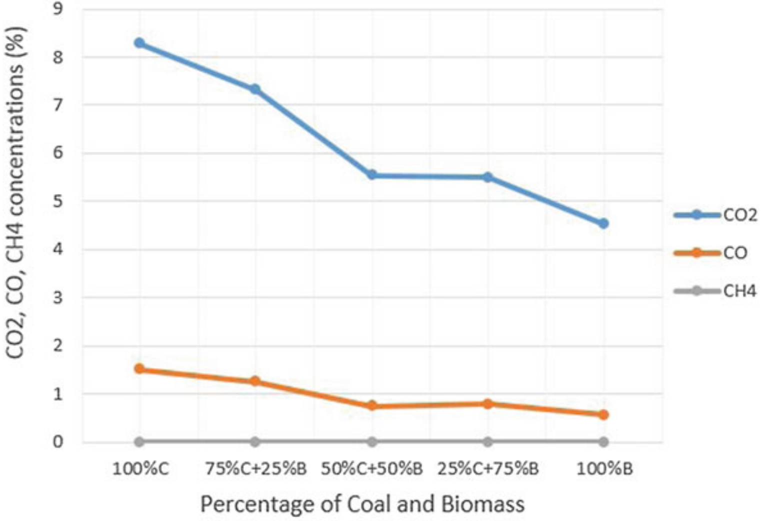


**Fig. 11.8** Energy output of **a** biomass/coal mixture and **b** pure biomass for various fuel reactor temperatures

mixture always added up to 100 gm/hr. All other parameters were adjusted according the biomass/coal flow rate.

Figure 11.9 shows the effect of different mass fractions of coal and biomass on gas concentrations. As the percentage of biomass increases, percentage of $CO_2$ and CO in the fuel reactor decreases due to factors discussed earlier. $CO_2$ decreases because

(a) Gas Concentrations in Fuel Reactor



(b) Gas Concentrations in Air Reactor

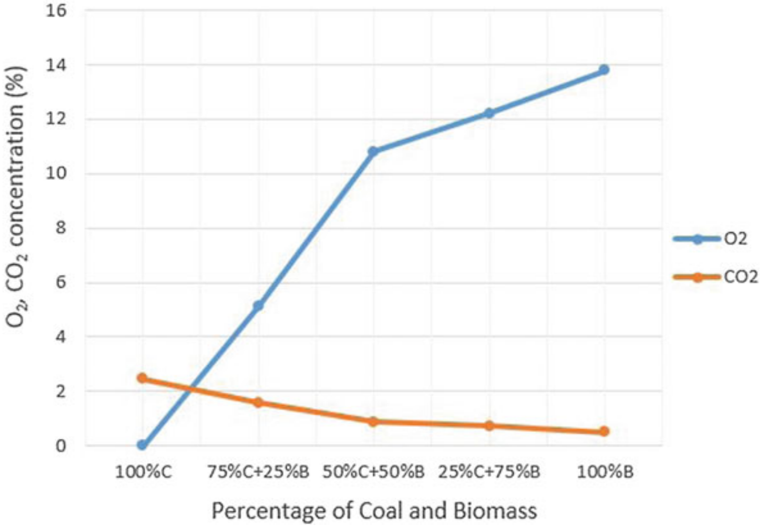


**Fig. 11.9** Effect of using different mass fractions of coal and biomass on gas concentrations in the **a** fuel reactor and **b** air reactor

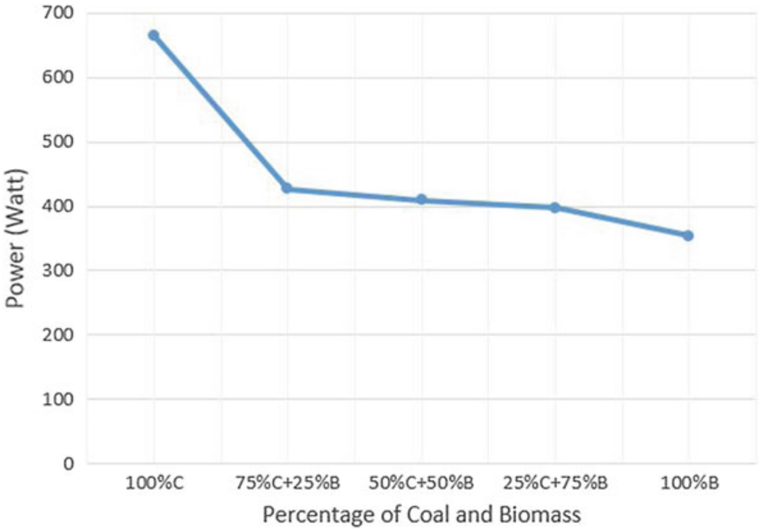


**Fig. 11.10** The effect of different mass fractions of coal and biomass on energy output

conversion efficiency rate of biomass is very low at the temperature used, 900 °C, whereas coal's conversion efficiency rate is relatively high. $O_2$ concentration in the air reactor increases as the biomass fraction increases because when more biomass is used, less OC particles are reduced by CO in the fuel reactor. When these particles are moved to the air reactor, less oxygen is consumed by the reduced OC particles as there are less of them. At 100% coal, there is 0% oxygen in the air reactor because all the OC is completely consumed. $CO_2$ concentration in the air reactor decreases as more biomass is added due to biomass' higher carbon conversion efficiency at 900 °C.

Figure 11.10 shows the effect of different mass fractions of coal and biomass on energy output. As expected, at 100% coal, there is lot more energy output compared to when some amount of biomass is added. Adding more biomass only decreases the energy output by a relatively small amount.

## 11.4 Conclusions

In this paper, a laboratory scale experiment on CLC was simulated using ASPEN Plus. In the experiment, a 1/1 ratio of biomass/coal mixture and pure biomass were used as solid fuels. The experimental results considered the effect of fuel reactor temperature on gas concentrations in both the fuel and air reactors. The process simulations validated the experimental results for gas concentrations, the conversion efficiency, and carbon capture efficiency. When using a biomass/coal mixture as fuel, $CO_2$ and CO concentration in the fuel reactor increased and $CO_2$ in the air reactor decreased as fuel reactor temperature increased. When pure biomass was used, $CO_2$ concentration decreased in both the fuel and air reactors while CO concentration increased with increase in the fuel reactor temperature. Due to poor oxygen transport capacity of the iron based oxygen carrier hematite, the conversion efficiency decreased for both the biomass/coal mixture and the pure biomass as the fuel reactor temperature increased. Carbon capture efficiency increased for both types of fuels (mixture and pure biomass) as the fuel reactor temperature increased. Energy output for both types of fuels increased with increase in fuel reactor temperature; however the energy output decreased for biomass/coal mixture beyond 960 °C temperature of fuel reactor. Results also showed that higher mass fraction of biomass produces less $CO_2$, but also a lot less energy than 100% coal as expected.

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# Chapter 12
# Process Simulation of Chemical Looping Combustion for a Mixture of Biomass and Coal with Various Oxygen Carriers—Part II

**Kartik Deshpande, Ramesh K. Agarwal, Ling Zhou and Xiao Zhang**

**Abstract** Chemical Looping Combustion (CLC) is an emerging technology that has shown great promise for the capture of almost pure $CO_2$ in combustion of fossil fuels in power plants. In this chapter, the CLC process is modeled in ASPEN Plus and then validated using experimental data from the combustion of three types of biomass as fuels, and Hematite ($Fe_2O_3$) as an oxygen carrier (OC). The three types of biomass used in the simulation are Pine Sawdust, Almond Shells, and Olive Stones. The effect of the fuel reactor temperature on gas concentrations (namely $CO_2$, CO, $H_2$, and $CH_4$) in the fuel reactor, and the carbon capture efficiency are examined. It is found that all three biomass types have very high carbon capture efficiencies, with Pine Sawdust and Almond Shell reaching nearly 100% capture efficiency for temperatures equal to or greater than 950 °C, while Olive Stones reaches a capture efficiency of nearly 100% at temperatures greater than 980 °C. It is also found that fluctuations in $CO_2$ concentrations in the fuel reactor vary across the three biomass types. The effect of using $Mn_2O_3$ as the OC in place of $Fe_2O_3$ was also investigated. It was found that switching the oxygen carrier to $Mn_2O_3$ caused the concentrations of CO and $H_2$ in the fuel reactor to decrease slightly, while the concentration of $CO_2$ increased slightly. Furthermore, changing the OC to $Mn_2O_3$ had no effect on the carbon capture efficiency. Additionally, a mixture of coal and biomass at 895 °C was used with each of the two oxygen carriers, and the results were compared. It was found that the system using $Fe_2O_3$ had a greater power output than the one using $Mn_2O_3$, and that power output increased as the fraction of coal in the coal-biomass mixture increased.

**Keywords** Chemical looping combustion · Process simulation · Biomass · Coal · Carbon capture efficiency

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## 12.1 Introduction

Global climate change and greenhouse gas emissions are the important issues of international concern (Schuur et al. 2015). $CO_2$ is a byproduct of fossil fuel combustion and is released into the atmosphere from power plants and other manufacturing plants such as steel, cement, fertilizer etc. which is very detrimental to the environment as it contributes to global warming. To mitigate global warming, the 2015 Paris Agreement announced an agenda to limit average global temperature increases to 2 °C by greatly decreasing the worldwide greenhouse gas emissions (Schuur et al. 2015; Lyngfelt 2014). To attain this objective, it was proposed that existing processes for carbon capture and sequestration must be improved to reduce $CO_2$ emissions from large power plants. Various methods of combustion have been tested, but one of the most efficient among them has been shown to be Chemical Looping Combustion (CLC). CLC has been shown to capture almost pure, concentrated $CO_2$, in contrast to other means of $CO_2$ separation from flue gas, such as the oxy-combustion, chemical absorption, and physical absorption (Linderholm et al. 2016; Lyngfelt and Leckner 2015). In addition, CLC process requires less energy to capture $CO_2$ and costs less than the alternative methods, thus making CLC a very promising technology for carbon capture and its subsequent sequestration (Velasco-Sarria et al. 2018).

CLC systems consist of an air reactor and a fuel reactor. A solid oxygen carrier (OC) is used in the fuel reactor to provide the oxygen for combustion in the fuel reactor. The oxygen carrier is reduced in the fuel reactor, and then is sent back to the air reactor to be oxidized. Once re-oxidized, it is sent back to the fuel reactor and the process continues. This process is known as the recycle redox reaction and is given in Eq. (12.1) (Banerjee and Agarwal 2015; Meng et al. 2015).

$$2\mathrm{Me}_x\mathrm{O}_y \leftrightarrow 2\mathrm{Me}_x\mathrm{O}_{y-1} + \mathrm{O}_2 \tag{12.1}$$

Choosing the proper oxygen carrier can have a substantial effect on the performance of a CLC system. For an oxygen carrier to work effectively, it must have a high reactivity and redox rate, as well as high resistance to thermal sintering and attrition. Typically, metal oxidizers are used as oxygen carriers; the most commonly used metal oxidizer is Iron (III) Oxide ($Fe_2O_3$). Various other metals have been shown to exhibit the properties of an effective oxygen carrier, such as Mn, Cu, Co, and Ni (Mayer et al. 2018; Costa et al. 2017; Alalwan et al. 2017, 2018; Linderholm et al. 2017). However, iron-based oxygen carriers are low-cost, and as such iron-based oxygen carrier such as Hematite ($Fe_2O_3$) is the most commonly used (Alalwan et al. 2018; Linderholm et al. 2017). CLC allows combustion to occur in a nitrogen free atmosphere, which prevents the formation of $NO_x$ gases. In addition, the separation of the air reactor and fuel reactor allows that there is no direct contact between the atmospheric air and fuel, and therefore it allows for higher concentration of $CO_2$ and $H_2O$ to be produced in the fuel reactor. $H_2O$ can be easily condensed and removed, which allows for almost pure $CO_2$ to be easily captured.

