The Handbook of Environmental Chemistry 99

Series Editors: Damià Barceló · Andrey G. Kostianoy

Pankaj Pathak
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Alternative Energy Resources

The Way to a Sustainable Modern Society

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The Handbook of Environmental Chemistry

Volume 99

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Alternative Energy Resources

The Way to a Sustainable Modern Society

Volume Editors: Pankaj Pathak · Rajiv Ranjan Srivastava

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Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last four decades, as reflected in the more than 150 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Series Editors

Preface

The conventional energy resources are finite and estimated to be finished within the next few decades. Such a report creates panic in modern society where energy is an unprecedented commodity in daily life. This situation is more severe for all the developed and developing countries, which are on its growing wheels with full pace by depending on conventional fossil fuels to fulfill their energy demands. Increasing population with a challenge to uplift their lives to have access to the basic amenities, huge growth in primary energy consumption, and the unstable geopolitical scenario specifically in the oil-producing countries of Middle East are unfavorable to the aim of Sustainable Development Goals. In this context, energy planning for global sustainability is a complex exercise, facing a plethora of challenges and issues in every corner of this world. The most common and conventional sources of energy (coal and petroleum) are non-sustainable that emits a huge amount of greenhouse gases. Links between energy and climate change have already been established. The adaptation to alternative energy makes more sense and renewable energy has been recognized as the most potential substitution of conventional energy. Therefore, increasing the contribution of cleaner energy to the energy-mix by the means of alternatives or renewables is of great focus, not only to ensure energy (electricity) supply at an affordable price but also with environmental responsibility.

This book is an ice-breaker for scholars, researchers, and academicians who are working on the new, alternative, renewable, and clean source of energy to ensure a sustainable future. Strata of topics have been included with an objective to cover the maximum aspects of future energy-mix.

The utmost remarkable structures of this book are associated with alternate energy resources, pros and cons of resources; utilize these resources to build a sustainable environment for modern society. Chapter “Potential and Transformational Needs of Alternative Energy in Developing Countries” deals with the potential and transformation needs of alternative energy resources in developing countries. Chapter “Mechanism of Photoanodes for Dye-Sensitized and Perovskites Solar Cells” emphasizes harnessing solar energy, its mechanism, and upgradation to make it sustainable. Chapters “Grid Integration of Wind Energy Conversion Systems” and “Offshore Wind Energy: Resource Assessment” focus on onshore and offshore wind energy resources and the integration of wind energy. In the chapter “Hydropower: A Renewable Energy Resource for Sustainability in Terms of Climatic Change & Environmental Protection,” we have given attention to environmental sustainability due to hydropower. Chapters “Biomass Energy Sources and Conversion Technologies for Production of Biofuels,” “Renewable Energy from Woody Biomass of Poplar and Willow SRC Coupled to Biochar Production,” and “Ligninolysis Potential of Ligninolytic Enzymes: A Green and Sustainable Approach to Bio-transform Lignocellulosic Biomass into High-Value Entities” are discussing different methods of utilizing biomass to convert into energy and biofuel, different mechanisms harness bioenergy is discussed. Chapters “Waste-to-Energy: Suitable Approaches for Developing Countries” and “Biomass-Derived Triglyceride: A Source of Renewable Aviation Fuel and Biodiesel” describe different technologies for the conversion of wastes (municipal organic waste, plastic) into energy and biofuel. Moreover, energy from wastewater is generated by using microbial fuel cells, which is discussed in the chapter “Microbial Electrochemical Systems (MESs): Promising Alternatives for Energy Sustainability”. Further reverse osmosis concept through membrane technology to generate alternate energy is discussed in the chapter “Generation of Osmotic Power from Membrane Technology”. The environmental impacts associated with alternative bioenergy are discussed in the chapter “Environmental Impact and Challenges Associated with Bio-based Energy.” Chapter “Role of Chemistry in Alternative Energy: The Thermodynamics and Electrochemical Approach” emphasizes the role of chemistry to harness sustainable green energy. Chapter “Renewable Energy as a Sustainable Alternative: A Way Forward” concludes the significance of alternative energy scenarios and future prospects for a modern sustainable society.

Nevertheless, the material collected in this volume will convey deep knowledge of alternative energy and its associated upgradation done in the recent past to build sustainable modern society.

On the whole, the material composed in this book will bring in-depth understanding and extension of knowledge in the field of alternative energy resources and different techniques to harness renewable energy. Dr. Pankaj Pathak and Dr. Rajiv Ranjan Srivastava individually acknowledge the authors and reviewers for contributing their valuable time, knowledge sharing, and their interests to bring this book into the present shape.

Amaravati, India — Pankaj Pathak
Da Nang, Vietnam — Rajiv Ranjan Srivastava

Contents

Potential and Transformational Needs of Alternative Energy in Developing Countries

Sadia Ilyas, Hyunjung Kim, and Rajiv Ranjan Srivastava

Contents

Abstract The entire world is in a quandary for the interdependent terms of "energy-to-all" and "climate change." The developed countries are somehow in a better situation as they are energy surplus and being able to pay against their carbon emissions. This situation is certainly not existing in developing countries. They

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must have to overcome the energy poverty to pace their growth rate; however, they do not have access to the clean energy, resulting in a contribution to climate change by using the high carbon-emitting fossil fuels. In this context, the development of alternative energy technologies in developing countries in this current decade is now major uptake as a crucial component in providing an integrated solution to ensure the "energy-to-all" and to limit the "climate change" issue. This chapter aims to discuss the potential of developing countries in the field of alternative energy and their real needs of the hour for energy transformation to alternatives. The cases of several countries, more specifically the African and mid-Asian countries, are discussed, those having the high potential for alternatives but facing the energy crunch along with a high population density of the mid-Asian countries.

Keywords Alternative energy, Emissions reduction, Energy-to-all, Sustainable development

1 Introduction

Energy is the quantitative term that must be transformed into an object for performing work or heating any other object. The law of energy conservation states that "energy can neither be created nor be destroyed, only it can be converted from one form to another form." *Sustainable energy* can be an extension of the energy conservation, which states that "the use of energy in terms of meeting the present needs without compromising the future generation to meet the demand." The conventional fossil sources of energy, viz., coal, petroleum, and natural gas, which fulfil the largest energy demand worldwide do not fit to be sustainable source of energy due to the characteristics that after conversion of energy from one form to another, they all are going to be exhaust and significantly affects the future demands. Moreover, these sources are criticized for intense emissions of the greenhouse gas emissions (GHGs) and uncertainties of the economic feasibility and availability due to dependence on foreign supply [1]. This situation becomes more critical by knowing the fact that nearly one billion populations worldwide is lacking access to electricity and about 3 billion population rely on smoky fuels, viz., charcoal, wood, and cow dung as the cooking fuel, causing the estimated yearly deaths of seven million people. Notably, energy production and consumption cause 70% of the total GHGs emissions. Hence, sustainable and affordable clean energy has also been kept under Goal 7 of the United Nations Sustainable Development Goals [2].

1.1 Perennial Problems with Conventional Fossil Fuels

Among the fossil fuels, coal, petroleum oil, and natural gas have remained the largest source of energy production, where coal is abundantly distributed worldwide albeit

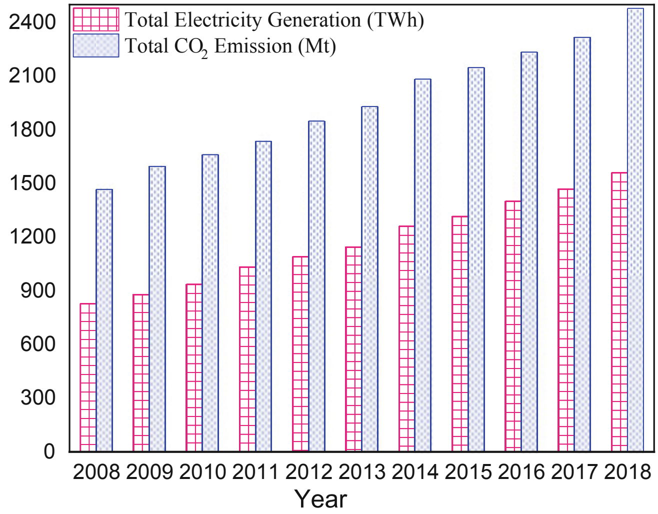


Fig. 1 Worldwide electricity generation and CO_2 emissions data (reproduced with permission from [4])

exhibits dreadful effects. Coal mining is not environmentally friendly itself that poses a serious threat to the ecosystems of the mine sites. Moreover, externalities like emissions of 800 tph CO_2 by a coal feed of 400 tph for generating 430 MW of electricity are the associated adversary of the coal-based power plant [3]. The global electricity production corresponding to the CO_2 emissions is presented in Fig. 1 and depicts the mammoth contribution of power plants in global warming [5]. It also pollutes air with the release of suspended particulate matter, water due to acid drainage of coal, and soil by the ashes and slurry disposals. In contrast to the abundance of coal, oil and natural gas are not distributed widely and limited to some geographic boundaries where finite availability is estimated for the next few decades only; hence, it cannot be taken as a sustainable alternative source of energy.

1.2 Alternative Energy

Sustainable energy is always interchangeably referred to *renewable energy* – "the energy derived from the natural resources that are infinite or, non-exhaustible," viz., sunlight and wind. Although renewable energy (RE) is often considered to be the alternative source of conventional energy, but actually all the renewable energy cannot be taken as the *alternative energy* that specifically avoids the fossil fuels to control environmental footprints. Biomass energy is such an example to be renewable but not the alternative energy (AE) as it may cause deforestation and emissions by burning of biomass/wood (thebalance.com, Renewable energy in the US economy). The marginal difference can be pictorially depicted in Fig. 2; however,

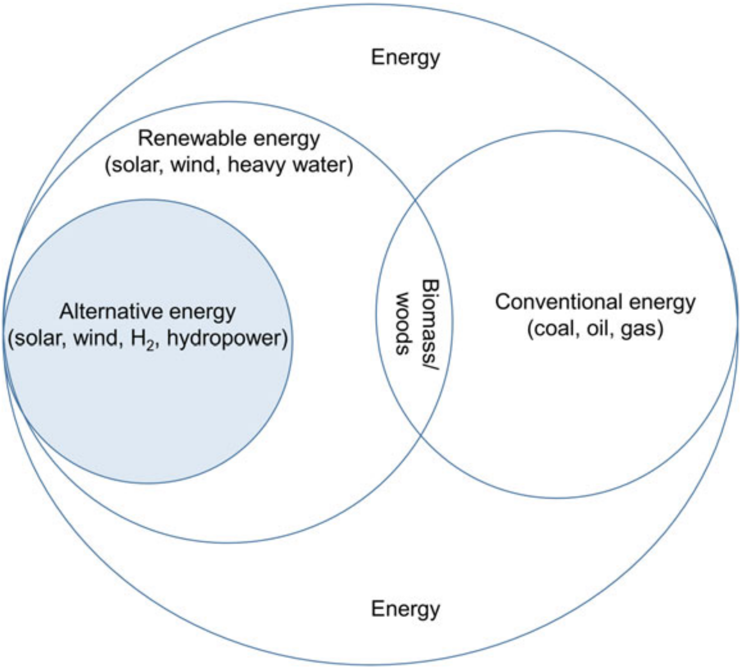


Fig. 2 A typical representation of the relation between different forms of energy sources

looking at the dominant role of bioenergy in the energy mix as the only renewable carbon source with a potential to emissions abatement, both the renewables and alternatives are simultaneously considered in this book as one. One of the reasons behind such consideration is the fact that the carbon in bioenergy derives from the sequestration of atmospheric CO_2 via the photosynthesis during the growth of biomass.

The alternative sources, like solar, wind, hydropower, geothermal, and hydrogen, are becoming attractive due to their low emissions, indefinite supply, and potentially stable pricing in the energy market. On the other hand, the alternative energy has shortcomings, viz., higher capital costs, an intermittent energy supply, and inefficient to supply a stable base-load energy demands [1, 6]. The benefits and limitations of the alternative sources are summarized in Table 1.

2 Importance and Imperative to Energy Transformation

Traditionally, energy is continued to be the core of the economic and industrial development of any country [7]. The countries with energy poverty have found to perform poorly on the development front and the prosperity index. In the modern era, the energy demand is not only limited to industrial growth and economic

Table 1 The main benefits and limitations identified for alternative energy sources

Types of alternative energy	Benefits	Limitations
Solar- capturing the radiant energy from sunlight to convert into the heat and electricity via the photovoltaic solar cells	Sunlight is functionally endless that can render fossil fuels obsolete	The efficiency is still low and needs a large space for harvesting the solar panels
Wind- capturing the energy of wind flow through turbines and convert into electricity	No emission to pollute the environment and large availability	A concern for birds and large space is required for wind turbines, mostly suitable for coastal areas
Hydropower- capturing the energy by turbines from the water flow through dam and convert into electricity	Versatile in operation from large dams to small check-dams	Disrupts natural water flows and non-reliable due to the changes in seasonal water flows
Geothermal- capturing the heat from the earth's crust and volcanic eruptions to operate the turbine for electricity production	It is naturally replenished and its underground existence does not leave any footprint on the surface	Costly infrastructure is required
Hydrogen- usually hydrogen is separated from water and can be used as fuel and electricity	Can be used for fuel cells able to powering the electric motor	It's a new technology and high-tech expertise with R&D investment is required

development, albeit it is now directly affecting human health and the surrounding environment. Clean, affordable, and reliable energy is therefore indispensable, in particular to the developing and underdeveloped countries. In order to pace their growth rate, they must need to fulfil the energy demand but in a sustainable manner. In lacking this, the economic and industrial growth can be achieved, but the prosperity of citizens cannot be secured. The alternative energy in terms of RE technologies has a vital role in future energy use and inextricably linked to economic prosperity [8]. The problem lies in the energy transformation from fossil fuels to RE/AE technology for electricity generation and fulfilment of the energy demand.

Spurred by policy support and innovations in a growing number of countries, AE technologies have been recorded significant advances with cost-cutting that consequently increases the deployments. However, the progress in AE is not homogeneous across countries and each sector. Many barriers still exist to hamper the deployments of AE, mostly in the developing and underdeveloped countries albeit the developed countries are confronting a different challenge. It shows the necessity to all the international community that belong to either the developing or the developed countries for coming together in a common effort to transform the global energy system in the coming years. In a report on "Energy for a Sustainable Future" to the Secretary-General's advisory group on energy and climate change [9], the challenges to energy transformation have been divided on the basis of different income groups: (1) lower, (2) middle, and (3) high. The imperative to energy transformation among those nations is summarized in Table 2.

Table 2 Energy transformation needs for different categories of countries based on their income group

Category	Description for energy transformation
Lower-income group countries	They need the energy expansion to meet the requirements of several billion people experiencing the energy poverty and living on access to traditional biomass only. Access to AE technology can be affordable to these groups of countries as it does not require to build up the strong infrastructure in terms of energy generation, storage, and transmissions
Middle-income group countries	They need to tackle the energy expansion to decouple growth from energy consumption through enhancement in energy efficiency and reduced emissions of GHGs. Mostly developing countries in this group are in a more critical situation as they need more energy consumption to maintain their imperative growth rate, but they are under scrutiny for their emissions to the environment
High-income group countries	Unique challenges are in front of this group of countries, mostly the developed ones. The fact is that they have largely invested in the energy sector in the 1960s–1970s. Hence, those investments lives are reaching the end and present opportunities to invest in new energy projects with low emissions like the RE/AE

While different countries may pursue the transformational paths in different ways, there is a large potential synergy from international cooperation on joint strategies and technology sharing that includes the lessons learned from old/current practicing policies and regulations, capacity buildup, financial approaches, and more coordinated research and development. All the countries of the three categories have the opportunity to a fundamental transformation of their energy system, allowing low- and middle-income developing countries to leapfrog current systems for achieving the access to affordable, cleaner, reliable, and sustainable energy. Such changes will require large shifts in regulatory front for all the economy with huge incremental investment on infrastructures that estimated to be about $1 trillion per year. As per the different categories of countries, the energy transformation is supposed to be uneven, which can lead to a wider "energy gap" between the developed and least developed/developing countries if the transformational changes will be poorly handled. On the contrary, a balanced transformational framework has the potential to achieve sustainable growth if handled well. It is also noteworthy to mention the socioeconomic angle on energy transformation. By the year 2050, an increase in welfare (15%), GDP (1%), and employment (0.1%) is estimated [10]. At the regional/country level, the outcome of the energy transition depends on the ambition of individual regions and the regional socioeconomic structures. The energy shift is always foreseen as the job snatcher which cannot be accepted by any country as it will adversely affect the socioeconomic system. This scenario has been rejected by IRENA [10], and job creation of 19.0 million in the rapid expansion of RE/AE against a loss of 7.4 million jobs in the field of fossil fuels by 2050 has been estimated. Therefore, transforming the socioeconomic scenario is one of the most potent benefits of energy transformation. The socioeconomic footprint from a

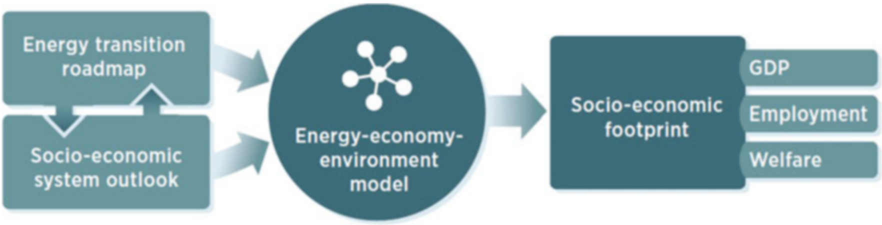


Fig. 3 A representation for obtaining the socioeconomic footprint through the combinational energy transition (reproduced with permission from [10])

combination of energy transition roadmap and a socioeconomic system is pictorially presented in Fig. 3 [10].

3 Status Quo of the Energy Transformation and Contributions of Developing Countries

Additions to AE capacity are nowadays exceeding the power generation through fossil fuels with a wider margin. The capacity addition from the starting of the twenty-first century until 2016 is depicted in Fig. 4a. In 2017, the AE sector added 167 GW capacities worldwide with 8.3% of robust growth over the previous year [10]. Approximately 94 GW solar, 43 GW wind, and 4 GW offshore wind capacity have been added [13]. In the contribution of the AE addition, the significant presence of developing countries with high economic/GDP growth rate is recognized. The growth recorded in different AE sectors is presented in Fig. 4b. It clearly shows that solar, wind, and hydropower are the three main sectors with high contribution growth than others. The country like India has projected its target for a total of 227.5 GW installed AE until 2022 [5]. At the same time, lowering costs open a new prospect of electricity supplies dominated by AE. Among the capacity addition of total 167 GW AE in 2017, the contribution of solar and wind was 52% of the total addition, while fossil fuel contribution decreased to only 40%. The reducing costs of alternatives can be understood by the average global auction pricing of some selected fields shown in Fig. 4a. In 2017, offshore wind projects were offered at market prices without requiring subsidy, while the concentrated solar power (CSP) including thermal storage was offered at <10 US cents/kWh [14]. Also, the global weighted average costs for onshore wind and SPV stood at 6 and 10 US cents/kWh, respectively, in the year 2017–2018, which is forecasted to significantly undercut these more [14]. Looking at the direct relation between the alternatives and economic growth, the trends clearly show that growth in this sector is continuously accelerating. Nevertheless, the current growth rates are insufficient to achieve the level of decarbonization required by 2050 (will be discussed later with the case study of India). The additional energy services other than electrification like heating and transportation will be required because electricity accounts only 20% of the total

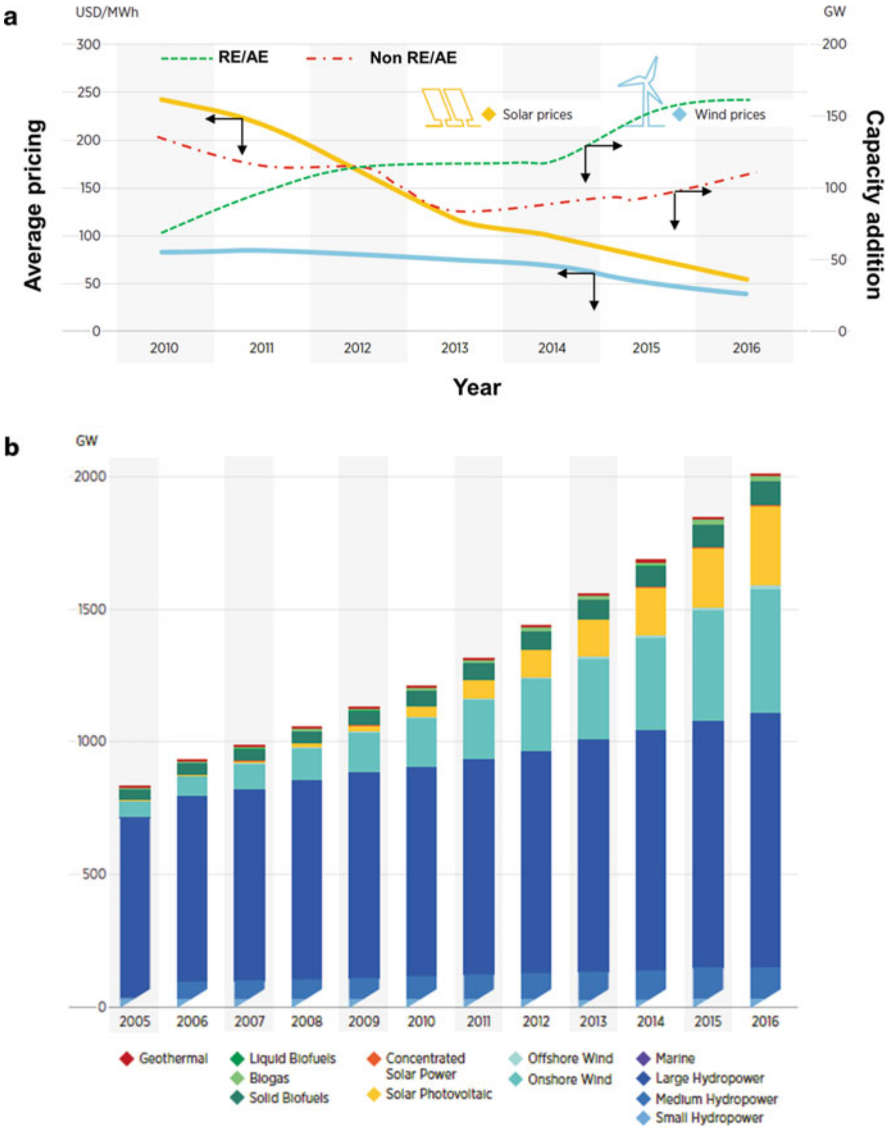


Fig. 4 (**a**) A representation for the capacity additions of RE and non-RE sectors and the average global pricing of selected alternatives, solar and onshore wind energy [11, 12]. (**b**) A representation for the sector-wise capacity additions by different RE/AE means [12]

energy consumption. Furthermore, increasing the electricity share and the AE supply as an energy mixture will raise the share of alternatives in end-use sectors. The industrial sector has been identified to be the most challenging one. The high energy demands of certain energy-intensive industries, the high carbon content of certain products, and the high emissions of certain processes make innovative solutions and life cycle thinking necessary. Heavy industries as a whole have advanced far to increase the usage of alternatives, but electrification and the development of innovative technological solutions for the renewable hydrogen and biochemical feedstock continue apace.

Nevertheless, the energy transformation in every corner of this world is slowly but significantly taking place; most of the transformation about two-thirds of the new capacity in three countries in the United States, China, and India are coming from the alternatives. This is quite an interesting fact that despite the aggressive transformation, both leading Asian countries China and India are also investing huge in coal power plants to meet their future energy demands. China is the undisputed leading the AE growth that accounts more than 40% of the total energy mix worldwide by 2022 [15]. China has surpassed its solar and wind target for 2019, while India's capacity is expected to be more than doubled by 2022 along with 90% of solar and wind as well.

4 Framework to Sustainable Pathways for Developing Countries

In order to design a framework to the sustainable pathways for energy transformation from conventional to the alternatives, Vandaele and Porter [16] have presented a comparative study between the United States and African countries like Morocco, Kenya, and South Africa. The pattern of energy transformation can be easily understandable due to a huge gap between the countries in terms of energy access and energy consumption.

4.1 African Countries

Kenya has over 40% of the population below the poverty line (BPL) with approximately 20% access to the electricity, while others are living on biomass and waste combustion [17]. The country generated 68% from RE sources out of the total 7.6 million MWh of electricity produced in 2012. As a part of scaling up renewable energy program SREP 2011 and Vision 2030 under the financial investments by the African Development Bank and World Bank [18], a capacity buildup of 23,000 MW is aimed until 2030 against the capacity of 1,840 MW in 2012 [19]. On the other side, Morocco consumed 25.4 million MWh of electricity in 2012 with only 20% from hydropower, and 4% from other alternatives are contributing to a total of 6,763 MW of electricity capacity [20, 21]. The country has the main challenge to shift its dependency of over 70% electricity from the oil supply from foreign countries. In comparison with Kenya and Morocco, South Africa is a middle-income country with 83% of the population having access to energy. However, the country fulfils 90% of electricity demands from coal power plants and emits a large amount of CO_2 [22]. Emissions reduction and the stabilized electricity supply are the two main goals for which the country has planned to diversify its primary energy sources by increasing renewables from 203 MW to 18,200 MW in 2030 [22]. South Africa has average solar radiation ranging from 4.5 to 7 kW h/m^2/day [23]. Numerous SPV stations of a total 919 MW operational capacity and 1,360 MW capacity are under construction stage. Solar water heating (SWH) has also implemented well in the country and matured with 242 MW of installed capacity [24]. Actually, the entire Southern African Development Community (SADC) region is struggling to overcome energy poverty despite having tremendous renewable resources. The International Renewable Energy Agency has estimated the solar potential of the SADC region to be about 20,000 TWh/year (as can be depicted from the irradiation map of South African region in Fig. 5), albeit $<1\%$ is currently installed, suggesting for a massive opportunity to solar energy expansion in the region [25].

Looking at the electricity consumption of the African countries, the United States is consuming a huge amount of electricity over 4 billion MWh in 2013. Although the country is one of the leading amongst tapping of AE, the United States mainly relies on coal (39%) based electricity production [26] while, natural gas is used to produce ~28% of the electricity mainly supplies to the industrial sectors [27]. AE sector is expected to grow at a rate of 67% albeit contributing only 16% of the total electricity generation in 2040 [28], showing that the world's leading country has also a lot to be done in the direction of energy transformation.

Vandaele and Porter [16] have proposed the comparative blueprint for energy transformation of the abovementioned four countries (as shown in Fig. 6). It has been proposed that the transformation in Kenya led by the geothermal energy from the Great Rift Valley. The smaller, decentralized, and microgrids would allow affordable access to a remote area and would require to install 400 MW/year of alternatives until 2040. For Morocco, the solar (800 MW) and wind (572 MW) installations would be the major inputs than the hydro (100 MW) and bioenergy (120 MW) by 2040. The alternative technologies that would benefit South African energy transformation include the increased energy efficiency, smart meters and grids, and hydrogen storage. The country would require a large installation of solar (1,400 MW) and wind (1,200 MW) capacity/year up to 2040. On the contrary, the per capita electricity consumption in the United States has estimated to decline with improved efficiency from 12,200 kWh to 8,000 kWh per year. However, the decommissioning of aging power plants will generate a demand for new installations, which would be contributed by the addition of solar and wind energy at a capacity of 12,500 MW and 18,000 MW per year, respectively, by 2040.

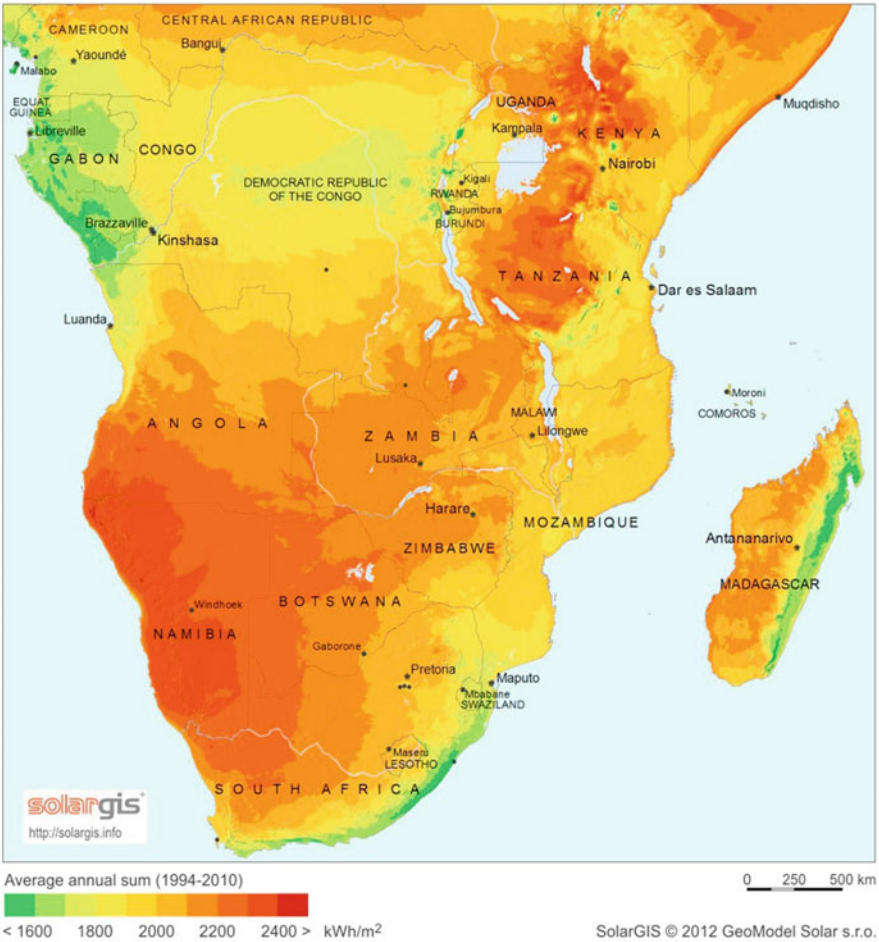


Fig. 5 The irradiation map of South African region (reproduced with permission from [25])

4.2 *Mid-Asian Countries*

Among the mid-Asian countries, Bangladesh is one of the dense population countries and facing both energy and economic poverty. Only 42% of the Bangladeshi population has access to electricity [29], while only 20% has grid connections [30]. The per capita electricity consumption is very low (146.5 kWh) far below that of the average of low-income countries, i.e., 392.4 kWh [31]. The energy growth rate of 316 MW/year against the demand of 7,500 MW/year is very drastic. Moreover, above 75% of electricity production depends on the finite source of natural gas and coal [32]. To bridge this huge gap for demand versus generation, Bangladesh is

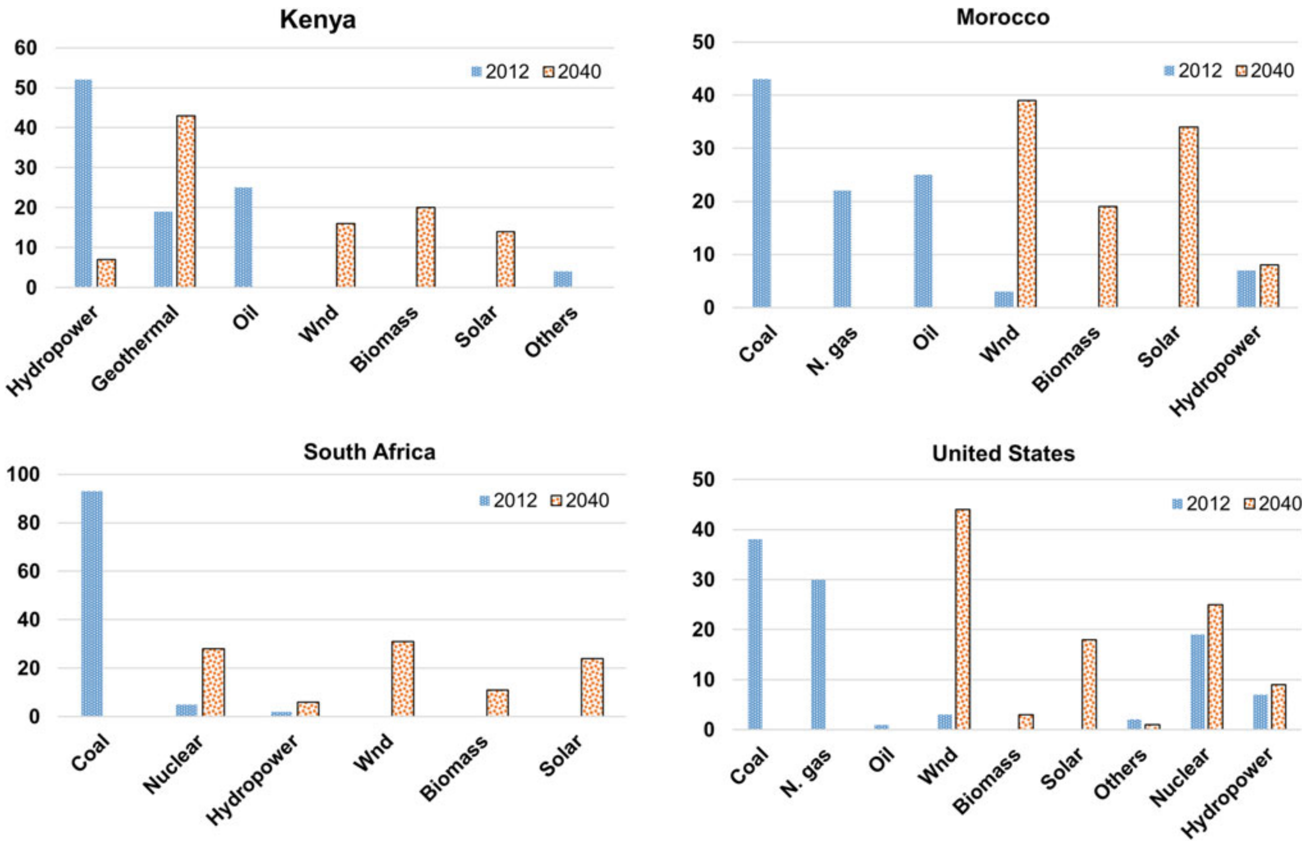


Fig. 6 Electricity generation by different means of energy sources (reproduced with permission from [16])

Table 3 The current status and capacity buildup projects of alternative energy in Pakistan (reproduced with permission from [42])

AE source	Capacity potential (MW)	Installed capacity (MW)	Under installation (MW)	Project feasibility (MW)	Progress
Solar	2,900,000	100	104	1,340	0.1 GW of SPV projects have been commissioned, and 0.3 GW project in Balochistan (Quetta) is planned
Hydro	60,000	6,556	20,733	6,564	20.7 GW of capacity projects are at various stages
Wind	346,000	106	900	2,500	0.1 GW of wind projects have been commissioned
Biomass	3,000–5,000	35	–	4.3	Only in Punjab province but grid connected project is yet to be commissioned

eyeing at the alternative sources as the country has plenty of opportunities to go for the renewables. The country has over 6.0 h average sunlight and wind speed of 3–6 m/s. Bangladesh requires an installed capacity of 1,000–1,200 MW alternatives to attain a dependable 800 MW of energy production [32]. Bangladesh receives an average direct normal irradiance/annum (DNI) of ~1,900 kWh/m^2 against the standard of 2,000 kWh/m^2 for 100 MW energy through the concentrated solar power (CSP) plant [33, 34]. Hence, an addition of 1,600 MW by the end of 2020 is on pipeline as the next phase of 450 MW addition by 2015 [35].