Bio-energy with $CO_2$ capture and storage (BECCS) opens the possibility for negative $CO_2$ emissions involving the removal of $CO_2$ already emitted into the atmosphere (Adánez-Rubio et al. 2018). Biomass is a very plentiful resource, and various studies have shown that it can be used as an effective fuel source. Additionally, more $CO_2$ is consumed in the creation of biomass than released during its combustion, which leads to overall negative carbon emissions. Shen et al. (2009) used pine sawdust as biomass for CLC in the 10 kWth unit, and discussed the influence of the fuel reactor temperature on the $CO_2$ capture and combustion efficiency. Adánez-Rubio et al. (2014) used milled pine wood chips as biomass in a 1.5 kWth chemical looping with oxygen uncoupling (CLOU) process. Biomass combustion was completed to form $CO_2$ and $H_2O$ without the presence of any unburnt material including tars. High carbon capture efficiencies were achieved using very low oxygen carrier inventories and without a carbon separation unit. Sarvaramini and Larachi (2014) used Birch wood as fuel for CLC test; the results showed that the volatiles were burnt over solid iron oxide oxygen carriers between 400 and 600 °C converting up to 99% of volatile carbon into $CO_2$. Schmitz used different biomass fuels in CLC, mainly biochar of different sizes and black wood pellets and achieved the highest carbon capture efficiency of 99 and 100% in the 10 and 100 kWth units, respectively. Several system studies have demonstrated the high potential of biomass in CLC, which could enable $CO_2$ capture and thus result in overall negative $CO_2$ emissions at the lowest possible cost (Schmitz and Linderholm 2018).

The present work aims at further contributing to the knowledge of biomass based CLC by using process simulation. First, the ASPEN Plus process simulation results are validated by using the experimental data from a 0.5 kWth unit CLC power plant, which employs three types of biomass, namely the Pine Sawdust, the Almond Shells and the Olive Stones. Then the effects of using $Mn_2O_3$ and $Fe_2O_3$ as oxygen carrier are simulated and compared. The influence of the fuel reactor temperature on the results is evaluated, including the gas concentrations, carbon capture efficiency and power output.

## 12.2 Materials and Methods

ASPEN Plus software was used to conduct the process simulation; it is widely used software for modeling an entire power plant at an industrial scale and allows for the prediction of performance of CLC process based power plant a priori before the full-scale deployment (Zhou et al. 2013; Yan et al. 2015; Kevat and Banerjee 2018). The experimental set up used by Mendiara et al. (2018) shown in Fig. 12.1 was used to establish a corresponding process model and flow sheet in ASPEN Plus. The experimental set up consisted of two fluidized bed reactors connected by a fluidized loop seal used to prevent the mixing of gases between the two fluidized bed reactors as shown in Fig. 12.1.

In ASPEN Plus, the flowsheet was setup as “Solids with metric units,” and the MIXCINC stream class was assigned to the simulation. The MIXCINC stream class

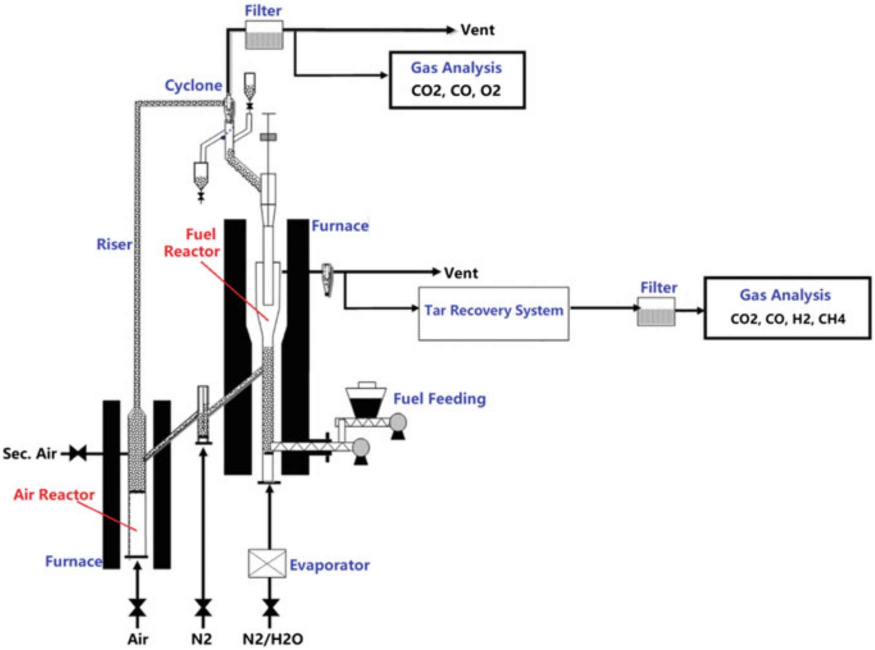

**Fig. 12.1** Schematic view of apparatus used in Mendiara et al.'s experiment (Mendiara et al. 2018)

allows for both conventional and non-conventional streams to be used in the simulation. The non-conventional stream class was used to model the biomass, while the conventional stream class was used to model all other streams in the simulation. For simplicity, the IDEAL base calculation method was selected, and this allowed for calculations to be done using the Ideal Gas Law. Due to inherent limitations in the ASPEN Plus software, multiple blocks were used to model the fuel reactor. For the fuel reactor, a RYIELD reactor was first used to model the pyrolysis and devolatilization of the fuel. The products of the RYIELD reactor were moved to RGIBBS reactor which was used to model the gasification of the decomposed fuel. The products of the RGIBBS reactor were then moved to RSTOIC reactor which was used to simulate the fuel combustion. These three blocks together represent the fuel reactor. The air reactor was modeled as a single RSTOIC reactor. An overview of these components and their respective functions is shown in Table 12.1. The model constructed in ASPEN Plus is shown in Fig. 12.2.

The first part of this research was the validation of the ASPEN Plus process model by comparing its results against the experimental data obtained by Mendiara et al. (2018). Three biomass types were used in the experimental data. These three biomass types were Pine Sawdust, Almond Shells, and Olive Stones. The biomass was modeled in ASPEN Plus as a non-conventional solid using ultimate and proximate analyses provided by Mendiara et al. (2018). These values are shown below in Table 12.2.

**Table 12.1** Process models used in various parts of the CLC process in ASPEN Plus

| Name | Model | Function | Reaction |
|---|---|---|---|
| DECOMP-1 | RYIELD | Biomass devolatilization and pyrolysis | Biomass → Volatile matter + Char |
| RGIBBS | RGIBBS | Gasification | Char + Volatile matter → $CO_2$ + $H_2O$ |
| FUEL-R | RSTOIC | OC reduction reactions and further combustion | Char (mainly C) + $H_2O \rightarrow H_2 + CO$<br>Char (mainly C) + $CO_2 \rightarrow 2CO$<br>$CO + Fe_2O_3 \rightarrow CO_2 + 2Fe_3O_4$<br>$H_2 + 3Fe_2O_3 \rightarrow H_2O + 2Fe_3O_4$<br>$CH_4 + 12Fe_2O_3 \rightarrow 2H_2O + CO_2 + 8Fe_3O_4$<br>$CO + H_2O \leftrightarrow CO_2 + H_2$ |
| AIR-R | RSTOIC | OC oxidation reaction | $0.5O_2 + 2Fe_3O_4 \rightarrow 3Fe_2O_3$<br>C (unconverted char) + $O_2 \rightarrow CO_2$ |

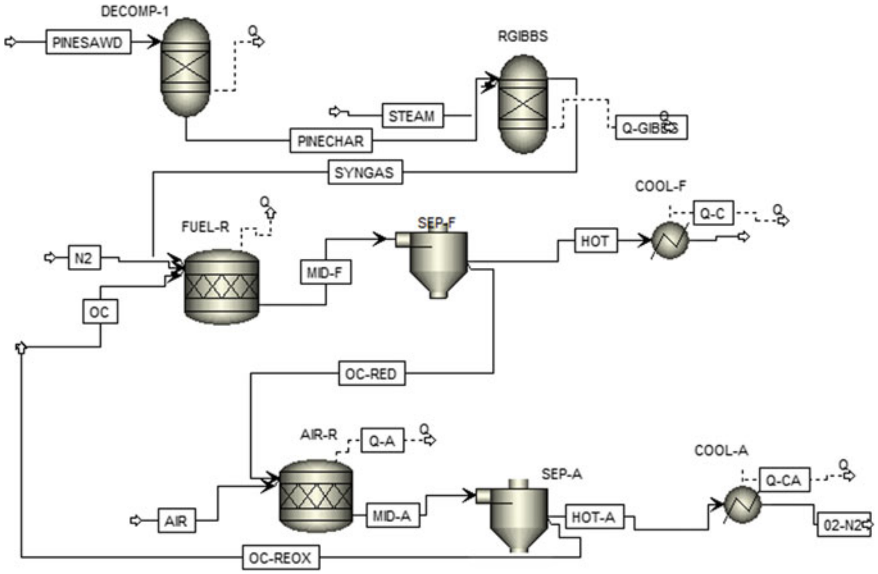

**Fig. 12.2** Flowsheet of experimental set up in ASPEN Plus

**Table 12.2** Ultimate and proximate analysis of the three biomass types (Mendiara et al. 2018)

| | Pine sawdust | Olive stone | Almond shell |
|---|---|---|---|
| *Ultimate analysis* (wt. %) | | | |
| Carbon | 51.3 | 46.5 | 50.2 |
| Hydrogen | 6.0 | 4.8 | 5.7 |
| Nitrogen | 0.3 | 0.2 | 0.2 |
| Sulfur | 0.0 | 0.0 | 0.0 |
| Oxygen | 37.8 | 38.3 | 40.5 |
| LHV (kJ/kg) | 19158 | 16807 | 18071 |
| *Proximate analysis* (wt. %) | | | |
| Moisture | 4.2 | 9.4 | 2.3 |
| Ash | 0.4 | 0.8 | 1.1 |
| Volatile matter | 81.0 | 72.5 | 76.6 |
| Fixed carbon | 14.4 | 17.3 | 20.0 |

In Mendiara et al.'s experiment (Mendiara et al. 2018), an iron ore known as Tierga was used as the oxygen carrier. Based on the data provided by Mendiara et al., Tierga ore is primarily a Hematite ($Fe_2O_3$) consisting of 76.5% Hematite by mass, with the remainder of the ore being a mixture of Silica ($SiO_2$), Aluminum Oxide ($Al_2O_3$), Calcium Oxide (CaO), and Magnesium Oxide (MgO) (Mayer et al. 2018). The oxygen carrier stream in the simulation included these impurities in order to simulate the experiment as accurately as possible. In addition, the biomass and OC flow rates were varied in Mendiara et al.'s experiment to maintain optimal OC to fuel ratio. Table 12.3 shows the input values for fuel reactor temperature for each biomass type for various flow rates of biomass and OC. In all simulations described in this chapter, the air reactor temperature was 950 °C.

After the validation, the next part of the paper focuses on the evaluation of the performance of CLC power plant using different oxygen carriers. For this purpose, Manganese (III) Oxide was used as the oxygen carrier instead of Hematite. Mn-ores also possess a relatively high reactivity, which makes them a potential alternative to Fe based oxygen carriers. In ASPEN Plus, the composition of the oxygen carrier stream was changed to $Mn_2O_3$, but it still included the impurities that were present in the $Fe_2O_3$ oxygen carrier stream. The reactions in the fuel and air reactors were changed to use the Mn based OC in place of the Fe based OC. The stoichiometry of these reactions remained unchanged. By changing the OC to $Mn_2O_3$, the concentration of gases in the fuel reactor was compared to the simulations that used $Fe_2O_3$ as OC. In addition, the power outputs of the two systems with two different OC at various temperatures were compared. Finally a third case was simulated to investigate how the power output varied using the two different oxygen carriers when a mixture of coal and biomass was used in place of pure biomass. For this part of the simulations, Shenhua bituminous coal was used. The ultimate and proximate analysis of this coal is shown in Table 12.4 (Gu et al. 2010).

**Table 12.3** Input values in ASPEN Plus model corresponding to the experimental values of Mendiara et al. (2018)

| Parameters | Pine sawdust | | | | Olive stone | | | Almond shell | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 895 | 910 | 955 | 985 | 905 | 955 | 980 | 905 | 955 | 985 |
| Biomass (g/hr) | 152 | 113 | 98 | 98 | 164 | 141 | 141 | 190 | 102 | 88 |
| OC (kg/hr) | 10.1 | 9.2 | 6.7 | 6.7 | 8.8 | 7.6 | 7.6 | 13 | 7 | 5.9 |

**Table 12.4** Ultimate and proximate analysis of Shenhua bituminous coal (Gu et al. 2010)

| *Ultimate analysis* (wt. %) | |
|---|---|
| Carbon | 69.75 |
| Hydrogen | 4.3 |
| Nitrogen | 1.03 |
| Sulfur | 0.52 |
| Oxygen | 13.81 |
| LHV (kJ/kg) | 27100 |
| *Proximate analysis* (wt. %) | |
| Moisture | 6.01 |
| Ash | 4.76 |
| Volatile matter | 35.1 |
| Fixed carbon | 54.13 |

## 12.3 Results and Discussion

### *12.3.1 Validation of the Experiment of Mendiara et al. (2018)*

As mentioned before, the first part of this work focused on the validation of the ASPEN Plus process model against the experimental data of Mendiara et al. (2018). In their experiment, biomass was combusted in the fuel reactor at various temperatures in order to determine the optimal temperature to capture the purest stream of $CO_2$. As was noted by Mendiara et al., the biomass and OC flow rates were decreased with temperature to maintain optimal OC to fuel ratio.

#### 12.3.1.1 Gas Concentrations from Pine Sawdust

For Pine Sawdust, the biomass was fed into the fuel reactor at 895, 910, 950, and 985 °C, while the concentrations of various gases, namely $CO_2$, CO, $H_2$ and $CH_4$ were measured in the stream leaving the fuel reactor. The concentrations of these compounds that were determined by Mendiara et al. are graphed with the concentrations obtained from the simulation in Fig. 12.3. The simulations closely agree with the experimental data at lower temperatures, while slightly deviating at higher temperatures. This discrepancy can be attributed to an under production of methane ($CH_4$) in the simulation model. The production of methane has the largest difference between the experimental data and the simulation results and its concentration continues to decrease as the fuel reactor temperature increases. The concentration of methane continues to stay below the experimental value as the temperature increases; however the concentrations of other products rise above the experimentally observed value. The concentrations of these products do not deviate from the experimental values by a substantial amount, with the concentrations of $CO_2$, CO and $H_2$ all being within

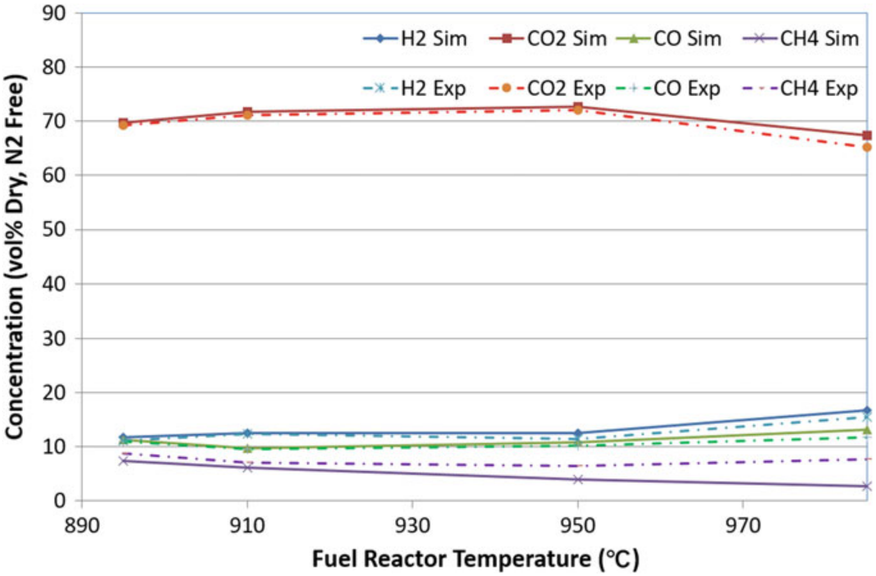

**Fig. 12.3** Comparison of gas concentrations in the fuel reactor for pine sawdust from ASPEN Plus and experimental data (Mendiara et al. 2018)

1.5% of their experimentally observed values. This indicates that the results of the simulation obtained are an accurate validation of the experimental results obtained by Mendiara et al. $CO_2$ concentration is shown to increase from 895 to 950 °C at which point the $CO_2$ concentration reaches its highest value and then begins to decrease. As such, the purest $CO_2$ stream is obtained at fuel reactor temperature of 950 °C. This is consistent in both the experimental results as well as in the simulations. Overall, the concentrations of $CO_2$, CO, and $H_2$ in the fuel reactor agree fairly well with the experimental results as shown in Fig. 12.3.

#### 12.3.1.2 Gas Concentrations from Olive Stone

For Olive Stone, the biomass was fed into the fuel reactor at 905, 955, and 980 °C. The concentrations of $H_2$, CO, $CO_2$, and $CH_4$ are shown in Fig. 12.4. As was the case with the Pine Sawdust, methane was still under produced. The concentrations of the other gases obtained from ASPEN Plus also did not match as well as they did in case of pine sawdust, however the largest deviation was still only 2.0% in case of $CO_2$ at 980 °C, which indicates that the model constructed in ASPEN Plus was an accurate representation of the experimental setup. It is shown in Fig. 12.4 that $CO_2$ concentration is the highest at 905 °C, and it decreases gradually with increase in temperature.

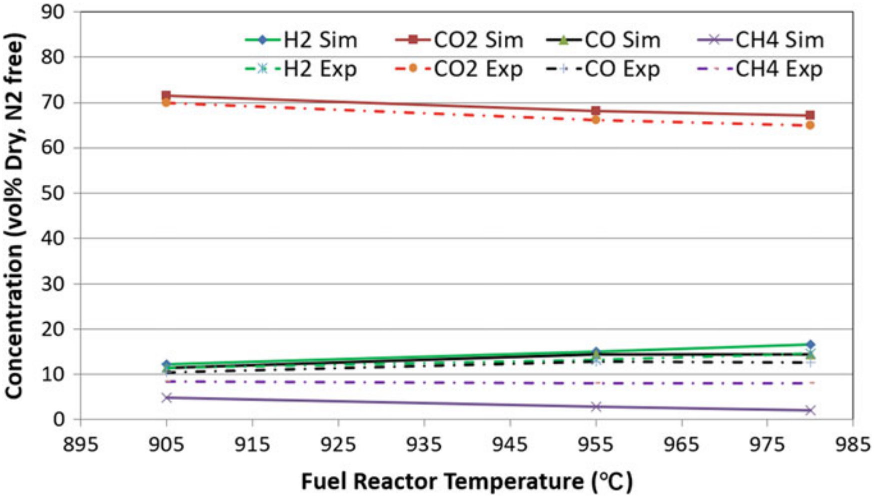

**Fig. 12.4** Comparison of gas concentrations in the fuel reactor for Olive Stones from ASPEN Plus and experimental data (Mendiara et al. 2018)

### 12.3.1.3 Gas Concentrations from Almond Shell

For Almond Shell, the biomass was fed into the fuel reactor at 905, 955, and 985 °C. The concentrations of $H_2$, CO, $CO_2$, and $CH_4$ are shown in Fig. 12.5. Once again, the simulated value of concentration of methane was lower than the experimentally

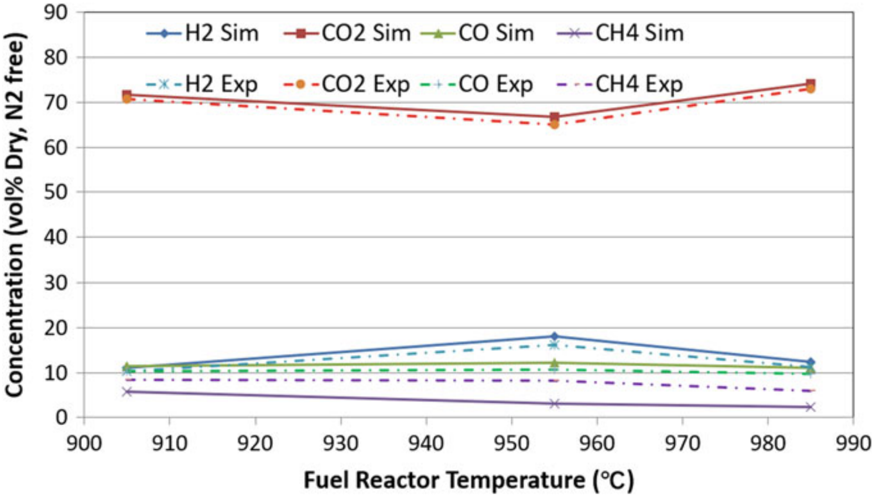

**Fig. 12.5** Comparison of gas concentrations in the fuel reactor for almond shell from ASPEN Plus and experimental data (Mendiara et al. 2018)

determined value. However, the data obtained from the simulation model fits the experimental data fairly well, with the largest deviation in concentration being 1.8% for $H_2$ at 955 °C. The $CO_2$ concentration initially decreases with temperature, until it reaches its lowest value at 955 °C. From this point onward, the $CO_2$ concentration increases as the temperature approaches 985 °C as shown in Fig. 12.5.

#### 12.3.1.4 Carbon Capture Efficiency ($N_{cc}$)

One method of evaluating the performance of a CLC system is to determine its Carbon Capture Efficiency ($N_{cc}$). The equation for determining the carbon capture efficiency is given below (Mendiara et al. 2018).

$$N_{\mathrm{cc}} = \frac{\left[F_{\mathrm{CO_2},FR} + F._{\mathrm{CO},FR} + F_{\mathrm{CH},FR}\right]_{out}}{\left[F_{\mathrm{CO_2},FR} + F_{\mathrm{CO},FR} + F_{\mathrm{CH_4},FR} + F_{\mathrm{CO_2},AR}\right]_{out}} \tag{12.2}$$

where $F_{x,\,FR}$ is used to denote the molar flow (mol/h) of gas $x$ in the fuel reactor, while $F_{\mathrm{CO_2},AR}$ is used to denote the molar flow (mol/h) of $CO_2$ in the air reactor. $CO_2$ in the air reactor is a byproduct of residual char combusted in the air reactor. Since a CLC system consists of interconnected fluidized beds, some char is carried from the fuel reactor into the air reactor by OC particles. At higher temperatures, more char is converted into carbonaceous gas in the fuel reactor, and as such, increasing the temperature of the fuel reactor decreases the amount of char that can reach the air reactor. Thus, increasing the fuel reactor temperature decreases the concentration of $CO_2$ in the air reactor, and thereby increases the Carbon Capture Efficiency. For both Pine Sawdust and Almond Shell, the Carbon Capture Efficiency reached approximately 100% at temperatures equal to or greater than 950 °C, while Olive Stones reached a $N_{cc}$ value of approximately 100% at 980 °C. This difference could be due to the fact that pine sawdust and almond shell have greater volatile matter content than olive stones; 81.0% and 76.6% compared to 72.5%, respectively. The simulation results for Carbon Capture Efficiency as a function of the fuel reactor temperature match the experimental results obtained by Mendiara et al. quite closely, as shown in Figs. 12.6, 12.7 and 12.8. For Almond Shell biomass, the simulation data fits the experimental data most closely, with the two graphs essentially overlapping.

### *12.3.2 Effect of Different Oxygen Carriers on CLC Plant Performance*

After validating the process simulation model against the experimental data, the ASPEN Plus simulations were performed by changing the OC from $Fe_2O_3$ to $Mn_2O_3$.