Pakistan is an important mid-Asian country under the low-middle-income group. However, the Pakistan situation is better than Bangladesh but not very good as the country is facing formidable energy challenges to maintain its sustainable socioeconomic development. The electricity supply is a quarter short of the demand [36], whereas, the per capita energy consumption is only 501.6 kg-oil far less than the world average of 1,790.1 kg-oil [37]. Pakistan traditionally relies on oil-based energy contributing 30.8% of the total energy mix which is mostly imported from the Gulf countries. Currently, in the energy mix, natural gas is contributing the highest, 49.5%, along with the liquefied petroleum gas, 0.5%; hydropower, 10.5%; coal, 6.6%; and nuclear, 1.9% [38]. As per an estimation, the country has a shortage of 13,000 MW electricity, which is adversely affecting the GDP by 2% of the overall growth and a loss of 400,000 employments [39]. To cope with the burgeoning gap between the energy demand and supply, Pakistan has taken several steps under the National Energy Security Plan 2005 2030 [40, 41]. Increasing the contribution by the alternative sources is one of the major targets taken into account. Although the progress is slow, it is witnessing some significant changes albeit a lot has to be done for meeting the target of "energy-to-all." The recent progress in front of alternatives in Pakistan is summarized in Table 3 [42]. The initiatives to the energy transformation from fossil fuels to the alternatives are also getting additional support from the recent cost-cuttings with the AE technologies. This makes the alternatives more

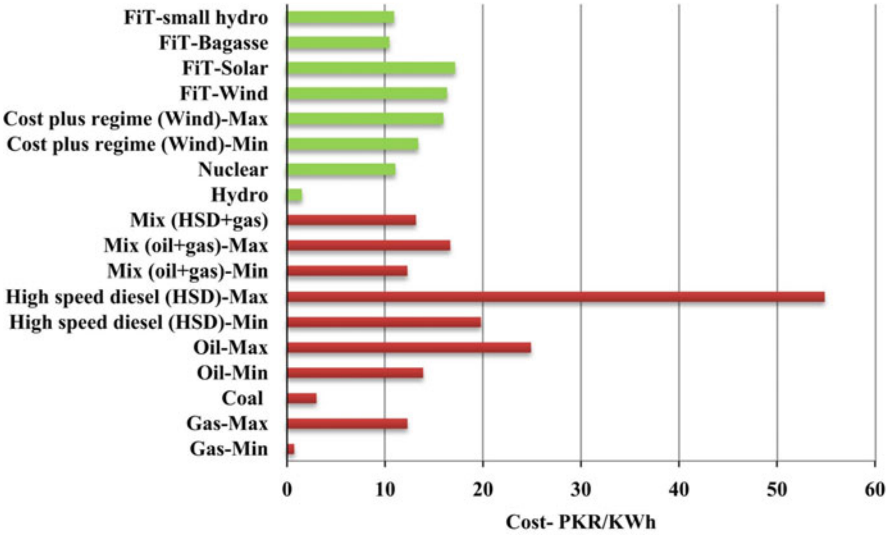


Fig. 7 Cost competitiveness of alternative and conventional energy sources in Pakistan (reproduced with permission from [42])

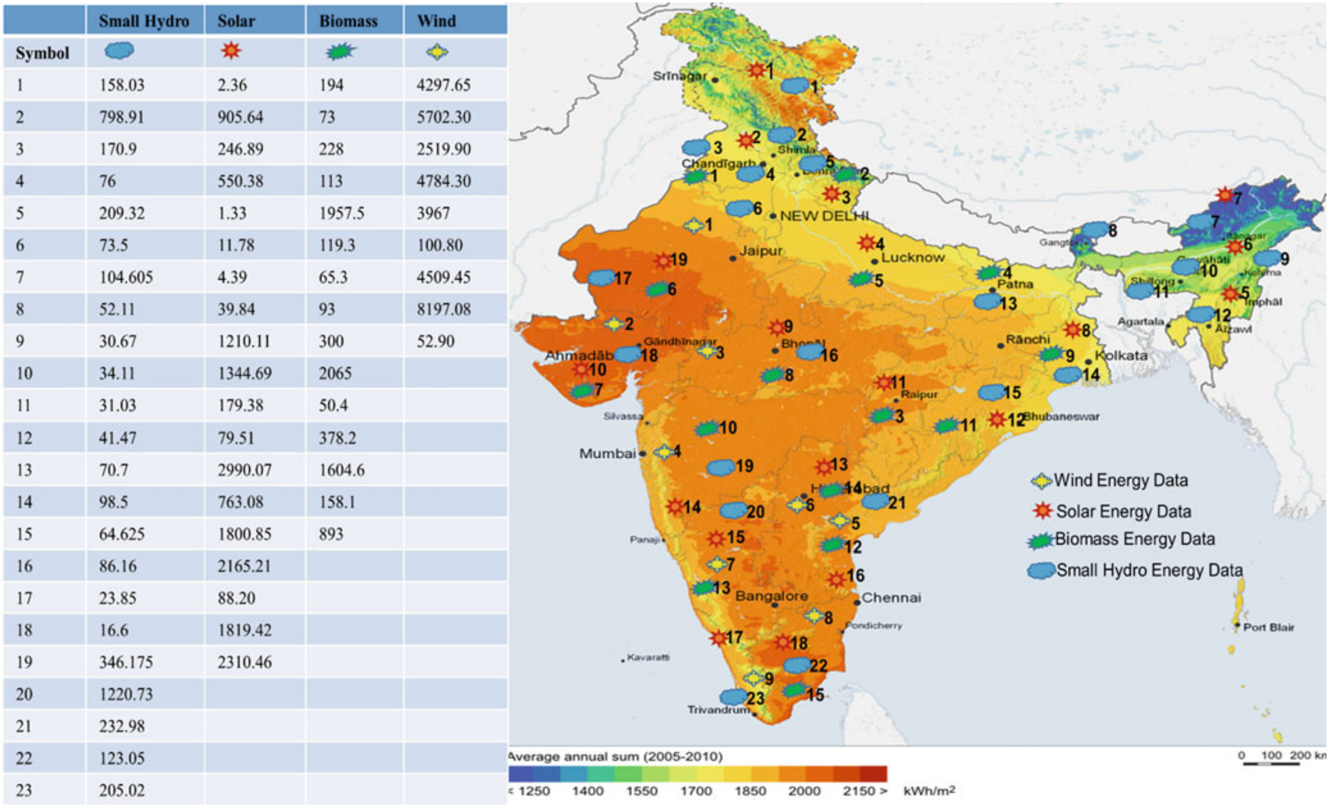
attractive at the socioeconomic front. The cost competitiveness of AE in comparison with conventional energy is depicted in Fig. 7.

Not only in the Indian subcontinent but worldwide India is one of the fastest-growing economies that also hold 1.35 billion of population, and accordingly the energy demand is massive to sustain the growth rate. Currently, 58% of energy supply is through the coal-based power plants along with 13% by the large hydropower projects [43, 44]. Despite of generating about 7.5% of the global energy, the country is facing a plethora of challenges due to a spiked consumption in primary energy nearly twice in recent times [45–47]. Hence, looking at the non-sustainable energy source of coal (many reserves are low grade), dependence of water streams on the monsoon patterns, and import dependence for petroleum products, India is making concerted efforts for securing its energy future with the alternatives.

India is blessed with all forms of alternative sources [48]. Solar and wind are particularly having more potential and plenty of available sources. With 250–300 clear sunny days, average temperature ranging 25–30°C, and solar incident ranging 4–7 kWh/m^2/day, India is estimated to have 750 GW of energy potential using sunlight [49]. A 7,000 km long coastline with an average wind speed of above 3 m/s, India has great potential for wind energy as well [50]. The progress in this area is significant, and it is estimated that the target of 60 GW wind energy by 2022 is achievable [51]. Due to an agrarian economy of India, plenty of inter alia husk, cotton, jute, straw, coconuts shells, bamboos, and *Jatropha* plants present a huge potential for 30 GW of bioenergy with a target of 10 GW by 2022 [52]. The monsoon rain gives birth to several small rivers and water streams in the remote mountaineer area; to tap the hydropower from such small streams, India has identified the potential to generate ~15,000 MW of hydropower with 11% installed capacity [53]. The alternative energy map of India presented by Chabhadiya et al. [5] is shown in Fig. 8, which clearly depicts that the country is aggressively using its alternative sources as per the suitability criteria [45, 52, 54, 55].

China is one of the global leading countries registering the energy transformation in aggressive mode; however, the pace of the economic and industrial growth along with the most populated country of this world pushes China to a continuous shifting towards the alternatives. Zeng et al. [56] have divided China's energy transformation into four stages:

1. First stage (1949–1979): During this period, hydropower in rural areas was developed at a slow rate due to the non-availability of capital and inefficient technology and management. A project, namely, Gutian cascade hydropower project, started in 1952 at Fujian Province could be completed after 30 years in 1973. Consequently, a total installed capacity of small hydropower was not more than 7 million kW until 1979 with an output of 0.23 million kW/year.
2. Second stage (1980–1989): During the sixth 5-year plan of China, the goal of energy conservation was aimed to stop the depletion of fossil fuels, and hence, substantial investments were made to develop the alternative sources [57]. It resulted in the construction of five large- and medium-sized cascade hydropower plants on the Yellow River [58]. By the end of the second stage, wind energy projects were also established to generate a total capacity of 9,100 kW electricity [59], whereas the flat plate solar water heater production was also started with a slower deployment [60].
3. Third stage (1990–1999): In continuation of the second stage, China could install a total of 23,500 MW hydropower capacity by 1999 [61]. However, the main revolution was marked in wind energy where the household generation of wind energy turns to wind farming to generate 40,000 kW wind energy until 1999. Despite such remarkable transformations, the rural energy crisis could not be eliminated [62].
4. Fourth stage (2000–2015): This phase of energy transformation is the most important as China has installed its alternatives from 120,000 MW to 375,000 MW between the years of 2005 and 2013 and registered the growth in all fronts. China became the largest producer of small hydropower, while wind energy has been assuming a larger share of the total capacity in recent years, reaching 91,400 MW [63]. Solar technology also took a big step forward where China reached 42 million square meter of solar heaters by 2009 from only 6.1 million square meters in 2000 [60]. Currently, China has the largest market share for solar water heating [64] along with an installed SPV capacity of 28,050 MW [65]. Also, China is generating a total of 4,150 kW tidal energy. In a recent study conducted by Wang et al. [66], it is revealed that China has gone to a simultaneous transformation of energy in all the region (except Tibet and Xinjiang); however, the eastern region of the country has relatively high growth of alternatives (Fig. 9).



	Small Hydro	Solar	Biomass	Wind
Symbol	☁	✹	✸	✦
1	158.03	2.36	194	4297.65
2	798.91	905.64	73	5702.30
3	170.9	246.89	228	2519.90
4	76	550.38	113	4784.30
5	209.32	1.33	1957.5	3967
6	73.5	11.78	119.3	100.80
7	104.605	4.39	65.3	4509.45
8	52.11	39.84	93	8197.08
9	30.67	1210.11	300	52.90
10	34.11	1344.69	2065	
11	31.03	179.38	50.4	
12	41.47	79.51	378.2	
13	70.7	2990.07	1604.6	
14	98.5	763.08	158.1	
15	64.625	1800.85	893	
16	86.16	2165.21		
17	23.85	88.20		
18	16.6	1819.42		
19	346.175	2310.46		
20	1220.73			
21	232.98			
22	123.05			
23	205.02			

Fig. 8 The alternative energy map of India with the capacity buildup data (reproduced with permission from [5])

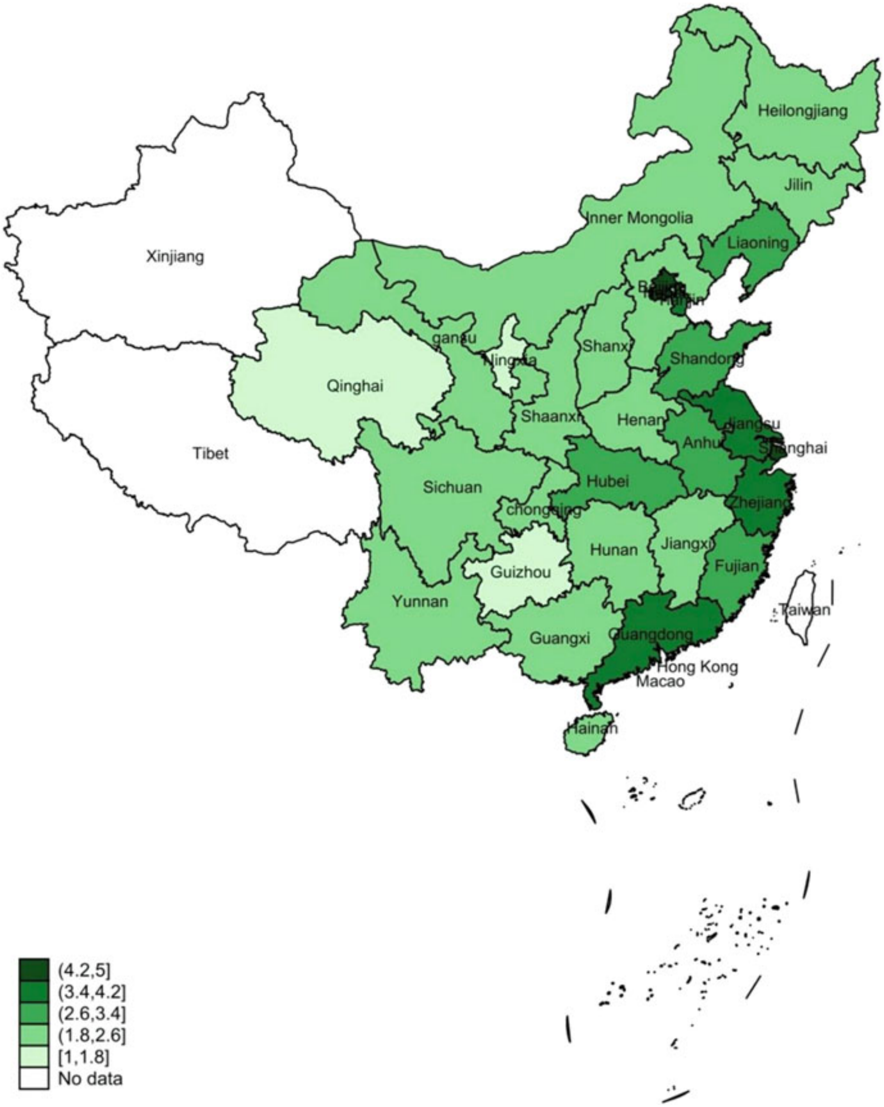


Fig. 9 The energy transformation indices of China (reproduced with permission from [66])

In the 13th 5-year plan, China has proposed the feedstock-to-final bioenergy pathways according under the China Bioenergy Development Roadmap 2050 [67]. As per the planning potential presented by Kang et al. [68], the significant transformation in total bioenergy production for the year 2020–2050 has been predicted approximately to be 9,200 PJ from 4,203 PJ. The estimated bioenergy potential of China is presented in Table 4. As can be seen from the table, biogas

Table 4 Bioenergy planning potential of China (reproduced with permission from [68])

Types of bioenergy	Planning potential of bioenergy (in PJ) with timeline			
	2020	2030	2040	2050
Bio-fired electricity	1,555.63	2,076.95	1,753.15	1,644.05
Bio-fired heat	422.95	638.14	573.56	586.45
Biogas	1,858.24	3,390.78	3,818.94	4,095.59
Bio-liquid fuel	366.15	1,005.98	2,236.97	2,872.81
Total	4,202.97	7,111.85	8,382.62	9,198.9

would be the most productive bioenergy in 2050 with a fact that China has the large number of operating digesters [69].

It is evident that immense push for building up the alternatives' capacity is going on, but despite the positive steps, unfortunately they are far behind to achieve the sustainable energy transformation goal if it comes to analyze the sharing of AE/RE in final energy use of the particular country/region. Since the installation capacity does not exactly belong to final energy use, it is imperative to focus on the distribution of final energy consumption as well. A comparative representation of indicators relevant to energy transition for major countries/region in the global map of renewables is shown in Fig. 10. It can be depicted from Fig. 10 that a lot has to be done to achieve the sustainable energy transition pathways, including the requirement of huge investments in the name of decarbonization of energy.

4.3 Contribution to Emissions Reduction of GHGs

Electricity generation by applying the AE technology is considered to be the major contributory for minimizing greenhouse gases (GHGs) emissions (in terms of carbon dioxide equivalent, CO_2e). As estimated, the amount of electricity produced by coal-burning, emitting 1.4–3.6 pounds of CO_2e/kWh, can be produced by alternative means with reduced emissions as low as 0.02–0.04 pounds of CO_2e/kWh [70]. This is a huge difference, and hence, the development of alternative sources is imperative to replace carbon-intensive energy. The scenario has been actualized by some developed countries. For example, by the utilization of 27.3% of alternatives in 2014, Germany dropped its GHGs emissions to the second lowest level since 1990 albeit the country's economy grew by 1.4% [71].

In a recent study, Chabhadiya et al. [5] have evaluated the case of energy transformation scenario of India in terms of India's commitment to the Paris Climate Treaty (COP21) for reaching back at the level of 2005 emissions. Notably, India has aimed to reduce its 33–35% emissions by 2030 under the United Nations Framework Convention on Climate Change (UNFCCC) and COP21. For which, India is working to install 40% of its electricity capacity by alternatives [2, 72, 73]. A new target of 227.5 GW installed capacity by 2022 is expected with an annual increase of 25%

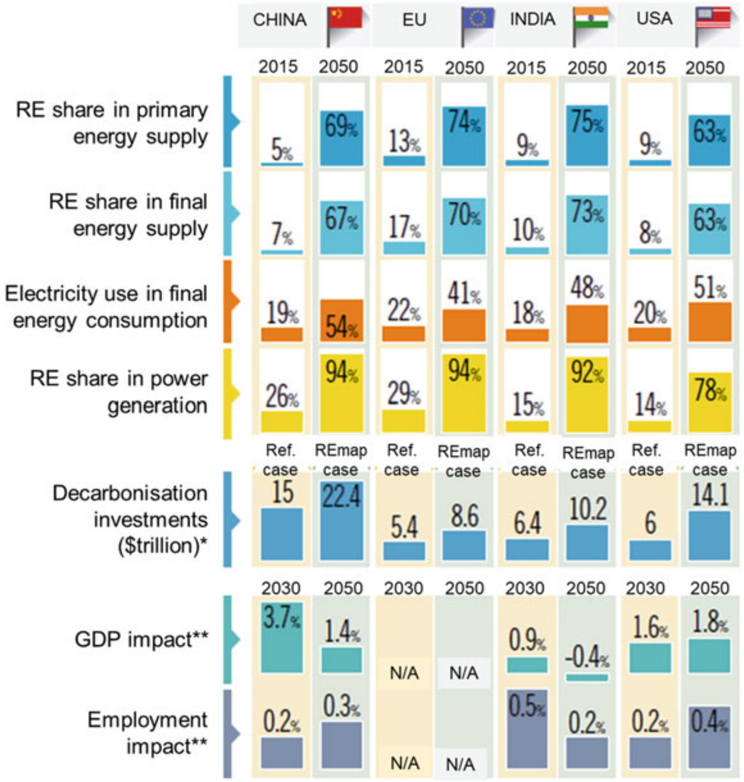


Fig. 10 Key indicators relevant to the energy transition in selected countries, where * denotes the investments including investments in RE, energy efficiency and infrastructure, and energy flexibility to integrate renewables in the power sector, while ** represents the difference in GDP and employment (reproduced with permission from [10])

in total energy generation, while no new thermal power plants will be built until 2027 except those already in progress [74]. In order to determine the impact of aforementioned initiatives on the GHGs (in terms of CO2e), a regression analysis of the energy generation and emissions within the time frame of the year 2005–2016 has been conducted by Chabhadiya et al. [5] using the primary data of BP Statistics Report [75].

Three different scenarios have been anticipated in the Indian energy sector, and the contributed emissions have been calculated for each case. Case I assumes for a 10–20% alternatives growth between the year 2018 and 2020 followed by constant estimated growth of 25% until 2035. In this case, the conventional energy sector would be having an equal contribution to the energy generation without any decline (Fig. 11), revealing no benefit in terms of emissions control that cannot meet the sustainable development pathways.

Case II assumes a 10–20% AE growth within the period of 2018–2020, thereafter, increasing by the expected 25% growth until 2035. Moreover, India is committed to

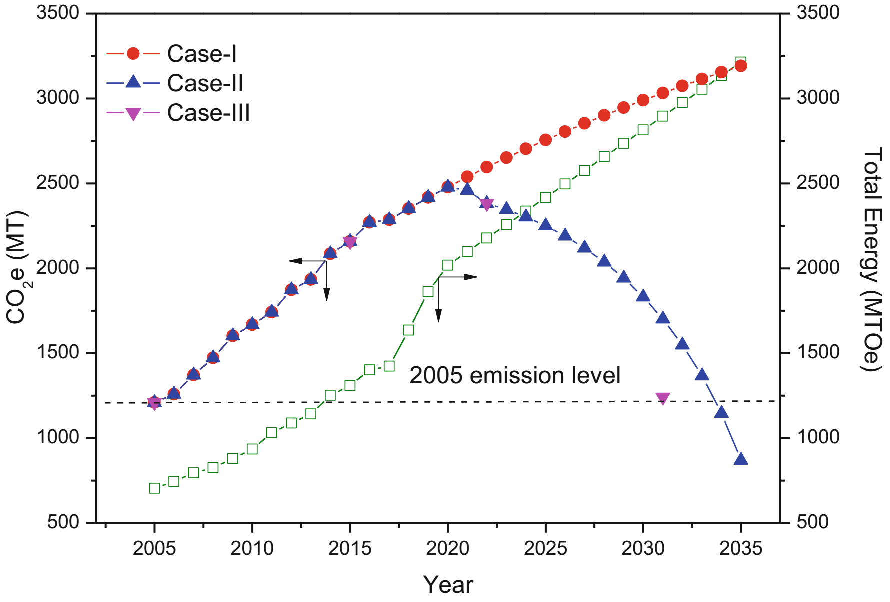


Fig. 11 Scenarios for emissions contribution with respect to yearly energy demand of India (reproduced with permission from [5])

a 13% energy mix by 2022 [74] which anticipates that the alternatives will replace the coal-based energy by 5% for the year 2021 and a further 13% AE/RE mix contribution by 2022 with an annual growth rate of 5% and without any new capacity addition of thermal power plants. Results based on this assumption (shown in Fig. 11) depict a remarkable reduction in emissions with respect to the consistent growth in total energy production. The emission is found to decrease from 2,157 Mt. to 1,830 Mt. CO_2e within 15 years of time frame starting from 2015, albeit this cannot help India to reach the GHGs' emission to the committed level of 2005 in accord with COP21 [5].

Case III deals with the emissions target of 2030 for reaching back to the level of 2005 emission as per the COP21 accord (Fig. 11). The regression analysis of the energy mix data reveals that this target is too optimistic which will require a huge jump of 68% alternatives in the energy mix of India bringing down emissions to 1,240.44 Mt. CO_2e by 2030 (at the level of 2005). However, as per the current scenario, the achievement of 68% alternatives in the energy mix seems to be difficult to match even if India would achieve the capacity buildup of 227.5 GW alternatives by 2022. It indicates that achieving the sustainable pathways for developing is quite a difficult task that requires more brainstorming and a multidimensional approach [5].

5 Summary

The energy poverty of developing countries combined with their eagerness to pace the economic growth has tremendous pressure on their energy programs. The growth with sustainability goal is additionally compressing them to keep their emissions as low as possible. This makes a necessity for a quick and effective energy transformation towards the alternatives and energy mix instead of relying alone on the conventional source of high emissions fossil fuels. The acute poverty in African countries and a huge population living below the average income in the mid-Asian countries without access to clean energy are actually a mammoth task for uplifting them and providing access to sustainable energy. The good aspect is that these countries have plenty of alternative sources by efficient utilization with advanced technologies; they can overcome their long-standing problem in terms of access to clean energy to a large population. Solar, wind, and small hydropower sources have especially more availability, and the decreasing cost of technology and equipment can be a panacea to solve their problem. Countries like China, India, and South Africa with their competitive economy and technological understanding can provide a better solution in the respective regions. The studies have clearly shown that energy transformation has a clear and direct role in the emissions reduction for providing sustainable growth pathways and mitigating the risks of climate change.

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Mechanism of Photoanodes for Dye-Sensitized and Perovskite Solar Cells

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Contents

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Abstract The demand for fossil fuel consumption is continuously increasing due to the growth of the world's population. Carbon dioxide (CO_2) gas emission from conventional energy sources eventually will amplify the Earth's natural "greenhouse" effect and hence will result in global warming. Therefore, to reduce the risk of climate change, photovoltaic solar cell (PV) devices have been developed. Surprisingly, PV system has capability to conduct useful electricity from natural sunlight source, which provides clean, sustainable, and renewable energy instead of combusted conventional fossil fuel sources. Nowadays, both dye-sensitized cells (DSSCs) and perovskite solar cells (PSCs) were investigated more intensively than the first- and second-generation solar cell systems due to their flexibility, transparency, and lighter weight materials. In fact, photoanode elements played an essential role in determining the strength of light-harvesting absorption and generating excited electron charge carriers' mobility between dye/perovskite and respective transparent conductive oxide (TCO) glasses. Apart from that, binary/ternary transition metal oxide material selection (TiO_2, ZnO, SnO_2, MgO, WO_3, etc.) of photoanode in DSSCs and PSCs is also a crucial factor for photogenerated electrons. However, still metal oxide materials have some drawbacks such as high recombination rate which resulted in losses of overall photoenergy conversion efficiency (PCE) performance. In fact, the PCE of existing either DSSC or PSC devices still have rooms to improve compared to first- and second-generation solar cells. This chapter briefly discussed the operational principle, material selection, key problems, and also the insight to commercialization of organic PV devices.

Keywords Dye-sensitized solar cells, Metal oxides, Perovskite solar cells, Photoenergy conversion efficiency, Photovoltaic cell mechanism

1 Introduction

1.1 Background and Motivation

For the past 15 decades, humans have fully relied on conventional energy sources (oil, gas, coal, and other fossil fuels) to generate electricity and power to fulfill our living requirements. The availability and accessibility of conventional energy manner is accelerating the nation and even country development. Since the use of energy resource has become one of the essential parts of human life, the demand for fossil fuel consumption is embedded, resulting in greenhouse gas emissions that

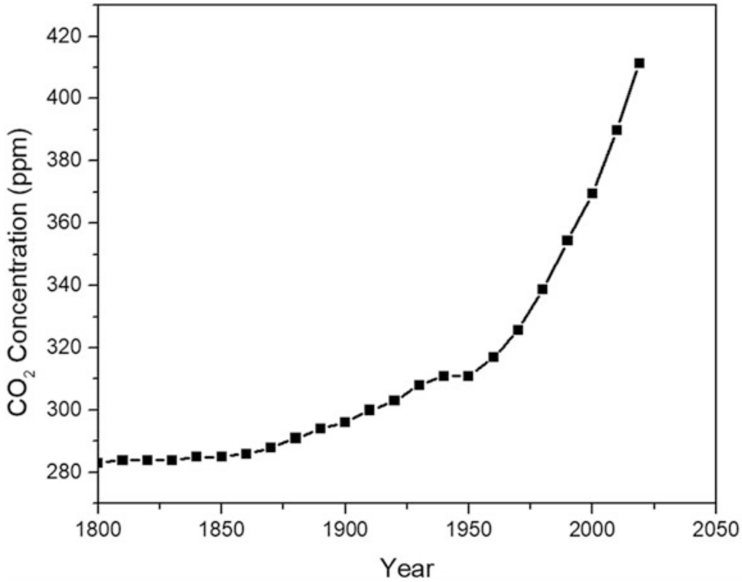


Fig. 1 Atmospheric concentration of CO_2 levels from 1800–present (adopted from [1–4])

tremendously affect our current energy supply. These phenomena resulting the "greenhouse" effect, where the formation of carbon dioxide (CO_2) due to the combustion of fossil fuels that released in atmosphere and re-radiates to the atmosphere. Henceforth, greenhouse gases are trapped in the atmosphere, causing the temperature to rise.

Definitely, climate change which is the long-time rise of global temperature will cause global warming. The earliest concentration of atmospheric CO_2 was recorded at 285 ppm (parts per million) (year of 1840 data), but recently, it dramatically increased to 411.4 ppm (44.35%) (December 2019) as shown in Fig. 1.

Moreover, there are also other gases that directly contribute to global warming such as methane (CH_4), nitrous oxide (N_2O), and chlorofluorocarbon (CFC). The devastating effects of global warming will cause the glaciers to melt, long-term droughts, frequent wildfires, and rise of ocean's temperature.

Continuous on dependence towards fossil fuel, the ecological will always facing a serious crisis on the greenhouse effects and global warming issues. One of the alternative ways is driving forces in promoting sustainable development. Therefore, executing research for generating green and renewable energy resources has been of major concern for researchers, which can provide useful energy in sustainable manner. The cleanest energy source is solar energy, which is abundant and natural, which can be converted into valuable energy such as electricity.

Green energy coming from sunlight which is an everlasting renewable source that can be converted into useful energy is named solar energy. However, the converting of natural renewable energy forms into a controllable and reliable energy resources such as power electricity while keeping low-cost production for high scale production is the remain a challenge in the last two decades. Of course, there are still other core challenges that need to be solved like energy fluctuation, location dependency, and huge investment requirement. Thus, the emerging solar technologies have the potential to be cost-effective [5]. In this chapter, the overview and theoretical study of third-generation photovoltaic cells will be briefly discussed. Accordingly, the material used of photoanode and operation principle of the device will be addressed.

1.2 Photovoltaic Cells (PVs)

A PV cell is an energy-harvesting technology that enables to convert sunlight into useful electricity through a process as shown in Fig. 2. In practical terms, the solar cell is harvesting under visible light, which will produce both current and voltage to generate electric power. Few processes have been required in order to achieve a working device. Most importantly, a material could absorb the visible light and release an electron to be moved to a higher energy state (conduction band). Next, the higher energy electron from an internal solar cell will circulate toward the external circuit. Then, the electron will then lose its energy at the external circuit and returns

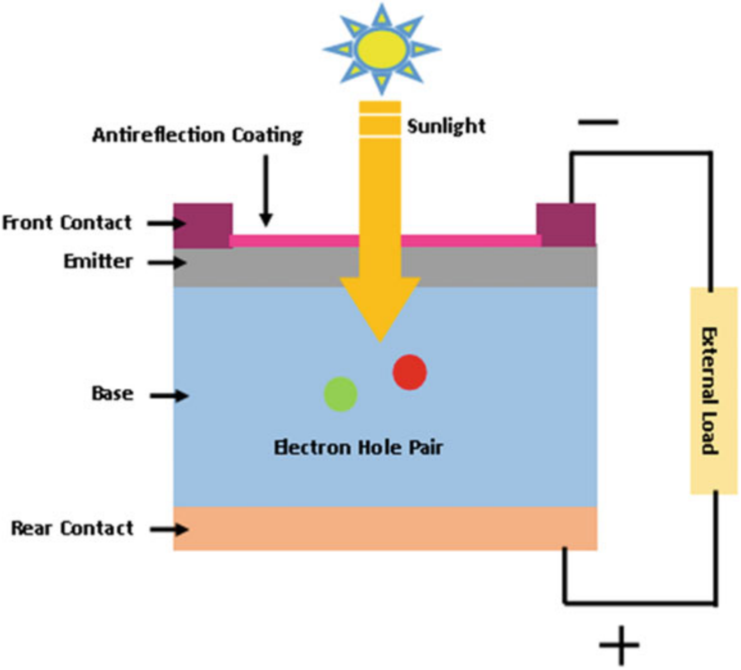


Fig. 2 Cross-sectional view of photovoltaic cell

to its original state. In fact, almost every single type of PV cell has semiconductor materials as fundamental basis to form *p-n* junction. The basic operation of PV cells is:

- The harvesting of cells under light and generated charge carriers
- The collection of light in generated charge carriers and formation of electric fields
- The generation of a large voltage across the solar cell and dissipation of power in the load

1.3 Overview of Organic Photovoltaic Cells

The emerging solar PV cells based on organic semiconductor can provide a low-cost alternative for solar PV [6]. Basically, the thickness of active layer for a typical PV cells is around 100 nm, which is about 1,000 times and 10 times thinner than the crystalline silicon and thin film PV generations, respectively. In the low temperature without any vacuum of organic semiconductors, they are potentially for large-area PV production. Due to this reason, there is considerable interest in organic PV devices. However, the ideal efficiencies of organic solar cell demonstrated are about 2–3 times lower than the Si wafer-based solar cells. Thus, further improvement in efficiency performance for organic PV cell is needed. The organic solar cells were first discovered in 1975 with 0.001% efficiency performance, but in 2019, 8.7%.

2 Material Selection

In dye-sensitized solar cells (DSSCs), the most widely used as photoanode is titanium dioxide (TiO_2), which has been extensively studied and considered as the most popularly used for preparation processes because of its unique electrical, optical, and physical properties [7–9]. Besides, zinc oxide (ZnO)-TiO_2 composite layer has also been extensively used as photoanode in DSSCs due to its high electrical and optical properties. As we have known, ZnO metal oxide has two times greater electron mobility than TiO_2 which is in the range of 205–300 $cm^2\ V^{-1}\ S^{-1}$. Furthermore, ZnO metal oxide helps in faster electron transport and reduces charge recombination.

During the last decades, metal oxides have received a lot of attention from researchers and scientists because of their distinct thermal properties and chemical stability [10]. Their exclusive characteristics include a high dielectric constant and electronic reactiveness and good electric, superconductivity, optical, and electrochromic features derived from d-shells that have been partially filled [11]. Due to its outstanding properties, it has been widely explored for organic PV cells. In addition, hybrid organic/inorganic perovskite solar cells (PSCs) are promising materials due to their great optoelectronic characteristics and ease of manufacturing. Generally, the molecular formula of PSCs is ABX_3, where the A represents the organic unit, B the metal (Sn or Pb), and X the halide unit [12]. With this, well-structured PSCs can easily achieve an efficiency of 23.3%, but two important issues need to be addressed before commercialization such as device performance and stability.

Basically, metal oxides with wide bandgap are commonly used in PSCs in order to absorb more light. In this case, a wide bandgap of metal oxide material could play an important role in PSCs. Metal oxides can be relatively applied either as hole transport material (HTM) or electron transport material (ETM) active layer in PSCs. Still, the selected material also needs to fit the requirements and should be suitable to be used as HTM or ETM layer. The first requirement would be a suitable band alignment. As an example, the valence band maximum and conduction band minimum of PSCs must be greater than for HTM and also ETM. Next, it must be a good charge mobility material. In order to have a fast photogeneration and transport of charge carriers and also suppress the recombination between HTM and active layer, a good charging flexibility is required. In contrast, a comparable crystallinity of metal oxides is one of the crucial factors to improve the PSC performance [10].

Besides, metal oxide is utilized in the interfacial layer between the two elements of PSCs in order to enhance efficiency and stability. Han et al. reported that MgO material formed as the ETM layer and proved that the fill factor (*FF*) and open-circuit voltage (*Voc*) of PSCs were dramatically enhanced [13]. Guarnera and his co-workers sandwiched the Al_2O_3 metal oxide between the absorber layer and the HTM layer to prevent metal migration into the PSCs [14]. Moreover, it also can further protect the absorber layer from infringement of moisture and thus increase the stability of device [15, 16]. Furthermore, researchers also use chromium oxide-based metal contact (Cr_2O_3/Cr) with metal electrode [17]. Surprisingly, long-term stability under direct illumination is achievable.

For the first invention of PSC device, Miyasaka research group introduced TiO_2 as an ETM layer in 2009 [18]. After 2009 and later, the efficiency of PSCs was still low. The liquid electrolyte of HTM is widely used to resolve the degradation issues instead of the solid type. Five years later, mesostructured PSCs, like thick pine-hole-free perovskite film, were accredited with more than 16% efficiency with the aid of solvent technology [19]. For the following years, an efficiency of 20–22% was reported accordingly by tailoring the composition of PSCs [20]. Currently, several researchers have developed an ETM layer using mesostructured TiO_2 in order to generate highly efficient PSCs [21]. Nonetheless, mesoscopic TiO_2 restrict some applications since some processes require high temperature. Still, TiO_2 provides poor mobility of electron charge, which can delay electron movement and definitely increase charge recombination. Several researchers tried to figure out a new metal oxide with wide bandgap instead of TiO_2 to overcome these issues [19]. On the other hand, the band alignment of some available metal oxide materials has been used as ETM in PSCs as shown in Fig. 3.

Over the years, efficiency of PSC-based ZnO reached to 21%, while the stability of the ZnO-based PSCs remained [22]. Tin oxide (SnO_2) was introduced in 2015 as an alternate material instead of TiO_2 in PSCs, even if it was less relevant than ZnO or

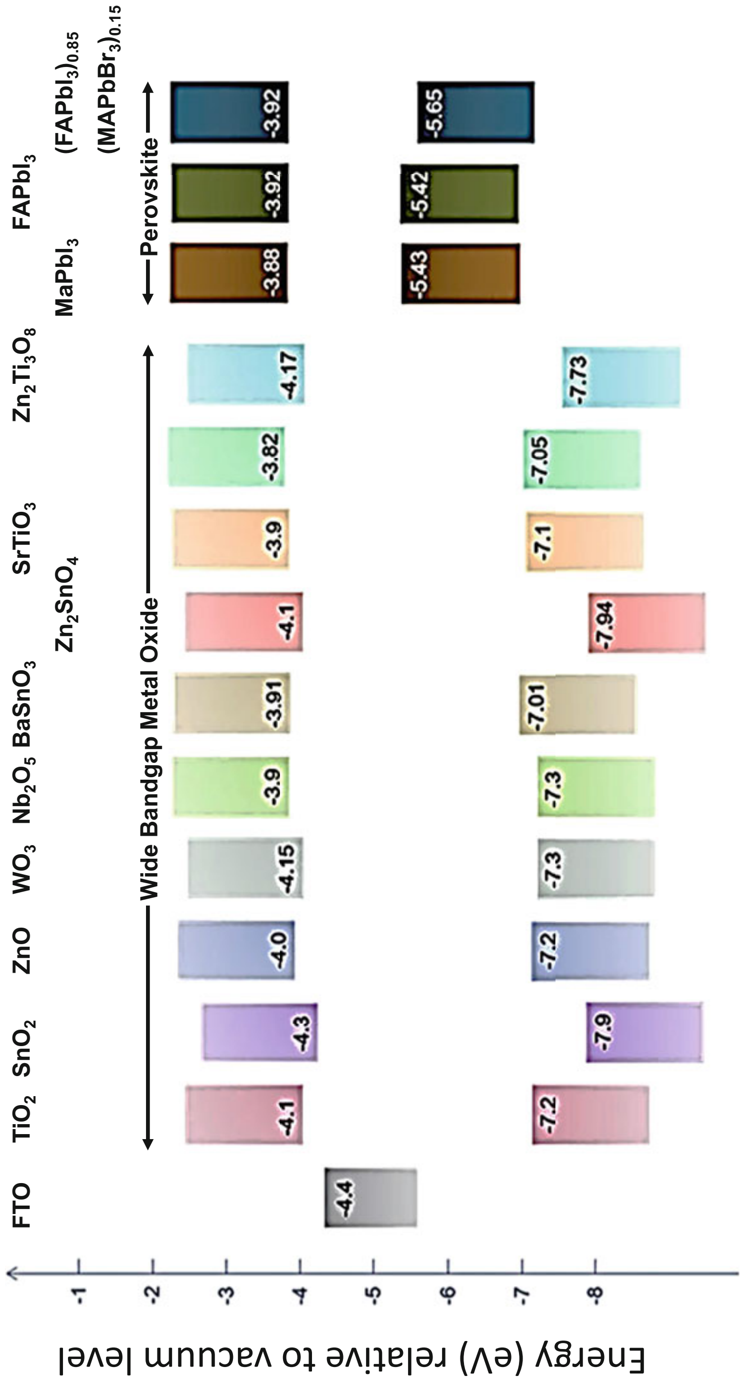


Fig. 3 Availability of metal oxide materials used as ETM in PSCs (adopted with permission from [10])

TiO_2 in PSCs. The efficiency of PSCs based on SnO_2 is rising from 18% to 21% over time, and it gains much attention due to its high electron mobility, wide bandgap, and stability. Other than that, a number of binary metal oxide have been studied as PSCs' ETM layer including tungsten(IV) oxide (WO_3), niobium pentaoxide (Nb_2O_5), indium (III) oxide (In_2O_3), and biopolymer (CeO_x) [23]. One of the effective ways to improve the overall performance is to use binary metal oxide having a dopant concentration. Some scientists have stated that Mg-doped TiO_2 and ZnO have higher CBM, which enhances the resistance of the charging recombination and the PV efficiency of resulting PSCs with an improved *Voc* [15, 16].