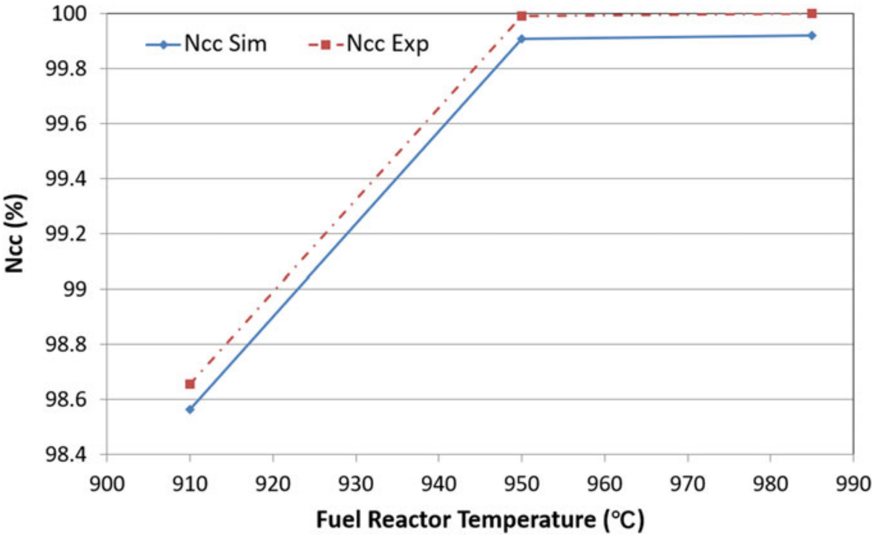

**Fig. 12.6** Carbon capture efficiency for pine sawdust

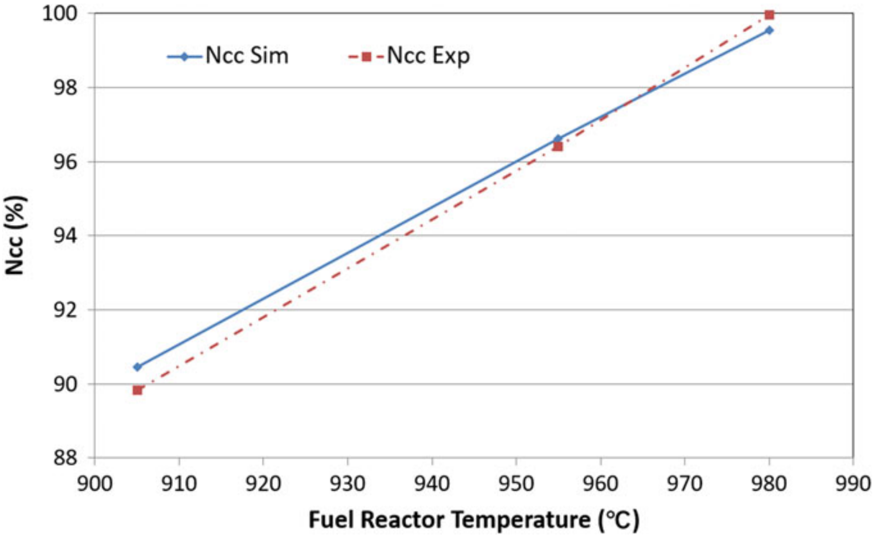

**Fig. 12.7** Carbon capture efficiency for olive stone

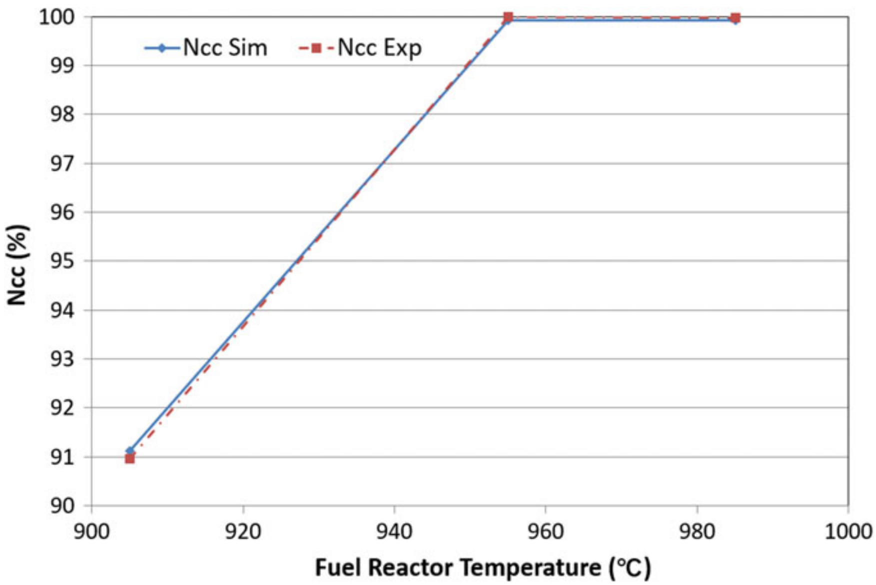

**Fig. 12.8** Carbon capture efficiency for almond shells

Pine sawdust was used as the biomass of choice in this investigation since the gas concentrations from simulations for this biomass most closely matched the experimental results using $Fe_2O_3$ as OC.

By changing the OC from a Fe based compound to a Mn based compound, the concentrations of CO and $H_2$ in the fuel reactor decreased slightly, while the concentration of $CO_2$ increased. The $CH_4$ value remained essentially unchanged. This indicates that $Mn_2O_3$ is more reactive as an OC and converts more CO to $CO_2$ than a Hematite based OC. However, since the maximum $CO_2$ concentration using $Mn_2O_3$ is only about 0.8% greater than what was obtained using $Fe_2O_3$, the use of a Mn based OC in place of a Fe based OC does not provide significant benefits. The Carbon Capture Efficiency remained identical between the two oxygen carriers, but since these values were essentially 100% at temperatures greater than 950 °C, this is just an indication that $Mn_2O_3$ is equally effective in converting residual char to carbonaceous gases as $Fe_2O_3$. The concentrations of $CO_2$, CO, $H_2$, and $CH_4$ in the fuel reactor are shown in Figs. 12.9, 12.10, 12.11 and 12.12. The results of the simulation using $Mn_2O_3$ are compared with the results from simulation using $Fe_2O_3$ in these figures.

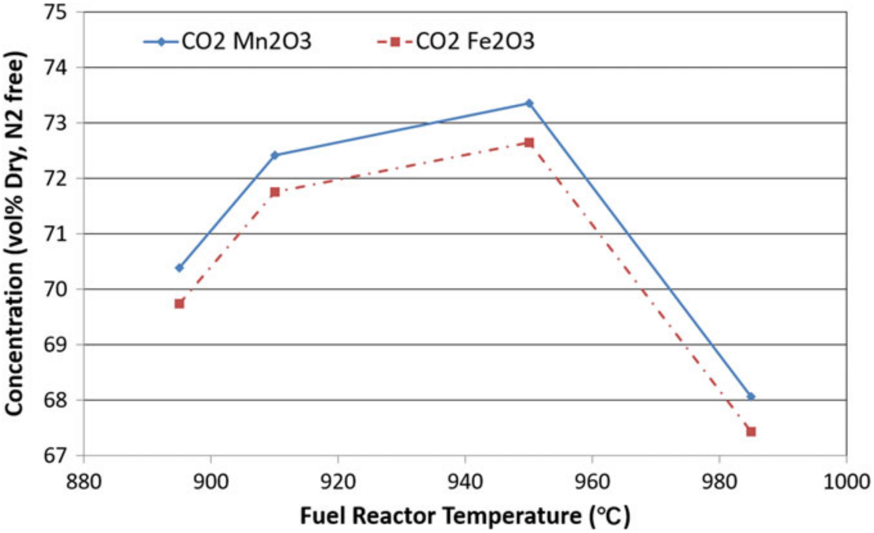

**Fig. 12.9** $CO_2$ yield from Mn based OC compared to Fe based OC

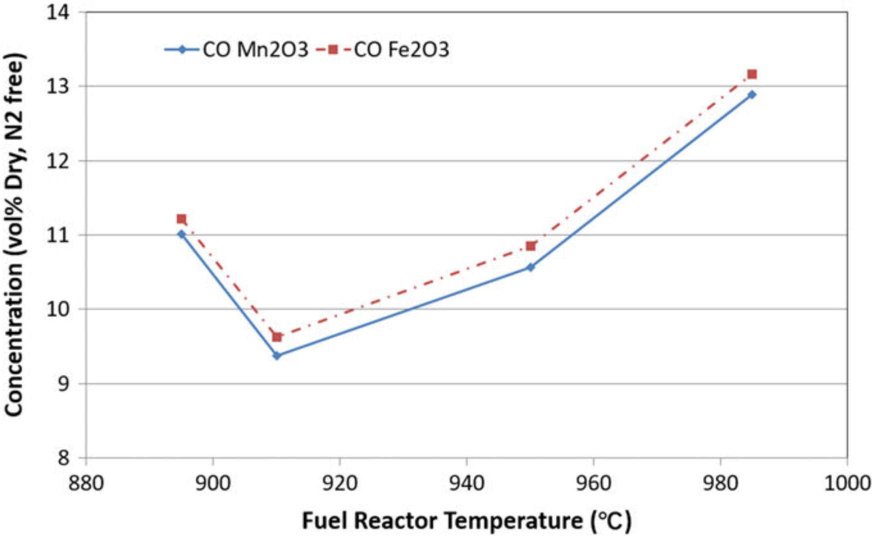

**Fig. 12.10** CO Yield from Mn based OC compared to Fe based OC

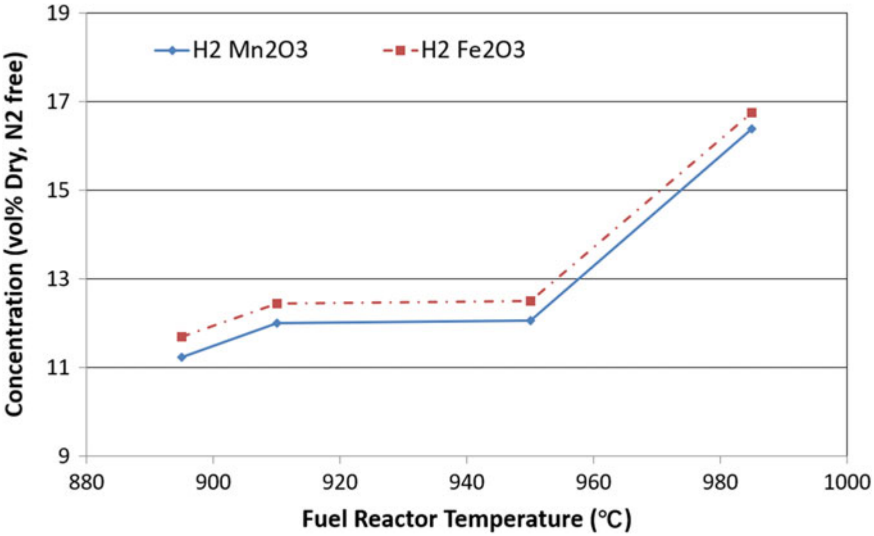

**Fig. 12.11** $H_2$ yield from Mn based OC compared to Fe based OC

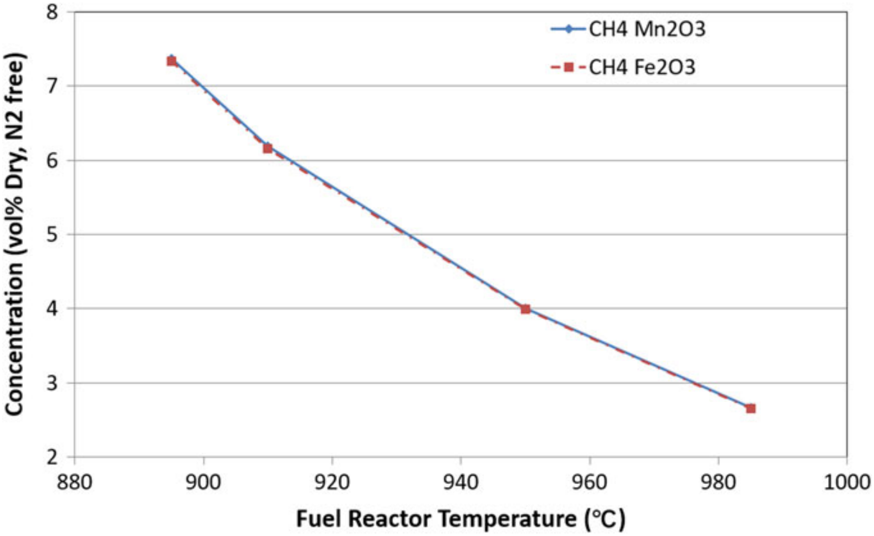

**Fig. 12.12** $CH_4$ yield from Mn based OC compared to Fe based OC

### *12.3.3 Power Output*

#### 12.3.3.1 Pure Biomass

To further investigate the performance of the CLC plant including the effect of using $Mn_2O_3$ in place of $Fe_2O_3$, the thermal power output of the system was determined at different temperatures. Once again, the biomass of choice was Pine Sawdust. To maintain the consistency in the process simulation model in ASPEN Plus, biomass flow rate was decreased with temperature as specified by Mendiara et al. (2018). These flow rates were shown previously in Table 12.3. The power output falls sharply with increase in temperature as shown in Fig. 12.13. Additionally, it can be seen from this figure that the CLC system using $Fe_2O_3$ gives a higher power output than the system using $Mn_2O_3$. At 895 °C, the power output is at its maximum value for both OCs, approximately 2220 Watts using $Fe_2O_3$, and approximately 1531 Watts using $Mn_2O_3$. It can also be observed that the power output falls to negative values for both scenarios once the temperature in the fuel reactor reaches 950 °C. This is an indication that the energy released from the combustion of the biomass at that particular flow rate of 98 g/hr. is not sufficient to make up for the energy required to heat the fuel reactor to 950 °C and beyond.