Ternary metal oxides are the other interesting candidates because of the ease of changing their electrical properties and band structure by changing their composition. In 2014, strontium titanate ($SrTiO_3$) has been introduced to have a PSC efficiency of 7%. In the meantime, researchers also explored ternary oxide ($Zn_2Ti_3O_8$) and barium titanate ($BaTiO_3$); however, their efficiency performance was low. Additionally, tin-based (Sn^{2+}) ternary metal oxides have been considered as possible candidate as ETM layer in PSCs due to its CBM of Sn-based oxide mainly from interaction of Sn (5 s-O2p) orbital, resulting in large conduction band dispersion and poor effective mass performance. Over the years, $BaSnO_3$ (BSO) and La-$BaSnO_3$ (LBSO) ternary structures achieved PSC efficiencies of 12.3% and 15.1%, respectively. In 2015, a highly reactive precursor produced with lowered processing temperature (90°C), their group successfully obtain for the binary ZnO-SiO_2 (ZSO)-based PSCs with efficiency of 15.3% [24]. So far for low-temperature processing, there was achieved an ideal efficiency of 21% for PSCs, where it is integrated by Lanthanum (La)-doped $BaSnO_3$ (LBSO) composite materials [25].

Moreover, numerous binary and ternary metal oxides were explored as an alternate layer instead of TiO_2 although they have lower performance than TiO_2-based PSC device. Comprehensive work and analysis of surface alteration/doping is needed in order to enhance the properties of current metal oxides. Particularly, ternary metal oxides included two cation sites; there are several possibilities for the transformation by partial cation replacement. High processing temperature makes it difficult to achieve the desired composition in the single phase of a ternary oxide. For ternary metal oxides, the development of synthetic low-temperature processing technique is necessary. In addition to the improvement of the properties of the current metal oxides, a great effort must be done to achieve both high performance and consistency and find attractive metal oxide materials with better optical and electrical properties than TiO_2.

3 Photoanode Preparation Methods

Photoanode is the major constituent in DSSCs and PSCs which performs a principal role in charge collection and transport. Among the varieties of semiconductors used as photoanodic materials, TiO_2 has been extensively applied due to its broad availability, high photostability, wide band gap energy, high thermal stability, low toxicity, and low cost [26]. TiO_2 comprises three phases, including anatase, rutile,

Table 1 Photoanode preparation methods for DSSCs and PSCs

Chemical method		Physical method	
Gas-phase precursors	Liquid-phase precursors	Gas-phase precursors	Liquid-phase precursors
1. Chemical vapor deposition (CVD) 2. Atomic layer deposition (ALD) 3. Thermal oxidation	1. Electrochemical deposition (ECD) 2. Solvothermal /hydrothermal 3. Chemical bath deposition (CBD) 4. Successive ionic layer adsorption and reaction (SILAR) 5. Spray pyrolysis 6. Sol-gel coating 7. Template method 8. Self-assembly 9. Mechanical methods	1. Physical vapor deposition (PVD) a. Thermal evaporation b. Sputtering c. Pulsed laser deposition (PLD) d. Cathodic arc deposition (Arc-PVD) e. Thermal spraying f. Nanoparticle deposition system (NPDS)	1. Spin coating 2. Dip coating 3. Doctor blade printing 4. Screen printing 5. Electrospray deposition (ESD)

and brookite. Anatase is considered to be thermodynamically stable and more photoactive than the other two phases. Apart from phase composition, the functional properties of a photoanode are strongly dependent on its material properties such as crystallite size, morphology, surface area, porosity, etc. which in turn are controlled by the technology selected for the photoanodic materials.

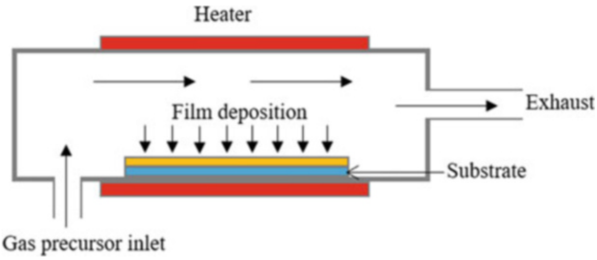
There are some common preparation techniques which have been employed in DSSCs and PSCs, either chemically or physically. For chemical processing, chemical reaction is utilized to synthesize and grow the photoanodic materials. Meanwhile, physical technique employs visible phenomenon to produce and deposit the photoanodic materials. Both chemical and physical preparations of photoanode are categorized under their medium or precursors of gas and liquid phases. The chemical and physical methods used to prepare photoanodes for DSSCs and PSCs are summarized in Table 1.

3.1 Chemical Methods

3.1.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) made its first breakthrough in 1880s by Sawyer and Man where they deposited carbon and metals on lamp filaments to improve its duration (Sawyer and Man). Reaction of CVD takes place between the gaseous reactant and the substrate surface [27]. Figure 4 shows the schematic diagram of the CVD system. CVD method is the preferred technique due to its flexible nature and vast advantages. However, CVD still possesses a few drawbacks. The advantages of CVD method are the formed thin film structures are dense without inclusion of impure elements, and it is able to produce different types of coatings at low

Fig. 4 Schematic diagram of chemical vapor deposition system



processing temperatures with single layer, multilayer, composite layer, and nanostructured layer [28]. The major disadvantage of CVD method is that it uses toxic, corrosive, and explosive precursor gases.

There are few techniques under CVD method to prepare photoanodes such as drop casting and low-pressure CVD (LPCVD), flat-flame diamond CVD, thermal CVD, metal organic CVD (MOCVD), initiated CVD (iCVD), and atmospheric pressure CVD (APCVD). Among these CVD techniques, LPCVD is the most desirable technique as no carrier gases are used, and it produces a uniform film deposition with less contamination. LPCVD operates in the range of 0.1–10 Torr with resistance-heated heaters [29]. MOCVD deposits a thin epitaxial layer utilizing organometallic compounds and hydrides. It is able to govern the thickness of the film for most favorable structure designs [30]. APCVD operates at low temperature, below 600°C, to deposit oxides, and binary and ternary silicate glass coatings.

3.1.2 Atomic Layer Deposition

Atomic layer deposition (ALD) was first invented by Stanislav Koltsov and Valentin Aleskovsky in the 1960s at Leningrad Technological Institute (LTI) in the Soviet Union [31]. ALD reacts between two chemical precursors (reactants). The precursors react with the substrate surface in a layer-by-layer (sequential) manner. The alternating exposure is repeated to deposit a thin film. The process of ALD includes four important steps (Fig. 5):

1. Exposure of metal precursor
2. Evacuation process;
3. Exposure of other reactant (nonmetal precursor)
4. Purge of reactants and product molecules from the chamber

ALD provides a wide benefit such as possibility of producing high-quality materials with pinhole-free and low temperature processing and allowing interface modification. However, the lack of speed and confinement of deposition by the size of reaction chamber are the main drawbacks of ALD.

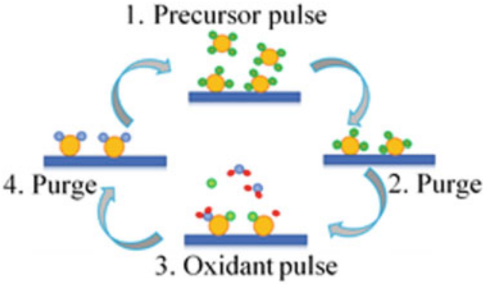


Fig. 5 Process of atomic layer deposition

3.1.3 Thermal Oxidation

Thermal oxidation is relatively a chemical process that is able to produce a thin layer of photoanode. It was first discovered by an Egyptian engineer, Mohamed Atalla, in the late 1950s for surface passivation of silicon semiconductors [32]. This method forces the diffusion of an oxidizing agent into the substrate under high temperature for reaction to occur. Commonly, titanium paste is applied on the substrate and it is placed in a thermal oxidation furnace filled with oxygen (oxidizing agent) to deposit TiO_2 layer on the substrate.

3.1.4 Electrochemical Deposition

Electrochemical deposition (ECD) can deposit a thin coating of metal, oxide, or salt onto the surface for conducting a substrate by means of electrolysis. The process involves reduction of ions in the solution as in Eq. (1).

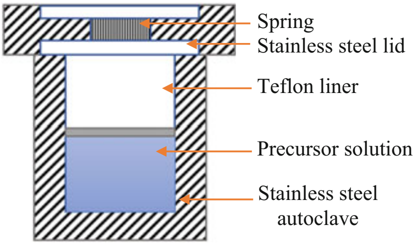
$$M^{z+}{}_{\text{solution}} + ze \rightarrow M_{\text{lattice}} \tag{1}$$

The ECD method is considered the simplest, viable alternative to vacuum-based deposition and can be conducted at room temperatures and pressures. Moreover, the ECD variants such as electroplating, electrophoretic deposition (EPD), and electrolytic anodization can be deployed for synthesizing of materials. EPD technique applies an electric current that charges the colloidal particles, and then charged particles are transported toward the photoanode, discharged, and formed a useable film. Meanwhile, in electrolytic anodization, the negative ions in the electrolyte oxidize the photoanode and hence develop a nonporous oxide film on it.

3.1.5 Solvothermal/Hydrothermal Methods

An autoclave is used for solvothermal/hydrothermal synthesis as shown in Fig. 6. For this context, both solvothermal and hydrothermal syntheses are branches of inorganic synthesis. Solvothermal synthesis occurs in a nonaqueous solution

Fig. 6 Schematic diagram of a stainless steel autoclave



(non-water as solvent) and acts as an oxidation barrier. On the other hand, hydrothermal synthesis occurs in aqueous solution above the boiling point of water, 100°C, at 1 bar of pressure [33]. This method induces solubility through applied heat and pressure up to its critical point. Furthermore, it can accurately control the size and shape distribution of the resultant product. Although there are drawbacks using this method such as the need of costly autoclave, it is still extensively used and studied by numerous researchers. There are a few types of hydrothermal synthesis [34]:

- Crystal growth
- Treatment
- Precipitation-hydrothermal crystallization
- Hydrothermal + ultrasonic
- Hydrothermal + microwave

The first discovery of ultrasonic technique in air and water was in 1880 by Jacques and Pierre Curie after the development of piezoelectric effect [35]. It uses ultrasound in the range of 20 kHz and above to agitate particles in a liquid in order to improve the mixing and accelerating chemical processes. There are two different types of sonicators which are probe sonicator (direct sonication) and bath sonicator (indirect sonication). Ultrasonication requires high-power ultrasound into a liquid medium, which the sound waves are transmitted throughout the fluid and create alternating high-pressure (compression) and low-pressure (rarefaction) cycles. Besides, small vacuum bubbles are created while at low-pressure cycle. Rapid vibration causes cavitation. The collapse of thousands of cavitation bubbles releases tremendous energy in the cavitation field. The ultrasonication of liquids gives favorable effects such as homogenization, dispersing, deagglomeration, milling, emulsification, extraction, lysis, disintegration, and sonochemical effects [36].

3.1.6 Sol-Gel Coating

Chemical solution deposition is a wet chemical method used in photoanode synthesis. It is the widely used method for photoanode preparation in DSSCs and PSCs. Sol-gel process produces highly pure and homogeneous product and has a strong adhesion and low-temperature processing. The process starts from the precursor

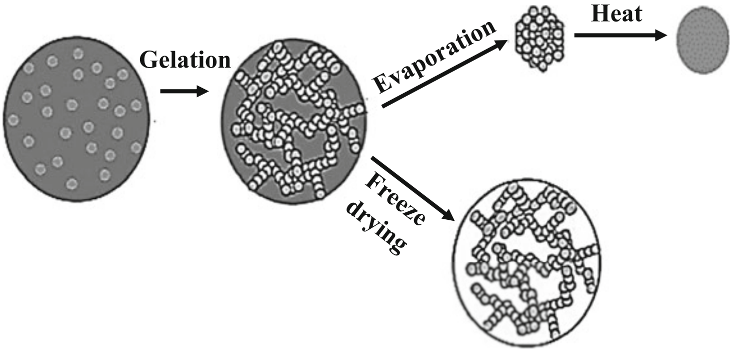


Fig. 7 Schematic of sol-gel process

(chemical solution) to obtain a suspension through dispersion and then form gel-like slurry solution through gelation (Fig. 7). This process results in linkage of metal ions and the precursor with oxo- or hydroxo-bridges [37]. Sol-gel process is integrated with other physical deposition methods such as doctor blade technique, spin coating, and dip coating.

3.2 Physical Methods

3.2.1 Physical Vapor Deposition

Physical vapor deposition (PVD) is a vacuum coating method and divided into evaporation and sputtering. Evolution of vacuum technology first begun in 1640 by Otto von Guericke for water pump application, and then Michael Faraday was able to glow plasma in a vacuum tube in 1838 [38]. Generally, thermal evaporation technique is conducted under a vacuum which allows the vapor particles to move directly to the substrate as a target and be melted through electrical heating. Although thermal evaporation is a simple and low-cost method, however, it has a poor adhesion, is prone to contamination, and possesses a poor step coverage. On the other hand, sputtering produces high-quality deposition material and gives better step coverage with good adhesion. However, sputtering has high risk for substrate damage from ionic bombardment. Sputtering was introduced in 1852 using two types of sputtering: DC magnetron sputtering and radio frequency (RF) sputtering. Figure 8 shows schematic diagram of thermal evaporation and sputtering.

3.2.2 Doctor Blade Technique

Doctor blade technique was followed from the idea of tape-casting machines discovered by Glenn Howatt [39]. This method has various names such as tape

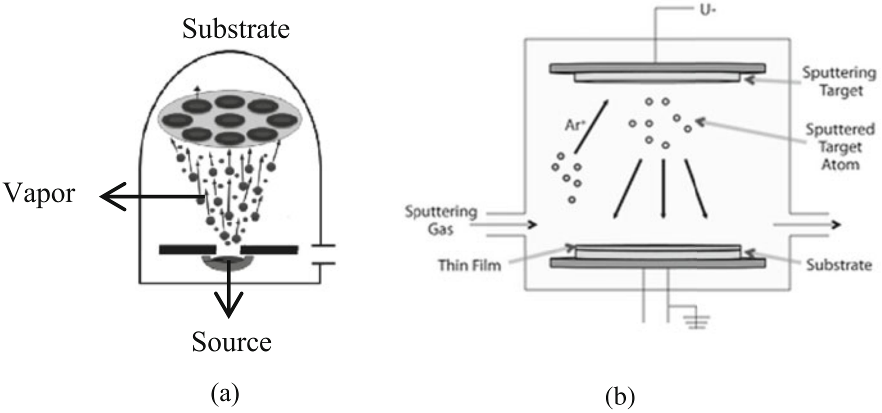
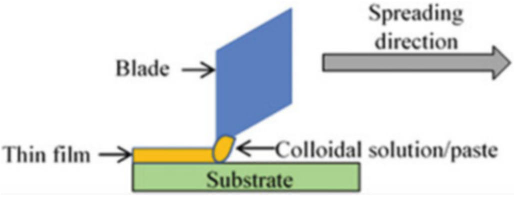


Fig. 8 Schematic diagram of (**a**) thermal evaporation and (**b**) sputtering

Fig. 9 Doctor blade technique



casting, knife coating, or knife-over-edge coating. The process involves three simple steps:

1. Colloidal solution deposition
2. Spreading the solution over the substrate
3. Drying the film

The method is simple and economical and straightforward. The blade works as paste spreading on the surface of the substrate homogeneously to form a thick film (Fig. 9). Besides that, doctor blade technique is a practical deposition method for mass production compared to its spin coating counterpart due to initial loss of coating. Despite its benefits, this technique has limitation at high solution/paste concentration where aggregation of particles occurs.

4 Mechanism of Dye-Sensitized Solar Cells

In general, DSSCs are capable of transporting and producing electrons and absorbing light to the load at greater voltage and transporting back the electron in the cell at poorer voltage. The materials required is the nanocrystalline TiO_2 where it is placed on the photoelectrode to deliver the essential big surface part to dye molecules. In

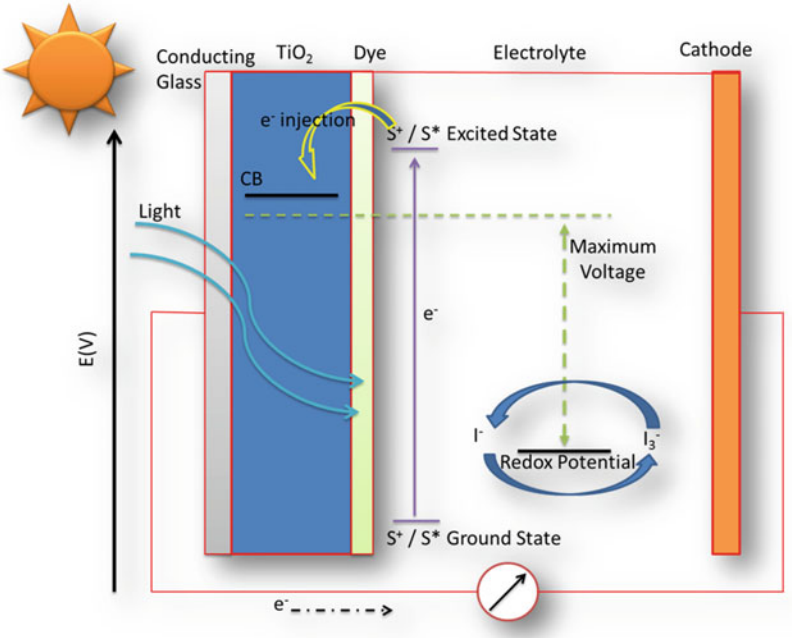


Fig. 10 Schematic illustration of the operation principle of DSSCs

Fig. 10, the dye molecules are moved from the uppermost employed molecular orbitals to the lowermost vacant molecular orbital states during absorption of light (photons).

The conversion of photons into current is shown in the following steps:

1. The photon is absorbed by a photosensitizer. Because of the absorption of photon, e^- get elevated from the S^+/S ground state to the $S^+/S*$ excited state of the dye.
2. The excited electrons with a lifespan of a moment (nanosecond) are injected into the (CB) conduction band of nanoporous TiO_2 electrode which lies below the excited state of the dye, where a small fraction of the solar photons is absorbed by TiO_2 from the UV region. Based on the process, the dye becomes oxidized.

   Excitation process:

$$\text{Photon} + S^+/S \rightarrow S^+/S^* \tag{2}$$

Injection process:

$$S^+/S^* \rightarrow S^+/e^-(TiO_2) \tag{3}$$

3. Based on the injection of electrons, they are conveyed between TiO_2 nanoparticles and diffuse in the direction of the translucent conducting oxide. Electrons reach the counter electrode (CE) from the outer circuit.

   Energy generation:

$$e^{-}(TiO_2) + CE \rightarrow e^{-}(CE) + TiO_2 + \text{electrical energy} \tag{4}$$

4. The electrons at the CE reduce I_3^{-} to I^{-}; therefore, the dye regeneration takes place due to the receiving of e^{-} from I^{-} ion redox mediator, and I^{-} gets oxidized to I_3^{-} (triiodide ions, oxidized state).

$$e^{-} + S^{+}/S^{*} \rightarrow S^{+}/S \tag{5}$$

5. I_3^{-} (oxidized mediator) diffuses in the direction of the CE and decreases to I^{-} ion.

$$2e^{-} + I_3^{-} \rightarrow 3I^{-} \tag{6}$$

The drive of e^{-} in the CB of the widespread bandgap nanostructured semiconductor is accompanied by the diffusion of charge-compensating cations in the electrolyte layer near the nanoparticle surface. For that reason, the generation of electric power, P_E, in DSSCs causes no permanent transformation of substance alteration. Solar cell efficiency of more than 11% has been demonstrated in DSSCs [40].

For energy diagram of DSSCs, the photoanode absorbs photons to produce electron-hole pairs (excitons) during exposure to daylight where an electron is excited from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) as shown in Fig. 11. These electron-hole pairs can be combined into excitons or can free electrons and holes to produce a current due to the difference in the exciton's binding energy of the perovskite materials. This kind of process is like the advancement of electron from the valence band (VB) to the conduction band (CB) in inorganic semiconductors.

5 Mechanism of Perovskite Solar Cells

The first PSC in solid-state solar cells is used in 2012 [6, 18]. The schematic of the PSC is shown in Fig. 12. Since then, a common form (ABX_3) is used to represent a combination of materials as shown below.

The most commonly used material in PSCs is methylammonium lead iodide perovskite ($CH_3NH_3PbI_3$), which is located between the ETL layer (mesoporous or TiO_2) and HTL layer. If the carrier recombination probabilities of other perovskite

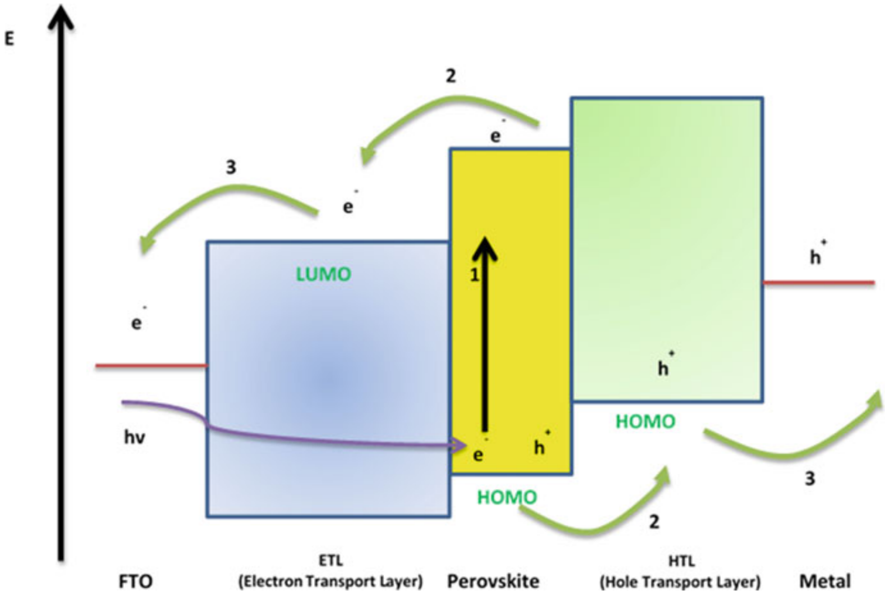


Fig. 11 Band diagram and main process of DSSCs. (1) Free charge generation and absorption of photon; (2) Charge transport; (3) Charge withdrawal

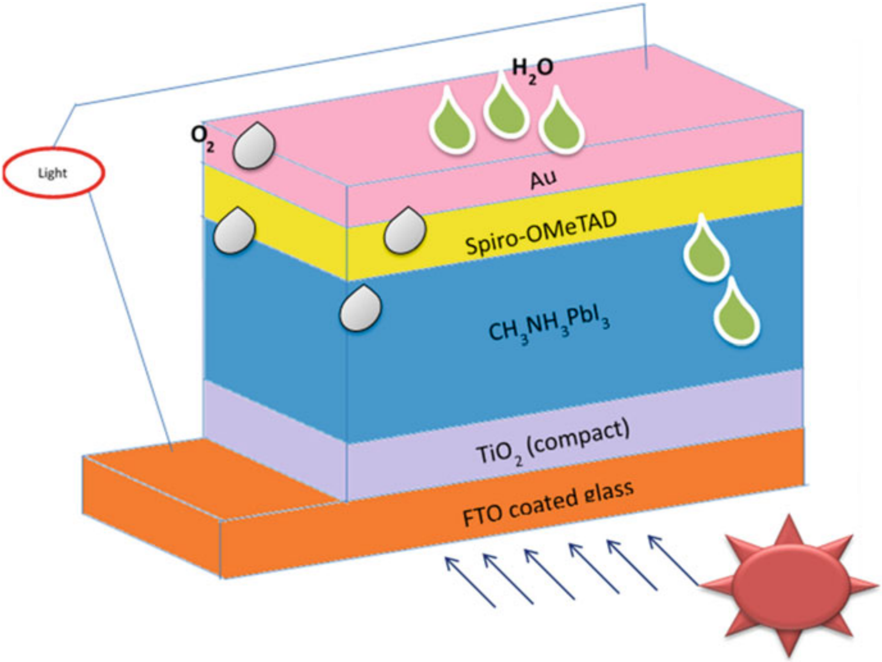


Fig. 12 Schematic diagram of the operation principle of PSCs

materials and methylammonium lead halides ($CH_3NH_3PbX_3$, where the X is Cl^-, Br^-, or I^-) are smaller (leading to a higher carrier mobility), the diffusion lifetime and space of the carrier become longer. Therefore, the length of the diffusion of carriers is the indication of the performance of PSCs.

6 Conclusions

In this chapter, the background and overview of organic PV cells and materials' selection layer, preparation methods, and working principle of DSSCs/PSCs device have been briefly presented. It is discussed that organic-based PV technologies especially DSSCs and the latest invention, PSCs, have received a great attention by tuning the electrode layer. According to the optical properties, metal oxide materials promising as good photocatalytic activity that ease to absorb more visible light into photovoltaic devices with low recombination rate. It is much hoped that with the improved efficiency performance along with the reduced cost of these emerging PV solar cells, solar energy will be a dominant and a sustainable source of renewable energy.

Acknowledgment This research work was financially supported by the BOLD2025 Grant (No. 10436494/B/2019008), fundamental research grant scheme (No. 20190111FRGS), and BOLD2025 publication (No. RJO10436494) under Universiti Tenaga Nasional Sdn. Bhd., Malaysia.

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Grid Integration of Wind Energy Conversion Systems

V. S. K. V. Harish and Amit Vilas Sant

Contents

Abstract The market of renewable energy sources is increasing day by day due to the global energy crisis and the environmental pollution factors affecting the globe. Out of the renewable sources, wind energy has shown a substantial increase in contributing for the production of electricity. Around 60 GW of wind power installed capacity was added in 2019 with a total global figure reaching 651 GW, worldwide. Wind energy conversion system (WECS), as the name suggests, taps the on-site wind mechanics to convert wind energy into mechanical power of rotation. Mechanical power of wind turbines is then converted into electrical energy through genera-tors. Present chapter deals with technological aspects of design and operation for grid-integrated WECSs. Basic principle underlying the working of a wind energy power system is outlined. Primary elements and components involved in construction of a generic wind energy power plant are introduced. Integrating intermittent renewable energy power plants like WECSs require power electronic converters which act as an interface between wind turbine generators and the main power grid. Electrical properties of wind generators dictate the performance of a grid-integrated

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WECS, and thus, the operational aspects of power quality, reliability and stability become underlying objectives for design of power electronic interfacing converters. Operational aspects in terms of active and reactive power management have been outlined. Issues of power fluctuations, flicker and harmonics with necessary concern to transmission line grid codes are analysed. Techno-economic feasibility analysis for linking the wind turbine generators to the grid reported in the literature have been discussed in detail.

Keywords Modelling and simulation, Power converters, Power quality, Techno-economic analysis, Wind energy conversion systems

1 Introduction

Electricity generation sector majorly depends on oil and gas, and hence, the environmental impacts are expected to be dangerous. In order to control the harsh effects of environmental degradation, it is very necessary to switch onto a cleaner energy source. Harnessing electrical power from wind energy has gained interest in several nations around the world. 90 countries around the world has recognized wind energy system as an energy resource industry, and 30 countries have more than 1 GW of wind power installed capacity, out of which 9 nations have installed 10 GW of wind energy-based power systems (Karin et al. 2019). As of September 2019, total cumulative onshore and offshore wind energy installations have been reported with a capacity of 591 GW, worldwide [1]. Digitization and other associative technological advancements have led to unlocking more volume in wind energy business, through improved designs, enhanced asset and risk management with improved maintenance. Africa and the Middle East have installed close to 900 MW of wind energy capacity in 2019 as compared to 962 MW capacity in 2018 [2]. Studies have forecasted an increase of 160% more of the current installed capacity in these regions [2].

Countries which have dominated the wind power installations in 2018 are Brazil, China, Germany, India and the USA. China has been the leader with around 210 GW of wind power installed capacity [3] followed by the USA which achieved about 100 GW of wind power installed capacity [4]. Competitive pricing, technological advancements and low curtailment risks have supported speedy wind power installations in China. Renewable portfolio standards and production tax credit have been the major drivers to enhance the competitiveness of wind power industry in the USA (refer Fig. 1).

Developing economies like India and China are experiencing a gap in supply and demand of energy and, thus, a restricted supply of electricity to the consumers [5]. Such a situation, if not addressed, can adversely affect the economic growth. Expected increase in energy demand, limited or nascent growth in supply, high cost

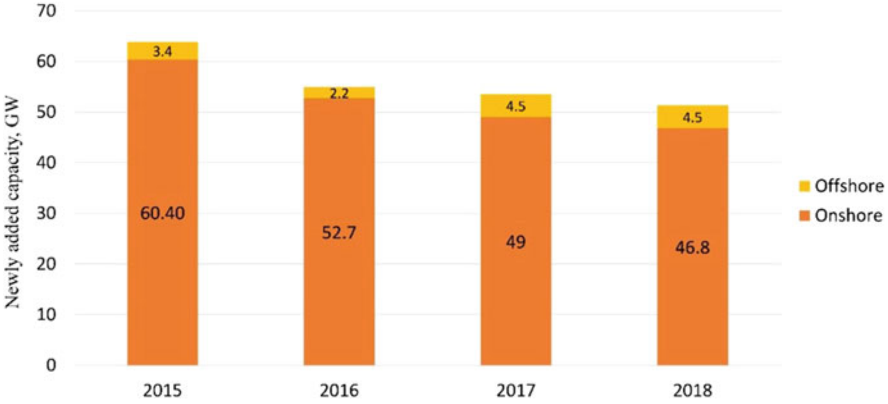

Fig. 1 Newly added worldwide wind power installed capacity since 2015 [4]

of capacity addition and negative environmental impacts of fossil-fuel-based power generation highlight the utilization of renewable energy sources (RES), implementation of energy efficiency and energy conservation technologies and measures [6]; distributed energy sources and application of demand response or demand side management are other ways to bridge the gap of demand and supply during the peak period [7]. Wind power plants can be integrated with demand side management strategies to improve microgrid system's performance and reduce cost of generation. Small-scale low power wind turbines are being installed in high rise buildings to generate electric power in locations with very good wind contour profiles.

1.1 Wind Energy Conversion System

A wind energy conversion system (WECS), as the name suggests, converts the kinetic energy available in the wind into rotational mechanical energy through turbine blades which in turn is converted into electrical power through a generator (and a gearbox). Windmills are also WECSs with an only difference that the rotational mechanical power of shaft is used for non-electrical purposes such as pumping water, milling and driving other machineries.

Wind turbines tap the energy in blowing winds using blades, and low-pressure pockets are formed on one side of the turbine blades. These pockets pull the turbine blade towards it, thereby enforcing the rotor of the wind turbine to rotate. Blowing wind also exerts a force against front side of the turbine blade. This force called as drag is much weaker than the lifting force which causes the rotor to turn. Lift and drag forces are combined, and the turbine rotates like a propeller. Mechanical gears used are employed to increase the rotation speed of the system in order to possess the

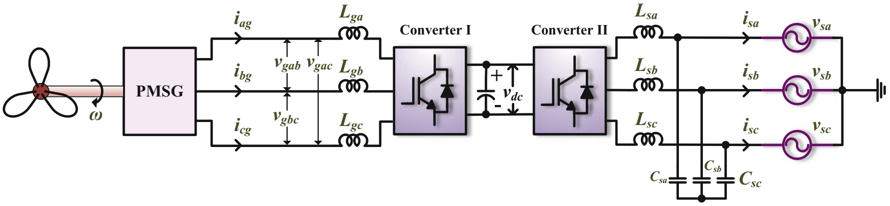

Fig. 2 Power structure of grid tied PMSG-based wind energy conversion system

capability to generate AC electrical power. The speed increases from around 15 rpm to 1,800 revolutions a minute.

A typical wind turbine consists of a streamlined casing called a nacelle, which is placed on top of a tower. Nacelle contains components such as gears, brake, rotor and generator, and for high-power wind farm, facilities are large enough for a helicopter to land. A controller is used to maintain speed of the turbine rotor below a certain value to avoid damage caused by high-speed winds. Hydraulic/mechanical/electrical brakes are used to interrupt the rotor rotation during emergency conditions. An anemometer is used to timely measure the wind speed, and the wind speed data is passed on to the controller.

Typical layout of a grid tied permanent magnet synchronous generator (PMSG)-based WECS is shown in Fig. 2. Firstly, the kinetic energy of wind is converted to mechanical energy through wind turbine, which acts as a prime mover for the PMSG system. PMSG, having hard magnets either mounted on the surface or buried inside the rotor structure, converts the mechanical energy into electrical energy. As the wind velocity varies over time, the mechanical power output of the wind turbine and the electrical power output of the PMSG also varies. Thus, variable voltage variable frequency supply is available at the stator terminals of PMSG. The Institute of Electrical and Electronics Engineers (IEEE) developed a standard IEEE-1547 [8], which deals with the standards pertaining to the grid integration of distributed energy resource; only active power can be injected by a distributed energy resource. Hence, for the grid integration of PMSG, the frequency and voltage level needs to be regulated [9].

Also, the flow of active and reactive power needs to be controlled. This is achieved with the help of two converters, Converter-I and Converter-II, connected in back-to-back configuration. The Converter-I is the machine side converter which ensures that the maximum power point tracking is employed and rotor speed is regulated. This is achieved by controlling the phase, frequency and amplitude of the currents being drawn from PMSG. This converter further ensures that sinusoidal currents drawn from the PMSG are sinusoidal, thereby minimizing the losses on account of harmonic currents. The Converter-II, which is controlled to act as a grid side converter, regulates the dc link voltage, v_{dc}, and controls the active power being injected in the grid.

The phase, frequency and magnitude of currents being injected in the grid are controlled to control the active power injection at unity power factor. This

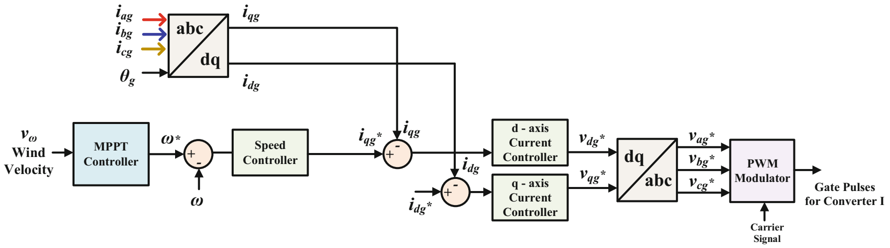

Fig. 3 Control structure for Converter-I

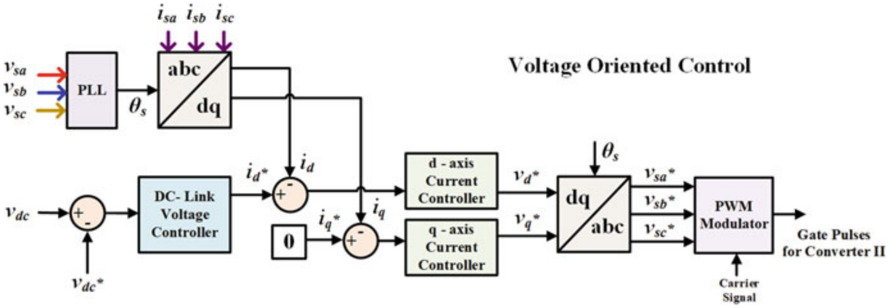

Fig. 4 Control structure for Converter-II

necessitates that the injected currents are sinusoidal and no reactive power is delivered to the grid. This further results in minimal grid pollution on account of grid integration of wind energy conversion system [10]; a grid tied microgrid structure for an educational institute was proposed by [11].

Further, Fig. 3 shows the control structure employed for Converter-I. The speed and position sensor senses rotor position, θ_g, and rotor speed, ω. Based on the instantaneous wind velocity, the maximum power point tracking (MPPT) controller determines the reference speed for PMSG which is the optimal speed to ensure that maximum power is extracted. The actual rotor speed and the reference speed are compared, and the resulting speed error is processed by the speed controller to determine the reference q-axis current. The sensed stator currents, i_{ga}-i_{gb}-i_{gc}, undergo abc to dq0 transformation to determine the *d*-*q* axes currents, i_{dg}-i_{qg}, being supplied by the stator. Theses *d*-*q* currents are compared with the respective reference values, and the resulting current errors are individually processed by the current controllers to determine the reference d-q axes voltages, v_{dg}^* - v_{qg}^*. These d-q reference voltages undergo dq to abc transformation to determine the reference voltages v_{ag}*- v_{bg}*- v_{cg}*, which are further processed by the PWM modulator for the generation of gate pulses for the Converter-I.

Moreover, Fig. 4 shows the control structure employed for Converter-II. The instantaneous grid voltages v_{sa}-v_{sb}-v_{sc} are processed by phase lock loop (PLL) algorithm to determine the instantaneous phase angle, θ_s. With the help of θ_s, the current being injected into the grid are transformed from abc to dq0 reference frame. The dc-link voltage, v_{dc}, measured across the capacitor C_{dc} is compared with the reference value, and the resulting voltage error is processed by the dc-link voltage controller to determine the reference value of d-axis current, i_d*. As no reactive power is to be injected into the grid, reference value of q-axis current, i_q*, is maintained at zero. The actual and the reference d-q axes currents are compared, and the resulting errors are processed separately by the d-axis and q-axis current controllers. Thus obtained reference voltages v_d* and v_q* are transformed to abc reference frame, v_{sa}*-v_{sb}*-v_{sc}*, which are further processed by the PWM modulator to generate the gate pulses for the Converter-II. This chapter is primarily focused on a WECS that would generate electrical power.

2 Design, Modelling and Simulation of a WECS

For maximum utilization of wind power dynamics and electrical power generation, angular velocity of the wind turbine plays a vital role. There are two types of wind turbines, viz. fixed-speed wind turbine and variable-speed wind turbine. Variable-speed wind turbine systems have the ability to supply reactive power on demand and address peak load through the drive train. Maximum power point tracking (MPPT) algorithms are developed to extract maximum power from a WECS by generating a reference voltage point for the converter. Ye et al. [12] developed a MPPT strategy by controlling the excitation current of a hybrid excitation synchronous machine-WECS. Generator voltage is converted into DC which is then fed to the utility through a voltage source inverter. The excitation current needed for the machine is provided by a buck circuit. Inverter current is maintained in phase, and the DC link voltage is managed using a PI controller. A LC filter and a PI controller are used for harmonics mitigation and generating a constant excitation current. *d*- and *q*-axis control loops are developed to control the converter outputs. Developed MPPT strategy compares previous and current power output and ensures that the difference is within a certain prescribed limit. If not, control action is taken. MPPT algorithm is demonstrated on a 3 kW DC motor for wind emulation with appropriate torque control.

Performance of a designed WECS is evaluated under different wind speeds and conditions [13]. A 1-kW PMSG-based WECS simulator was developed comprising a small turbine, servo motor, rectifier, MPPT-controlled boost converter, battery bank and a PWM DC-AC converter. PMSG has been considered for the study due to its larger power-to-weight ratio, reliability and efficiency. Boost converter raises the rectified voltage which is then supplied to the inverter. A pulse-width modulation (PWM) signal is provided by the PI-controller to drive the boost converter with an aim to maximize the output power using MPPT. Inverter provides an interface between the load and DC link voltage. PI-controller regulates the user-end voltage using control loops which handles the wind variations and power disturbances by controlling the current values. PSIM [14] software package was used to simulate the

WECS. However, the study assumed ideal characteristics for switches and diodes of the inverter, and an additional DC/DC power converter was used for BESS. Wind speed was varied from 5 m/s to 11 m/s and was varied to be exponentially decreasing for testing dynamic performance of the developed WECS. Maximum errors of 0.3 pu and 0.15 pu were recorded for speed and torque, respectively.

Doubly fed induction generator (DFIG)-based WECS possess several advantages over PMSG-based WECSs. Reddy and Kumar [15] developed a DFIG-WECS with a variable speed, horizontal axis-type wind turbine. Power electronic interfacing converters are made use of to integrate a WECS to the main electrical power grid. Performance and control of a two level converter and a matrix converter were compared as an interface between the grid and the DFIG. A back-to-back voltage source converter (a two-level convertor) consisted of a rectifier and an inverter, connected through a dc link. AC/DC rectifier on the generator side controls the rotor speed, and DC/AC inverter on the grid side maintains the dc link voltage constant, irrespective of the magnitude of generator side voltage. The matrix converter is comprised of nine bidirectional switches acted as an AC/AC converter to control magnitude, frequency, phase angle and input displacement angle. Matrix converter was employed to act as a substitute for the dc link used in a typical two level converters. The control of these converters is provided by the space vector pulse width modulation (SVPWM) technique. During its operation, six switches out of eight are active switching space vectors and reference voltage is selected as per which the switching states of the inverter are decided. The performance of the two converters is simulated in MATLAB/SIMULINK. Firstly, the simulation is conducted on a two-level converter. The current and voltage waveforms are plotted, and the total harmonic distortion (THD) for the generated voltage and current was evaluated to be 1.06% and 2.27%, respectively. For load voltage and current, THD was 0.27% and 0.42%, respectively. Using SVPWM matrix converter, THD for generator voltage and current was reduced to 0.69% and 1.02%, respectively. Also, for load voltage and the current, THD lowered to 0.17% and 0.29%, respectively.

A variable speed WECS yields 10%–12% more output energy than a fixed speed WECS and is less expensive [16]. PMSG machines are regarded to be aptly suitable for a variable speed WECS due to high efficiency and reliability with less weight and size [17]. During transfer of electrical power into the grid or the load, various converters are used out of which the matrix converter is considered to be a better choice as it is free from commutation problems, light in weight, fast transient response and compact in size.

In addition, Kumar et al. [16] developed an adaptive fuzzy logic controller along with a reversed matrix converter to obtain MPPT point. Space vector pulse width modulation (SVPWM) was used to improve the performance under different conditions. A wind turbine emulator was used to drive the PMSG, and performance of the turbine was tested for steady and dynamic states. dSPACE DS1104 real-time board consisting of a chopper DC drive with four-quadrant control was used as emulator. Twelve-switch voltage boosted-matrix converter (six on the front as voltage source rectifier and other six on the rare end as current source inverter (CSI)) was used. At any particular instant, one switch from the upper end and one from the lower end conducts. When the switches are from different phases, power is transferred to the load and vice versa. The adaptive fuzzy logic controller is comprised of a voltage regulator and an angular frequency controller. Using the perturb and observe method, the reference angular frequency was calculated, and output power was monitored as per the change in the frequency. Matrix converter generated maximum power by regulating active power through a signal obtained from the SVPWM. The adaptive fuzzy logic controller generated the SVPWM phase angle by processing an error function. In this manner, by constantly using the reference angular frequency, maximum power from the wind is captured.

System responses for both steady state and during unbalanced load conditions were observed. THD value for steady-state response was 2.3%, and power factor of 0.996 was achieved. Whereas, for unbalanced load conditions, load voltages were quite stable, the matrix converter was completely capable of handling voltage and frequency during balanced, unbalanced and one phase-out conditions.

DFIG-based WECS with active power management strategy was developed by Tamaarat and Benakcha [18]. Vector method was adopted to manage the active and reactive power, independently. A three-blade wind turbine and a DFIG with stator windings directly connected were modelled with a power converter connected to the rotor windings of the DFIG. Grid side converter handled the reactive power flow between the converter and the grid, whereas the rotor side converter focused on extracting maximum power out of the system. Active and reactive powers were stated as per rotor currents of DFIG. Direct control method was used to compare the reference and actual values of active power and reactive power. In vector control, the quadratic component is responsible for active power and direct component for reactive power. Wind speed is varied from 6 m/s to 8.5 m/s, and waveforms for wind gust, power coefficient, angular speed, active power and reactive power were observed. Variations in current and voltage with respect to rotor speed were observed. External disturbances like wind speed, density and frequency variations are provided in order to check the robustness. Developed scheme was not completely robust against wind speed variations and did not provide adequate performance for dynamic characteristics, but it is better to estimate the speed instead of measuring as anyways the measurements are not that accurate.

Small-scale low-power WECSs have also been designed to act as micro-generation source for home energy management system. Kusakana [19] developed an energy management model of a 2 kW residential WECS with battery storage. Battery energy storage has been used to solve the problem of intermittency in power output of a typical WECS [20, 21]. Local load profile and wind resource along with feed-in tariff (FiT) and time of use (ToU) were regarded as inputs to the developed energy management model. MPPT operation was achieved using DC/DC converter. An inverter was used to connect the WECS to the main power grid. Total power generated was supplied to the MPPT converter to extract maximum power. If the WECS generated power greater than the required quantity, it was split and fed into the DC/DC converter and the battery for charging. Other times of the day, power was imported from the grid to satisfy the load demand. Developed non-linear model was evaluated using a WECS system that interacted with the grid, in South Africa, as a case study. For the case study, the simulation results displayed that cost reduction was achievable up to 95%.

3 Control Design for a WECS

In a WECS, it is necessary to control action of the wind turbine, and control strategies need to be developed to obtain maximum output. Power output from a WECS is dependent on the accuracy with which peak power points of the system are tracked. This tracking is exercised by developing a maximum power point tracking (MPPT) algorithm which operates irrespective of the type of generator being used. MPPT controllers are designed for parameter control of tip-speed ratio (TSR), hill-climb search and power signal feedback method. Numerous studies have been reported in developing MPPT algorithm strategies by varying parameters of the WECS system components.

Mathematical model for connecting a small-scale wind energy generator to the grid through transformers and transmission lines is shown in Fig. 5. As illustrated from the outline of power structure of grid tied PMSG-based WECS (Fig. 2), any grid tied inverter is a voltage source inverter (VSI) operated in current controlled model. This inverter acts as a controlled current source and, hence, is represented as a current source in the equivalent circuit diagram of Fig. 5.

In Fig. 5, I_{inj} represents the injected current which is the output of the VSI (output of Fig. 2). L_{MV_T}, L_{HV_T} and L_{UHV_T} represent medium voltage, high voltage and ultra-high voltage transformer, respectively, and R_{MV_l}, L_{MV_l} and C_{MV_l} are the medium-voltage transmission line resistance, inductance and shunt capacitance, respectively. Similarly, R_{HV_l}, L_{HV_l} and C_{HV_l} are the high-voltage transmission line resistance, inductance and shunt capacitance, respectively. V_G is the grid voltage level. It is to be noted that the model represented by Fig. 5 is based on a typical layout for connecting a small wind park structure to the grid [22] using passive components such as transformers and transmission line cables.

Boubzizi et al. [23] analysed PI, first- and second-order sliding mode control of the aerodynamic torque to achieve maximum efficiency through optimal performance of the wind turbine. Second-order sliding mode control (super twisting strategy (STW)) leads to better performance with elimination of undesirable chattering. *d*-axis dealt with reactive power and *q*-axis with torque estimation. In PI controller, field-oriented approach was used where *d*-*q* axis is decoupled and

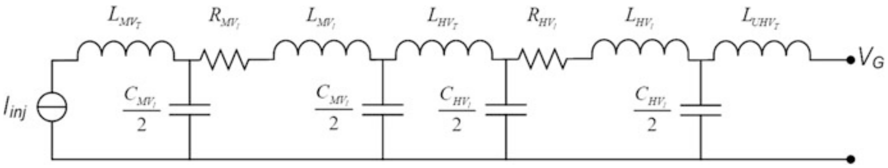

Fig. 5 Mathematical model of a WECS connected to the grid

parameters of the controller are computed using pole compensation approach, whereas for first-order sliding mode control, equivalent and switching control signals are used as sliding surfaces. Due to the presence of a sign term in the switching control signal, chattering phenomena takes place. This problem was eliminated in the second-order sliding mode control. This control strategy required information only on the sliding surface, reducing complexity and mitigating chattering effect as the control action now acts on a larger number of derivatives. MATLAB was used to implement the developed strategies, and robustness of the system was compared by varying the rotor resistance and mutual inductance. Wind speed was varied from 8 m/s to 13 m/s. Simulation results showed that the tracking performance of the second-order sliding mode control ensured better torque and rotor current than PI and first-order sliding model control. PI controller produced dynamic errors as well as overshoots which were absent in sliding mode control strategies.

Cheikh et al. [24] developed a control strategy to achieve maximum power output from a 3 kW PMSG-based WECS. Speed of PMSG was tuned to an optimum desired value by varying the chopper's equivalent load resistance. Stochastic nature of wind was mapped as a combination of rapidly variable component (to model turbulence) and a long-term changing component (to model seasonal variations). *d-q* reference frame-based equivalent circuit was used to illustrate dynamics of PMSG, and a non-linear state space model was developed. In order to linearize the PMSG equivalent circuit model, a differential geometric feedback technique was adopted. Lie derivative of the output state-space equation was computed along the direction of system vector and input vector field. However, due to the dependency of the feedback controller on the parameters of the system, such as the high-speed shaft inertia, it was strongly affected by any uncertainty of the parameter. Error vectors of modelled PMSG speed and optimal speed based on tip-speed ratio (TSR) were computed and minimized using Lyapunov theory to handle uncertainties. Output electrical power and the electromagnetic torque of the developed WECS were driven close to optimal operating points by changing the value of the resistance. Such an exercise was obtained for different wind speed and TSR values. Developed control strategy was validated against first-order sliding mode controller by maintaining the coefficient of power to its maximum value and TSR value to optimally obtained value. Chopper equivalent resistance value was varied to obtain the optimum TSR and PSMG speed and, hence, maximum power output from the developed WECS. Transient disturbances were observed for rapid variations in coefficient of power, TSR and PMSG's speed values.

Youssef et al. [25] developed a variable-step perturb and observe MPPT algorithm, for a grid-tied 1.5 MW WECS, which involved search space in a synthesized power speed curve. Synthesized curve was bifurcated into different regions, and the step-size was varied according to the position of operating point in the regions. PMSG was connected to the utility grid with the help of a back-to-back voltage source converter (VSC). Similar shape was maintained with changes in wind velocity while changing in location. Speed control concept was illustrated using a PMSG dynamic model. For eliminating reluctance torque, the d-axis current was forced to zero. Inverse park transformation was used to regulate actual machine current with reference. Low oscillations were seen upon applying small fixed speed step-size. MPPT time response improved upon large fixed speed step-size application. A new formulated curve divided the operation region into four sectors. Sign of difference between curves determined the perturbation. WECS was connected to the grid using an inverter (grid-tied). MATLAB/Simulink was used for demonstrating the developed MPPT algorithm and was validated for system performance with conventional perturb and observe MPPT algorithm.

In a standalone WECS, wind turbine is connected to the generator feeding an isolated load. Control of system voltage and frequency is an extremely important task in order to obtain optimal power generation and delivery. Model predictive control (MPC), as a technique, has been employed for control of WECSs with a limitation of requiring larger computational efforts. Electrical drives help the MPC to function as a fast system with shorter time steps, thereby improving the strategy's computational performance in term of speed, accuracy and memory requirements. Kassem [26] developed a MPC strategy to manage and control WECS parameters. VAR compensators, connected to the induction generator terminal, were employed to regulate the system voltage by controlling the firing angle. For controlling the system frequency, rotor speed has to be controlled which eventually depends on the power output and blade angle. A functional MPC was designed which uses Laguerre functions to minimize the computational steps. For a larger prediction range, exponential data weighing is used to manage the numerical problems. The system was simulated on MATLAB/SIMULINK in order to test the effectiveness of MPC strategy. Wind speed was varied from 6 m/s to 8 m/s and was tested for a step change of load impedance. As the wind velocity increases, firing angle of the compensator decreases with increase in rotor speed.

A robust non-linear adaptive controller was designed by Ayadi and Derbel [27] for controlling the power output of a PMSG-based variable speed wind turbine (VSWT). The controller was designed on the backdrop of a back-stepping strategy as compared to conventional vector approach, feedback linearization control and sliding mode control. Lyapunov function was used for derivation of fundamentals and stability analysis of the developed controller. A mathematical model of wind turbine was developed through which optimum rotor speed and maximum power output were obtained by considering optimal values of blade pitch angle and tip speed ratio for MPPT. Field-oriented control strategy is majorly used for PMSG-based WECSs. Such a strategy consists of two inner current loops and an external mechanical loop to control torque and speed regulation. Both non-adaptive- and adaptive-based cases were considered where the system parameters were varied in the adaptive case, only. An additional step for adaptive part is taken into account in which a new Lyapunov function is introduced for parameter adaption. Comparatively, adaptive case gave better accuracy for PMSG, and the system efficiency was improved.

Kahla et al. [28] have used fuzzy logic to develop a MPPT strategy along with the standard on-off controls in order to mitigate drawbacks of the standard methods which are presence of discontinuous sign function leading to chattering effect and poor system robustness. Using fuzzy logic enhanced the capabilities of a conventional on-off control by eliminating chattering effect. Fuzzy controller generates reference torque, and the hysteresis controller generates PWM pulses by comparing the three-phase currents to minimize any discrepancy. Conventional on-off control has two components: equivalent control component and alternate high-frequency component. Fuzzy logic controller adds an alternate high-frequency component to make the control component of WECS to work at optimal operating point and eliminates the unwanted sign value resulting in no chattering.

Sensors employed for data acquisition and signal processing can cause errors. Approach against erroneous sensor measurements for resilient operation of PMSG-based direct-drive WECSs was presented by Saha et al. [29]. A sliding mode observer (SMO)-based state and fault estimation system, indirect vector control approaches and a fault mitigation algorithm for generator and grid side voltage source converters (VSCs) were designed. Vector control approach is simple, however, PMSG-based WECS failed to operate reliably and efficiently due to erroneous sensor measurements. Current, DC link voltage and speed sensors' malfunctioning were considered. State and fault estimation system based on SMO and mitigation of fault along with indirect vector control algorithms regulated the electrical torque to maintain optimum generator speed for maximum power extraction. Grid-side VSC was controlled for power flow regulation when operated in the grid-connected mode and for voltage and frequency regulation when operated in the islanded mode. Function of SMO was error estimation in the generator due to faulty sensor measurements. Uncertainties in modelling and parameters were not considered. Simulation studies were performed on a grid-connected PMSG-based WECS. Proposed approach was found to be sufficiently good to nullify the impact of faulty sensors' erroneous measurements.

For a dual stator induction generator (DSIG)-based WECS, Benakcha et al. [30] developed comparative analysis of linear and non-linear control based on PI control and back-stepping control, respectively. Wind turbine is modelled, and the relationship between tip speed ratio, wind speed, power coefficient and power was developed. DSIG comprises two static stator windings which are displaced at an angle of 30° and a moving rotor winding. Field-oriented control was performed by controlling the d-q axis currents which eventually controls the flux and torque. For back-stepping control of DSIG, Lyapunov function was used for defining error between reference and actual speed and also the reference rotor flux and actual one. The DSIG rated at 1.5 MW is simulated on MATLAB/SIMULINK choosing the displacement between the windings as 30°. Firstly, by taking three fixed speeds, the PI controller and the back-stepping controller are compared. Back-stepping control had faster response, while the response time was improved for both PI and back-step cases with increase in the wind speed. Secondly, the wind varied speed profile is considered which results in constant dc voltage, active and reactive powers in acceptable limits and lower value of THD for PI control method.

4 Power Quality for Grid-Tied WECS

Traditionally, power quality is defined as any change in the power (voltage, current, or frequency) that interferes with normal operation of electrical equipment [31]. Every equipment and machinery that is driven by electrical power has a certain limit of susceptibility which in turn defines the necessary level of power quality. It can be noticed from the definition that power quality can be specifically regarded as a power quality disturbance. IEEE developed a standard named *IEEE Recommended Practice for Monitoring Electrical Power Quality IEEE 1159–1995* which defines power quality in terms of interruptions, sags and swells, long duration variations, impulsive transients, oscillatory transients, harmonic distortion, voltage fluctuations and noise [32].

Variations in wind speed lead to fluctuations in the output power of a WECS which is given as Eq. (1).

$$P_{\text{wind}} = \frac{1}{2}\rho A v^3 c_p \tag{1}$$

where, P_{wind} = wind power output, W; P = density of air, kg/m^3; A = area of the rotor, m^2; v = wind velocity; and m/s, c_p = Betz-factor power coefficient, usually in the range of 0.4–0.5.

Variations in wind speed cause the parameter v to change, and thus, output power of the WECS changes significantly (as P_{wind} is proportional to v^3). Now, when power changes with velocity, injected current, Iinj, becomes variable which causes the grid voltage to drop leading to *flicker* effect due to grid impedance variations. A current, I, flows into the grid when an impedance Z is connected to the WECS (of Fig. 5), which is given as Eqs. (2) and (3).

$$P = V \cdot I \cdot \cos\phi \tag{2}$$

$$\Rightarrow I = \frac{P}{V \cdot \cos\phi} \tag{3}$$

Changes in power, P, result in corresponding change in current of Eq. (3).

$$\Delta I = \frac{\Delta P}{V \cdot \cos\phi} \tag{4}$$

Such variations in current lead to flicker effect and harmonics which are also dependent on the type of generator used and grid-coupling in Fig. 2. Also, due to non-linearity of loads, harmonics are generated. Harmonics are undesired non-sinusoidal signals which can be represented using Fourier transforms as a combination of sine and cosine mathematical functions. Harmonics are represented mathematically in terms of total harmonic distortion (THD), amplitude and partial weighted harmonic distortion (PWHD) of voltage and current signals. Figure 6 illustrates representation of fundamental (desired) signal and harmonics (third, fifth and seventh harmonic) with respect to their phase, degrees.

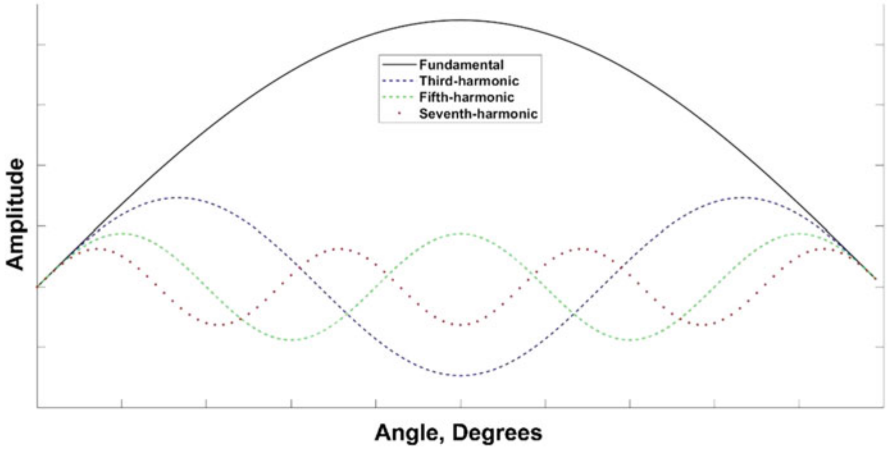

Fig. 6 Mathematical model of a WECS connected to the grid

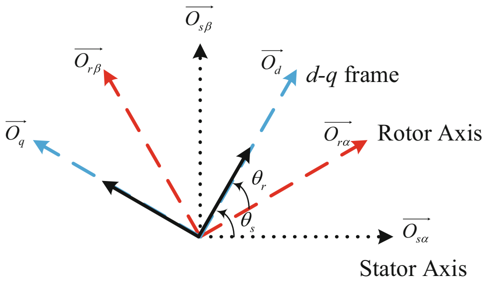

Fig. 7 Orientation of the d, q frame

Due to the intermittent nature of wind energy, power electronic interfacing circuits are employed to connect the wind power generator to the grid. Incubation of power electronics and, specifically, electronics has raised the issue of grid-tied WECSs [33]. Several articles have been reported on development of control strategies like PWM rectifier controlled by direct power control-space vector modulation (DPC-SVM) to eliminate harmonic currents [34]. Due to non-linear nature of the loads, an electric power system suffers from harmonics-related issues. Passive filters due to series or parallel resonance and no complete elimination of harmonic currents find limited applications as compared to active filters for harmonics mitigation [35].

A hybrid control strategy was developed by Mesbahi et al. [34] for grid side converter to control the dc link voltage with active filtering function. A doubly fed induction generator (DFIG)-based WECS was developed using the *d-q* reference frame (Fig. 7). Wind-generated active and reactive powers were controlled using rotor currents by a PI controller. Instantaneous active and reactive powers of the load were controlled though DPC strategy which involved comparison of estimated power values with new reference powers and variables using a hysteresis controller. Voltage vectors were obtained using these differences and looked up in the switching table. MATLAB/Simulink was used to model the strategy, assuming a constant speed DFIG system.

In a wind energy conversion system (WECS), the main aim is to deliver constant voltage and power to the load connected to it. In order to maintain the voltage constant, rotor flux-oriented method is mostly used in the systems. Idjdarene et al. [36] developed a direct torque control method to control the DC voltage of an isolated induction generator integrated with a flywheel energy storage system. The flywheel storage was responsible for power quality control in case of variations in wind speeds. Developed WECS consisted of a wind turbine, rectifier, inverter, induction generator and a flywheel storage. As speed of the wind fluctuates, power output experiences oscillations and to control speed, a reference speed was obtained. Vector model of the induction machine was used to develop the control strategy. Torque was estimated from flux and current values using the *d-q* model of the induction machine. Three-phase voltage inverter provided voltage vector, and the switching table was preferred for operation in the four quadrants. Flywheel energy storage system was modelled using the flywheel initial energy and reference speed expressions. The machine was operated beyond its rated speed, and a field weakening operation was required for constant power function.

5 Power System Dynamics and Contingency Analysis for a Grid-Connected WECS

Producing electricity using wind energy is nowadays used widely throughout the world and is considered as the most clean and efficient form of renewable energy. In a grid-connected WECS, there is a significant chance of *fault occurrence* in the transmission system. With increased penetration of large wind farms for power generation, power system engineers are developing fault diagnosis studies applying various algorithms to estimate the state of the power system. Also, for such forms of energy, it is equally important to test whether it is reliable and if yes till what extent. Such an exercise enhances the power system security levels. An electric power system operates in five different states ,viz. *normal/secure* state, *alert* state, *emergency* state, *extremis* state and *restorative* state (Fig. 8). A power system is said to be secured when all the components are operating within acceptable limits and all the system variables are within prescribed ranges [37, 38].

Aval et al. [39] developed an analytical approach to develop a reliability assessment tool which would also evaluate risks associated with a DFIG-based WECS. Contingencies in terms of wind speed and wind turbine outages were considered, and a Weibull-Markov method was adopted and tested to a Vestas V90-2 MW wind turbine structure. The homogenous Markov method is used for frequency evaluation and state probability using analytical matrix operations. Developed approach was

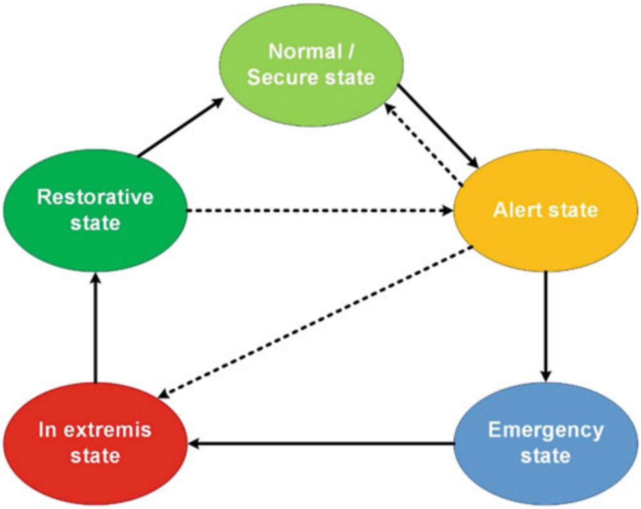

Fig. 8 Power system operating states

applied to a six-bus test system with nine transmission lines and generators ranging from 5 MW up to 40 MW. The analytical approach was demonstrated as different case studies scaling up and down the generators connected to the bus 1 and 2. Outputs were recorded in terms of forced outage rate, mean time between failures per hour, mean time to repair per hour and maintenance per week required. Twenty wind power generators of 2 MW each were considered with failure rates for different components of the WECS under study.

Fault detection and diagnosis of a grid-connected WECS is also significant. A robust power system state observer was developed by Wu et al. [40] for FDD and, also, to provide stability in case of external disturbances. For the adaptive fault diagnosis, a detection system was designed based on the power system state vectors. Lyapunov stability theory was applied to test the feedback gain matrix and stability checks whereas for fault estimation, asymptotical stability was checked for accuracy. Closed loop stability of the system under study was tested for active tolerant control to ensure surety of normal operation of the faulted power system. Proposed system was simulated for a variable-speed and fixed-paddle WECS connected to a transmission system and was tested for two fault conditions: actuator fault and shaft fault. No experimental analysis or case studies were considered in the study.

A typical WECS comprises huge number of components, sensors and actuators which makes the system more complex and difficult to handle. Faults occurring in the sensors affect the operation of the turbines which eventually lowers the productive generation. To address such faults, Wang et al. [41] have developed a sensor-based process monitoring fault-tolerant control strategy to handle the faults and improve overall system performance. A linear time invariant system model was developed with an aim to identify the left co-prime factorization which shall lead to accurate estimation of the process outputs. Developed algorithm designs the process predictor, performs residual evaluation and handles the threshold setting of the system. Further, there are two proposed strategies for FTC. Supplementary sensor-based PM FTC replaces the measurements of the faulty sensor with the supplementary sensor once the fault is detected. The transfer function model of the secondary sensor is shown in the paper. But, to use extra sensors instead of the faulty sensors cannot always be the choice due to economic and structural considerations. For such cases, soft sensors based on the data-driven process monitoring have been used. It works by producing another process variable once the fault is detected. To check the performance of the proposed strategies, a benchmark simulator provided by MATLAB was used. Hydraulic pitch system is considered in this article for which input is the pitch angle control command and the measured pitch angle acts as the output. From the figures obtained, it could be noted that the monitoring technique proposed is quite reliable and also successful in detecting the faults. The results obtained for the FTC plotted for two cases shows that the supplementary sensor-based technique is the best. Also, the use of soft sensors gives a satisfactory result.

As the wind energy penetration increases, the power system's (grid) frequency gets affected. Wind generators participate in the control of frequency control through advancements in technology. Verma and Kumar [42] developed a load frequency control strategy for a two area interconnected power system based on DFIG. A deviation signal is generated by comparing the system and load frequency, and the DFIG would inject power into the grid to provide necessary inertial support to the system. Developed control strategy is based on inertial control, power reserve control and communication control. DFIGs provide only primary control for frequency, but majority of control is provided by the conventional power plants. Using power electronic converters, kinetic energy stored inside the variable speed wind turbine (VSWT) is used for inertial control, pitch control and speed control. During inertial control, either the inertial response of VSWT is used, or droop characteristics are taken into consideration. In pitch control, active power is limited to a pre-defined value, and reserves are used when the system frequency changes. VSWT blades are turned as per the wind speeds for less or more exposure of the surface as per the power system's requirement. A two area interconnected system model having both the reheat type conventional generators and non-conventional generators like DFIG are simulated. A load perturbation of 2% is given to observe the characteristics of the DFIG and the conventional generators.

You et al. [43] have studied the control problem for non-linear systems' actuators. The problem was robust and fault-tolerant, while parameters were uncertain. For describing the WECS, the fuzzy model by Takagi-Sugeno [44] was used. Algorithms based on fuzzy dedicated observer and fuzzy PI observer were developed to analyse the system's state along with the fault reconstruction of actuator. Stability of fuzzy robust scheduling fault-tolerant controller for the system was proved using various mathematical techniques such as Taylor series and linear matrix inequalities. Fault in the WECS was categorized into three types as per Pozo and Vidal [45] and Pérez et al. [46]. Takagi-Sugeno fuzzy model used *if-then* fuzzy inference rules for non-linear system description taking into account the unmeasurable state variables and system uncertainties. Parallel distribution compensation method was used to design the fault-tolerant controller. Boundary conditions for closed loop stability were proven by Lyapunov theory [47] and Taylor series [48]. The system state model was assumed to be observable. The captured mechanical power was depicted as per Betz theory [49].

6 Techno-economic Analysis of Wind Energy Conversion Systems

Apart from possessing technical and environmental advantages, a typical wind energy conversion system should also possess economic and financial feasibility for better adoption and easy implementation. Quantitative metrics, such as economic cost per kWh of power generation, annual energy generation, capital costs including costs of components, generator cost, tower cost, battery and inverter cost, installation and other costs, are evaluated to compute the net present value (NPV) and levelized cost of electricity (LCOE) generation. Financial analysis includes metrics which are computed as certain percentages over the capital costs. Such metrics include depreciation cost, interest less inflation cost, operation and maintenance cost and likewise [7].

Quantitative metrics such as annual energy output, wind power density per unit area, capacity factor and plant load factor are evaluated to assess the technical performance of a WECS. Historical wind and meteorological data are used to estimate and model the wind characteristics, and LCOE is evaluated. Ohunakin et al. [50] evaluated LCOE and NPV for various geographical locations in Nigeria. WECS's plant life, maintenance costs, construction and infrastructure cost, wind speed, turbine life and discount rate were taken into consideration for evaluations. Wind turbines of ratings ranging from 20 kW to 2 MW were considered with different hub heights. As the value of life of wind turbine and capacity factor increases, LCOE decreases, and similarly when the operation, maintenance, infrastructure and turbine costs increases, LCOE also increases.

Taner [51] applied escalation method of inflation to economically analyse the optimal investment cost for developing a 3 MW WECS in the Cappadocia region of Turkey. The method estimated annual generation of around 7,884 MWh for the period of 2014–16. WECS energy region was based on the compatible wind potential as well as important performance characteristics installation, as described by Mathew and Philip [52]. The problem of plant area impact on farms was solved by its location on barren land with sufficient wind flow [53]. Owing to the environmental impacts on plant and animal life, it was analysed that the location of wind farms should be away from residential areas. In order to offer energy advice to the factory, data analysis calculation was considered important. The electrical energy unit cost was understood to be suitable for the Cappadocia region which served as the prime cause for its wind energy potential's effectiveness. Statistical SPSS® software [54] was used to evaluate data accuracy rendered by Republic of Turkey

Ministry of Forestry and Water Affairs General Directorate of Meteorology for the period of June 2012 to April 2015. Analysis of variance (ANOVA) was used to determine the wind velocity mean differences. Difference between the present cost of deferred plan and present value of current plan was defined as the cost for economic analysis.

7 Summary

Since last decade, there has been tremendous increase in installations of offshore and onshore wind energy conversion systems (WECS) due to several reasons such as green energy generation of high power, good wind potential and ability to harness offshore wind and also as a micro-generator. In this chapter, concept of generating electrical power using wind speed is introduced. Configuration and layout of the components involved in a typical WECS has been illustrated. Latest research articles on modelling and simulating a WECS was presented. For a grid-connected WECS, it is mandatory to control the active and reactive power components to satisfy the demand and also the electrical grid codes. Researchers around the world have deployed control strategies based on conventional control such as on-off, PI-control and also advanced strategies like sliding mode control, model predictive control and fuzzy logic. Due to the intermittent nature of wind energy, power electronic interfacing circuits are employed to connect the wind power generator to the grid. Incubation of power electronics and, specifically, electronics has raised the issue of grid-tied WECSs. Several articles have been reported on development of control strategies like PWM rectifier controlled by direct power control-space vector modulation (DPC-SVM) to eliminate harmonic currents. Fault analysis, detection and control for a grid-connected WECS have also been discussed.

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Offshore Wind Energy: Resource Assessment

Garlapati Nagababu and V. S. K. V. Harish

Contents

Abstract Recent advancements in technologies and increased attention towards renewable energy sources have made offshore wind energy systems as one of the largest and significant electrical power generators. In this chapter, fundamentals of offshore wind energy physics along with resource assessment methodology are described in detail. The process of resource assessment consists of the use of different data sets, different resource and energy estimation models. Wind, being an intermittent resource for power generation, mandates statistical methods to estimate the parameters with uncertainties. Researchers have employed several methodologies to assess offshore wind power density using resource estimation models and geographical information systems. Present chapter will be beneficial in getting familiar with the wind resource data analysis and different aspects of resource assessment.

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1 Introduction

Wind energy is implied type of solar energy generated due to the warming of the earth exterior and rotation of earth on its axis [1]. The air in the contact with surface absorbs the heat and moves upwards, whereas the denser and colder moves downwards; this generates vertical movement of the air. Moreover, the distribution of heat around the globe is different as the equatorial part gets more heat than the polar regions. Owing to achieve equilibrium, the denser air moves towards the less dense air which generates the lateral movement of air. These both vertical and lateral movements of air particles are termed as wind. Additionally, the rotation of earth on its axis generated Coriolis effect (CE) that causes winds to deviate towards right side (clockwise) of its direction in northern hemisphere and towards left side (counterclockwise) of its direction in southern hemisphere (refer Figs. 1 and 2). CE is most significant near the polar regions and nominal near the equator.