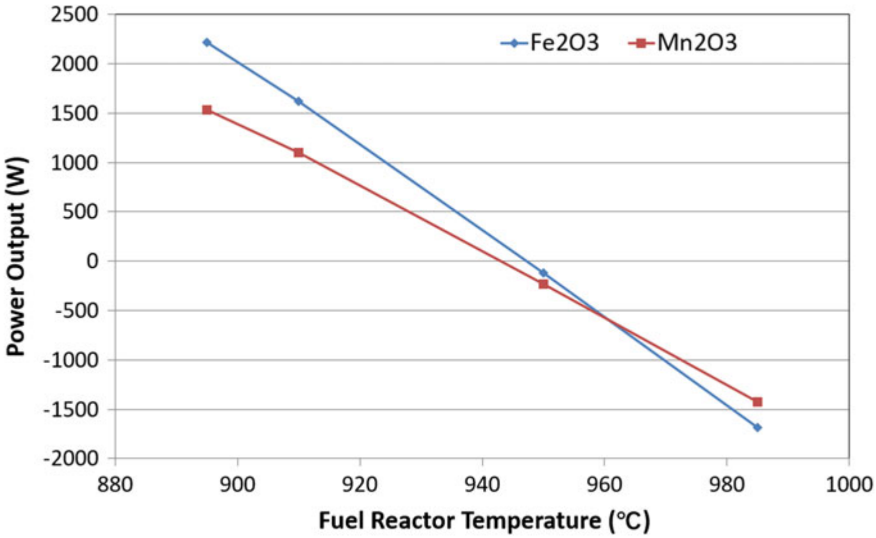

**Fig. 12.13** Power Output from ASPEN Plus for pine sawdust using Fe and Mn based OCs

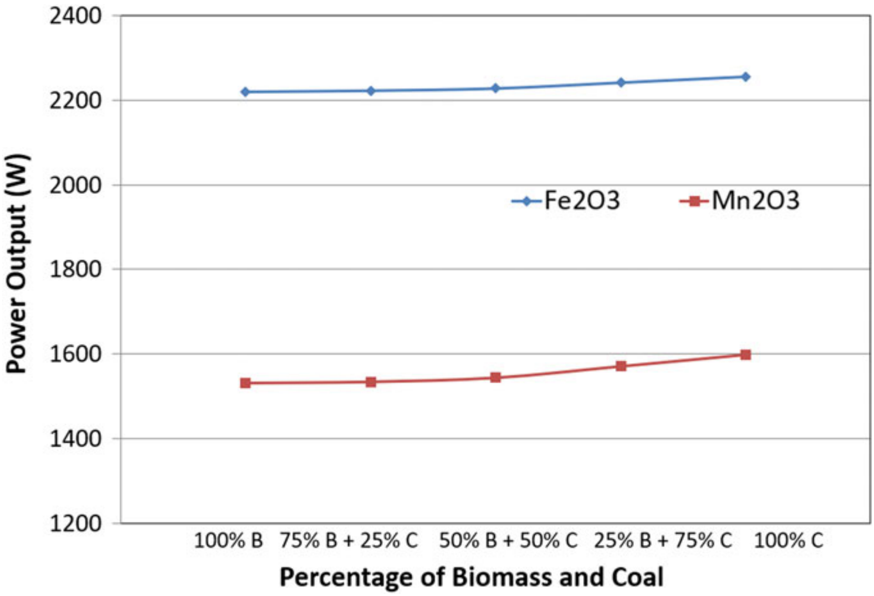

**Fig. 12.14** Power output from mixture of biomass and coal using Fe and Mn based OC

#### 12.3.3.2 Mixture of Coal and Biomass

Simulations were also performed using a mixture of biomass and coal. The fuel reactor temperature was set at 895 °C and an OC flow rate of 10.1 kg/hr. was used. The total biomass and coal flow rate always added up to 152 g/hr.

Figure 12.14 shows the power output obtained from a mixture of biomass and coal when both $Fe_2O_3$ and $Mn_2O_3$ were used as OC. It can be seen that the maximum power output obtained using $Mn_2O_3$ as OC is substantially lower than the maximum power output obtained with $Fe_2O_3$ as OC. In addition, as the fraction of coal in the fuel stream increases, the power output also increases as expected. This is due to coal's higher LHV, meaning that more heat is released when coal is combusted compared to when pure biomass is combusted. Since the use of $Mn_2O_3$ as OC resulted in the system to produce far less power compared to that with $Fe_2O_3$ as OC, it can be concluded that $Mn_2O_3$ is not a suitable alternative to $Fe_2O_3$ as an oxygen carrier.

## 12.4 Conclusions

In this chapter, a complete CLC system with biomass as fuel was simulated using ASPEN Plus software. Pine Sawdust, Almond Shells, and Olive Stones were used as the three types of biomass. This work investigated the effect of fuel reactor temperature on the concentrations of $CO_2$, CO, and $H_2$ in the fuel reactor, and on the Carbon

Capture Efficiency ($N_{cc}$) for the three types of biomass using $Fe_2O_3$ as oxygen carrier. The process simulations were validated against the experimental data obtained by Mendiara et al. (2018) for gas concentrations and carbon capture efficiency. When using the pine sawdust as fuel, $CO_2$ concentration in the fuel reactor increased until 950 °C, and then decreased as the temperature approached 985 °C. When almond shells were used as fuel, the $CO_2$ concentration decreased with temperature until the fuel reactor reached 955 °C. From this temperature onward, the $CO_2$ concentration increased with the temperature. For olive stones as fuel, the concentration of the $CO_2$ in the fuel reactor decreased as the temperature of the reactor increased. For all three biomass types, carbon capture efficiency increased with temperature, with pine sawdust and almond shell reaching almost 100% carbon capture efficiency at 950 °C, while olive stones reached this value at 980 °C. In addition, the effect of using $Mn_2O_3$ as the oxygen carrier was also investigated. It was found that the use of $Mn_2O_3$ as oxygen carrier caused the concentrations of CO and $H_2$ in the fuel reactor to decrease, while causing the concentration of $CO_2$ to increase. This indicates that using $Mn_2O_3$ in place of $Fe_2O_3$ increases the efficiency of the conversion of CO to $CO_2$. Carbon Capture Efficiency remained the same between the two oxygen carrier types, but since this value is already close to 100%, it is likely that there is miniscule quantity of unconverted char in the fuel reactor and therefore the carbon capture efficiency is not expected to change significantly. Finally, the power output from both pure biomass and a mixture of coal and biomass was determined to examine the effect of $Fe_2O_3$ and $Mn_2O_3$ on power output, as well as the change in power output for various percentages of coal and biomass in the mixture. It was found that $Mn_2O_3$ produced a significantly lower amount of power compared to $Fe_2O_3$, and increasing the percentage of coal in the mixture increased the power output as expected.

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# Chapter 13
# Analytical Methods in Biodiesel Production

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**Abstract** Biodiesel is a clean burning fuel that can be obtainable from renewable sources and utilized in diesel vehicles. The physical characteristics of biodiesel are indistinguishable from petroleum diesel, therefore, it is currently considered as a best alternative fuel. However, the quality of the biodiesel is very important in order to commercialize and get acceptance for marketing. There is a necessity to undertake a quality analysis of biodiesel to assess the chemical properties. Several existing analytical methods that are to evaluate the characteristics of biodiesel is mainly categorized into chromatographic and spectroscopic methods. Appropriate analytical

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techniques can be adopted to measure the impurities preciously even at lower concentrations. Hence, this chapter describes the developments in biodiesel analysis including chromatography methods such as gas chromatography (GC), gel permeation chromatography (GPC), liquid chromatography (LC), size exclusion chromatography (SEC), supercritical fluid chromatography (SFC), thin layer chromatography (TLC) and spectroscopic methods such as infra-red (IR) spectroscopy, fluorescence spectroscopy, inductively coupled plasma mass spectrometry (ICP–MS), ultra-violet (UV) spectroscopy and proton nuclear magnetic resonance (P–NMR). Other methods namely viscometry, refractive index, titration for determining free fatty acids, wet chemical methods, enzymatic methods, and methods used to test for oxidation stability and new low-cost and greener alternatives in the analytical field are also discussed. Further, this chapter contemplates the assessment of various available methods, accounting their merits and demerits, and provides some improvements and selection of suitable analytical methods for biodiesel production.

**Keywords** Biodiesel · Analytical methods · Chromatographic methods · Spectroscopic methods · Transesterification

## 13.1 Introduction

All over the world, several countries are involving to utilize the biofuel technology in order to resolve the problems on hiking of energy and fuel costs due to reduction of fossil fuels, which are world's non-renewable resources (Goswami et al. 2017a). The recent researches are focused to finding alternative fuels instead of using conventional petroleum fuel (Selvaraj et al. 2019). Currently, the manufacturing and usage of advanced and alternative fuels are crossed more than a dozen. Among them, biodiesel is considered as important potential alternative fuel for diesel engine and receiving great attention in worldwide (Knothe 2001). The physical characteristics of biodiesel are similar to the petroleum diesel that makes requirement of no changes in the diesel engines. Therefore, biodiesel is technically well adopts and becomes a best substitution to replace petroleum/convention diesel. However, there are some issues to be rectified on $NO_x$ emissions, cold–flow properties, oxidative stability and majorly commercialization of biodiesel, which costs more than conventional diesel. In addition, the biodiesel can be obtained simply from the common feedstocks. Nevertheless, the relative ease of biodiesel production can camouflage the significance of retaining high quality standards for any fuel provided to a current diesel engine. It is important to the development of the biodiesel industry that all fuel produced and sold meet the quality standards (Goswami et al. 2017c).

### 13.1.1 Biodiesel

Biodiesel is defined as diesel equivalent fuel derived from renewable resources namely vegetable oils and animal fats (Pinto et al. 2005). The primary sources of the biodiesel are vegetable oils such as soybean oil, rapeseed oil and tropical oils. Further, the inexpensive feedstocks such as animals' oils and fats, particularly recycled greases or used vegetable oils are received attention as sources of biodiesel. It is a liquid biofuel contains alkyl esters of long chain fatty acids produced from either vegetable oil or animal fats by chemical reaction called "transesterification" (Van Gerpen 2005). It is a process of reacting triglyceride molecule with an excess of alcohol in the presence of a catalyst (KOH, NaOH, $NaOCH_3$, etc.) to produce glycerol and fatty esters. For the transesterification process, methanol is an efficient, economic and most commonly utilized alcohol and it also yields methyl esters viz. methyl soyate and rapeseed methyl ester. Synthesis pathways of biodiesel and chemical reaction with methanol are schematically shown in Figs. 13.1 and 13.2, respectively.

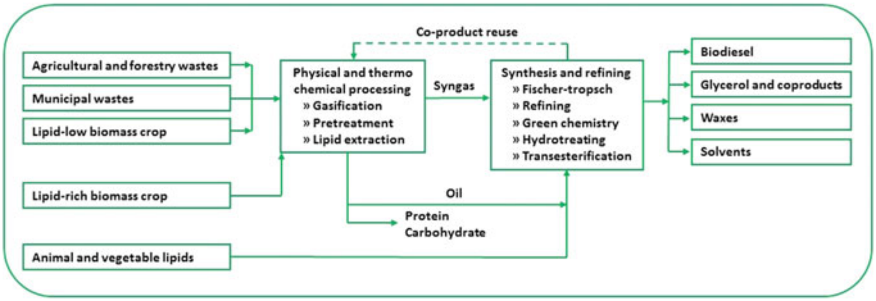
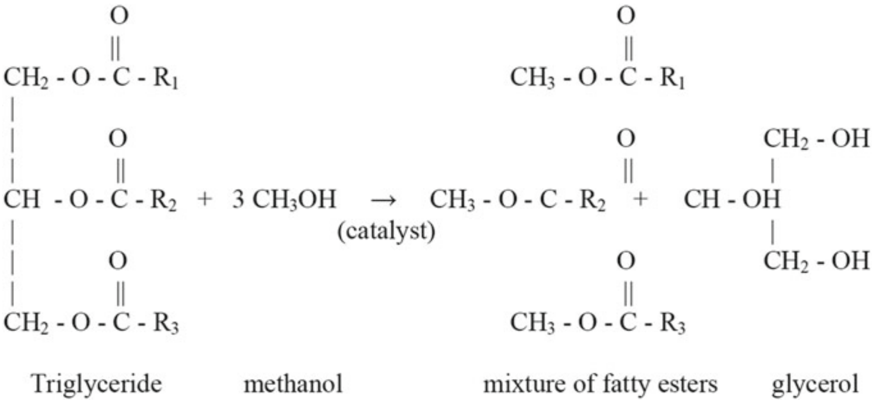


**Fig. 13.1** Schematic of synthesis pathways of biodiesel



$$\begin{array}{l} \mathrm{CH_2-O-\overset{O}{\overset{\|}{C}}-R_1} \\ | \\ \mathrm{CH-O-\overset{O}{\overset{\|}{C}}-R_2} \\ | \\ \mathrm{CH_2-O-\overset{O}{\overset{\|}{C}}-R_3} \end{array} + 3\,\mathrm{CH_3OH} \xrightarrow[\text{(catalyst)}]{} \begin{array}{l} \mathrm{CH_3-O-\overset{O}{\overset{\|}{C}}-R_1} \\ \mathrm{CH_3-O-\overset{O}{\overset{\|}{C}}-R_2} \\ \mathrm{CH_3-O-\overset{O}{\overset{\|}{C}}-R_3} \end{array} + \begin{array}{l} \mathrm{CH_2-OH} \\ | \\ \mathrm{CH-OH} \\ | \\ \mathrm{CH_2-OH} \end{array}$$

**Fig. 13.2** Representation of transesterification reaction

In the transesterification reaction, monoacylglycerols, diacylglycerols and intermediate glycerols are produced, which are presented in the final biodiesel product (methyl ester) in small quantities. These partially retained and unseparated glycerol, unreacted triacylglycerols, residual alcohols, free fatty acids and catalyst are contaminates the finally produced biodiesel. It makes serious operational problems with accessories like filter clogging/fuel deterioration and engine deposits. Consequently, the American Society for Testing and Materials (ASTM) in the United States (US) and some European Union (EU) countries including Italy, Germany, France, Czech Republic and Austria, standards have been established that limits the contaminant quantity in biodiesel (Goswami et al. 2019; Howell 1997). The standard limits are framed on the presence of specific impurities by inclusion of items viz. free fatty acids limited by acid value, residual alcohol limited by flash point, glycerol and acylglycerols limited by free and total glycerol and residual catalyst limited by ash value. Therefore, the quality determination of biodiesel is a greater issue to successfully commercialize the biodiesel fuel. There is high requirement to produce continuous good quality biodiesel with no operational issues to obtain the approval for marketing. The recent research has been focused to monitoring and analysis of transesterification process and biodiesel, respectively. Moreover, it is important to continuing the study and optimization of production processes of biodiesel due to its renewable nature and favorable attribution to the environment (Ibeto et al. 2009).

### *13.1.2 Biodiesel Properties*

In general, biodiesel holds the superior lubricating characteristics compare to the available low viscosity diesel fuel in the market (Knothe 2005). The properties of the biodiesel is mainly depends on the utilization of feedstocks during the production process and analysis methods. Since biodiesel exhibits better solvent properties, which can liquefy the filter clogging or fuel deterioration and engine deposits in a vehicle fuel system, where petroleum-derived diesel cerates deposits. Other attracted characteristics of biodiesel are biodegradable, renewable, nontoxic and water immiscible fuel. The color varies between dark and gold depends on the feedstock used in biodiesel production process. It shows excellent combustion properties compared to the low sulphur petroleum diesel due to holding higher cetane rating. The flash point of the biodiesel (>130 °C, >266 °F) is considerably greater than petroleum-derived diesel fuel (−45 °C, −52 °F) that makes safety to handle. It has high boiling point and low vapor pressure. The calorific value and density of biodiesel is around 37.27 mg $L^{-1}$ and 0.88 g $cm^{-3}$, respectively.

### 13.1.3 Quality Standards

The compression ignition diesel engines are potentially facilities the usage of biodiesel as an alternative fuel (Knothe 2001). ASTM and international standards for biodiesel are D6751 and ISO 14214, respectively, which are the general standards considered in the US as basic comparison of petroleum diesel and biodiesel. The quality requirements of biodiesel are regulated by Deutsches Institut für Normung (DIN) standard in Germany. There are diverse assortments of standards for the biodiesel produced from various oils, namely, FME (Fat methyl ester, vegetable and animal products according to DIN V51606), VME (vegetable methyl ester, purely vegetable products according to DIN E51606) and RME (rapeseed methyl ester from rape products according to DIN E51606). The standards verifies the essential features in the biodiesel production process and satisfaction comprising complete reaction, elimination of residual catalyst, glycerin and alcohols and nonexistence of free fatty, etc. The specification similarly takes account of a higher sulfur grade (S500), allowing up to 0.05 wt% sulfur in the biodiesel.

### 13.1.4 Requirement of Analytical Techniques

To determine the chemical characteristics of the biodiesel, there is a necessity to perform its quality evaluation. This quality assessment includes determination of specific gravity, viscosity, refractive index, ash content, flash point, cetane number, calorific value, iodine value, saponification value, acid value and fatty acid composition/individual essential oils, etc. (Goswami et al. 2017b). These characteristics are assisting to evaluate the biodiesel quality and particular biodiesel blends. The important chemical characteristics of biodiesel and its significance are enlisted in Table 13.1.

### 13.1.5 Percentage of Sulfur

The weight content of sulfur in percentage for diesel fuel used in on-road applications is restricted through regulations framed by Engine Manufacturers Association. The restriction of unsaturated fatty acids is essential because of probabilities to glycerides polymerization by higher heating of unsaturated fatty acids that may forms deposits/deterioration (Goswami et al. 2017b).

**Table 13.1** Chemical characteristics of biodiesel and its importance

| Characteristics | Definition | Significance |
|---|---|---|
| Melt point | Temperature at which the oil in solid form starts to melt | Important physical property and used for the indication of purity |
| Cloud point | Temperature at which waxes starts to crystallize | Indicates the lowest temperature of the fuel for operability |
| Flash point | Minimum temperature at which the fuel will ignite on application of ignition source | Used as a safe index for biofuels and indicates the level of purification |
| Iodine value | Amount of iodine, measured in grams, absorbed by 100 g of given oil | Used as a measure of the chemical stability properties of different biodiesel fuels |
| Viscosity | Measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size | The higher the viscosity, the higher is the tendency of the fuel to form engine deposits |
| Aniline point/cetane number | Relative measure of the interval between the beginning of injection and auto ignition of the fuel | The higher the cetane number of the fuel, the shorter the delay interval and the greater its combustibility |
| Density | Weight per unit volume | Oils that are denser contain more energy |
| Ash content | Measure of the amount of metals contained in the fuel | High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear |

## 13.2 General Aspects of Analytical Techniques

In general, biodiesel comprising two main classes of analytical techniques namely, chromatographic and spectroscopic. Additionally, some other techniques are reported in the literatures to evaluate the physical properties of biodiesel. The appropriate techniques can able to consistently measure the quantity of contaminates presented in the biodiesel even at very lower concentration with inexpensively (Knothe 2006). There are no novel techniques are currently available to fulfill this excellent features. Thereby, some concessions must be considered while choosing the technique to analyze biodiesel. The main classes of analytical methods such as chromatographic and spectroscopic techniques are usually called in organic analytical chemistry owing to the relative techniques such as gas chromatography mass spectrometry (GC–MS), gas chromatography infrared spectrometry (GC–IR), and liquid chromatography mass spectrometry (LC–MS) (Goswami et al. 2018). Some studies have dealt with utilization of hyphenated methods for analyzing biodiesel due to expensiveness of instruments and requirements of technically skilled persons to analyze the obtained data. This is circumstance fact that hyphenated techniques are assist to solving uncertainties residual after analysis by standalone chromatographic techniques. To meet the necessities of biodiesel standards, the quantification of specific compounds are not essential, however the classes of compounds quantification is very important.

## *13.2.1 Chromatographic Methods*

The chromatography is a technique that can be applied for the separation of mixture on the basis of relative amounts of each solute distributed between a moving fluid streams. In the literatures, the first report on the basis of chromatographic analysis is conducted by Freedman et al. (1984). They carried out the analysis of the transesterification of oils by a thin layer chromatography with flame ionization detection (TLC/FID) lactroscan instrument. Further, TLC/FID was applied to correlate bound glycerol content to acyl conversion determination by gas chromatography. The combination of analytical techniques both gas chromatography and high-performance liquid chromatography for the biodiesel have already reported in some literature. On the other hand, the gel permeation chromatography used for analysis of transesterification products has been reported as an analytical tool. Some chromatographic methods that are widely used in biodiesel analysis are discussed as follows.

### 13.2.1.1 Gas Chromatography

Gas chromatography (GC) is used in the analysis of fatty acids and alkyl esters content in the source (oil (or) triglycerides) and product (biodiesel) of the transesterification process. It is mainly used to estimate the conversion of biodiesel by inline determination of compounds formed during the process (Bala et al. 2017). Monounsaturated, diunsaturated and saturated fatty acid composition and polyunsaturated fatty acid (PUFA) content of biodiesel is evaluated by GC (Chopra et al. 2011). Additionally, the percentage distributions of individual components are measured using GC. The building blocks of the alkyl esters are analyzed using the characteristic variation of the individual compounds in response to the retention time of the individual compounds. The spectrum of the fragmentation mass is measured and notated by the symbol m/z ratio of molecular ion at specific level of exposed energy. The fragmentation of triglycerides with its intermediate products in the transesterification reaction can be found using the Mclafferty rearrangement method (Maulidiyah et al. 2017). The selective components of final product (biodiesel) are also identified using GC analysis. The untransesterified compound such as sterol glycosides are identified using GC (Montpetit and Tremblay 2016). In another study, the identified untransesterified compounds (sterol glycosides) are removed using the GC techniques (Saeong et al. 2017). GC in combination with flame ionization detector (GC–FID) is used for monitoring the selected ions. The unresolved peaks of the chromatogram can also be identified using the retention time and Kovats indices character of the selective compound on the range of peak from GC technique. It shows its importance for the following characteristic features; reduced time for analysis, complete separation with simultaneous identifications of compounds and the reliable determination of compounds. Hence, it becomes an important analytical method in determining the fuel blends with diesel composition (Kanateva et al. 2014). GC in combination with isotope dilution mass spectrum (GC–IDMS) can be used in the identification of trace elements. It is found to be similar with the GC–FID. The characteristic properties of the operation are validated by the linearity, range of operation and their corresponding response factor. It is also tested for the limit of detection for the process, limit of quantification of the process, precision of the quantification, reliability of data, uncertainty of data and robustness of the process. These properties make GC–IDMS to be a good process for determining the trace compounds of the biodiesel (Morales et al. 2015).

#### 13.2.1.2 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is used in the determination of average molecular weight and molecular weight distribution of biodiesel, using polystyrene as a standard (Dang et al. 2016). GPC is also used in the quantification of ethyl esters, acylglycerols and free glycerols of the tranesterified product. The detection limit of the process is found to be in the range of 0.02 mg/mL (Escorsim et al. 2015). GPC is used in the sample preparation for the analysis of biodiesel. It also maintained the reproducibility of biodiesel by the sample recovery in the transesterification process. It is also used in the estimation of glycerol content in biodiesel, produced by the transesterification process. This method of determination showed good similarity with the process of quantification done by attenuated total reflectance Fourier Transform infra-red (ATR–FTIR) spectroscopy (Dube et al. 2004). GPC is applied in the determination of oligomers. It is analyzed for the estimation of diglycerides, which in-turn showed the completeness of the transesterification process. GPC is also used in the determination of aging of biodiesel with respect to the oligomers (diglycerides) determination. The highest molar mass of the sample is detected at the 40th hour of aging and it is found to be 1600 Da. These are the estimation of diglycerides and other oligomers making to be a good method for monitoring the process of transesterification (Eskiner et al. 2015). GPC in combination with refractive index detector (GPC–RID) is used in the determination of density and fatty acid profile of biodiesel. The usage of RID in combination with GPC have also paved way for the identification of Poly-Dispersity Index (PDI) of poly-oligomers in biodiesel (Tesfaye and Katiyar 2016). The major drawback of the GPC is that it can separate only the compounds by its group (or) family in relation to its size and permissibility. The compounds of identity (or) uniqueness cannot be separated as an individual compounds (Mohanan et al. 2016; Patel et al. 2018).