The offshore wind energy means the wind energy available at the marine regions, i.e. water surfaces of seas and oceans. Offshore wind energy is an ample and untapped source of renewable energy available all over the globe in different intensities. The harvesting of offshore wind energy is an intricate engineering and scientific challenge [2]. This chapter is focused on the current status offshore energy, different aspects of wind resource assessment, energy estimation models and future trends in the field.

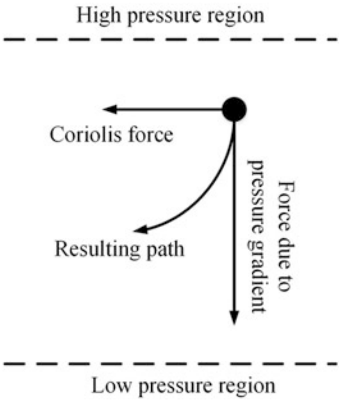

Fig. 1 Impact of Coriolis effect on the wind direction

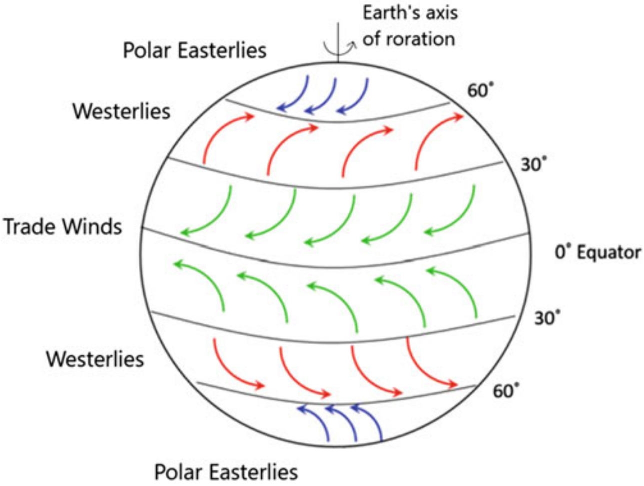

Fig. 2 Depiction of wind patterns with Coriolis effect

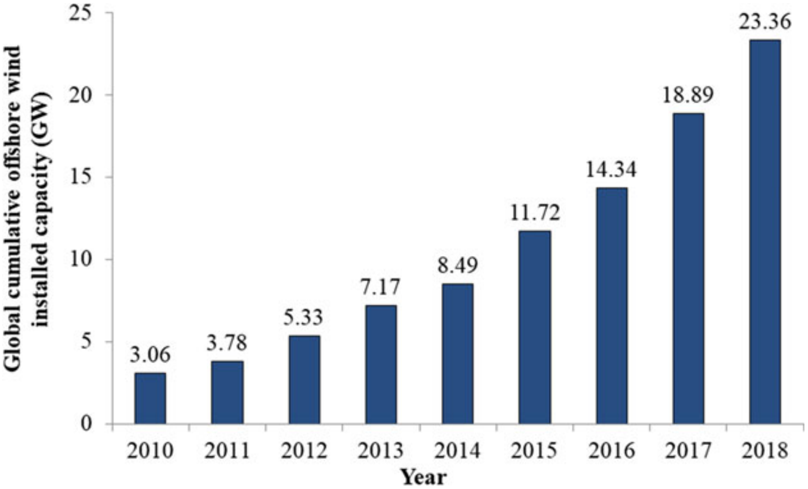

Fig. 3 Global aggregate offshore wind power installed capacity (2010–2018)

1.1 Background

The field of offshore wind energy is still in an infant phase and not older than two decades as shown in Fig. 3 [3]. There are incredible opportunities in offshore regions but numerous complications to be seized. While focusing on the offshore wind energy resources, the differences from onshore resources like environmental conditions, project infrastructure, project design, power evacuation facilities and safety measures have to be considered [1].

1.2 Status of Offshore Wind Energy

In the European oceanic regions, majority of the wind power plants are situated in North Sea, Irish Sea and the Baltic Sea. In Europe, the United Kingdom, Germany, Denmark, the Netherlands, Sweden and Belgium have majority of the offshore wind power capacity [3, 4]. Except these European countries, only China has significant installed capacity. The United States is the only country having the wind power project in the American offshore region. Further, the country-wise current offshore wind power installed capacities is listed in Table 1.

2 Offshore Wind Energy Conversion System

One of the largest-scale renewable energy technologies, the offshore wind energy conversion system (O-WECS), possesses several advantages over onshore WECS. Typically, an O-WECS has higher wind speeds with lower wind shear and innate turbulence which enhances its ability to take advantage of larger wind turbine arrangements. Also, studies have proved that an O-WECS of same capacity has lower environmental impacts as compared to an onshore WECS [6]. Apart from large power generation capability, the O-WECS can also assist in increasing the reliability of supply for remote and rural areas [7]. Although, O-WECS possesses such attractive merits, large-scale deployment has witnessed critical engineering challenges such as large investment costs due to specialized equipment and machinery, expensive support structures, untrained manpower to work at offshore conditions, maintenance issues and specialized techniques and measures for combating corrosion. The International Electrotechnical Commission defines an offshore wind

Table 1 Country-wise offshore wind power capacity scenario in 2018 [5]

Region	Country	Cumulative offshore wind power installed capacity (MW)
Europe	United Kingdom	7,963
	Germany	6,380
	Belgium	1,186
	Denmark	1,329
	Netherlands	1,118
	Other European countries	302
Asia-Pacific	China	4,588
	South Korea	73
	Other Asian countries	171
North and South America	United States	30

turbine in its IEC 61400-3:2009 [8], which has been replaced by IEC 61400-3-1:2019) as “wind turbine with a support structure which is subject to hydrodynamic loading”. An offshore wind turbine can be fixed using supporting structures at the seabed or else they may *float*, as well.

Power calculations for an O-WECS involve similar techniques, laying foundation from the fundamentals of fluid mechanics. Temporal and spatial variations of the wind characteristics such as speed, orientation and turbulence over a specific period of time are recorded at particular time [9]. All these factors affect the power generation potential for an offshore wind turbine with turbulence dictating the design of the turbines. Statistical methods are used to model the wind characteristics with uncertainties. Monte Carlo simulations, Gaussian distributions, Gaussian mixture curves and Weibull functions have been majorly used to model the wind speed frequencies for a location under study. Shape and scale factors of the probability distribution functions, used for modelling the uncertainties in the wind characteristics, are fixed according to the long-term mean wind speed (based on sampled timely averages). Wind speed, direction, mass flow rate and density are used to calculate the power of the wind per unit square metres. External design conditions such as ocean waves and currents, characteristics of subsea soil, ice floats, and salinity in water are considered for wind turbine design which affects the wind power calculations indirectly through associative changes in wind shear.

Total area spanned by the wind turbine blades (blades are the primary components of a wind turbine rotor), swept area, solidity factor, tip-speed ratio, drag and roughness of the blade’s surface are significant factors which affect the rotor design for an O-WECS; refer to Fig. 4. Losses in the rotor blade, airfoil characteristics, materials used for manufacturing and the type of control used for wind turbine rotor are other factors.

Rotor of a WECS is responsible for converting the kinetic energy of the wind into rotational mechanical energy and the torque gained by the rotor is transmitted to the shaft, usually through a gearbox. Gearboxes are mechanical transformers which are employed to increase the speed of the shaft connecting the generator. Wound-rotor induction generators of an O-WECS convert rotational mechanical energy of the shaft into electrical power using electromagnetic induction principle. Rotation speed of the generators is dependent on the magnetic pole pairs and the frequency of the alternating current generated. Power electronic converters are used to connect the power generated by the generator to the electrical power grid. Converters are also employed with filters to cancel out the harmonics in the alternating current generated thereby enhancing the quality of power generated. This is very important if the O-WECS power needs to be evacuated to the main power grid and does also makes a true economic sense.

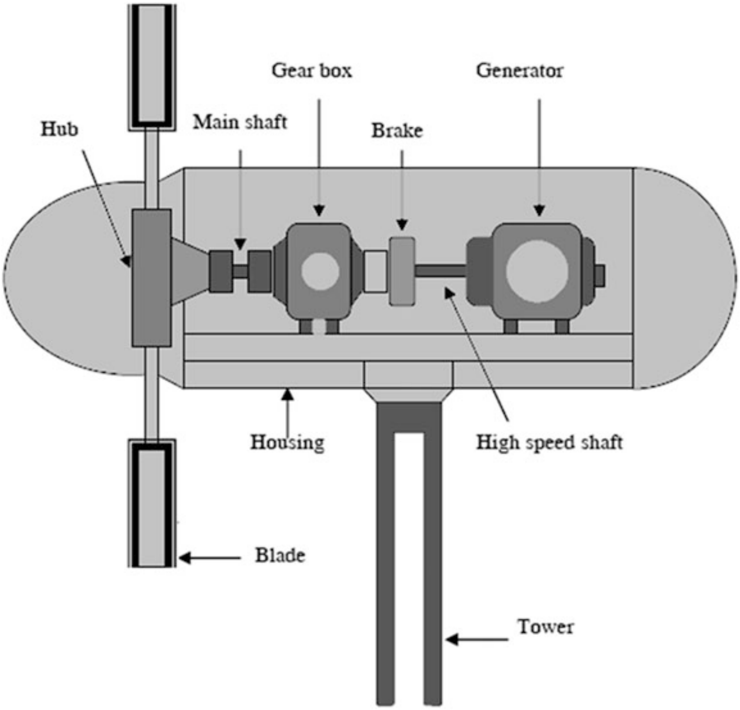

Fig. 4 Structure of typical horizontal axis wind turbine

3 Wind Resource Assessment

The wind resources exhibit very stochastic nature. Wind speed (WS) and direction may vary erratically with time at any location. Basically, wind resource assessment is the measurement of the wind energy available on some particular location or the target region. Measurement of wind resource comprises of recording and analysing the fluctuations in WS and changes in wind directions with reference to time at any particular point or multiple points or through a focused region [1]. Wind distribution is a crucial element in resource assessment along with the intensity of WS. Due to the disparities in WS fluctuations, two identical wind turbines positioned at different locations with equal average WS may harvest completely altered amount of energy [2]. Besides the daily and seasonal fluctuations, the wind distribution may vary year with years, even to the range of 10–30% [10]. Therefore, prior to the establishment of wind power project, long-term wind resource assessment is essential.

3.1 Different Types of Data Sets

Wind resource assessment is conducted using the data collected from different sources. Primarily there are three sources of wind data: on-site measurements, weather station networks, and numerical climate models [11]. Method of data collection varies for onshore and offshore regions; refer to Fig. 5. Onshore wind measurements are done using the anemometers mounted on wind mast at different heights and sensors placed on meteorological stations. The measurement of wind parameters in offshore region is more difficult as compared to the onshore regions due to apparent reasons of atmospheric uncertainties. It is done by means of the deployment of different types of buoys as per the conditions (distance from shore and depth of water). Generally, for near shore lower depth regions, the met buoys are used; whereas for higher water depth regions, moored buoys are employed. Moreover, some of the offshore meteorological stations, some other type of work stations (e.g. petrochemical units) and the moving ships are the source of limited wind data [12]. There are several methods of wind measurement that are applicable to both onshore and offshore regions, which are remote sensing recording, reanalysis data sets and other climate models. Remote sensing measurement involves the use of satellites, i.e. scatterometer [13, 14], SODAR (sonic detection and ranging) and LIDAR (light detection and ranging) instruments [11, 15]. Reanalysis data sets are an assimilation of long-term historical meteorological observational data, using a single consistent assimilation scheme. Depending on the focused region or location,

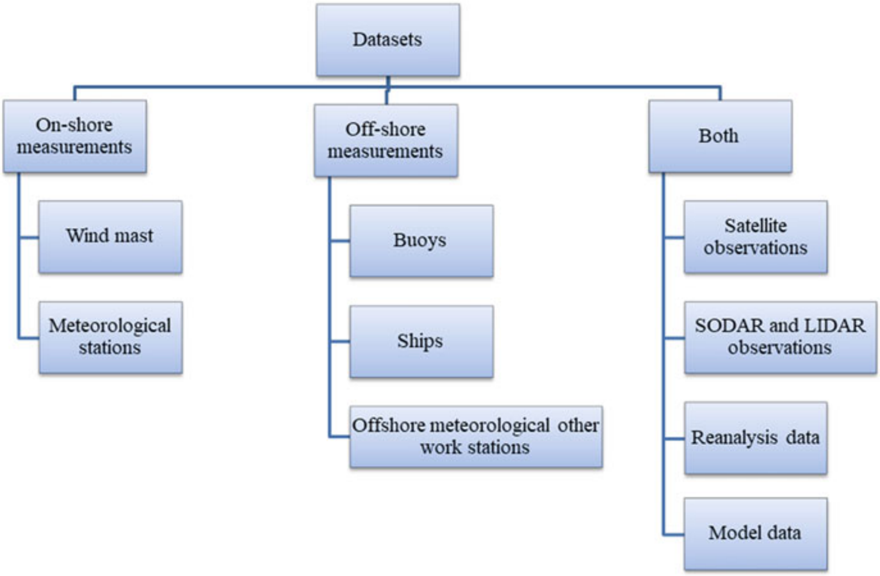

Fig. 5 Different types of data available from various sources for onshore and offshore regions

any one or multiple data sets are used for the resource assessment. Model data sets are generated through the mathematical models developed using atmospheric physics on the raw data available from different sources.

3.1.1 Satellite Data

Recently, satellite data has been employed comprehensively for the offshore wind resource assessment due to the advancement in marine resource measurement techniques. A laboratory based in Denmark (Risø National Laboratory), along with a number of associated institutes, steered SAT−WIND research programme and proved the feasibility of utilizing satellite observed data, together with surface wind recording data accumulated through scatterometers, altimeters, passive microwave remote sensors and synthetic aperture radars (SAR), during mid-years of last decade.

A global evaluative study on ocean wind power at multiple heights, usable speed ranges and siting depths utilized QuikSCAT satellite data and observed global mean wind power density (WPD) of 776 W/m^2 at 100 m height (1.6 times of the same at 10 m height) [16]. Among the available space-borne radar systems (e.g. scatterometers, passive microwave radiometers), SAR satellite imagery provides relatively higher resolution wind atlases [17]. A study focused on Baltic Sea found out SAR data to have higher accuracy with observed WPD of 300–800 W/m^2 [18]. Further, the same group of researchers utilized synergetic satellite data (Envisat ASAR, ASCAT and QuikSCAT) in order to increase the data samples and attain higher resource assessment accuracy with lower statistical uncertainty [19]. An evaluative wind energy resources assessment in the Ionian Sea of Western Greece found QuikSCAT satellite data to overestimate the wind resource by 8–13% with reference to buoy data [20]. Higher uncertainties of wind retrievals were observed at lower WSs (below 5 m/s). Further, it was detected that WS recoveries from QuikSCAT at nearshore stations (54 km) are not much accurate with reference to offshore regions owing to the ground contagion. Jiang et al. [21] performed a distributive study on offshore wind power with QuikSCAT Level 2 satellite recordings (9 years data with 0.5° horizontal resolution). The study concluded Fujian Province to have superior wind potential than the other offshore regions of China.

Soukissian and Papadopoulos [22] have examined the impacts of alternative sources of wind data on wind resource analysis on four sites of Aegean Sea. The satellite data was found to be overestimating, while the model data were underestimating the WS with respect to buoy measurements. Available offshore WPD in any region must be evaluated very cautiously while utilizing the alternative data sets. Otherwise, it may mislead the results. Realistic linear relationships are established among the buoy observations and numerical weather prediction (NWP) simulation data and satellite recordings for homogenization and calibration of latter data sets.

The accuracy of satellite data for offshore regions evaluated by different researchers is summarized and presented in Table 2. For offshore studies, the statistical parameters such as R, standard deviation, bias and correlation coefficient

Table 2 Overview of the studies on the accuracy of satellite data for offshore regions

Authors	Data	Scope	Temporal		Spatial	Reference for correlation	Correlation		RMSE (m/s)	Standard deviation (m/s)	Bias (m/s)
			Duration	Resolution	Resolution (degree)		R^2	Pr			
Pimenta et al. [23]	QuikSCAT	South-Eastern Brazil	1999–2007	Daily	0.5 × 0.5	Oil platform, buoys	-	0.81	-	-	0.35
Jiang et al. [21]	QuikSCAT	China	2000–2008	Daily	0.5 × 0.5	Wind masts	0.71	-	-	1.3	-
Carvalho et al. [24, 25]	QuikSCAT	Peninsula coast	2000–2008	12 h	0.25 × 0.25	5 buoys	0.89	-	1.89	1.77	0.61
	CCMP		1987–2011	6 h	0.25 × 0.26		0.88	-	1.72	1.72	0.1
	NCDC−BSW		1987–2011	6 h	0.25 × 0.25		0.89	-	1.93	1.74	0.83
	IFREMER−BWF		1999–2009	6 h	0.25 × 0.26		0.9	-	1.75	1.69	0.39
Chang et al. [26]	ASCAT	South China Sea	2009–2013	12 h	12.5 × 12.5 km	7 coastal meteorological stations	-	0.8	-	1.83	−0.4
	ENVISAT SAR		2009		150 m		-	0.75	-	2.09	−0.3
Gadad and Deka [27]	OSCAT	Karnataka state, India	2011–2012	12 h	0.5 × 0.5	INCOIS real-time automated weather station data	-	0.6	1.9	-	-
Carvalho et al. [28]	ASCAT	Iberian Peninsula	2007–2015	12 h	0.25 × 0.25 0.125 × 0.125	Buoys	0.93	-	1.26	1.18	0.42
	OSCAT		2010–2014	12 h	0.125 × 0.125		0.83	-	2.21	1.98	0.87
	CCMP		1987–2011	6 h	0.25 × 0.25		0.84	-	1.17	1.72	0.34

(continued)

Table 2 (continued)

Authors	Data	Scope	Temporal		Spatial	Reference for correlation	Correlation		RMSE (m/s)	Standard deviation (m/s)	Bias (m/s)
			Duration	Resolution	Resolution (degree)		R^2	Pr			
	Blended Sea winds (NCDC-BSW)		1987–2015	6 h	0.25 × 0.25			-	2.83	2.57	1.06
Soukissian et al. [29]	Blended sea winds (NCDC-BSW)	Mediterranean Sea	1995–2014	6 h	0.25 × 0.25	Buoys	-	0.88	1.818	-	−0.191
Guo et al. [30]	QuikSCAT	Global ocean	1999–2009	12 h	0.25 × 0.25	NDBC buoys	0.78	-	0.39	-	0.23
	ASCAT-A		2007–2015		0.25 × 0.25		0.77	-	0.33	-	0.09
Remmers et al. [31]	ASCAT	Irish waters	2012–2017	12 h	0.125 × 0.125	Buoys	0.81	-	0.36	-	−0.07
Surisetty et al. [14]	QuikSCAT	India	1999–2009	12 h	0.125 × 0.125	Buoys	-	0.87	1.39	1.62	0.7
	OSCAT		2010–2014	12 h			-	0.84	1.56	1.49	0.49
	ASCAT-A		2010–2016	12 h			-	0.88	1.37	0.71	0.14
	ASCAT-B		2012–2016	12 h			-	0.87	1.43	0.83	0.2
Elsner [32]	Blended sea winds (NCDC-BSW)	Africa	1995–2005	6 h	0.25 × 0.25	Buoys	-	-	-	-	-
Zaman et al. [33]	Satellite altimetry data	Malaysia	1993–2011	Monthly	2 × 2	Buoy	-	0.835	1.385	-	0.55

- not found

(either Pearson's R or R2) are the very frequently utilized techniques. Different studies on satellite data for offshore (see Table 2) show correlation coefficient in the range of 0.6 to 0.81, standard deviation in the range of 1.3 to 2.09 m/s, root mean square error (RMSE) from 1.72 to 1.93 and bias −0.4 to 0.83 m/s. From literature, it can be observed that IFREMER−BWF satellite data is well correlated with buoy data in Peninsula coast with a correlation coefficient of 0.9.

3.1.2 Reanalysis Data

Reanalysis data is the assimilation of ground meteorological stations, deployed buoys, transit ships and satellite data sets into general circulation model and delivers long-term high spatial resolution data with higher reliability [34]. The National Centers for Environmental Prediction (NCEP)-Department of Energy (DOE) and the European Centre for Medium-Range Weather Forecasts (ECMWF) offer WS component with temporal resolution of 6 h, from the year 1979 [35]. Moreover, it eases the evaluation of seasonal and annual variability of wind climate over different regions due to its spatial and temporal homogeneity. Reanalysis data can be utilized for global [36] as well as certain target region or country like Europe [37, 38] and the United States [39, 40].

Carvalho et al. [24] compared different analyses (NCEP-GFS and NCEP-FNL), reanalyses (ERA-Interim, NCEP-R2, NCEP-CFSR and NASA-MERRA), satellite data (CCMP, NCDC, IFREMER and QuikSCAT) and WRF modelled offshore winds with buoy data along the Iberian Peninsula coast. They found WRF modelled data is best alternative to buoy data. Further, NCEP-GFS or NCEP-CFSR data showed better wind power flux, so that, these two datasets can be used as an alternative to WRF modelled data. A study using high spatial and temporal resolution NCEP-CFSR reanalysis data concluded that CFSR reanalysis data is consistent with observation data and provides reliable wind data for offshore regions of China [41]. On the contrary, the 30 years duration CFSR data have been observed to be less accurate at higher elevation in the United Kingdom, when compared to the synoptic weather stations (12 offshore and 264 onshore) [42]. ERA-Interim reanalysis data delivers the most reliable initial and boundary layer simulation of near-ground wind properties [24, 25].

Several researchers have evaluated distinct reanalysis and mesoscale models for assessing wind properties for different regions (refer for the summarized overview in Table 3). RMSE, bias and a correlation coefficient (either Pearson's R or R2) are the most commonly used parameters for the study or error matrix in offshore studies. Here, it can be observed that the RMSE and bias are comparatively lower in almost every case for the mesoscale data.

Table 3 Overview of the studies on the accuracy of reanalysis data for offshore regions

		Temporal		Spatial				Correlation		
Author	Data	Duration	Resolution	Scope	Resolution (degrees)	Reference for correlation	RMSE	Pr	R^2	Bias (m/s)
Hawkins et al. [43]	NCEP−FNL + WRF	10 years	6 h	UK	0.1	Buoys, lightships, platforms	1.33	-	0.9	−0.02
Menendez et al. [44]	ECMWF ERA-interim + WRF	20 years	Daily	Spain	15 km	Buoys	-	0.7–0.9	-	0–1
Staffell and Green, [45]	Downscaled MERRA	20 years	Hourly	UK	Site	Buoys	-	-	-	1.6
Carvalho et al. [24, 25]	NCAR(R2) + WRF	10 months	Hourly	Iberian Peninsula	0.083	5 Buoys	2.43	0.76	-	0.34
	ERA−interim + WRF						1.85	0.88	-	0.48
	CFSR + WRF						1.94	0.87	-	0.6
	MERRA + WRF						2.01	0.86	-	0.59
	NCEP−FNL + WRF						1.89	0.87	-	0.53
	NCEP−GFS + WRF						1.89	0.88	-	0.56
Carvalho et al. [24, 25]	NCEP−NCAR (R2)	1 year	6 h	Iberian Peninsula	2.5	5 Buoys	3.43	-	0.6	0.87
	ERA−Interim		6 h		0.75		2.45	-	0.8	0.58
	CFSR		Hourly		0.5		1.85	-	0.9	0.16
	MERRA		Hourly		0.6		1.93	-	0.9	0.52
	NCEP−FNL		6 h		1		2.3	-	0.9	0.98
	NCEP−GFS		6 h		0.5		1.89	-	0.9	0.22
Stopa and Cheung [46]	CFSR	1979–2009	Hourly	Peru	0.5	1 Buoy	1.37	0.81		6.14%
				Hawaii		4 Buoys	1.37	0.86	-	−3.90%
				Gulf of Mexico		5 Buoys	1.52	0.87	-	0.43%
				NW Atlantic		5 Buoys	1.73	0.89	-	4.23%
				Alaska		5 Buoys	1.7	0.91	-	3.90%
				NE Pacific		5 Buoys	1.5	0.91	-	2.38%

- not found

3.1.3 Wind Power Potential

Researchers have used different methodologies to assess offshore WPD by employing different resource estimation models and Geographical Information System (GIS) approach. There are various parameters that affect the installation of offshore wind farms. For evaluating WPD at particular location or region, there are some aspects (i.e. sea utilization authorization, technology, economics and environment) that have to be studied.

An evaluative study performed on offshore wind resources of Southeastern Brazil using QuikSCAT satellite data for mapping the wind energy properties over large oceanic extent found that the coastal area of Brazil has an overall potential of 102 GW electrical energy generation [23]. Using bathymetry and properties of current wind electric technology maps of WS, WPD and practical turbine output can be determined. Dvorak et al. [47] created an offshore wind resource assessment for California by combing multiyear mesoscale modelling results, validated using offshore buoys with high-resolution bathymetry. Similarly, a group of researchers investigated offshore wind climate along the coast of Kanto area by a mesoscale model considering economic and social criteria estimated by GIS [48]. The study identified overall annual wind resource along the coastline of Kanto, which is about 287 TWh without considering the socio-economic aspects. Mesoscale model is observed to be performing well while determining the offshore WPD. Capacity factor (CF) can be considered as an index for evaluation of the economic feasibility of wind farm. Onshore wind farms can be said to be economically feasible if CF is more than or equal to 20%.

Microscale wind flow model and the coupled numerical mesoscale atmospheric model with long-term global reanalysis climate data set were employed by Waewsak et al. [49], in order to generate high-resolution wind resource maps of the Gulf of Thailand at varying heights above sea level. The study further pointed that, using a multi-criteria decision- making method, the possible regions for grid-attached wind power generation can be identified. Estimated technical power potential for the Gulf of Thailand is about 7,000 MW with annual generating capacity of 15 TWh. Kim et al. [50] have presented and additional strategies for site-selection process for feasible offshore wind farm sites in the coastline regions of Jeju Island, South Korea. The site-selection criteria can be categorized in four divisions: (a) energy resources and economics, (b) preservation zones and topography safeguard, (c) human actions and (d) aquatic environment and oceanic ecosystem. The spatial methods of GIS can be used for investigating the resources available in the particular country or region. However, among prescribed four categories, the energy resource availability and economics are also integral part of the process.

In addition to the mesoscale models, the wind power potential can also be derived by means of satellite data. Gadad and Deka [27] assessed the offshore wind resources of Karnataka, India, by adopting Oceansat-2 scatterometer (OSCAT) data and GIS approach. Prior to utilization, the OSCAT satellite data is validated by real-time meteorological station data, collected from Indian National Centre for

Ocean Information Services (INCOIS) for India. The estimation of wind power generation calculated for RE power 5 MW wind turbine (based on class of water-depth) for the considered region is 9.091 GW for monopole foundation (0–35 m), 11.709 GW in jacket-type foundation (35–50 m), 23.689 GW in advanced jacket-type foundation (50–100 m) and 117.681 GW for floating foundations (100–1,000 m).

Different researchers evaluated the offshore wind power potential using different methodologies for different countries are summarized and presented in Table 4. It can be observed that majority of researchers used log law for extrapolating wind speed to required height.

3.2 Significant Parameters Involved in Resource Assessment

The most concerned parameters in resource assessment are WS and wind direction. The values of wind power density and power potential are calculated for specific location or region at particular hub height with the help of WS data for given time period. Wind power potential (P) is the quantitative amount of power that can be generated by means of wind energy. Wind power density (WPD) is the wind power potential available per unit area of the plane at right angles to the wind direction.

$$P = \frac{1}{2}\rho A U^3 \tag{1}$$

$$WPD = \frac{P}{A} = \frac{1}{2}\rho U^3 \tag{2}$$

where, U is wind speed (m/s) and A is the area of the plane (m^2).

Further, the characteristics of atmospheric boundary layer are integral part of resource assessment process due to its impact on the intensity of WS. The atmospheric boundary layer, which is also termed as planetary boundary layer, is the lowest part of the atmosphere in contact with earth surface. The physical characteristics of air in atmospheric boundary layer like relative humidity, temperature, velocity and density vary quickly with space and time [3].

Variation in WS in vertical direction is defined by wind shear, as a function of height from the surface [11]. There are two methods of wind shear calculation: (1) power law and (2) log law. Power law is a popular method for presenting the relation between WS and height. The expression for the WSs v_1 and v_2 at height h_1 and h_2, respectively, can be presented as follows:

$$\frac{v_2}{v_1} = \left(\frac{h_2}{h_1}\right)^{\gamma} \tag{3}$$

Table 4 Summary of studies reported for evaluation of offshore wind power potential

Source	Scope	Model	Wind data with spatial resolution	Vertical profile	Wind turbine model (capacity in kW)	CF (%)	Exclusionary factor	Available potential (GW)	AEP (TWh)
[23]	Brazil	GIS	QuikSCAT (0.5°)	Log law	GE 3.6 s (3,600)	52	10 to 46%	102	-
					Repower 5 M (5,000)	44			
[47]	California	Mesoscale model version 5 (MM5) weather model, GIS		Log law	RE power 5 M (5,000)	Variable	33%	75.5	661
[51]	China EEZ	GIS	QuikSCAT (1 km)	Log law	RE power 5 M (5,000)	37.5	Shipping lanes, bird path, submarine cables, coast buffer	-	1,566
[20]	Ionia Sea		QuikSCAT (0.25°) and buoy wind data	Log law	Vestas V112 (3,000)	35–52	-	-	20
					Siemens SWT–3.6 –107 (3,600)				
					General Electric GE 3.6 sl (3,600)				
					Multibrid (5,000)				
					RE power 5 M (5,000)				

(continued)

Table 4 (continued)

Source	Scope	Model	Wind data with spatial resolution	Vertical profile	Wind turbine model (capacity in kW)	CF (%)	Exclusionary factor	Available potential (GW)	AEP (TWh)
[52]	Inner Mongolia, China		Surface observational data	Power law	CONE−450 (450)	45	-	-	-
					NM600/43 (600)	-			
					YT/850 (850)	64			
					NODEX−N70/ 1,500 (1,500)	-			
					GAMMA−60 (1,500)	-			
					SL 3,000/90 (3,000)	-			
[48]	Coast of Kanto, Japan	Mesoscale meteorological model RAMS, GIS	ECMWF (2.5°)		MWT – 92/2.4 (2,400)	>25, 30, 35	Excluding areas with fishing rights, natural park regulations and harbour operations and 10 km offset distance from the coastline	-	287
[49]	Gulf of Thailand	Mesoscale compressible community (MC2) model, GIS	NCEP/NCAR R1 global reanalysis data (2.5°)	Log law	-	25	-	7	15

- not found

where γ is wind shear exponent which depend on the type of surface. For, open shear regions, wind shear is taken as 0.08 [11].

Log law is an optional substitute to power law for the evaluation of wind-speed variation with height, which is based on the logarithmic boundary layer profile and uses surface roughness length (z_O) as an important parameter. The expression for log law can be given as follows:

$$\frac{v_2}{v_1} = \frac{\ln\left(h_2/z_o\right)}{\ln\left(h_1/z_o\right)} \tag{4}$$

The value of surface roughness length depends on the type of surface. The smoother the surface, the lower the roughness length. The value of roughness length for water areas (offshore regions) is taken in the range of 0.1–0.3 mm, which represents roughness class 0 [53].

The air moving near the surface experiences unexpected variations in wind velocity and direction due to turbulence created by obstacles and surface roughness. Presence of turbulence reduces the wind power potential and also generates fatigue forces on wind turbine components. The turbulence intensity gets influenced by shape and size of obstacles. The turbulence zone might be spread over up to 2 times the height of obstruction in upwind direction and about 10–20 times in downwind direction. The impact of turbulence in vertical direction reached around 2–3 times the height of the obstacle. Mathematically the intensity (*TI*) of the turbulence can be represented in terms of mean WS ($\overline{U}$) and standard deviation (σ) as follows:

$$TI = \frac{\sigma}{\overline{U}} \tag{5}$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}\left(U_i - \overline{U}\right)^2}{N-1}} \tag{6}$$

where N is the number of observation of WS.

3.3 Resource Estimation Models

According to a review presented by Landberg et al. [54], various wind resource estimation methods are folklore, only measurements, measure-correlate-predict (MCP), global data sets, wind atlas approach, models based on in situ data, mesoscale models and combined mesoscale-microscale models. Further, depending on the different sources of data, various resource estimation models are classified in three categories, namely, mesoscale models, computational fluid dynamics (CFD) models and microscale models [11]. The objective of resource estimation models is to take the wind data available from different sources for locations and generated the wind data for desired location. The generated data consist of WS at multiple heights (or WS at particular height with wind shear) and wind directions.

Mesoscale models provide weather projections with spatial resolution of 20–20,000 km and temporal resolution from hours to days. Mesoscale takes reanalysis data, altitude data and surface roughness data to provide model's external forcing by means of boundary conditions. Mesoscale Compressible Community (MC2) model, Karlsruhe Atmospheric Mesoscale Model (KAMM) and Mesoscale Model5 (MM5) are the widely utilized mesoscale models. CFD models consist of turbulence models having Reynolds-averaged Navier-Stokes (RANS) equations with and used for finer spatial resolution applications [11]. CFD models are applied while modelling the airflow across a complex terrain and thermal effects. CFD models take digital terrain models, roughness maps and wind data as the inputs. The products of the model are steady-state time-independent results of WSs and directional distributions.

Microscale models resolve small-scale contours and roughness geographies. The models are applied to the scales in the order of 100 km and are utilized for large wind farm regions spread over hundreds of kilometres. Wind Atlas Analysis and Application Program (WAsP) is the most commonly used microscale model and was initiated in the late 1980s [55]. Few other famous wind assessment software tools like windPRO and WindFarmer employ WAsP engine [11]. Mesoscale models can be combined with the microscale models as per requirement [54]. KAMM and WAsP is the most widely used combination of mesoscale and microscale models.

3.4 *Wind Energy Estimation Models*

Wind energy estimation models are the methods to be used for the resource assessment by means of collected data. The data might be obtained from any single or multiple sources as elaborated in Sect. 3.1. There are multiple methods available for the estimation of wind energy as listed below and elaborated in the following subsections:

- Wind turbine-based resource estimation
- Direct or non-statistical method
- Statistical method
- Extreme wind-based estimation

3.4.1 Wind Turbine-Based Energy Estimation

This approach is implemented to assess the productivity of wind turbine in terms of maximum power potential and power generated through wind turbine by means of time series wind data (averaged WS values). Now, the power available in the wind with velocity, U, is given by Eq. (1) [3]. However, the actual amount of power generation (P_w) relies upon power curve of given wind turbine. In stall-regulation wind turbine, the power generation reduces on further increment in WS from the rated value. However, in pitch-regulation-based wind turbine, the power generation remains the same as the rated power between rated and cut-out WSs. The power curves are generated using the test data of wind turbines as per the guidelines of International Electrotechnical Commission (IEC), Geneva [56].

3.4.2 Direct or Non-statistical Energy Estimation

While having the large number of data values, the averaging approach is utilized. For N number of WS observations U_i, the data is averaged over the time interval of Δt. The expressions for the parameters evaluated in this resource estimation approach are as given below.

The mean WS, ($\overline{U}$), over long-term WS data is given as Eq. (7):

$$\overline{U} = \frac{1}{N}\sum_{i=1}^{N} U_i \tag{7}$$

The standard deviation of WS (m/s) is given as Eq. (8):

$$\sigma = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(U_i - \overline{U}\right)^2} \tag{8}$$

The mean WPD (W/m^2) is Eq. (9):

$$\frac{\overline{P}}{A} = \frac{1}{2}\rho\frac{1}{N}\sum_{i=1}^{N} U_i^3 \tag{9}$$

Average power generated by wind turbine (W)

$$\overline{P}_w = \sum_{i=1}^{N} P_w(U_i) \tag{10}$$

where $P_w(U_i)$ is power computed from power curve as elaborated in Sect. 3.4.1.

The energy generation E_w (in J or Wh)

$$E_w = \sum_{i=1}^{N} P_w(U_i)(\Delta t) \tag{11}$$

3.4.3 Statistical Method for Energy Estimation

Statistical analysis is utilized to estimate the amount of energy that can be generated at particular location if the wind turbine is installed, with the help of WS data at desired height. The statistical approach consists of probability distribution of WSs. Probability distribution (PD) presents the likelihood of the occurrence of particular WS. It is described using probability density function (PDF) and cumulative distribution function (CDF). PDF represents the probability of the existence of a particular WS ($\rho(U)$) during the observed time period at particular location and height, whereas the CDF presents the probability of observing WS value less or equal to a particular value ($F(U)$). Rayleigh and Weibull distributions are the most widely employed probability distributions. PD is further utilized for the calculation of estimated power generation as discussed in Sect. 3.4.4.