#### 13.2.1.3 Liquid Chromatography

High performance liquid chromatography in association with ultraviolet detector (HPLC–UV) is used in the inline monitoring of biodiesel during transesterification process. The reaction is monitored as the function of time. Since, the compounds are eluted rapidly; it is used for monitoring the transesterification process. HPLC–UV with rapid elution on core shell column saved both time and reagents of the process. Inline monitoring of biodiesel production using HPLC is efficient than the process with GC; since no derivatization required for analysis with HPLC (Allen and Ott 2012). The conversion of oil to their corresponding alkyl esters is also determined by the HPLC–UV technique. It is correlated by the determination of monoglycerides, diglycerides, triglycerides, methyl esters and free fatty acid content of biodiesel, analyzed by HPLC–UV. The unprocessed free fatty acids of biodiesel, fatty acid alkyl esters (biodiesel), glycerides, phosphoglycerides and lysophosphoglycerides contents of biodiesel are also estimated using HPLC (Haas et al. 2000). The reverse phase HPLC with UV detector is used in the analysis of tocopherols content, a contaminant in biodiesel (Pauls 2012). Brassinosteroids, a residue in biodiesel is also quantified using HPLC. The quantification is carried out using the selective labeling of the compound. This method of estimation is found to be selective and sensitive for the derivatives (Laura and Fulvia 2015). HPLC in combination with the mass spectrum (HPLC–MS) is used to analyze the ultrafine particle for their metabolism. It is used to explore the basic molecular activities of the particles. It is also used in monitoring the selected reaction with its retention time as a function for profile. Hence, this targeted profiling of metabolism of selective particle by HPLC–MS made it as an analytical method in profiling transesterification process (Zhong et al. 2017). HPLC in combination with evaporative light scattering detector (HPLC–ELSD) is compared with HPLC–UV in determining the blended fuels. HPLC–UV cannot analyze the blended petrodiesel with the biodiesel. But, HPLC–ELSD can differentiate and analyze the triacylglycerides, fatty acid alkyl esters and petroleum diesel content in the blends. Hence, HPLC–ELSD is proved to be better than the HPLC–UV (Foglia et al. 2005). HPLC with refractive index detector (HPLC–RID) is used in the separation and determination of fatty acid alkyl esters (biodiesel), during transesterification. HPLC–RID is found to be reliable with lower noise, showing stable running system. It also consists of a simple operation with the sensitive reactions (Fu et al. 2008). HPLC–ELSD is used in determination of monoacylglycerides, diacylglycerides and triacylglycerides, whereas HPLC–RID is used in estimating glycerol content of the biodiesel (Lv et al. 2017).

#### 13.2.1.4 Size Exclusion Chromatography

Size exclusion chromatography (SEC) is used in the separation of glycerides and fatty acids from the mixture of final product (biodiesel), produced by transesterification. It separates fatty acid alkyl esters, glycerol, monoglycerides, diglycerides and triglycerides along with the estimation of its content (Pinzi et al. 2011). High pressure

SEC (HPSEC) is also employed in the analysis of fatty acid content of the biodiesel (Gonçalves et al. 2014). Size exclusion high pressure liquid chromatography (SE–HPLC) is also used for profiling fatty acid content of biodiesel. It is used for determining the percentage of polymers in the biodiesel using polystyrene as a standard. The glycerides content in the alkyl esters are also identified using SE–HPLC in combination with RID (Michelin et al. 2015). SEC in combination with ELSD (SEC–ELSD) is used in estimating the free fatty acid content, monoglycerides, diglycerides and triglycerides of the final product (biodiesel) in transesterification reaction (Viêgas et al. 2015). The main drawback of SEC is the lack of quantification of individual glycerides in the biodiesel mixture (Sáez-Bastante et al. 2014).

#### 13.2.1.5 Supercritical Fluid Chromatography

Ultra-high pressure supercritical fluid chromatography (UHPSFC) is studied for its variance on using various detectors such as ELSD, mass spectrum (MS) and photodioide array (UV) detectors for determining acylglycerols. UHPSFC–MS is found to be better than the other detectors. It is also found to be efficient than the HPLC–MS and high temperature gas chromatography–mass spectrum (HTGC–MS). Since, it can be used in separating and detecting the lipophilic analytes content. It is used in estimating the glycerol, free fatty acid, monoglycerides, diglycerides and triglycerides contents of biodiesel. Carbon dioxide is used as primary mobile phase in separating neutral and amphipathic lipids. It is also applied in separating carotenoids of the product (biodiesel) (Ashraf-Khorassani et al. 2015).

#### 13.2.1.6 Thin Layer Chromatography

Thin layer chromatography (TLC) is used to study the process of transesterification with the spot analysis. The variance in the spot for varying retention factor is considered for profiling the transesterification reaction implied in producing biodiesel (Kuepethkaew et al. 2017). The production of biodiesel is mainly deviated by the presence of glycerides. Hence, the presence of free fatty acid, monoacylglycerides, diacylglycerides and triacylglycerides for the respective source of oil is checked and validated by the TLC analysis (Guil-Guerrero et al. 2017). Free fatty acid, monoglycerides, diglycerides, triglycerides, fatty acid alkyl esters, carotenoids, sterol esters, tocopherols, retinoids and other polar lipids are separated, qualified and identified using TLC for TLC quality characterization of source (oil (or) triglycerides) (Vicente et al. 2009). TLC in combination with FID is used in rapid screening of chemical composition. The screening analysis and quality assessment of biodiesel is done using the estimation of hydrocarbons, fatty acid alkyl esters, free fatty acid, triglycerides, diglycerides, monoglycerides and polar lipids in biodiesel and biodiesel blends (Yang et al. 2013). TLC and its image processing analysis pave a way to monitor the transesterification process with TLC–FID. The area of the triglyceride spot can signify the completion of transesterification process (Reddy et al. 2010). The low accuracy

**Table 13.2** Comparison of chromatographic techniques

| Method | Advantages | Disadvantages |
|---|---|---|
| GC | • All fatty acids can be separated<br>• Mass fragmentation can be detected using Mclafferty rearrangement<br>• Selective compound can be detected | • Purification and processing of samples are required |
| GPC | • Average molecular weight and its distribution can be determined<br>• Glycerol and oligomers can be quantified<br>• Product can be reproduced and recovered<br>• Density and PDI could be found using GPC–RID | • Separation is only based on size and permissibility |
| LC | • No derivatization is required for monitoring transesterification<br>• Tocopherols and brassinosteroidscan be detected<br>• Glycerides and glycerol contents can be detected | • Samples should be processed for glycerides analysis |
| SEC | • Glycerides and fatty acids can be separated<br>• Percentage of polymers in biodiesel can be predicted | • Individual glycerides cannot be quantified |
| UHPSFC–MS | • Efficient than HPLC–MS and HTGC–MS. Since, it could separate lipophilic analytes | • High cost detectors are required for analysing the analytes |
| TLC | • Profiling of transesterification reaction can be done<br>• TLC–FID can detect hydrocarbons and lipids | • Lower accuracy with humid sensitivity |

and the sensitivity of analysis towards humidity made the process drawback in analysis of biodiesel. The linearity of the sample is also poor. The cost of TLC–FID is also high, which made it unfit for commercialization (Yang et al. 2013). Table 13.2 presents the comparison of widely used chromatographic techniques and their merits and demerits.

### 13.2.2 Spectroscopic Methods

Spectroscopy is a scientific measurement technique. It studies the absorption and emission of light and other radiation by matter, as categories to the dependency of these processes on the wavelength of the radiation. While monitoring transesterification reaction, the spectroscopic methods such as nuclear magnetic resonance spectroscopy and near-infrared spectroscopy are highly utilized for biodiesel analysis. In recent times, standalone spectroscopic methods including nuclear magnetic resonance and near-infrared spectroscopy are used for biodiesel. The widely utilized spectroscopic methods are discussed as follows.

#### 13.2.2.1 Infra-red Spectroscopy

##### Fourier Transform Infra-red Spectroscopy

Fourier Transform Infra-red (FTIR) Spectroscopy is used in the analysis of biodiesel to find the functional group annotation with its corresponding wavelength (Kumar et al. 2013). FTIR is also used in predicting the moisture content of the biodiesel. The fat (or) source of the sample is dissolved in the solvent (propanol) to identify the moisture content. The presence of a peak in the absorbance wavelength range of 3000–3700 $\text{cm}^{-1}$, can provide the occurrence of moisture content in the sample by FTIR spectra (Mirghani et al. 2011). FTIR is also used in monitoring the transesterification process. The prediction of triolein and methyl oleate content in the biodiesel, helped in monitoring the transesterification process (Reyman et al. 2014). The steryl glucosides in methyl esters are also checked with the FTIR analysis. The intermediates of transesterification such as monoacylglycerides, diacylglycerides and triacylglycerides are also monitored by the FTIR spectroscopy (Saeong et al. 2017). The ageing of biodiesel is also validated by the FTIR spectrum analysis. The oil (or) fat in combination with biodiesel, diesel regeneratives and hydrogenated vegetable oil is used for the analysis of ageing of biodiesel. The ageing of biodiesel can be occurred with the formation of acids that can be found using the FTIR spectrum analysis (Singer et al. 2015). FTIR in association with horizontal attenuated total reflectance (HATR–FTIR) is employed in the prediction of composition of the biodiesel. The degree of unsaturation of the biodiesel is also predicted by HATR–FTIR (Ruschel et al. 2015). FTIR combined with photoacoustic spectroscopy (FTIR–PAS) is applied in the study of degradation of oil (or) fat. The purification of biodiesel and washing of glycerol is also validated by FTIR–PAS. The efficiency of FTIR–PAS is found to be greater than the prediction of degradation of oil by attenuated total reflectance FTIR (ATR–TIR) (Lima et al. 2008).

##### Mid Infra-red Spectroscopy

The spectral absorbance at the range of 900–1500 $\text{cm}^{-1}$ is said to be a mid-range Infra-red (MIR) spectral region. It is also mentioned as a “finger print region” of the oil and fatty acid alkyl esters involved in the biodiesel production process (Baskar et al. 2016). Larger bands of absorbance spectrum for biodiesel analysis are found in the MIR region. The spectral incidence, higher intensity and specificity of the signals made the MIR spectroscopy as an appropriate analytical method for analyzing biodiesel. Horizontal attenuated total reflectance combined with MIR spectroscopy

(HATR–MIR) is used in biodiesel analysis. The adulteration in biodiesel with oil is quantified using HATR–MIR. The quantification limit of the process is found to be good at 1–3 (w/w%) of an adulteration (Guimarães et al. 2015). Attenuated total reflectance in combination with MIR (ATR–MIR) spectroscopy with the help of principal component analysis (PCA) is used in the recognition of frying oil. ATR–MIR in combination with partial least square (PLS) multivariate calibration are used in determining the content of an individual oil such as; soybean, palm and hydrogenated vegetable oils (Hocevar et al. 2012).

#### Near Infra-red Spectroscopy

The region above 4000 $cm^{-1}$ of absorbing wavelength is named as Near Infra-red (NIR) region. The combination of NIR and fibre optic is used in the determination of diesel blends in the mixture of biodiesel and petroleum diesel. It is also applied in the analysis of ethyl ester and diesel fuels in the mixture (Knothe 2001). NIR is analyzed in the absorbance range of 4000–12,820 $cm^{-1}$. The crude sample, without any pretreatment is analyzed for the prediction of methyl ester, free glycerol, total glycerol, monoglycerides, diglycerides and triglycerides of the biodiesel, using NIR (Pinzi et al. 2012). NIR along with fibre optic probe is applied for monitoring methyl ester content for analyzing the transesterification process. The difference in oil and biodiesel composition is also predicted using NIR. Thus by these measurements NIR is found to be a good analytical method in analyzing biodiesel. It can be operated easily with the rapid measurements of data showing accuracy and reliability. The samples used for analysis are not destructed however, the usage of NIR is found to be for a specific compound (Knothe 1999, 2001).

### 13.2.2.2 Fluorescence Spectroscopy

The biodiesel composition is quantified for ethanol and fatty acid alkyl ester concentration using fluorescence spectroscopy. The process of estimation of ethanol concentration using fluorescence spectroscopy does not require any separation (or) alteration of compounds (Kumar and Mishra 2012). The samples are analyzed at the gas stations of the spectroscopy. The variation could be recorded in the fluorescence spectra due to the change in viscosity of the oil and fatty acid alkyl ester (Scherer et al. 2011). The fluorescence can be observed for the oil and fatty acid alkyl esters in the wavelength range of 370–800 nm, with the excitation around 350 nm. The fluorescence for the glycerine can be noted at the range of 400–600 nm. The processing of sample for emission and excitation spectra of oil, biodiesel and glycerine does not require any dilution (Chimenez et al. 2012).