Rayleigh distribution is the easiest method of PD as it requires only single input variable, which is average WS. Expressions for PDF and CDF are given as Eq. (12) and (13):

$$p(U) = \frac{\pi}{2}\left(\frac{U}{\overline{U}^2}\right) \exp\left[-\frac{\pi}{4}\left(\frac{U}{\overline{U}^2}\right)^2\right] \tag{12}$$

$$F(U) = 1 - \exp\left[-\frac{\pi}{4}\left(\frac{U}{\overline{U}^2}\right)^2\right] \tag{13}$$

Weibull distribution uses a couple of parameters: shape and scale parameter, for the distribution of the available data. Due to the utilization of two input parameters, Weibull distribution presents the wind regime better than the Rayleigh distribution which is based on only one parameter (mean WS). Expressions for PDF and CDF are given as Eq. (14) and (15), respectively:

$$p(U) = \left(\frac{k}{A}\right)\left(\frac{U}{A}\right)^{k-1} \exp\left[\left(\frac{U}{A}\right)^k\right] \tag{14}$$

$$F(U) = 1 - \exp\left[-\left(\frac{U}{A}\right)^k\right] \tag{15}$$

where k is shape parameter and A is scale parameter (in m/s).

3.4.4 Wind Turbine Power Estimation

The average power generated through wind turbine can be computed using Eq. (16).

$$\overline{P}_w = \int_0^\infty P_w(U)p(U)dU \tag{16}$$

where $P_w(U)$ is power curve of selected wind turbine. Further, the average wind turbine power can be used to derive the performance of the turbine in terms of capacity factor (CF). CF is described as the ratio of actual power generated through wind turbine for given WS to the power generated by wind turbine at rated WS (rated power, P_R), over a given time duration, Eq. (17).

$$CF = \frac{\overline{P}_w}{P_R} \tag{17}$$

The expression of wind turbine power curve $P_w(U)$, in terms of WS, U, is given as Eq. (18):

$$P_w(U) = \frac{1}{2}\rho A C_p \eta U^3 \tag{18}$$

where η is the drive efficiency of wind turbine (given as Eq. (19)), A is the cross-sectional area of turbine rotor, ρ is the air density and C_p is rotor power coefficient (given as Eq. (20)):

$$\eta = \frac{\text{GeneratorPower}}{\text{RotorPower}} \tag{19}$$

$$C_P = \frac{\text{RotorPower}}{\text{PowerinWind}} = \frac{P_{\text{rotor}}}{\frac{1}{2}\rho A U^3} \tag{20}$$

3.4.5 Extreme Wind Speeds

Generally, the wind energy estimation models are based on WS values. However, extreme wind is also an important parameter to be considered while designing the wind turbine, since the turbine is to be subjected to those extreme wind events. Extreme wind stands for the highest value of WS occurring over longer time period. Extreme winds are generally expressed as reoccurrence (or repetition) period. The extreme wind is highest WS averaged for given time span, with yearly probability of occurrence of 1/N years.

3.5 Key Issues in Resource Assessment

Major issue in wind resource assessment across the world is the lack of consistent and dependable data [57]. As discussed earlier, there are limited source of offshore wind data. Moreover, the experimental methods of data collection face environmental problems and hence cannot record long-term continuous data. Therefore, the long-term wind resource assessment has to be conducted based on reanalysis data or model data, which are less preferable than the measured data and has to be validated [15].

4 Summary

Offshore wind harvesting for energy generation is picking up interests in many parts of the world. The concept of offshore wind energy conversion system was introduced, and significant parameters involved in modelling such a system were outlined. Primary focus was to outline different methods of wind resource assessment to assess and analyse the wind data in terms of speed, orientation and other characteristics. While focusing on the offshore wind energy resources, the differences from onshore resources like environmental conditions, project infrastructure, project design, power evacuation facilities and safety measures have to be considered. Also, the wind resource data used for the resource assessment can be obtained either from any single source or through multiple sources. Different types of data are available from various sources for onshore and offshore regions. Multiple methods involved in collection and analysis of wind speed data have been categorized as wind turbine-based resource estimation, direct or non-statistical method, statistical method and extreme wind-based estimation method. The global amount of wind resource availability has been estimated to be of 10^{15} kWh/year, which is significantly higher than the global electricity consumption of 55×10^{12} kWh/year. Hence, there is a long way to go in terms of wind power deployment.

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Hydropower: A Renewable Energy Resource for Sustainability in Terms of Climate Change and Environmental Protection

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Contents

Abstract Hydropower refers to energy conversion from flowing water into electricity. Due to water recycling by the Sun, hydropower is widely accepted as a form of renewable energy. A sustainable project is possible only when there is appropriate planning, efficient system design to tackle societal and environmental issues, and continuous adaptation to changing conditions. It is important to update knowledge

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regarding the ecological and societal issues involved in setting up hydropower plants. All stakeholders' interests and future courses of action depend on these aspects. In this chapter, information from sources such as books, journals and other publications is reviewed to provide a detailed account of extensive water management and the capacity for electrical generation from water, technological changes that have developed hydropower into a major renewable energy source, the ways in which how hydropower contributes to a comprehensive energy scenario and associated issues such as the problems of global climate change and environmental damage.

Keywords Climate change, Environmental protection, Environmental issues, Hydropower, Renewable energy, Social issues, Sustainability

1 Introduction: Hydropower as a Vital Energy Source

As of late, hydropower has become an issue in the world, particularly in political gatherings, broad communications, the scholarly community, and social and natural developments. Numerous individuals from different divisions of society have brought up issues of whether hydropower is a benign and sustainable form of energy given that it does have some adverse effects on the environment. These inquiries centre on questionable aspects of hydropower's sustainability and value. Many see the advantages of hydropower dam development and support further development; at the same time, others declare that hydropower dams are unsafe for society and for the environment and that governments should therefore stop developing them.

Hydropower has always been a vital source of energy and is a natural result of solar-powered radiation [1]. Solar light–based radiation is expended at the land or sea surface, warming the surface and evaporating water where it is present. A gigantic amount of energy – close to half of all solar radiation arriving at the Earth's surface – is used in natural evaporation of water and drives the hydrological cycle [2, 3]. The underneath potential of hydropower is enormous as nearly two third of earth is water. But a limited potential is only explored till now. Some water soaks into the ground and forms groundwater, while other water forms surface run-off and flows into water bodies. Global and local wind systems, generated and maintained by differences in atmospheric pressure arising from planetary rotation and spatial variations in absorption of solar energy, move air and its water vapour content over the surface of the Earth up to an altitude of several kilometres.

Finally, the water vapour forms clouds and falls as precipitation – about 78% on the oceans and 22% on the land [2, 3] – transporting water from water bodies to the land surface of the Earth and also resulting in a huge flow of water back to the oceans via streams and groundwater overflow. It is the flow of water in streams and rivers that produces hydropower – or, more accurately, it is the inevitable downward movement of water from the land to the ocean, driven by gravity.

2 Hydroelectricity Generation: A Technological, Environmental and Climate Change Perspective

According to a 2011 report from the International Energy Agency (IEA) [3], hydropower accounts for 16% of all global electricity generation sources, as depicted in Fig. 1.

Generally, hydropower processes are part of a limited framework. Hydropower is the rate at which hydraulic energy is generated from a specific process of downward flow of water and involves its speed or placement, or both, by massive turbines. Hydropower can be utilized to control hardware or to create electricity, or both, at the same time. The mechanical application is mostly valid for small-scale hydropower plants, where the power that is produced is utilized to control small-scale mechanical equipment and machines for squeezing, processing, granulating and sawing applications. In certain instances, the yield shaft from a small-scale hydropower turbine is extended into two headings to provide both mechanical power and electricity generation.

Massive hydropower plants are typically utilized for power generation. For generating hydropower, a turbine yield shaft is attached to a generator. The electricity that is generated is transmitted via systems consisting of different parts such as switchyards, transformers and transmission lines. A well-planned and well-run hydropower plant is considered one of the least expensive ways of generating electricity [4], maybe because the fuel (falling water) can be obtained without direct expenses related to purchasing fuel. The cost of power generation by massive hydroelectric power ventures is US$0.02–0.19/kWh [5]. The generally low power

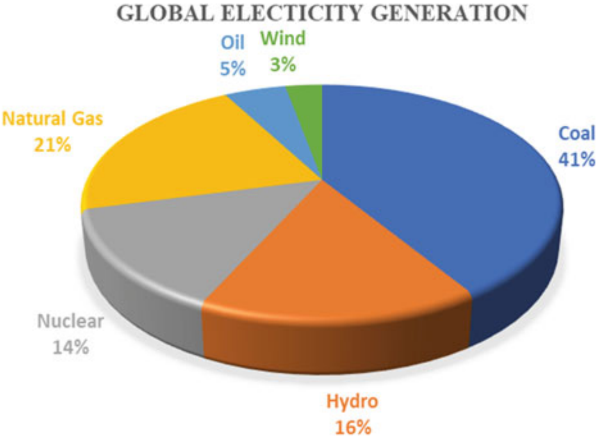


Fig. 1 Global electricity production scenario (adapted from [3])

generation cost might be one reason why hydroelectricity is considered a base burden for the majority of power service organizations. Hydroelectric power plants can react to demand fluctuations a lot more quickly than other power generation frameworks – for example, thermal power plants [6, 7]. This makes hydropower a flexible energy conversion technology and clarifies why hydroelectric power plants are utilized for peak power generation in various instances. Further, hydroelectric power generation is a highly efficient energy conversion process since it changes mechanical work directly into electrical energy, both of which are high forms of energy. The energy transformation framework efficiency of a well-run hydroelectric power plant can be around 85%, while the framework efficiencies for thermal power plants are under half that [8].

3 Classification of Hydropower Projects

Each hydropower venture is unique because it is site specific, so the classification of these plants is mostly based on size and the source of the power-producing water, including whether it involves use of large reservoirs. Different countries and organizations use different criteria to describe the scale of hydropower schemes, as shown in Table 1.

Numerous countries, particularly in Europe, consider 10 MW the cut-off point for small-scale hydropower and consider larger hydropower frameworks large-scale ventures. The use of installed electrical capacity as a classification criterion is significant because it is utilized in regulatory and legal documentation (for example, rural electrification acts and power supply contract agreements). These differences in the classification of hydropower schemes result in differences in the sizes of such schemes considered low-significance frameworks for the purposes of the Clean Development Mechanism (CDM) [10].

Table 1 Small-scale hydropower as defined by installed capacity according to various countries and the International Energy Agency

Country/organization	Installed capacity (MW)
Belgium, Greece, Ireland, Netherlands, Portugal, Spain	≤5–10
Brazil	≤25–30
Canada	≤45–50
China	≤45–50
France	≤5–10
India	≤20–30
Norway	≤5–10
UK	≤15–25
USA	≤25–30
International Energy Agency	≤15–25

Adapted with permission from [4, 9]

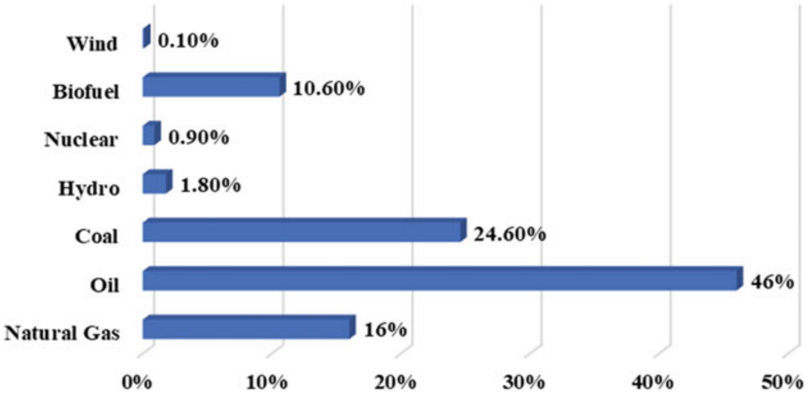
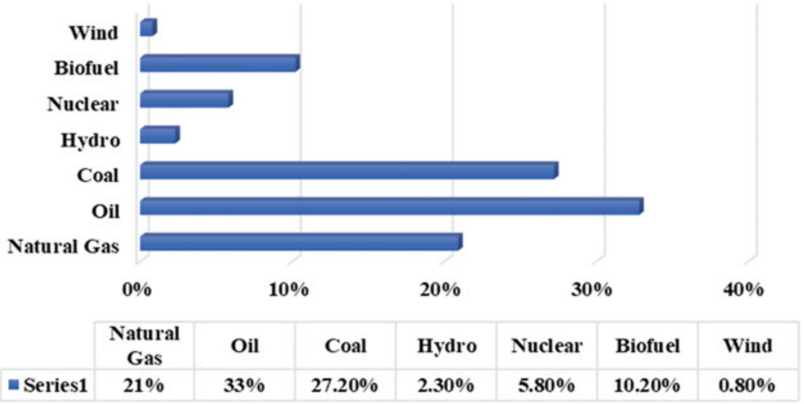


Fig. 2 Global primary energy supply mix in 1973 (adapted from [3])



	Natural Gas	Oil	Coal	Hydro	Nuclear	Biofuel	Wind
■ Series1	21%	33%	27.20%	2.30%	5.80%	10.20%	0.80%

Fig. 3 Global primary energy supply mix in 2009–10 (adapted from [3, 9])

Classification of the scale of hydropower plants on the basis of the head refers to the relative levels of the inlet and outlet, which determine the water pressure that propels the turbines to rotate and generate electricity.

According to the IEA [3], hydropower accounted for 1.8% of the world’s primary energy mix (representing the sources of all energy consumption in industry) in 1973, increasing to 2.3% in 2009–10, as shown in Figs. 2 and 3.

3.1 Run-of-River Hydropower

Run-of-river (RoR) hydropower produces hydroelectricity from river flow without use of a dam; rather, it depends on precipitation, groundwater flow and run-off, which are very dynamic and can change frequently. Thus, RoR hydropower is dependent on a variable flow of water current and generally includes some short-term water storage to help cater for additional power requirements, especially in summer. Because of natural temporal variations in water flow, these systems may be less active than other types of system that depend on strength of water flow or the framework of flow through the outlet. RoR systems are therefore best suited to rivers with little flow variation or large reservoirs such as lakes [11]. Because they do not require a lot of construction, RoR hydropower schemes can have both financial and environmental advantages over other hydroelectricity-producing frameworks with the same installed capacity [12, 13]. RoR hydropower generation is utilized in various countries such as Malawi, where the Shire River (an outlet from Lake Malawi) is used for power generation [9]. Also, nearly 65% of independent electricity production in British Columbia, Canada, comes from RoR hydropower, while other sources provide the remaining 35% [12]. Because of their financial advantages, RoR hydropower plants are often utilized in small-scale hydropower frameworks [9] and may involve a combination of two redirection frameworks to streamline energy generation at the site. Mostly, a stream of water flow and an open reservoir are used, with a moderately short penstock [13].

3.2 Storage Hydropower

In a storage hydropower system, water is stored in a reservoir behind a dam to produce hydropower. The reservoir determines the flow; thus, storage hydropower plants have more power dependability than RoR hydropower plants. Storage hydropower ventures are commonly utilized when there are large variations in water flow in the middle reaches of a waterway system [14]. The design of these hydropower plants to optimize yield and production efficiency depends greatly on the local topography [14]. Storage hydropower systems offer far greater energy benefits than ordinary RoR designs. One of the crucial points of interest in storage hydropower is the capacity for potential energy storage in the water behind the dam. In addition, storage hydropower systems can manage flow in the waterway downstream of the dam and thus improve the reliability of energy generation at downstream sites. In this way, various RoR power plants can be introduced downstream in a cascade structure, utilizing the same water to create new hydropower with a consistent yield.

3.3 Pumped Storage Hydropower

Pumped storage hydropower plants are not energy sources per se; rather, they are primarily pressure-driven energy storage devices [9]. In terms of both design and financial aspects, pumped storage hydropower has been described as the only large type of grid-based electrical energy storage currently available to power utilities

[15, 16]. In this type of system, water is pumped under high pressure from a lower reservoir to a higher reservoir at times when there is a high flow of water but low power demand. This hydropower is stored for later use when high power generation is needed. Some types of turbine can double up as pumps for producing hydropower. In an ideal scenario, any electrical power plant can utilize pumped storage capacity innovation. Although the energy loss caused during the pumping procedure makes the pumped storage a net energy consumer, this type of framework can supply massive energy storage with flexibility at a low working cost [14]. For a hydropower framework that includes pumped storage, the main concern is the high investment cost in comparison with other hydropower designs with the same installed capacity. Only certain types of site are suitable for installation of pumped storage hydropower systems. Mountainous locations are best for this type of system to utilize the geography for potential energy storage. The amount of separation between the reservoirs is an important factor in the pumped storage design because greater distances entail greater investment costs and greater energy losses during pumping, making the system less economically viable and less efficient to operate. In addition to its suitability for fulfilling peak power demands, pumped storage hydropower systems allow efficient management of power generation because they produce an almost steady yield of power.

4 Huge Potential of Hydropower as a Renewable Energy Source

Hydropower is based on the renewable energy source of the hydrological cycle, which is powered by solar energy, so it obviously acts as a natural source of energy [17]. Because the hydrological cycle is perpetual, it is considered a sustainable energy source, according to the standard definition. Hydropower frameworks are generally installed in-stream in high-current waterways, water system channels and water supply frameworks. Unconventional hydropower frameworks are also known as zero-head hydropower systems or hydrokinetic power systems.

Africa, which has the greatest need for sustainable sources of electricity production for development – has huge potential for further implementation of hydropower. However, to date, the contribution of hydropower to its energy supply has been limited by lack of funding and facilities [18], and such constraints also limit the application of hydropower elsewhere in the world. In Oceania and South America, the average regional hydropower capacity factor varies within a range of 30–50%.

A hydropower plant may not have a 100% capacity factor, irrespective of water availability, because of factors such as (1) closure of the plant for routine maintenance, (2) reduced power demand in rainy seasons and (3) reduced electricity prices in other scenarios. The global total installed hydropower capacity in 2009 was estimated to be 926 GW by the World Energy Council [18] and 956 GW by the IEA [19]. A more conservative figure of 860 GW was proposed by the International

Table 2 Top ten countries classified by installed hydropower capacity and by hydropower share of total energy mix in 2010

Country	Installed capacity (MW)	Country	Hydropower share of total energy mix (%)
China	210	Norway	99
Brazil	84	Brazil	84
USA	79	Venezuela	74
Canada	74	Canada	59
Russia	50	Sweden	49
India	38	Russia	19
Norway	30	India	18
Japan	28	China	16
France	21	Italy	14
Italy	20	France	8
Rest of the world	302	Rest of the world	14
Whole world	936	Whole world	16

Adapted with permission from [9, 21]

Hydropower Association [20] as a reasonable reflection of the true situation. The estimated global installed capacity excluded pumped storage facilities, which were variously estimated to account for around 120 GW or 150 GW [20]. The World Energy Commission estimated that in 2009, the overall total hydropower power generation was around 3550 TWh/year [18]. If the yearly generation is compared with the global technical generation potential, it can be seen that the latter value is more than four times the former one, showing good prospects for hydropower development. Lists of the top ten countries classified by installed hydropower capacity and by hydropower share of the total energy mix are provided in Table 2.

From Table 2, it can be seen that some developed and emerging nations (e.g. Brazil and Norway) depend greatly on hydropower for their power supply. According to the Intergovernmental Panel on Climate Change (IPCC), the fundamental reasons for this are the availability of abundant water bodies and high energy consumption [17].

According to data from a 2011 IEA report [3], by 2010, across all continents, Asia had the greatest hydropower production and installation capacity in the world, whereas Australia and Africa had the least, as shown in Fig. 4.

5 Conventional and Futuristic Technologies

To understand the potential and contribution of hydropower, an outline of important techniques and factors influencing hydropower generation is required and thus is briefly included here. Hydraulic turbines are an essential requirement for generating variable electrical energy; hence, a lot of work to improve the design and efficacy of

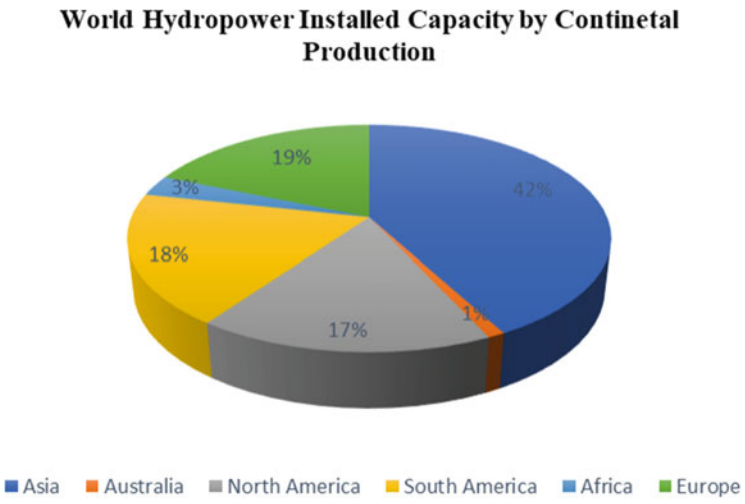


Fig. 4 Installed hydropower capacity on different continents in 2010 (adapted from [3, 9])

modern hydraulic turbines is ongoing [1, 22, 23]. During operation in off-design conditions, a moderate- or high-level residual swirl takes place in the draft tube mainly because of a mismatch between the swirl evolution through the wicket gates and the extracted angular momentum at the turbine runner [24], subsequently causing an abruption that decreases the efficacy [24–26] and massive fluctuations of inside pressures [27–32]. Consequently, an unsteadiness phenomenon occurs in hydraulic turbines forced to operate far below their best efficacy point (BEP). The pressure fluctuation leads to vibrations that damage the mechanical components [33–36], failure of the runner blade [37, 38] and thus power swinging [23, 39, 40].

Turbine operation is hindered by self-induced instabilities during off-design operational regimes and various transient conditions such as start-up, load rejection, emergency shutdown and runaway [41–48]. Following such adversities, both the structural integrity and the lifetime of a hydraulic turbine become diminished as consequences of fatigue damage [45, 48–51]. A number of techniques have therefore been examined to mitigate these effects and can be distinguished into two types: (1) active control techniques and (2) passive control techniques, mainly depending on the pattern of energy injection into the main flow [52]. The basic difference between the two types of technique is that passive control does not require auxiliary power and a control loop, whereas active control requires an external energy source (commonly, either air or water is injected). Various developed passive and active control techniques are listed in Table 3.

Besides the aforementioned techniques, recently a new control technique – magneto-rheological control – has been introduced [44, 47], in which a magneto-rheological brake (MRB) is used to slow down the speed of the runner blade to control the swirling flow configuration and associated self-induced instabilities [82, 83]. This diminishes the axial flux of the circumferential momentum with

Table 3 Types of control method and their advantages and disadvantages

Control method	Control technique	Advantages	Disadvantages	References
Stabilizer fins	Passive	Diminished draft tube surge	Local hydraulic losses, effective only in limited regimes	[53]
J-grooves	Passive	Diminished draft tube surge	Local hydraulic losses, effective only in limited regimes	[54, 55]
Runner cone extensions including free rotation concept	Passive	Diminished draft tube surge	Lateral forces, decreased kinetic energy recovery within the cone, effective only in limited regimes	[56–61]
Stator installed immediately downstream of runner	Passive	Diminished draft tube surge	Hydraulic losses, effective only in limited regimes	[62]
Adjustable diaphragm	Passive	Diminished draft tube surge in a wide range of regimes	Hydraulic losses	[1, 63]
Water injection with flow feedback	Passive	Diminished draft tube surge in a wide range of regimes, no volumetric losses, self-regulating	Not yet identified	[1, 63–65]
Air injection/admission	Active	Diminished draft tube surge in a wide range of regimes	Volumetric losses, amplification of self-excitation at a few operating points	[66, 67]
Tangential water injection at cone wall	Active	Diminished draft tube surge	Volumetric losses	[68]
Axial water injection with high/low velocity	Active	Diminished draft tube surge	Volumetric losses	[1, 69–73]
Water injection with flow feedback and additional energy	Active	Diminished draft tube surge	Not yet identified	[64, 74]
Water jet with tangential component	Active	Diminished draft tube surge	Volumetric losses	[75]
Inverse modulation of water jet	Active	Diminished draft tube surge, modulated frequency targeting a specific value	Volumetric losses	[76–78]
Two-phase air–water injection	Active	Diminished draft tube surge in a wide range of regimes	Volumetric losses	[1, 78]

(continued)

Table 3 (continued)

Control method	Control technique	Advantages	Disadvantages	References
Water injection at trailing edge of wicket gates	Active	Diminished rotor–stator interaction effects	Volumetric losses	[79–81]

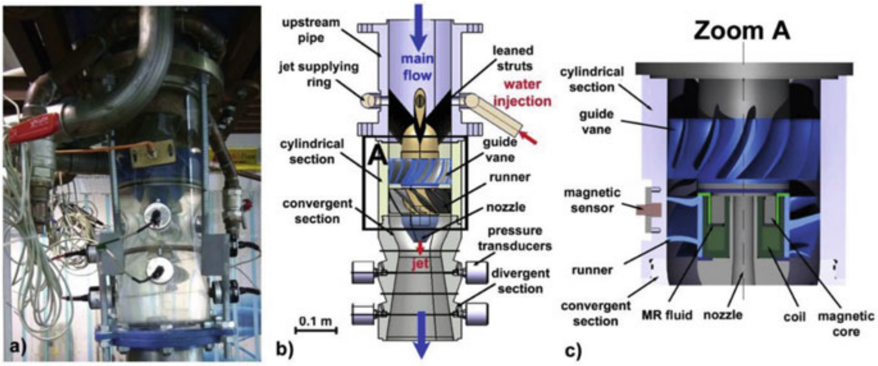


Fig. 5 Swirl generator test rig designed to investigate different control techniques (adapted from [1]). **a** Test section installed on the test rig. **b** Axial water injection. **c** Magneto-rheological control

controlled speed of the runner. Further, to optimize the swirling flow ingestion by the draft tube in order to maintain the flow with minimum loss of draft and maximum recovery of pressure, in the presence of a wide range of discharge values, the Francis turbine with tandem runners has been introduced [24]. This differs from others such as the counter-rotating microturbine [84], pump turbine [85] and bulb turbine [86]. Different control techniques, including axial water injection and the magneto-rheological control technique, are shown in Fig. 5.

In fact, most hydropower plants are old and were designed decades ago to work under very different conditions from the requirements of the present scenario. Therefore, dramatic improvements in flexibility with storage capacity and advanced system services to support integration of variable renewable energy are the key challenges for most hydropower plants, albeit that hydrodynamic phenomena limit their flexibility. Thus, hydroelectric infrastructure development is becoming more compliant with changing and dynamic context conditions – such as the market, climate and environmental safeguards – through new designs and operational paradigms.

As extension or further upscaling of the operational range/capacity may entail additional stresses on electromechanical equipment, digitization of hydropower production and storage systems – including turbines, generators and controls – avoids these stresses by accurately and safely mimicking the dynamic behaviour of the equipment [87]. Upgrades incorporating next-generation digital technologies –

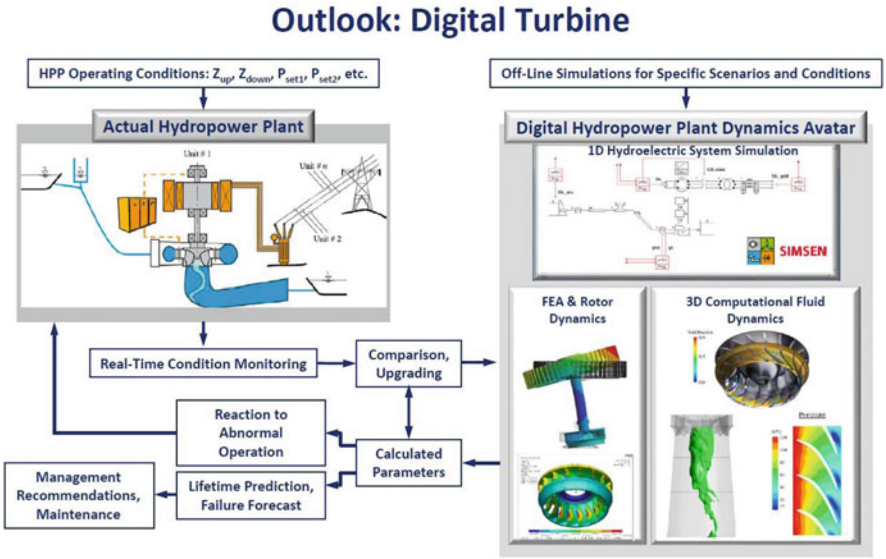


Fig. 6 Information flow and exchange with use of a digital avatar of hydropower plant dynamics (adapted from [1])

including tools for lifetime prediction, modelling, data analysis, predictive maintenance and optimal condition monitoring – can efficiently contribute to enhancing robustness and reliability [88–90]. It is estimated that increased hydropower technology performance due to digitalization will boost new features with more flexibility for hydropower plants and enhance the role of hydropower in the energy mix. Kougias et al. [1] have presented an overview of a digital turbine for information flow and exchange with use of a digital avatar for a hydropower plant, as depicted in Fig. 6.

6 Ecological and Societal Perspectives on Hydropower

The social and ecological implications of hydropower are very significant, as they have a large scope. Positive effects need to be identified and established in such a manner that both the environment and society will benefit. The size of the plant, time and site qualities are very important for hydropower [91, 92]. The ecological and societal implications are very important as they are the most vital factors for sustainability of hydropower plants. This has a moderating effect where expenditure is restricted. Development of hydropower plants includes designing them to have positive effects on the ecological balance and society. Land is cleared and human settlements may be uprooted to prepare for such developments. Flooding of land to create dams may decimate biological systems, demolish foundations and uproot established settlements, besides causing local business loss.

Furthermore, financial and social difficulties caused by the creation of a 'blast' town in the local area are common effects of a massive hydropower venture. During the activity period of the hydropower venture, some waterway areas experience hydrological shifts. Downstream water flow is very helpful in hydropower generation. It inevitably affects social and environmental activities, with financial implications. It is mandatory to safeguard aquatic life. As a consequence, engineers involved in the hydropower venture are obliged to devise a moderation programme and to evaluate and report on the natural and social consequences of the venture. Resettlement of uprooted ecosystem inhabitants is one of the most difficult activities involved in overseeing hydropower plant projects [93]. Massive hydropower ventures become very sensitive issues when the effects range from physical safety of dams to various ecological and social implications [93].

Environmental and social appraisals are required for massive hydropower ventures and can be a very delicate issue. In terms of ecological and social effects, small-scale hydropower frameworks look appealing, mainly on the basis of the assumption that 'little is lovely'. A small-scale venture has less natural and social effects, yet it creates less power. Thus, it may be imperative to find solutions to the ecological effects of a hydropower framework. Right now, the environmental benefits are looked at impartially, per unit of power produced. In any case, where small-scale hydropower ventures do not require resettlement, they are considered socially more worthy than massive hydropower ventures.

7 Climate Effects of Hydropower

As far as research developments are concerned, hydropower – as a sustainable power source – is one of the advancements that create power while causing the least effects on the global environment. However, massive energy storage systems do result in emission of greenhouse gases (GHGs) such as methane and carbon dioxide because of covered fundamental issue disintegration without enough oxygen [94]. At present, it is argued that hydropower reservoir emissions of both methane and carbon dioxide should not be considered greenhouse effects.

According to the fourth assessment report from the IPCC, methane is much more harmful than carbon dioxide. However, emissions of both GHGs from hydropower plants have effects on the weather, and it is estimated that these effects persist for a century [95]. In a hydropower plant set-up, GHGs are emitted as a result of construction of storage reservoirs [96, 97] and also as water flows through the turbine runner during its action [98, 99]. Through contact with the turbines, the gases encounter low-pressure and high-temperature conditions, and, with the vigorous activity, fast degassing and emissions into the environment occur [99]. Thus, the water drawn from the reservoir to power the turbine must not be obtained from the deeper parts of the reservoir or lower parts of the stock. Despite GHG emissions at the turbines, some significant proportions of carbon dioxide and methane may remain broken down in the water and may be degassed further through the flow beyond the turbine. GHGs formed in storage reservoirs have been detected in areas far downstream of the reservoirs [100]. Pools in tropical conditions have been found to have significantly higher levels of GHG emissions than those in milder climate zones [101]. One potential reason for this is the higher water temperatures in tropical settings, which increase the pace of decomposition of organic matter [97].

In contrast to other power generation technologies, however, GHG emissions from hydropower plants are relatively low. Here, the existence cycles of GHG emission factors for a hydropower plant are around 15–25 g CO_2/kWhel. These values are far lower than those for petroleum product power, which usually range between 600 and 1200 g CO_2/kWhel [102]. Studies on life cycle GHG emissions from plant developments have reported widely varying values (ranging from 0.2 to 152 g CO_2 reciprocals/kWhel), conceivably because of differences in the assembly procedure, type and nature of the reservoir (for hydropower) [103]. Even when the most extreme estimations of GHG emissions are considered, emissions from hydropower are lower than those from nonrenewable energy sources. This explains the effect of hydropower plants in moderating environmental change.

8 Effects of Ecological and Climate Changes due to Hydropower Production

Hydropower production can have impacts on the Earth; conversely, nature can have negative effects on hydropower generation. Ecological disturbance is one of the significant difficulties confronting the world right now. It has been contended that this is because of the way that each segment of an economic framework – for example, farming, power generation, mining and the travel industry – works within an entire ecological framework and hence can upset nature. A considerable portion of the extent of environmental degradation is human instigated and results from human population increases and inappropriate profit-driven activities. Environmental degradation in natural ecosystems is largely due to unsustainable agriculture, use of inorganic fertilizers and excessive clearance of forests. Amphibian weed invasion of waterways is one of the serious issues confronting hydropower generation because of the resulting ecological damage. Extensive research has shown that in the future, a few regions of the world will experience increased run-off while others will experience decreased run-off because of unnatural weather changes [104–106].

At the same time, a large portion of Europe is anticipated to have expanded hydropower generation potential, while certain regions will experience decreased potential. In Australia, reductions are commonly expected, while New Zealand is expected to have expanded generation potential. South America is anticipated to experience decreased hydropower potential. Large areas in Southern Africa and West Africa will experience decreases, while East Africa is expected to have expanded generation potential. At a worldwide level, investigations have concurred that global hydropower generation potential is anticipated to increase, yet almost no such increase in hydropower is seen (under 1%, as indicated by Hamududu and Killingtveit [105]). Thus, it can be seen from these investigations that regardless of whether individual nations and regions will encounter significant changes in run-off, environmental changes may not prompt significant changes in the worldwide hydropower power potential. Various studies on the effects of climate change on hydropower production have presented different aspects of the effects in specific countries. However, the majority of these investigations have utilized worldwide flow models, which are less dependable although it is possible to downscale their output to the national level. If global flow models are used in hydropower planning, the results should be interpreted cautiously. In such cases, it is recommended to utilize numerous models to improve the reliability of the projections and, along these lines, to lessen the level of uncertainty. For instance, the analysis by Hamududu and Killingtveit [105] was based on utilization of 12 different models and concurrence of at least six of them on the general pattern of future run-off projections (an increase, a decline or no change). These investigators could not settle on a choice about a country if fewer than six models concurred on run-off pattern projections. Extreme weather events such as dry seasons, floods and hailstorms have differing effects on hydropower generation by affecting the amount and quality of water available to hydropower plants. Increases in the frequency and magnitude of such extreme weather events are connected to the effects of environmental change [8]. These events limit hydropower generation as well as increasing the operational expenses of the power framework. Adverse effects on opportunities for hydropower generation are already being felt in several nations such as Malawi, India, Costa Rica and Sri Lanka.

Natural dangers – for example, sedimentation and flooding – will probably increase because of changes in local hydrology caused by extreme weather events [107], and, with local environments being degraded, the capacity to adapt to the effects of environmental change is debilitated. The impact of such extreme weather events on hydropower generation can be severe, making hydropower frameworks in the affected areas genuinely defenceless. One adjustment measure involves utilization of multiple small-scale production units rather than one enormous production complex. Other adjustment measures include utilization of advanced turbine technology that can work in conditions of variable flow and poor water quality.

9 Conclusions

The worldwide energy supply relies on petroleum products and is answerable for a large portion of global ecological damage and environmental change. The worldwide demand for energy supply is expanding, but the energy stockpile cannot. Substitution of petroleum products and coal with clean energy sources – and, in particular, sustainable power sources – is required. Nowadays, use of hydropower is very prevalent for green construction. Because of its environmental sustainability and profitability, water resource–rich countries such as the Netherlands are using it for this purpose [108–111]. It also helps to sustain large organizations in that country and has proved to be a vital cog in that country's gross domestic product. Hydropower technology can likewise be part of an essential energy framework, performing a role as an energy storage device. However, two of the downsides of hydropower ventures are the moderately high investment cost and the associated hazards. Financially, small-scale hydropower innovation is appropriate for private enterprises working as free power providers. Further, small-scale hydropower innovation has the benefit of being applicable as an independent energy framework for provincial power supply. Consequently, hydropower can contribute towards expanding social energy access and security, moderating environmental change and decreasing destructive air contamination, providing new economic opportunities and, along these lines, effectively promoting the viability of development.

This chapter has discussed the effects of hydropower creation on local environments. It can be assumed that hydropower innovation is one of the most ecologically sound and socially acceptable forms of energy generation. Although the effects of hydropower ventures depend on the size and the site, massive hydropower ventures generally have more noteworthy effects than small-scale ventures. However, hydropower ventures are exceptionally vulnerable to dangers arising from ecological damage and environmental change. Extreme weather events, which are exacerbated by environmental change, have adversely affected hydropower generation in individual nations. Thus, cautious planning and design are required to ensure the viability of hydropower ventures. Environmental change is a genuine phenomenon, and ecological damage in hydropower catchment territories is unavoidable. Some countries are expected to experience increases in hydropower potential, whereas other countries are expected to experience diminished potential; however, both scenarios are associated with potential hazards. Consequently, hydropower planning should incorporate adjustment measures. This is an issue that warrants further research. Various adaptations such as variable-flow turbine designs and steady power generation have been discussed in this chapter. Cooperative efforts are necessary to ensure clean power generation and management of environmental changes affecting hydropower ventures.

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Biomass Energy Sources and Conversion Technologies for Production of Biofuels

Majeti Narasimha Vara Prasad

Contents

Abstract Food, fuel, fodder, fertilizer, and fiber are the most essential requirements for the sustenance of life. The global population of ~7.5 billion and its explosion is asserting pressures on natural capital, especially biotic and abiotic resources. The finite sources of fossil fuel reserves, as well as the environmental impact related to

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their increased consumption, are the implication for climate change. Therefore, governments and scientists are concentrating to develop "energy bioscience" for sustainability. Biomass conversion technologies for biofuels have long been proven at an industrial scale, and the alcohol has been able to compete with conventional gasoline. Biodiesel (fatty acid methyl or ethyl esters) and bioethanol have emerged as renewable and non-conventional energy sources in many countries. Non-conventional liquid fuels such as biodiesel and liquid biofuels have numerous advantages in the era of climate change. In Europe, the main feedstock for biodiesel production is different from "energy crops" such as sunflower and rapeseed. Production of "biofuels" appears to be sound in theory, but in practice, several bottlenecks are to be resolved in an ecologically sound manner from the crux of this chapter.

Keywords Alternative energy, Bioenergy, Biofuels, Conversion technology

1 Introduction

The United Nations General Assembly has set the target to achieve access to affordable and clean energy to all under the Sustainable Development Goals (SDGs) in the year 2015 [1]. Since then the shift to alternatives has taken full pace by tapping every means of renewables and alternative energy resources. Biomass and its conversion products are analogous to fossil fuels and also serve as feedstock for various industries. Biomass being renewable, such a strategy would minimize the use of nonrenewable energy. Biomass contributes to about 14% of the world's energy needs. Prominent examples of biomass-derived energy sources are (a) forest waste, (b) agriculture waste, (c) industrial waste, (d) municipal solid waste, (e) sewage sludge, and (f) food and animal waste. In the case of developing countries, about 43% of the energy requirement is fulfilled from traditional biomass-based energy generation in comparison with a mere 1% energy contribution in the energy mix of developed countries. Planning for enhanced biomass production involves the establishment of energy harvesting with plants having good coppicing and nitrogen-fixing properties. The biomass thus produced can either be used for direct combustion or subjecting to the appropriate conversion for biofuels production.

The more noteworthy use of biomass in developing nations leads to the establishment of large-scale energy plantations. Bioproductivity is painstakingly achieved through fast-growing short rotation trees, ideal for drought conditions. Nitrogen fixers with coppicing capacity will be an additional advantage. The yearly photosynthetic stockpiling of vitality in biomass is multiple times more than that of vitality use from all sources. This gauge plainly shows the huge capability of biomass as an asset for regenerable energy sources that need to be harnessed and consumed sustainably. Major metabolic pathways of photoautotrophs produce energy-rich chemicals and a variety of biomolecules. Thus, biomass is the world's fourth biggest reservoir of energy. Biomass conversion to a wide array of industrial feedstock, fuels, in addition to its importance in safeguarding the environment is globally recognized as a topic of priority. In the recent past, several reviews have highlighted the potential of biomass and bio feedstocks and conversion to biofuels.

2 Why Energy from Biomass?

The yearly photosynthetic stockpiling of energy in biomass is multiple times more than that of fuel use from all sources. This gauge plainly outlines the gigantic capability of biomass assets, whenever outfit and oversaw economically. Bioenergy is the world's fourth abundant source of renewable energy. In large-scale energy forests, single stem and coppicing plant species are being planted all over the world depending on the agroclimatic. However, among the single stem plant species, *Eucalyptus* is the most preferred in India and elsewhere for biomass production. Large-scale energy plantation demonstration projects [EPDP] have been implemented in different agroclimatic regions of India. The governments of India and other international organizations have provided financial and technical help.

In developed countries, the major thrust has been given through the policy on innovation, research and development, and field demonstration. The agricultural surpluses are considered in terms of conversion to ethanol and other energy-rich chemical feedstock. Bioethanol, algal biofuel biodiesel, next-generation biofuels and capacity building in energy bioscience. The relevance of bioenergy can be understood by the fact that plenty of tracts of marginal lands are accessible in various agroclimatic zones. Various multiuse species of plants have been distinguished that could possibly coordinate their cultivation on a rotational cycle to fit on the economic budget to rural people and easily accessible to the remote areas (Fig. 1).

3 Energy from Biomass

3.1 Terrestrial

There is a great demand of biomass as a fuel, fodder, fertilizer, fiber, food, and other resources for small and cottage industries. Biomass can be generated through agro-sylvo-pastoral system. Fuelwood in the urban sector can be substituted but not in rural areas. Therefore, firewood production for rural people is a major task. The following are some of the multiuse plant species that can be grown in EPP: *Acacia auriculiformis* (Bengal babul), *A. catechu* (Cutuch), *A. dealbata* (silver wattle), *A. leucophloea* (Safed babul), *A. mearnsii* (black wattle), *A. melanoxylon* (Australian block wood), *A. nilotica* (Babul), *A. senegal* (gum arabic), *A. tortilis* (Israeli babul), *A. farnesiana* (Cassie flower), *Albizia procera* (white siris), *A. lebbeck* (siris), *A. odoratissima* (black siris), *Alnus nepalensis* (Indian alder),

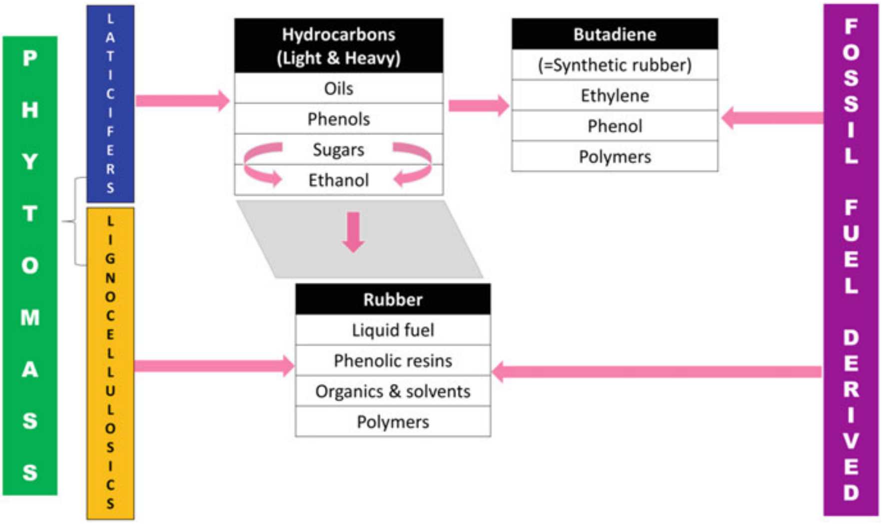


Fig. 1 Energy-rich phytochemical routes to fossil fuel analogues. Biomass energy sources can supplement fossil fuels

Butea monosperma (dark), *Cajanus cajan* (pigeon pea), *Casuarina equisetifolia* (Saru), *Dalbergia sissoo* (shisham), *Derris indica* and (kanuga, karanji, etc.). In the USA several hundred plants were screened for phytochemicals to substitute petrochemicals. In the Philippines, subabul wood is used for dendrothermal projects to generate power (3–5 MW).

3.2 Aquatic

Water energy farms pose a different kind of problems. The culture of water hyacinth and other macrophytes in public lakes would be unpopular as most of them are considered to be obnoxious weeds. The construction of artificial ponds for this purpose would be very expensive. Use of salt marshes and coastal lagoons may be cheap but could be environmentally disastrous since they represent ecotonal zones and are considered to be the highly important multiple-use ecological environment. These areas represent valuable faunal resources and serve as the breeding ground for several organisms which play a prominent role in the food chain on which several organisms depend. Once farming too has certain undesirable effects by changing temperature patterns and chemical balance of water. Large-scale farming depletes the nutrients in the vicinity, and immediate depths are a serious long-term problem, like soil depletion on land farms. Seaweeds like many other living organisms give off poisonous wastes. These could affect others both inside and immediately outside the farm area and create a specialized environment where only certain species can thrive. This subject has gained new dimensions in the recent past. Abundant aquatic biomass, e.g., water hyacinth, is harvested and digested in biogas plants for the production of low calorific value biogas [2–7].

3.3 Petrocrops

Petrocrops include plants bearing latex, seed oil, essential oil, and resin. In India, about 386 latex-producing plants have been notified belonging to the families Euphorbiaceae, Asclepiadaceae, Apocynaceae, Sapotaceae, Asteraceae, and Convolvulaceae. Catalytic cracking of solvent-extracted biocrude from different species of *Euphorbia* produced a number of hydrocarbon products that are useful in petrochemical industries. The potential latex-bearing plants are as follows: *Euphorbia lathyris*, *E. tirucalli*, *E. trigona*, *E. royleana*, *E. nivulia*, *E. catmandoo*, *E. caducifolia*, *E. neriifolia*, *E. antiquorum*, *E. antisyphilitica*, *C. gigantea*, *C. procera*, *Cryptostegia grandiflora*, *Pedilanthus tithymaloides*, *Monodenium* spp., and *Baliospermum montanum.*

3.4 Resiniferous Plants

Promising and potential resiniferous plants have a huge commercial scope viz., *Copaifera multijuga* (= Diesel tree). *Vateria indica, V. macrocarpa. Pinus roxburghii, P. kesiya* (Dhup lakadi). *Canarium bengalense, C. macrocarpus, D. alatus. D. costatus. Shorea robusta, S. assamica.* These plants and their parts possess a number of terpene compounds and their derivatives that can be used for producing a number of hydrocarbon compounds. For example, Copaiba tree (*Copaifera* sp.) growing commonly in South America produces hydrocarbon sap that can be used directly in diesel engines, hence called diesel trees. It has been estimated that 400 plants growing in an acre of land can produce 25 barrels of hydrocarbon sap/day.

3.5 Energy Crops

Crops that are rich in energy are corn, rice, cereals, sugar stick, sugar beet, cassava, and other sugar- and starch-producing crops. In the USA, corn is utilized for liquid fuel production. About 6 tons of corn yields around 2,200 L of ethanol. In Brazil, sugarcane production was multiplied to the extent that it resulted in hiking food costs resulting in the “food or fuel” crisis. Brazil, The United States of America, Philippines and Germany utilized a mixed blend of gas and ethanol. Such a mixed fuel was named gasohol or alcogas. Brazil’s national alcohol and “Proalcool” targeted running vehicles on gasohol and unadulterated alcohol. Cassava (mandioca, tapioca) is another crop rich in starch. It can be cultivated in a wide range of agroclimatic zones and does not require demanding inputs by the farmers. Around 10–12 tons of cassava can be harvested per hectare on wastelands which can serve as a substrate for 2,160 L of ethanol.

3.6 Non-agricultural Plant Resources

A number of non-agricultural plants produce non-edible oils, and some of the important are *Azadirachta indica* (neem), *Madhuca longifolia* (mahua), *Shorea robusta* (sal), *Derris indica* (kanuga), *Schleichera oleosa* (kusum), *Jatropha curcas* (physic nut), and *Simmondsia chinensis* (jojoba). Waste generated from agri-sylvi-pastoral system is difficult to handle because of its bulky and scattered in nature, low thermal efficiency and copious liberation of smoke. In order to achieve efficient bioresources, it is essential to compact biomass to manageable units with high thermal value. This process is known as briquetting. Briquettes can be used in bakeries, potteries, curing houses, breweries drying of vegetables, tea, tobacco, and spices for curing.

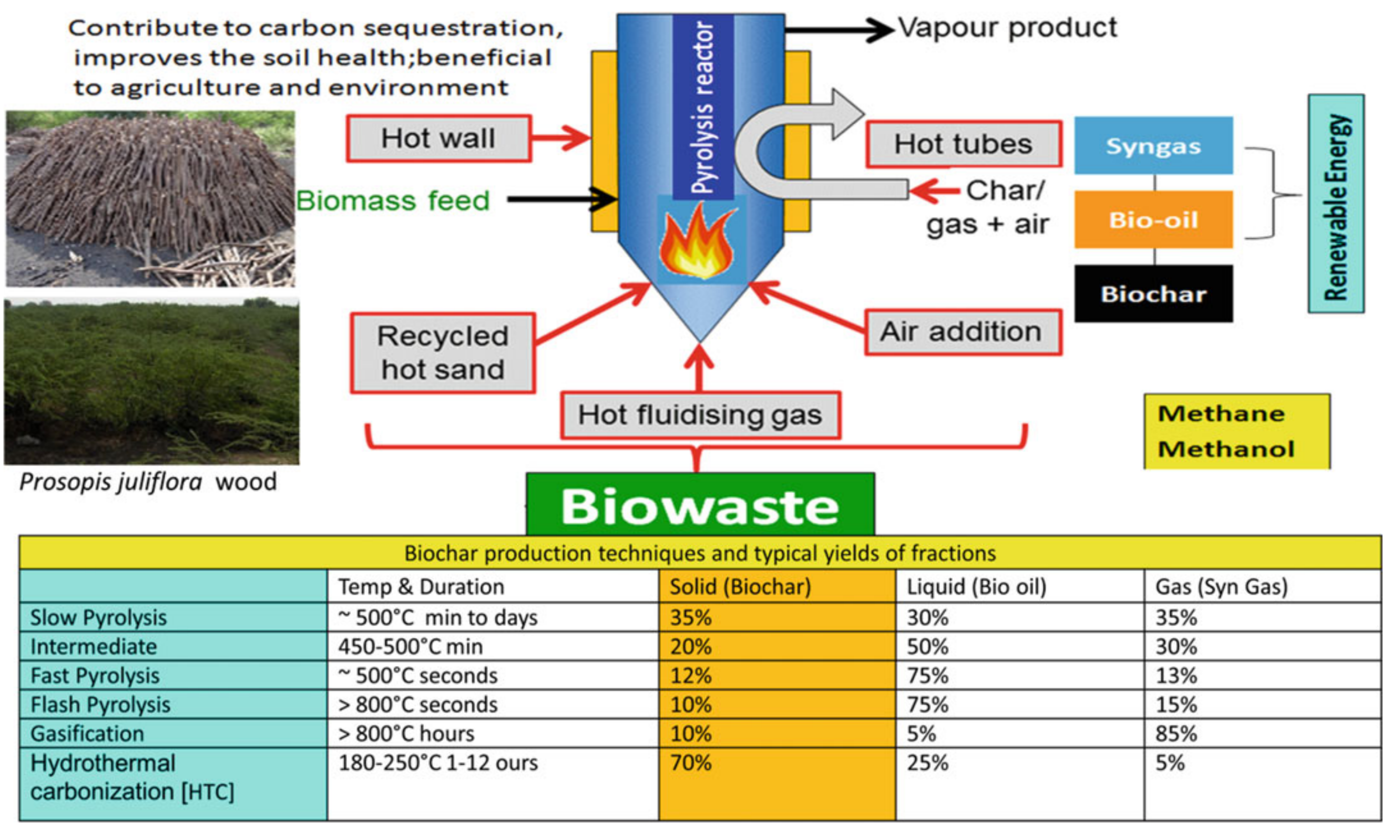
4 Biomass Conversion Technologies

4.1 Pyrolysis

Pyrolysis is an explicit process of biomass converted into the fluid (bio-oil), carbon-rich solid (charcoal), and vapor (flammable gas) through fractional ignition at temperatures around 500°C and without oxygen [8]. High temperatures permit the vaporization of the biomass, delivering gases, whose fumes are consolidated into liquids by liquefaction. The fluid fuel coming about because of this procedure can be utilized for different heating and power applications. Notwithstanding fluid energizes, the pyrolysis procedure likewise creates other ignitable items, for example, charcoal, gas, and numerous other worthy synthetics [9]. The schematic plan of the biomass pyrolysis process is shown in Fig. 2.

4.2 Biological Hydrogen

Biological systems producing hydrogen in light are (1) hydrogenase containing eukaryotic or algae, (2) cyanobacteria, (3) photosynthetic bacteria, and (4) biophotolysis. Algae (green and blue-green) are capable of splitting water to create hydrogen and oxygen. The enzyme for hydrogen creation in green alga is hydrogenase, while in blue-green it is nitrogenizing. Hydrogen is perceived as



Biochar production techniques and typical yields of fractions

	Temp & Duration	Solid (Biochar)	Liquid (Bio oil)	Gas (Syn Gas)
Slow Pyrolysis	~ 500°C min to days	35%	30%	35%
Intermediate	450-500°C min	20%	50%	30%
Fast Pyrolysis	~ 500°C seconds	12%	75%	13%
Flash Pyrolysis	> 800°C seconds	10%	75%	15%
Gasification	> 800°C hours	10%	5%	85%
Hydrothermal carbonization [HTC]	180-250°C 1-12 ours	70%	25%	5%

Fig. 2 Biochar and its by-products production techniques

one of the cleanest forms of energy which can be produced from biomass, a feedstock to accomplish sustainable bioeconomy (Figs. 3 and 4). Thermochemical innovations such as gasification and pyrolysis are the fundamental routes for

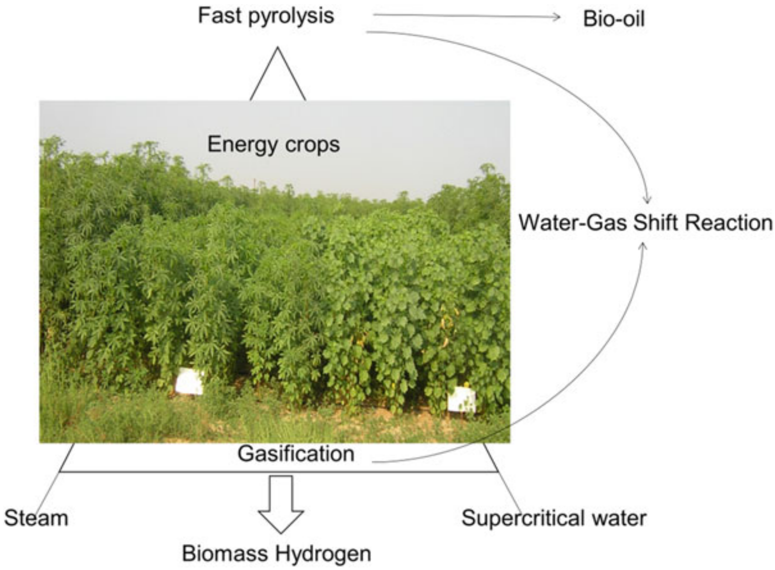


Fig. 3 Thermochemical routes for production of hydrogen from energy crop biomass

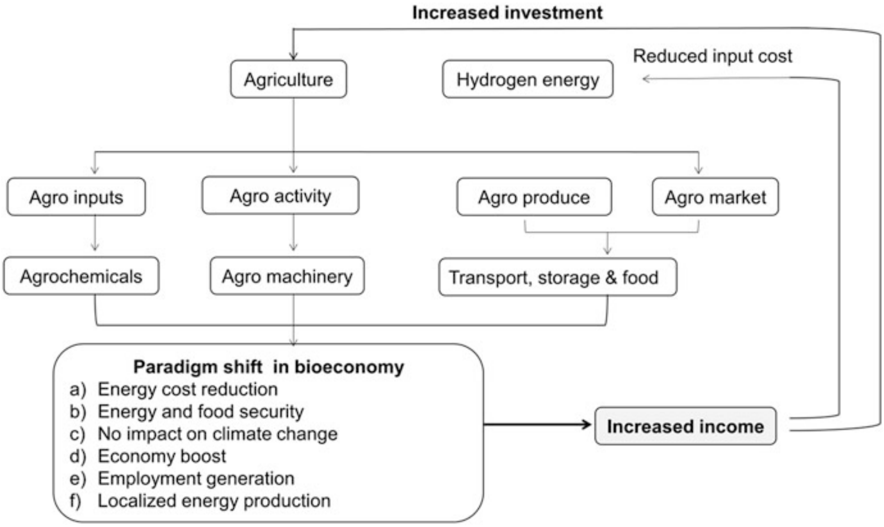


Fig. 4 Sustainability of hydrogen energy for ecodevelopment

hydrogen generation from biomass. Hydrogen from biomass can be utilized for fuel cells (FC), otherwise called polymer electrolyte membrane (PEM) fuel cells (PEMFC) [10–12].

4.3 Gasification of Biomass for Power Generation

Phytomass gasification (utilizing gasifiers of different capacities) produces power, and the gas can be used directly or for shaft power [13, 14]. The basic process and chemistry involved in gasification are:

- Conversion of biomass into combustible gas mixture called producer gas ($CO + H_2 + CH_4$)
- Involves partial combustion of biomass
- Four distinct process in the gasifier, viz.,
  - Drying
  - Pyrolysis
  - Combustion
  - Reduction

4.4 Lignocellulosic Conversion

Lignin is significantly vast on planet earth which can be considered as a substrate for different biochemicals via valorization including chemical changes for creation of bio-based polymers [15–17]. An audit of lignin science and its biorefining transformation advances are highlighted recently choices biochemical lignin valorization that has been recommended by Abejon et al. [15] and shown in Fig. 5.

Pathways for breaking holocellulose, lignin, and alpha cellulose gave promising results. Impacts of different response parameters on solvolytical depolymerization have been researched [18]. Bioconversion of lignin with oleaginous *Rhodococcus* has been illustrated [19]. Endeavors have been made with blend of enzymatic hydrolysis and ethanol organosolv pretreatments for delignification bringing about cellulose-to-glucose change. Lignin depolymerization and change by means of thermochemical strategies have been proposed by Pandey et al. [20]. Efficiency of extractives, molecule size and harvest hotspot for lignin and microcomponents, structural starches have been estimated [21].

Acid and enzymatic hydrolysis of lignocellulose (agricultural residue) for co-creation of liquid fuels and synthetics utilizing regular and biotechnological applications, for example, cell immobilization [21]. Microbial and enzymatic handling of biomass (lignocellulose) yields sugars for additional transformation to alcohol and different solvents contemporary need. Any sugar or starch can yield

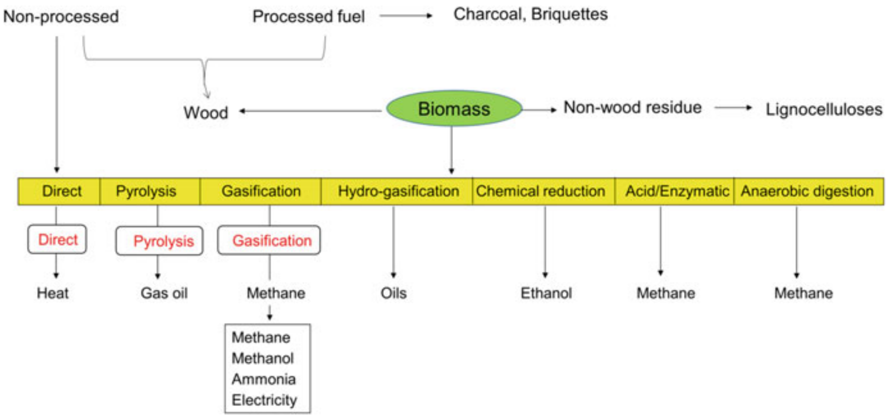


Fig. 5 Biomass conversion technologies and products

ethanol through regular yeast-based fermentation or through redesigned cell immobilization strategies, while the anaerobic process would create methane (gaseous fuel) and stillage/slurry (fertilizer). Sweet sorghum, corn, cassava, sugar beet Jerusalem artichoke, etc. are the significant crops. As of late, the strategy of cell immobilization was effectively utilized in numerous bioreactors for the production of liquid duels and synthetics. Cell immobilization with bacterial and yeast cells was very beneficial. Immobilization of cells and organelles is effective and extensively used in biotechnological applications. Sodium and calcium alginates, agar, polyurethane, polyvinyl structures, and so on have been utilized in various bioreactors for immobilizing cells and organelles. The criteria for choosing such material are that it ought to be non-poisonous to the living being immobilized, having maintenance limit, permeable and can be set up in explicit molecule size and shape.

4.5 *Nanotechnology for Biomass Energy*

Development of nanocomposite-based catalysts photoreactors with scattering light nanoparticle suspension accelerated the economic production of biodiesel and hydrogen production as listed in Table 1.

Table 1 Beneficial use of nanoscience for biofuel production

Research finding	Reference
Hydrogen production with the microalga *Chlamydomonas reinhardtii* grown in a compact tubular photobioreactor	Giannelli and Torzillo [22]
Conversion of biomass to biofuel by nanocatalysts – a review	Akia et al. [23]
CaO and MgO heterogenic nanocatalyst coupling on transesterification reaction of biodiesel from recycled cooking oil	Tahvildari et al. [24]
Ag/bauxite nanocomposite as a heterogeneous catalyst for biodiesel production	Bet-Moushoul et al. [25]
Engineered nanoporous materials mediated heterogeneous catalysts for biodiesel production	Sharma et al. [26]
Transesterification process using homogeneous and nano-heterogeneous catalysts for biodiesel production from *Mangifera indica* oil	Jadhav and Tandale [27]
Development of biochar-based nanocatalysts for tar cracking/reforming during biomass pyrolysis and gasification	Guo et al. [28]

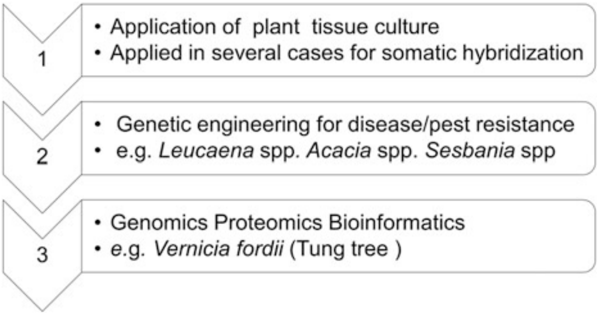


Fig. 6 Biotechnological interventions for enhancement of biomass

5 Biotechnology for Biomass Energy

Variety of biotechnological tools has been applied for solving the problems in the field of biofuels from biomass. The notable achievements are depicted in Fig. 6 [29–31].

6 Biomass Energy-Related Environmental Issues

Although biomass energy sources are abundant and plenty available, its conversion to the production of biofuels has certain limitations and disadvantages, as discussed below.

6.1 Monoculture

Serious allegations have been leveled against the implementation of large-scale plantations (e.g., 100s and 1,000s) of single species called "monoculture." Such projects could in fact have various negative consequences particularly when infected with fungal or bacterial diseases.

In the Philippines, *Leucaena leucocephala* (subabul, cubabbool, koobabul, etc.) is still the primary multipurpose tree species. The largest plantations of subabul are owned by the National Electrification Administration (NEA) (about 12,000 ha) and Manila Seedling Bank Foundation (about 2,000 ha). NEA uses subabul wood for its dendrothermal project. The harvested wood is used to generate steam or electricity. In 1987 the wood of subabul supported power plants of 200 MW capacity. By the year 2000, about 700,000 ha of subabul plantations and 2,000 MW electricity are planned. The psyllid (*Heteropsylla cubana*, insect) pest attacked this tree crop and devastated the lucrative market for leaf meal made from the leaves of Leucaena fetching about 12,000 pesos/year/ha. Seed banks of the Philippines also reportedly lost their business. Thus, monoculture could be devastating when an insect or fungal bacterial epidemic strikes the region. In India, Tamil Nadu's 12,000 ha of *Casuarina* and Gujarat's *Prosopis* plantations are worldwide known for supporting power-generating plants of 100 MW capacity.

6.2 Allelopathy

Leucaena leucocephala is the most popularly used plant species for energy plantations. Varieties like K B, K 28, K 29, and K 67 (Salvador type) and K 3, K 4, K 6, K 59, K 62, K 66, K 77, K 95, and K 101 (Peru type) are under cultivation in different parts. Plantation densities often range from 2,500; 5,000; 10,000; 20,000; to 40,000 plants per hectare. It has been observed that the density and diversity of the *Leucaena* ground floristic composition are controlled by planting density (see Table 2). The study of aqueous extracts of plant parts and soil from Leucaena plantations revealed the presence of phenolic acids, viz., gallic, protocatechuic,

Table 2 Phenolic acid content in leaves

Phenolic acid (μg/g)	*Eucalyptus camaldulensis*	*Acacia auriculiformis*	*Leucaena leucocephala*
Gallic	536.6	295.8	597.2
Protocatechuic	99.8	55.9	109.9
p-Hydroxybenzoic	76.8	ND	892.7
p-Hydroxyacetic	253.4	105.4	ND
p-Coumaric	6.8	19.8	55.9
Ferulic	ND	3.6	ND

p-hydroxybenzoic, vanillic, caffeic, syringic, p-hydrocinnamic, and ferulic acids, quercetin, and a number of phytotoxic flavonoids. These phytochemicals have allelochemical effects on the understory flora. Therefore, a high-density monoculture of Leucaena (beyond 5,000/ha) does not allow the growth of ground flora. This not only impoverishes the soil for nutrients but also hinders the nutrients cycle. Also due to allelochemical effects, seedling growth of certain forest species like *Casuarina glauca* and *Acacia confusa* was suppressed.

6.3 Disposal of Effluents

Ethanol production causes large-scale pollution. Every cubic meter of fuel produced from sugarcane generates 12–13 m of effluents. If this is discharged without treatment into aquatic ecosystems, it causes much pollution, in terms of BOD as in the case of sewage. Effluent from sugarcane industry is called stillage, and discharging it in water without treatment is a loss since it is a valuable fertilizer. Wood burning has been phased out in developed nations, since in large cities electricity is the environmentally friendly form of energy. Wood burning causes atmospheric pollution than does an industry.

6.4 Short-Rotation Intensive Culture

Short-rotation intensive culture (SRIC) means a silvicultural system based upon short clear-felling cycles, generally between 3 and 14 years employing intensive cultural practices such as superior planting material. European community released about 5 million ha of the arable land for SRIC. In Portugal and Spain, about 800,000 ha of *Eucalyptus* pulpwood plantations were successfully maintained. In several parts of Europe where Eucalyptus would be too frost tender, about 2,000 ha of experimental plantations of Poplars and Willows are maintained. Thus, the technology of SRIC is well established in several countries.

The environmental impact of SRIC must be taken into account. The plantations under SRIC would provide habitat or serve as shelter belts to adjoining crops. For example, *Casuarina* plantations on coastal belt of Andhra Pradesh and Tamil Nadu help as wind breaker. Some of the species recommended in SRIC fix nitrogen and thus enrich nitrogen status of the soil. Serious environmental objections have been raised especially with regard to *Eucalyptus*. These objections are often exaggerated. However, baseline and feasibility studies and research and development need to be strengthened before accepting or rejecting a plant species. Technical guidance to farmers must be made available in order to practice SRIC.

6.5 Energy Plantations as Sink for Carbon Dioxide

Global warming/greenhouse effect is much talked about these days which are due to carbon dioxide enrichment in the environment. It is estimated worldwide that about 8 Gt C (fixed) are emitted annually to the atmosphere (5.7 Gt) from fossil fuels and about 2.3 Gt from deforestation which amounts today about 20 million hectare per year. The net release of carbon due to tropical deforestation might be as high as 5 Gt annually in future if no control is possible. Biomass is considered to be relatively clean energy and can be made to add practically no carbon to the atmosphere and contributes insignificant S and NOx emissions in comparison with fossil fuels. Energy plantations/afforestation projects would absorb/recycle carbon dioxide and thereby diminish the greenhouse effects. Energy plantations of mixed types would produce multiple use products, and innumerable bioresources for use by living organisms contribute to the ecodevelopment of rural masses, soil conservation, and ecorestoration.

6.6 Use of Contaminated Substrates for Energy Crops

Integrated biomass energy parks are being planned on co-contaminated substrates (soil and water) by selecting suitable candidate species. Harvested biomass is processed into biofuels. Notable plant species experimented have been (a) *Ricinus communis* (Figs. 7 and 8), (b) *Jatropha curcas*, and (c) *Miscanthus giganteus* [2, 32]

In view of the information provided *vide supra*, various governments and scientists are concentrating to develop "energy bioscience" on a sustainable basis to supplement fossil fuels.

7 Conclusions

The field of energy bioscience progressed considerably encompassing bioethanol, algal fuels, biodiesel, and next-generation fuels. The major areas of energy bioscience researched upon and the importance of biomass for energy, its relevance to contemporary world, emerging biomass conversion technologies, and required biotechnology for enhancing bioproductivity are presented. Last but not least, the biomass energy-related environmental issues are also highlighted.

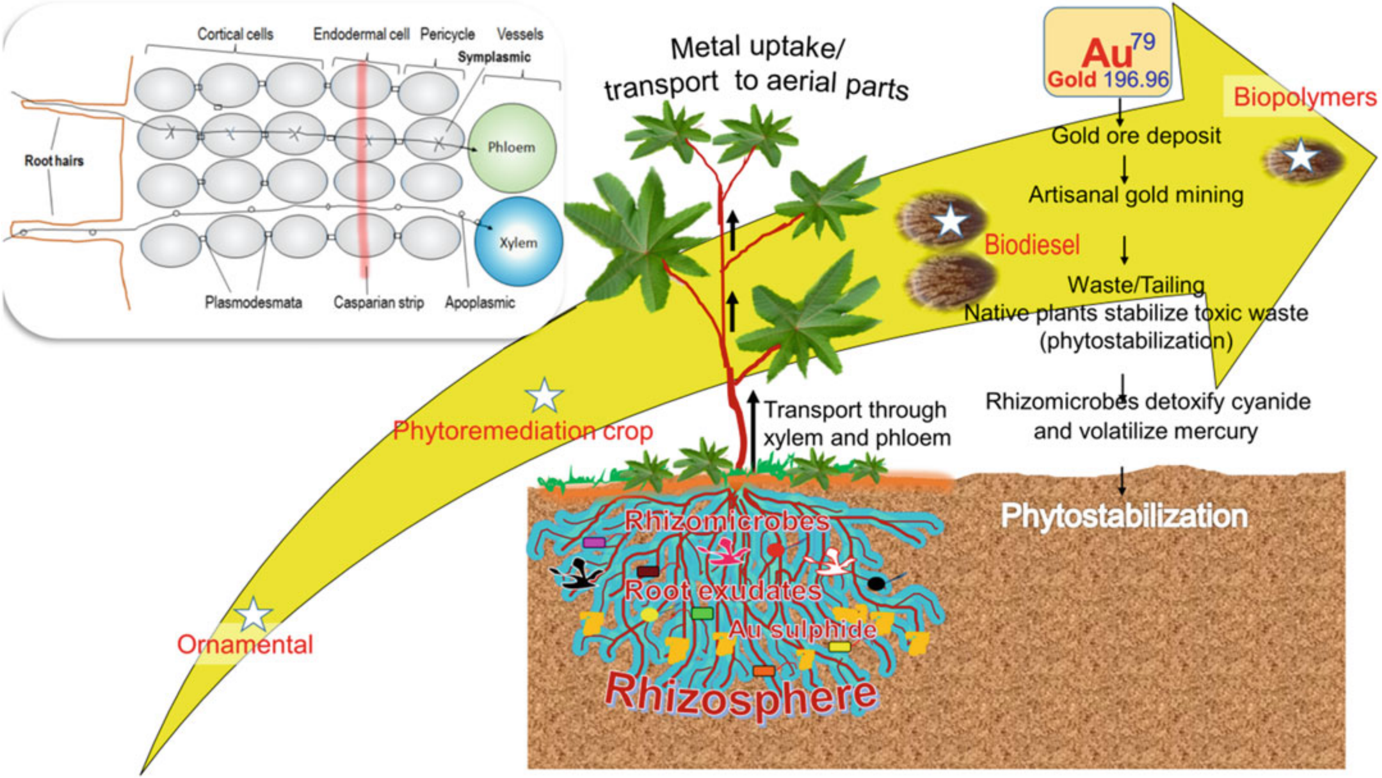


Fig. 7 Energy crop, e.g., *Ricinus communis*, is an important multipurpose plant not only for phytoextraction but also for vegetating industrially polluted soils

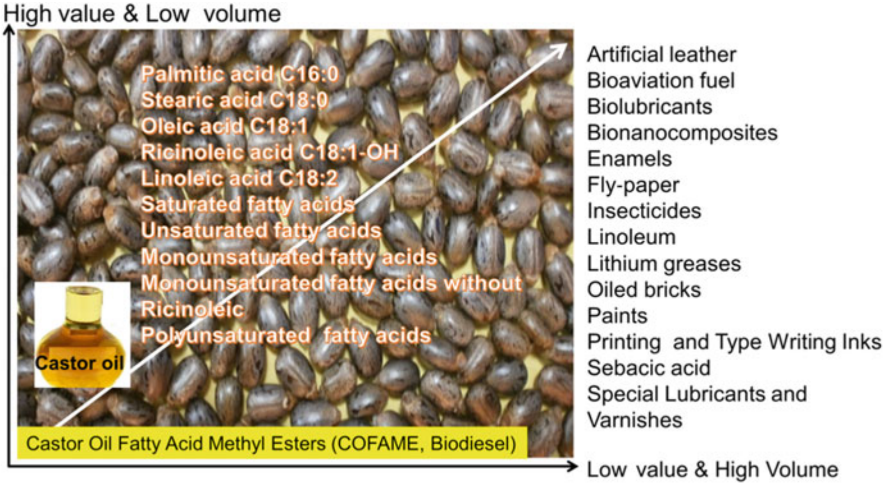


Fig. 8 Castor seeds producing a wide variety bioresources ranging low value, high volume materials such as castor oil fatty acid methyl esters (COFAME = biodiesel) to high value products as indicated in low volume

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Renewable Energy from Woody Biomass of Poplar and Willow SRC Coupled to Biochar Production

Kim Yrjälä and Huabao Zheng

Contents

Abstract Production of renewable energy has a fundamental role to play in mitigating climate change issues. Yet the role of modern bioenergy in decarbonizing the global energy system is not widely recognized. It is unfortunately not receiving the attention it truly deserves. The success story of wind and solar renewable energy increase should be revived by increase in bioenergy, which also can be a type of decentralized local energy production. A good option is to use woody biomass from

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short rotation coppice of poplar and willow, combined with phytomanagement, planting trees on brown fields and abandoned agricultural lands that may be contaminated with heavy metals or even organic pollutants. The plants and associated microbes help to remediate spoiled areas. The increased attention to sophisticated thermal treatment of biomass to produce biochar opens up new possibilities for woody biomass and forest residue treatment. They can be converted into energy in the form of volatiles, oils, and the carbonaceous material of biochar.