#### 13.2.2.3 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP–MS) is used to detect the presence of contaminants which are polluting environment and affecting the process of engine. The determination of potentially toxic compounds such as sodium, potassium, calcium, magnesium, phosphorous and sulphur are analyzed using ICP–MS. Some nutrient elements in oil and biodiesel are can be analyzed using ICP–MS (Maciel et al. 2013). In addition, direct inorganic elemental analysis can be done using ICP–MS with octopole reaction system (ICP–ORS). ICP–ORS is much efficient than ICP combined with optical emission spectroscopy (ICP–OES) in removing matrix and plasma based separation of interferences such as sulphur and phosphorous to enable the measurements of analytes. ICP–MS shows greater performance and wide elemental coverage than atomic absorbance spectroscopy (AAS) and ICP-atomic emission spectroscopy (ICP–AES). Octopole reaction system also has the limitation of analysing the interference, the presence of oxygen in the background membranes (Woods and Fryer 2007).

#### 13.2.2.4 Ultra-violet Spectroscopy

Ultra-violet (UV) spectroscopy is used for characterizing the oxidation stability (or) anti-oxidative property of the biodiesel. The absorbing character of the UV spectroscopy to determine the oxidation stability of a compound is carried out (Rodrigues et al. 2009). The concentration of biodiesel can be estimated using the UV spectroscopy. The concentration of the biodiesel is inversely proportional to the absorbance of the compound at a specific wavelength (Caires et al. 2014). The glycerol content of the product in the transesterification process is also estimated using the UV spectroscopy. The reaction mixture with 9,9-dimethoxyfluorene reagent and p-touluenesulfonic acid (PTSA) catalyst is analyzed using UV spectroscopy for the glycerol content. The limit of estimation of glycerol in biodiesel is at the range of 0.05 w/w% (Reddy et al. 2010).

#### 13.2.2.5 Proton Nuclear Magnetic Resonance

The progression of the transesterification process is monitored using the proton nuclear magnetic resonance (H–NMR). The fatty acid composition of the biodiesel is measured and identified using the H–NMR (Tesfaye and Katiyar 2016). The biodiesel concentration of the product during the transesterification process is also measured using H–NMR (Monteiro et al. 2009). In another study, the acidity of the sample (biodiesel) and the presence of acid content (acid value) in biodiesel is checked and measured using H–NMR (Viêgas et al. 2015). High field H–NMR shows poor mobility and it is also found to be expensive. Hence, mobile low field H–NMR is used in checking the quality of biodiesel. It shows clear differentiation between the oil, biodiesel, methanol and glycerol. The degree of unsaturation is found using H–NMR.

The fatty acid compositional information is the direct measurement of the biodiesel property. Signals corresponding to the protons such as glyceridic protons, methyl ester protons, olefinic protons and Bis-allylic protons are used to estimate the unsaturated fatty acid alkyl esters percentage of product (Linck et al. 2013). The main drawback of H–NMR is that it could not separate (or) differentiate the saturated compounds from the mixture (biodiesel) (Knothe and Steidley 2009). Table 13.3 presents the comparison of widely used spectroscopic techniques in the literature and their merits and demerits.

**Table 13.3** Comparison of spectroscopic techniques

| Method | Advantages | Disadvantages |
|---|---|---|
| FTIR | • Functional groups, moisture content and ageing of biodiesels are predicted<br>• Degree of unsaturation is predicted by HATR–FTIR | • Elemental and compound analysis cannot be done using FTIR |
| MIR | • Finger print region of biodiesel is in MIR range<br>• Adulteration of biodiesel and determination of soybean, palm and hydrogenated vegetable oil is done by MIR | • MIR differentiation with respect to carbonyl stretching is non-specific |
| NIR | • No pretreatment of sample is required<br>• Biodiesel and methanol content of the product is analysed using NIR | • Fatty acid profiling cannot be done using NIR |
| Fluorescence spectroscopy | • No alteration of samples is required<br>• Predicts the process of transesterification reaction | • Compounds involved in providing fluorescence of the product are not predicted |
| ICP–MS | • Potentially toxic contaminants such as S, Na, K, Ca, Mg and P are identified<br>• ICP–OES is more efficient than AAS | • Presence of oxygen in the compound interfere with the result |
| UV | • Oxidation stability, glycerol content and concentration of biodiesels are predicted using UV | • Determination of glycerol and biodiesel concentration requires the dye compound 9,9-dimethoxyfluorene for analysis |
| H–NMR | • Acidity of product can be predicted<br>• Biodiesel concentration and percentage of unsaturated fatty acid alkyl esters are measured using H–NMR | • It could not differentiate saturated compounds |

## *13.2.3 Other Methods*

### 13.2.3.1 Viscometry

Viscometry is utilized in analyzing the kinematic viscosity of biodiesel. This property of biodiesel is useful in measuring the process of transesterification. Since, the viscosity of oil (or) fat is higher than that of the viscosity of fatty acid alkyl esters. The kinematic viscosity of the product decreases with the increase in reaction time. Thus, the indirect measurement of product by kinematic viscosity as a function of time gives the transesterification profile for the process. The concentration of biodiesel is correlated with the kinematic viscosity of biodiesel to predict the transesterification process (Gabitova et al. 2017). The difference in the viscosity of the oil and fatty acid alkyl esters are found using viscometry. This method is said to be rapid. It is also found with the correlation of temperature and viscosity using neural network model. The only drawback of this method is the aggregation of particles around the walls of the container during analysis (Torrisi and Sabino 2012).

### 13.2.3.2 Refractive Index

The conversion of biodiesel is checked with the simple linear correlation of biodiesel concentration with the refractive index. The refractive index is measured for the product (biodiesel) at 303.15 K. The conversion of the biodiesel by the transesterification process is monitored by the change in refractive index of the product. This method is validated using the results of proton nuclear magnetic resonance (Xie and Li 2006). The thermodynamic interaction with the correlation of excess of refractive index states the reaction of intermolecular interactions in the biodiesel production process. The analysis of intermediate compound is also carried out using refractive index analysis (Vural et al. 2008). The characterization of refractive index helps in improving the flow visualization by imaging the internal flow in transparent nozzles. These characteristic property of refractive index is the important features for analyzing the biodiesel (Payri et al. 2016).

### 13.2.3.3 Titration for Determining Free Fatty Acids

Neutralization Number (NN) of biodiesel can be evaluated by the titration for determining free fatty acids (Komers et al. 1997). There are two approaches, one is using potentiometric and other is using two acid-base indicators such as neutral red and phenolphthalein are followed to quantify the strong and free fatty acids. The most consistent results are recorded by potentiometric method, whereas using the two indicators. The NU value determined by the titration method is reasonable higher in the range of 10–20% with the sample activity.

#### 13.2.3.4 Wet Chemical Methods

The iodine and saponification values are evaluated by the wet chemical methods. In the fatty acids mixture, the theoretical addition of iodine to the double bonds determines the iodine value, which can be acts as an indicator of the total amount of unsaturated fatty compounds. On the other hand, the average molecular weight of the fatty compounds determines the saponification value of the sample. Therefore, it must be considered to best use of iodine and saponification values since it's concurred of each other. These values are controlled by the biodiesel standard ASTM D6751. Various wet chemical methods are involved, however, these methods are presently replacing by chromatographic/spectroscopic methods due to providing improved information. In addition, the requirements of complex sample preparation in the wet chemical methods made as a time consumption process (Van Gerpen 2005).

#### 13.2.3.5 Enzymatic Methods

The description to test the completeness of the transesterification process by analyzing glycerol in biodiesel was reported earlier (Bailer and Hueber 1991). The enzymatic analysis was subsequently applied for the solid phase extraction of the reaction mixture. Formerly, this method was considered as simplest technique for glycerol analysis, however, there are some difficulties associated with reproducibility of this method (Lozano et al. 1996).

#### 13.2.3.6 Methods Used to Test for Oxidation Stability

The degradation of biodiesel can be determined by the oxidative stability, which relates to the requirement of time to decompose the biodiesel in the presence of oxygen at controlled heating.

Oxidation stability of biodiesel is measured by numerous ways and the vital one is Rancimat method. The oxidation stability of biodiesel can be measured in terms of induction time for the production of volatile organic acids under prescribed heat and oxygen, which is called Rancimat (EN 14112) technique. In this method the production of volatile organic acids are the byproducts of fatty acid ester. Another technique of Rancimat (EN 15751) measures the volatility of biodiesel by the prolonged stability of blends through extending the reaction tube up to 250 mm and the reaction time up to 20 h.

Oxidative stability of oils, lubricants and fats are also measured by high pressure differential scanning calorimeter (HPDSC). This analysis is performed with amendment in ASTM D5483 and considered as standard one for lubricating greases. In this analysis, a test cubicle containing properly weighed sample is heated up to the required temperature and pressure with oxygen. The exothermic reaction will take place, while keeping the sample at this prescribed conditions and the pressure drop is observed during the period is called oxidation induction time. There are other methods being identified for the measurement of oxidative stability of biodiesel. The discussed techniques are stepping stone methods for long term storage of biodiesel. The need for suitable testing equipment that must be more precise and faster will steadily increase once the biodiesel industry continues to develop.

#### 13.2.3.7 New Low-Cost and Greener Alternatives in the Analytical Field

In order to address the problems associated with established analytical techniques such as expensiveness, time taking, require skilled personals and no automation, the recent researches are focuses on development of chemical sensors. This technique is expected to be an attractive analytical tool in the biodiesel production process due to its easy operation, lower cost and ease in sample preparation and automation. Conversely, inadequate selectivity in complex media is highly delayed the practical use of chemical sensors i.e. the regularly used probes in bioreactors are only for pH and oxygen. To overwhelm the practical difficulties in the chemical sensor, the systems have been developed namely electronic tongues and electronic noses for the analysis of liquid and gas, respectively. Recently, they prove that there are able to classify the multicomponent media and conduct quantitative determination to monitoring the biotechnological processes (Rudnitskaya and Legin 2008). These excellent features make multisensory systems are the auspicious tool to monitoring the process while quantitative measurement and recognition of multicomponent media can be carried out simultaneously. However, more complexity and low reproducibility of composition of the biomass compared to other fermentation media, the applications of the electronic tongues and noses for the follow-up of production processes remain limited till day. Therefore, practical applicability of multisensor system is a big objection in the biotechnological industry and the future research needs to be directed to address the problems on reproducibility and stability in calibration and contamination of sensor surface in the complex media.

## 13.3 General Observations

There are several factors that can affect biodiesel quality viz., composition of feedstock (oil or fat), production processes, handling and storage. The assessment of biodiesel quality is realized by examining the chemical composition and physical properties of the fuel. There are some general problems on quality of biodiesel generating due to presence of unwanted components and some contaminants. As discussed earlier, partially retained and unseparated glycerol, unreacted triacylglycerols, residual alcohols, free fatty acids and catalyst are presented in the final product of biodiesel at trace level. Consequently, these parameters and their analytical techniques are addressed in standards along with alternative techniques have been explored. Furthermore, the monitoring of transesterification process and the blend level analysis are essential prospects on biodiesel analysis. Generally, GC and HPLC are used to analyze the most important parameters of biodiesel including glycerol and their acyl derivatives, fatty acids and fatty mono-alkyl esters. In fact, GC is mostly being utilized technique because of its high accuracy for minor component quantification. Howsoever, baseline drift, overlapping signals, and aging of standards and samples can antagonistically affect the GC accurateness. Additionally, GC analyses often require sample derivatization, primarily to afford trimethylsilyl derivatives of the hydroxyl groups. Though the procedure improves the chromatographic separation, it also increases the analysis time. Flame ionization detection is the best extensive detector utilized in GC, however the application of mass spectrometer has improved. Although HPLC is less deployed for biodiesel characterization, but it utilizes lesser analysis time than GC and also the sample derivatization is not needed. However, this technique might be applied for blend analysis of biodiesel obtained from different feedstock in comparison to than GC analysis. For HPLC analysis, various detectors were ascribed for biodiesel analysis, amongst which evaporative light scattering detection is quite appropriate. Spectroscopic methods such as NMR and IR based techniques are widely engaged to monitor the transesterification process and evaluation of bled level. NMR exhibits superior performance, however, it is an expensive instrument and requirement higher maintenance cost.

## 13.4 Summary

Numerous analytical techniques are employed to assess the quality and production monitoring of biodiesel. GC is the most commonly applied technique due to its accuracy in detecting very trace level of contaminants in order to meet the prescribed biodiesel standards. Although, the upgradation and enhancement of GC techniques is still under progress, however, no other techniques explored similar capabilities of GC including determination of all contaminants at low concentration, minimum instrumentation cost, minimum operating time and lesser laborious. The future research has to be focused on exploring methods to analyze the physical properties of the biodiesel. NIR/viscometry can be used for regular analysis with some realistic concessions because of user friendly and non-time-consuming technique that can be employable to monitor the biodiesel production processes.

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