Keywords Abandoned agricultural lands, Phytomanagement, Phytoremediation, Phytotechnology, Thermal treatment

1 Introduction

Until today, most of the world's energy supply has come from scarce resources like coal oil and gas. In a future low-carbon economy, bioenergy can play a significant role and contribute substantially to the global energy supply [1]. National energy production employs centralized large-scale systems or alternatively decentralized local small units. In circular economy, the smart use of resources becomes the paradigm where agricultural wastes actually become a resource with many opportunities, for producing not only ripe crops but also biomass for bioenergy [2, 3]. However, the role of modern bioenergy in decarbonizing the global energy system is neither widely recognized nor it receives the attention it deserves. IEA report reveals that bioenergy production will have the fastest growth among renewables in the global energy mix over forecasted period of 2018–2023. In 2023, it is estimated that bioenergy remains the largest source of renewable energy owing to its widespread use in heat and transport. IEA further identifies additional untapped potential for bioenergy to "green" the industry and transport sectors. A significant proportion of this potential relies on exploiting biomass waste as well as residue resources. Their uses give low lifecycle GHG emissions and have the potential to mitigate land-use change problems through improving waste management and air quality. When fully realizing this potential, modern bioenergy would complement the success experienced by wind and solar technologies. Modern bioenergy can aid to establish a more sustainable and secure energy system, something the world very much needs [4].

In this chapter, the opportunity for novel bioenergy production is outlined. Bioenergy creation from renewable resource of agricultural and forestry waste is elaborated in combination with production of forest tree biomass. Recent advances in remediation of contaminated lands using phytotechnologies are brought up where the production of biochar from agricultural and forestry waste can be the missing link for more energy-efficient and sustainable energy production from woody biomass.

2 Energy Potential of Woody Biomass

In Finland, the proportion of biomass in energy production is highest among industrial nations, and the role of wood is central. The proportion of renewable energy to total energy consumption was 2018 altogether 37%, and wood-based energy counted for 27% of total consumption. At the same time, wood covered three thirds of renewables [5]. Biomass-based fuels have traditionally included residues from the chemical and mechanical forest industry, and firewood used to heat homes. Over the last decade, these fuels have been complemented by forest chips from logging residues, biogas, biodegradable fractions of recycled waste, straw, and perennial energy crops such as reed canary grass. Biomass is also rapidly gaining importance as raw material for liquid biofuels in transport.

Wood pellets have been utilized for heating buildings in the Northern Hemisphere, where electricity is the common source of heating energy. Pellets substitute the oil in district heating networks. New technologies improve the power-to-heat ratio, and establishment of small power plants makes bioenergy a good option for locally distributed energy systems. The International Energy Agency (IEA) states that the world's primary energy supply is 13,555 MTOE (megatons of oil equivalent) in 2013, with 1829 MTOE coming from renewable energy. Burning biomass is most widespread contributing 73.4% of the total renewable energy; hydraulic power contributes 17.8%, while all other sources combined contribute 8.8% [6–9]. The IEA predicts that global electricity demand will increase to 42,000 TWh in 2050 and electricity generation using bioenergy will increase to 3,100 TWh. The increase is strong in the Asian region that includes China. There has been a gradual increase in percentage of renewable energy in the world's primary energy supply from 12.7% in 1990 to 13.5% in 2013.

Information box: **Biomass** Biomass is an organic matter that can be converted into energy, which includes food crops, crops grown specifically to produce energy, crop residues, wood waste and byproducts, and animal manure. Biomass may be used to produce heat, electricity, or liquid transportation fuel.

3 Utilization of Woody Biomass for Bioenergy: A Timely Perspective

A much revealing example of the renewable biomass utilization for bioenergy comes from Japan experiencing the breakdown of the Fukushima power plant 2011 in connection to earthquake. Tabata [10] recognizes in Japan three main waves of using woody biomass for energy. The first one occurred as a result of the oil shock in the 1970s [10], and that is when research and development for renewable energy started

50 years ago. The second wave co-occurred with the time of high oil prices in 2008 at the onset of global financial crisis. Greenhouses started using woody biomass for heating instead of heavy and light oils. The third wave finally came with the Great East Japan Earthquake and the following Fukushima nuclear power plant accident in March, 2011. The present wave caused an awakening of citizens' awareness of climate change and how to best deal with it. It was this disastrous accident that created the needed political momentum to change and improve renewable bioenergy legislation. This is a very good example of how public support is needed to enhance the continuation of woody biomass utilization for energy production.

Woody biomass energy utilization can slowly commence the conversion of the existing fossil fuel-based energy system into a biomass-based system. The scientific community needs, however, to be very careful in studying the total environmental impacts of bioenergy production including all sustainability aspects, such as life cycle assessment, economic benefit, and creating local and regional employment.

4 Poplar and Willow for Short Rotation Coppice (SRC)

Wood residues and pellets can be produced by short rotation coppice (SRC) of woody plants like poplar and willow [11, 12]. These woody plants ideally grow on abandoned agricultural land but not to compete with food production in agriculture. Brown fields are also suitable spaces for growing these energy trees, harvested at regular intervals for local energy production. In the first phase, the tree stand is established using selected high-performance seedlings. After certain time span, they are after cutting transported to industrial facility for energy production. The third phase is the restoration and replacement of trees to the energy tree plantation [13].

Combined heat and power (CHP) from biomass that is produce in sustainable way could be main constituents for renewable energy production approach. Their production and conversion of biomass to either liquid fuel or CHP is fundamental to get reasonable returns on energy investment [14].

Large amounts of residue from agricultural and forestry sources are currently available; 22 and 2.14 Mt. of dry matter from agriculture and forestry, respectively, in Italy [15] could be utilized for the production of biofuels or chips, CHP [16, 17]. It is necessary, however, in some way to guarantee the long-term sustainable supply of biomass for renewable energy production. To do this the sustainable option is to start growing new perennial energy crops particularly on marginal agricultural lands [18, 19]. The use of marginal lands for cultivation and bioenergy production has recently become a topic of interest for the scientific agronomic and agricultural economy communities. There is a growing availability of arable land in the Mediterranean regions, which is a consequence of the decline of cereal cropping systems and grain legume. This provides many opportunities to set up successful feedstock production on these unmanaged areas [20]. Very recent findings suggest that energy crops can be grown on marginal lands acquiring significant positive effects in terms of sustainability aspects. Challenges are the shortage of agronomic research especially on water use efficiency and biodiversity conservation. National and EU institutions and policies should more promote economic opportunities, and it is important to integrate local agro-ecosystems and farmers' involvement in these developments. The use of Life Cycle Assessment and certification schemes can give much needed sustainability indicators for the effective bioenergy production on marginal lands [20].

During the beginning of this millennia, short rotation coppice (SRC) crops were introduced on several farms in Northern Italy taking advantage of their low input requirement exploiting marginal lands [21]. In the total surface area of 6,695 ha in 2010, poplar was the most commonly chosen species for SRC since it had already been cultivated in the same area for the production of wood-based panels and paper. The suitability of clones of white poplar and willow to grow on marginal land in environmental conditions of Italy, the Mediterranean area, and Central Asian countries has been evaluated [14, 22]. The differences on dry, aboveground biomass among the investigated clones were statistically significant. The biomass amounts expressed as Mg per hectare (ha) ranged from 3.4 Mg ha^{-1} $year^{-1}$ for the clone PI 93.007 to 8.3 Mg ha^{-1} $year^{-1}$ for the clone 93.088.202; the mean was 5.4 Mg ha^{-1} $year^{-1}$. Some clones showed superior growth and yields compared to the reference clone 'Villafranca'. 'Villafranca' produces on average 5 Mg ha^{-1} $year^{-1}$ on other sites with the same cultural model. This SRC cultural model is suitable for biofuel feedstock (pellets and second-generation bioethanol), particularly if associated with phytoremediation [22, 23].

The increased biomass yields obtained by selected clones of white poplar and willow could contribute to a long-term, gradual sustainable replacement of fossil fuels in Mediterranean regions [14]. Woody biomass SRC can also protect soil and water resources creating new habitats for a wide range of species, particularly when traditional fertilization is minimized [13].

4.1 Willow Woody Biomass

The replacement of fossil fuels with biomass for energy production is an important strategy promoted by the European Union [24]. In this context, woody biomass from SRC is worldwide gaining interest for heat and electrical power generation. An additional global benefit is that the energy crops can also help to mitigate the effects of climate change by sequestering carbon dioxide during biomass growth. Willow (*Salix* spp.) cultivation receives a lot of attention, since willow is a fast-growing woody species that has commercially been planted to a significant extent in the European Union countries to produce biomass for energy [25, 26]. Willows are alternative nonfood cash crops in farming across whole Europe. Predominant SRC energy crop species include willow and poplar that are well suited for growth on lands with of different types of soil. The advantage is that they can successfully be produced on marginal/reclaimed lands that have become available, for instance,

Table 1 Biochar production from different sources of woody biomass

Biomass source	Country	Reference
Acacia	Brunei	Ahmed et al. [27]
Apple tree	China	Liu et al. [28]
Bamboo	China	Chen et al. [29]; Zhou et al. [30]
Beech	France	Margeriat et al. [31]; Zeng et al. [32]
Birch	Finland	Fagernas et al. [33]
Brazilian pepper wood	US	Yao et al. [34]
Cottonwood	China	Zhang and Gao [35]
Eucalyptus	India	Choudhary et al. [36]
	Spain	Amutio et al. [37]
	Spain	Gomezmonedero et al. [38]
	Australia	Werdin et al. [39]
Hickory	China	Hu et al. [40]
Mallee wood	Australia	Abdullah and Wu [41]
Miscanthus	Ireland	Trazzi et al. [42]
Oak	China	Shen et al. [43]; Wang et al. [44]
	Chile	Alejandro Martín et al. [45]
Pine	Spain	Marks et al. [46]; Ojeda et al. [47]
	US	Huggins et al. [48]
Poplar	Spain	Ojeda et al. [47]
	China	Chen et al. [29]; Kloss et al. [49]; Liu et al. [28]
Spruce	Canada	Keske et al. [50]
	France	Repellin et al. [51]
Tamarindwood	India	Acharya et al. [52]
Walnut	China	Huang et al. [53]
Willow	Belgium	Hamedani et al. [54]
	Finland	Hyvaluoma et al. [55]

when cereal crop cultivation has ceased in an area. The energy crop fuels can be channeled into different bioenergy systems for both heat and power generation, and this can take place from domestic to industrial scale [25]. A special sustainable case would be to produce biochar from short rotation coppice biomass (refer to Table 1). The produced biochar can be returned to soil for improvement of soil fertility and increase of soil carbon exemplifying with a circular economy [7].

Poplar and willow are proper energy crops in Northern and Western Europe climatological conditions. Especially in Sweden willow has been coined in the energy policy deliberations as an important source of alternative biomass for the production of wood fuel on farmland. Consequently, Sweden is the European leader in short rotation willow plantations for energy production, having more than 14,000 ha of willows on agricultural lands especially in the southern and central areas of the country [25].

SRC crops are typically planted in the spring at the beginning of the growing season. During the first winter, their stems are cut down to ground level that will initiate the growth of multiple stems (the crop is coppiced). Harvesting in SRC is done taking use of conventional machinery on the farms, to produce SRC rods, chips, or billets. Then they can be further chipped and/or dried as required preventing decomposition of the material. SRC energy crops have usually been harvested in 2–5-year intervals, with 3-year cycles being most common. The roots of SRCs can be left in the ground after harvest, where multiple new shoots will emerge through each progressive growth cycle. An SRC plantation will be potentially be viable for up to 30 years before a complete replanting becomes necessary [25].

5 Phytotechnology

Phytotechnology may help to provide valuable sources of renewable biomass for the bio-based economy in the broad realm of circular economy. This biomass has many uses like bioenergy, biocatalysis, and basic molecules for green chemicals, but also ecomaterials [56]. Several studies show the use of metal-enriched plant biomass cultivated for phytoremediation as potential fuel to produce bioenergy. The modes of energy production are thermal treatment like combustion [57], gasification [58], torrefaction [59], and pyrolysis [60, 61].

Information box **Phytotechnology** The term phytotechnology describes the application of science and engineering to examine problems and provide solutions involving plants. The term itself is helpful in promoting a broader understanding of the importance of plants and their beneficial role within both societal and natural systems. A central component of this is the use of plants as living technologies that provide services in addressing environmental issues (United Nations Environment Programme, UNEP).

Some new developments in situ bioremediation technologies have been coupled to renewable energy. Phytotechnologies have presented options using woody plants for remediation of contaminated soils. Woody plants like poplar and willow are used for treatment of heavy metal-contaminated land. The plant and associated microbes can by phytoextraction uptake harmful contaminating heavy metals (HM) like Cd, Hg, Ag, Pb, and Cr that are biologically non-essential and show toxicity even at low concentrations [62]. Phytostabilization is the technique when plants reduce the bioavailability of contaminants immobilizing them within the soil profile [63]. The plant structures form a stable mass with HM within the plant, and they will not enter the environment again. After treatment of contaminated lands with poplar and willow, the biomass can be channeled into energy production including biochar production.

5.1 Phytoremediation

Phytoremediation is the use of plants and their associated microbes for environmental cleanup [64–67]. This technology makes best use of various naturally occurring processes referred in Fig. 1 by which plants and their microbial rhizosphere flora degrade but also sequester organic and inorganic pollutants [69]. Phytostabilization is when inorganic pollutants like heavy metals are transformed into stabile forms that make them less available to bacterial flora and plants. Phytoextraction is when these heavy metals are deliberately taken up by the plant and stably stored in plant compartments like roots and the stem. Phytodegradation is the process when organic compounds are degraded by the use of plant-associated microbes. Phytoremediation is performed on both land contaminated with organic compounds like PAHs and petroleum hydrocarbons, respectively [70, 71], and lands containing heavy metals [72].

5.2 Phytomanagement

The European Renewable Energy Directive (RED), 2009 [73], encourages the restoration of degraded and contaminated land by cultivating biomass for biofuel and bioliquid in agreement with sustainability criteria to ensure biofuel/bioliquid production in a sustainable and environmentally friendly manner [74].

The use of trace element (TE)-enriched biomass is an important issue for avoiding TE re-dissemination in the environment. Several European field trials for phytoremediation using tobacco, birch, willow, and poplar have aimed to produce

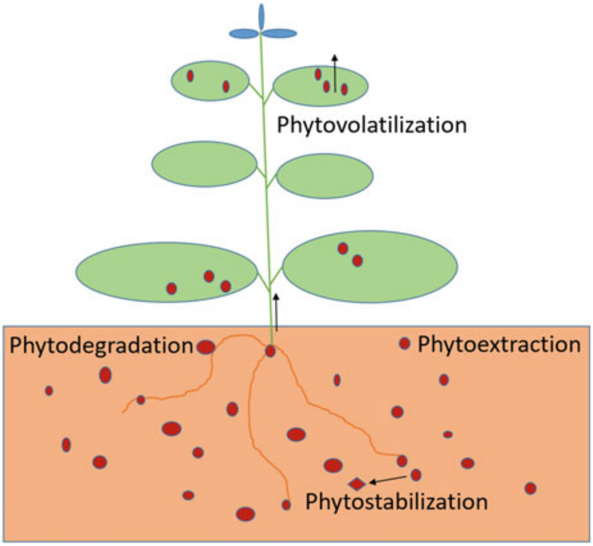

Fig. 1 Phytoremediation: Possible fates of pollutants during phytoremediation: the pollutant (represented by red circles) can be stabilized or degraded in the rhizosphere, sequestered or degraded inside the plant tissue, or volatilized (adapted with permission from Pilon-Smits et al. [68])

valuable biomass including metal and energy recovery [56]. Phytotechnology aims at linking the technologies to the production of valuable biomass products and deals with the fate of contaminants during industrial processes [75–77]. These projects address catalyst production using various energy recovery techniques that include combustion, torrefaction, and pyrolysis to produce biochar. Combustion experiments at an industrial scale with willow and poplar have been described [76, 78]. Apart from cellulosic pulp, the availability of co-products like lignin and sugars can stimulate the development of new emerging applications to the biorefinery approach.

6 Thermal Treatment of Woody Biomass

Torrefaction (290°C) and pyrolysis (450 and 800°C) trials were performed at pilot scale with a patented reactor (Fig. 2) on metal-enriched poplars from a contaminated soil managed by phytotechnologies and poplars cultivated on uncontaminated soil, for comparison [76].

Results showed that the evolution of the end product yield, i.e., biochar, bio-oil, and gas fractions, was depending on temperature rather than other parameters such as the origin or metal content of the tested poplars (Fig. 3). Torrefaction decreased the processed poplars weight, leading to metal-enriched torrefied biomass as a major end-product. At 450 and 800°C, the temperature governed the metal behavior.

At 450°C, metals were recovered in biochar, then in bio-oil, and finally in gases. The 800°C showed similar results for Cu, confirming that Cu does not easily

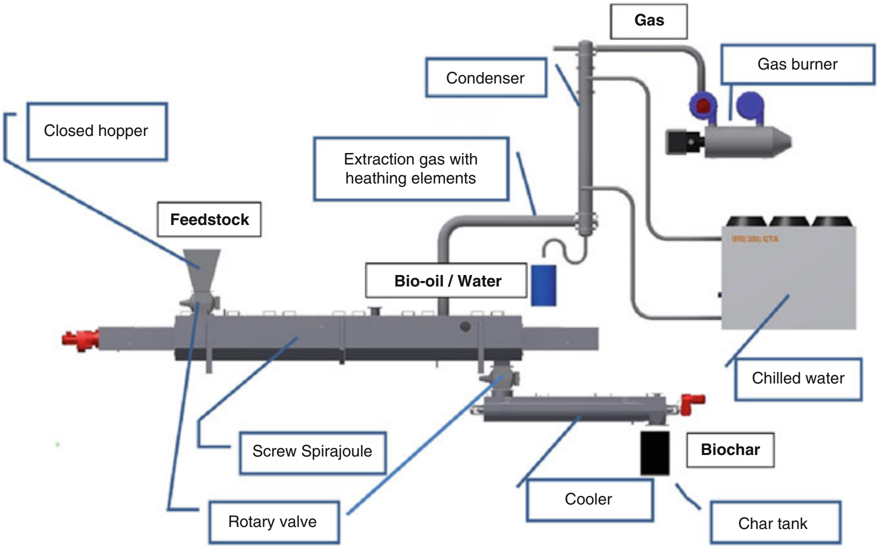

Fig. 2 Biogreen thermal process (adapted with permission from [76])

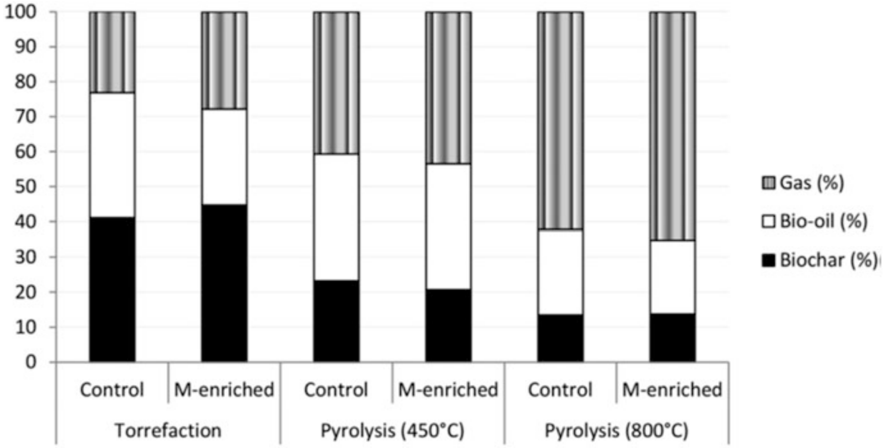

Fig. 3 End-product yields as a function of thermal processes, torrefaction and pyrolysis done with M-enriched poplar biomass (adapted with permission from [76])

volatilize. On the contrary, Zn, Pb, and Cd were mostly recovered in gases, which became the second metal recovery compartment.

The evolution of the end-product yield, i.e., torrefied biomass/biochar, bio-oil, and gas fraction, depended as expected mainly on the operating temperature. With increasing temperature, the torrefied biomass/biochar yield decreased, and gases increased, while biochar decomposition released volatile matters [79, 80]. Woody biomass is an excellent starting material for the production of biochar with varying properties (Table 1).

Concerning pyrolysis at 450°C, the Zn concentrations of control and M-enriched biochars were congruent with the weight loss occurring during pyrolysis, which verified the Zn conservation and that Zn volatilization was of minor importance [76]. Unlike Zn, Cd concentrations in biochars differed significantly between control and M-enriched. This result suggested that Cd contained in M-enriched wood chips was highly volatilized at 450°C. This also happened in thermal process at even higher temperature of 800°C. To guarantee the safe use of poplar biomasses in torrefaction and pyrolysis, the authors recommend performing Cd and other trace element analysis of all end products irrespective of the origin of the biomass [76].

6.1 Biochar

The biomass from SRC is an excellent starting material for the production of biochar from woody biomass [55]. Biochar is the thermal degradation product of organic materials in the absence of air (pyrolysis) [81]. It has favorable properties for soil treatment to increase fertility, soil quality, and soil health. The woody biomass is treated in 300–700°C pyrolysis reaction to produce volatiles, organic oils, and dry

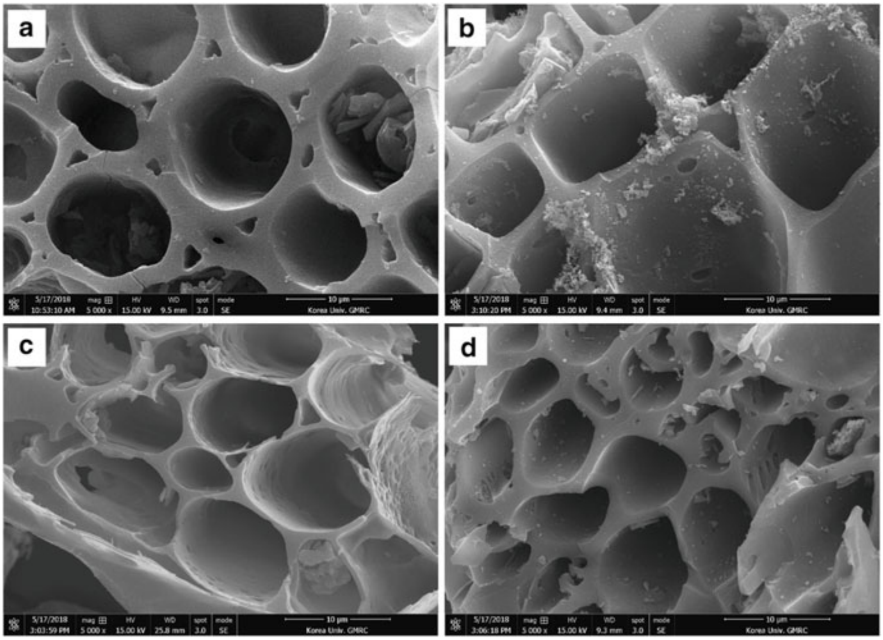

Fig. 4 Scanning electron microscopy (SEM) images of various types of biochars. (**a**) The mesquite wood chip biochar produced at 850°C; (**b**) 40% food waste +60% wood biochar produced at 850°C; (**c**) wood chip biochar produced at 850°C; and (**d**) dairy manure biochar produced at 600°C (adapted with permission from [82])

residue that is biochar. This product is very recalcitrant and can remain in soils for decades, having positive effects on soil quality, and at the same time, the returning of carbon to soil has mitigating effect on climate change.

Biochar is the thermal degradation product of organic materials in the absence of air (pyrolysis) [81]. Pyrolysis is one of the most promising technologies for the conversion of biomass into high-value products such as bio-oil, syngas, and biochar. In quantities, biochar can be produced through torrefaction or slow pyrolysis. The efficiency of biochar production from various biomass is much dependent on the temperature of pyrolysis, the types and composition of feedstock used, and reactor parameters (Fig. 4) [82, 83].

There are good prospects for application of biochar to agriculture because it may have a significant effect on reducing global warming through the reduction of greenhouse gas (GHG) emissions and the subsequent sequestering of atmospheric carbon into soil. When applied to soil, biochar can improve soil quality, soil health, and fertility and by that enhance agricultural production. The pH increase in acid agricultural soils mainly explains observed effects on soil fertility [84]. Biochar has in Eastern China be used to combat adverse effects of nitrogen deposition and to raise pH of acidifying soil [85]. Biochar has a role to meet the environmental challenges caused by agricultural and animal waste disposal. The waste can thus be recycled using pyrolysis into biochar, energy, and value-added products [83].

6.1.1 Biochar Production

Biochar is produced by the thermal decomposition (pyrolysis) of biomass in a reactor facility with little or no available air and at temperatures from 350 to 700°C. By choice of the feedstock and pyrolysis conditions, the production results in a desired carbon product for proficient use. Torrefaction again is the pyrolysis process at lower temperatures up to 300°C that significantly improves grind ability [86].

Charcoal produced from woody feedstock has been prepared and utilized already for several thousand years. Biochar is the carbonaceous product that in recent time has been used as fertilizer to improve the health and quality of soil. The pyrolysis process commences with the drying of biomass that contains liquid, and further heating starts releasing gases that are volatile substance contained in the solid biomass. Permanent gases (CO_2, CO, CH_4, and H_2) are formed, or alternatively organic compounds like methanol and acetic acid are produced. Cracking and polymerization of gases occur forming several products. They are permanent gases, liquid phase(s) like water and tar, and then the solid residue. The reaction pathways for these different products are partly competing where pyrolysis conditions, mainly temperature and residence time, influence what will be produced. Moreover, it has been seen that with increasing temperature, the porosity of biochar increases (Fig. 5). The option is to establish working guidelines that maximize the yield of desired products [86]. When the aim is oil production, the fast (or flash) pyrolysis is the way to go. The crucial thing is that condensable volatiles released need quickly to be cooled and in that way avoid cracking into light gases or polymerization into char. There rapid heating, typically just a few seconds, is used to reach the reaction temperature. As a result, the liquid yield may be up to 75% of the dry matter of the feedstock [87].

In biochar production, however, the main interest is the carbonaceous solid product. Porosity is a very typical feature of the carbonaceous biochar, which depends on feedstock and pyrolysis temperature. In the thermal pyrolysis reaction, the evaporation of water and the release of volatile components increase the stable carbon content. The polymerization of organic compounds in vapors and gases may lead to secondary char formation and in that way increase the yield of solids. Here the heating rate is typically low and the residence time long. Common temperatures for slow pyrolysis are around 500°C, but that depends eventually on desired properties of biochar. For biochar production, the biomass is not heated over 700°C. If pyrolysis is done at lower temperature range between 200 and 300°C, then the process is called torrefaction.

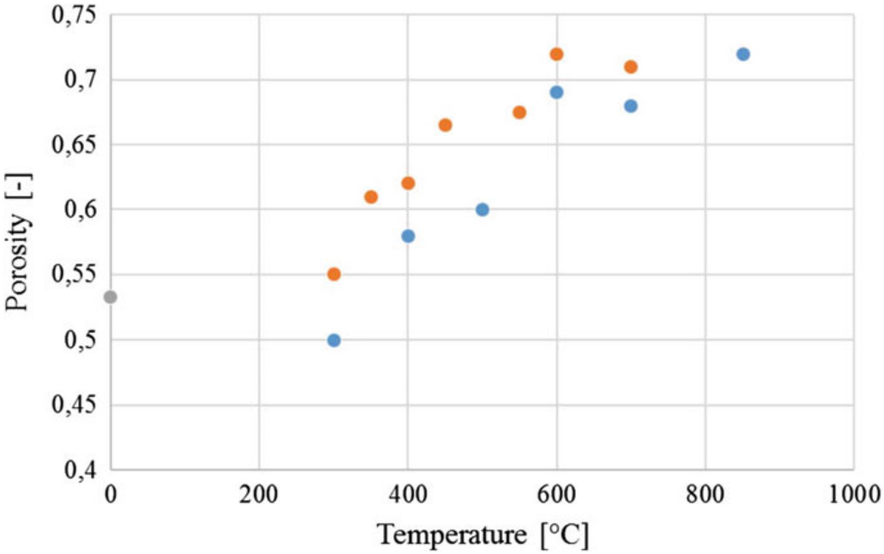

Fig. 5 Porosity of woody biochar (adapted with permission from [86])

7 Future Perspectives

The production of renewable energy from woody biomass of poplar and willow is a way to meet the EU demands and global demands of increasing the proportion of bioenergy among renewables and among total energy production. On global scale, there are other suitable plant species for biomass and energy, and especially interesting is the fast-growing bamboo plant that grows best in the subtropical region of Asia and America. The management of bamboo plantations connects well to stated sustainable development goals, especially in Asia, where bamboo is the biomass for the production of biochars, but at the same time a food source in the form of eatable shoots. Very recently, phytoremediation is put into practice using moso bamboo in heavy metal-contaminated soil opening up the possibility to also use marginal land in China in production of woody biomass for bioenergy production.

8 Conclusions

The concept here outlined for renewable bioenergy production consists of three fundamental building blocks combined to implement the idea of sustainable energy production. Short rotation coppice (SRC) is a well-known method for producing biomass for energy, but causing some economical constrains and challenges for farmers. The other well-known method is phytoremediation for combatting soil pollution of potentially toxic elements (PTE) which has not been used up to its full potential in agriculture, but so far mainly practiced by university scientists. The use of poplar and willow SRC for phytoremediation was very recently reported in Turin, one of the main urban centers of Northern Italy, demonstrating the usefulness of our presented concept in urban settings. The third building block, production of biochar by pyrolysis, is receiving increasing attention, because of positive sustainability impacts in agriculture and forestry. The option of combining these methodologies gives new opportunities for farmers in Europe and in parts of America and Asia where poplar and willow can be grown. The greatest challenge is evidently the stakeholder involvement, to teach and inform farmers of these available technologies, and to convince them that combined with biochar this type of energy production offers not only ecological but also economical sustainability. Renewable energy production by the concept of SRC biomass for biochar production is in accordance with the principles of the circular economy, but also very much along the idea of the 2019 Green Deal put forward by the European Commission.

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Ligninolysis Potential of Ligninolytic Enzymes: A Green and Sustainable Approach to Bio-transform Lignocellulosic Biomass into High-Value Entities

Muhammad Bilal and Hafiz M. N. Iqbal

Contents

Abstract The replacement of non-renewable fossil resources with a renewable organic carbon source is a grand challenge in terms of economic, ecological, and environmental motives. Among various renewable sources, the gainful utilization of lignocellulosic biomass seems a perfect choice both to the public and industrial domains for the eco-friendly production of industrially relevant chemicals, biofuels, and functional materials. Nevertheless, minimal processes have been recognized so far in the chemical industry for effective biomass consumption because of the

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complex and recalcitrant nature of lignocellulosic biomass. This scenario re-directed the researcher's attention to develop highly selective and promising bio-catalytic systems and green reaction bioprocesses to realize the biosynthesis of fuels and bio-chemicals from sustainable lignocellulosic materials. Ligninolytic enzymes assisted bio-delignification of lignocelluloses seems a new, environmentally responsive, and sustainable approach for effective processing of complex lignocellulosic-rich agricultural biomasses. This chapter spotlights the significance of agro-industrial waste biomasses and their gainful utilization for the synthesis of eco-friendly and economical products. Particular focus has been given on the ligninolysis potential of ligninolytic enzymes and bioconversion of lignocellulose biomass into high-value biofuels, specialty chemicals, designer composites, and functional materials. In addition to conclusive remarks, potential challenges and future perspectives in this promising field are also directed.

Keywords Biofuels, Delignification, Green chemistry, Ligninolytic enzymes, Lignocellulosic biomass, Sustainable environment, Value-added chemicals

1 Introduction

An increase in population size and the intensified consumer's necessities are expected to diminish fossil carbon resources in the coming years. In addition, environmental pollution, global warming, and ecological imbalance are the major problems of fossil fuel-based sources that pose a serious risk to the ecosystem [1]. Likewise, the extensive consumption of toxic chemicals and polluting non-degradable materials lead to severe ecological, health, and environmental problems. Therefore, mandatory factors, such as economic feasibility, ecological compatibility, and sustainability, should be taken into consideration in an interdisciplinary way to circumvent negative impacts before the formulation of alternative routes for chemicals, fuels, and materials synthesis [2]. Low cost, affordability, and good quality are the desired traits for the production of innovative platform products. Furthermore, it should be synthesized using bio-renewable and highly abundant carbon resources without having an adverse effect on the ecosystem, society, and wildlife. Being a renewable organic carbon source, lignocellulosic biomass can fulfill all the aforementioned criteria and is a potential solution to address the greenhouse gases and environmental pollution problems [3, 4].

Plant biomasses are renewable carbon sources that can be significantly used for the production of industrially relevant chemicals, biofuels, and valuable functional materials. Figure 1 shows various key steps involved in the processing of biomass to high-value entities. Lignocellulose principally containing three biopolymers (lignin, cellulose, and hemicellulose) indicates the most plentiful form of biomass. From the last several years, considerable progress has been made, across the globe, in utilizing

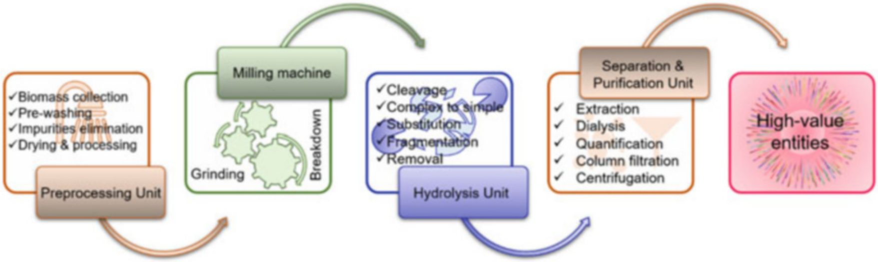

Fig. 1 Various key steps involved in the processing of biomass to high-value entities

biomass to synthesize chemicals and fuels. Beneficial consumption of lignocellulosic biomass appears an effective approach to save natural resources, global food production, and to avoid the environment from continual deterioration [5]. Nevertheless, the complexity and recalcitrant nature of lignocellulosic biomass caused a huge challenge for its efficient consumption and intensified the inevitability to develop highly selective and promising bio-catalytic systems and green reaction bioprocesses. With increasing consciousness and research experience, any product competing with the food supply, or interfering with the environment will be evaded in the future. In this respect, the exploitation of lignocellulosic waste biomass is an ideal option and thus strappingly advocated. This chapter discussed a green and sustainable approach to bio-transform lignocellulosic biomass into high-value entities by ligninolytic enzymes.

2 Lignocellulosic Biomass Resource and Compositional Analysis

At present, lignocelluloses are generally considered the most promising substrates for growing microorganisms as they related to low cost and relatively abundant availability. Figure 2 illustrates several requisite features that justify the potentialities of lignocellulosic biomass as a valuable source. Lignocellulose is the principal constituent in agricultural residues and a rigid structural complex in plants. Lignin (15–30%), hemicellulose (25–35%), and cellulose (25–50%) are the three essential organizational constituents of woody plants and agro-wastes accompanied by minor quantities of other constituents like minerals, acetyl groups, and phenolic compounds as shown in Fig. 3 [6–8]. Lignocellulosic biomass on average has 50–80% (on dry basis) carbohydrates, which are polymers of pentose and hexose sugar units. The cellulose and hemicelluloses are polysaccharides, which could be bio-transformed into sugars and eventually to ethanol by fermentation [9]. Cellulose is a polysaccharide that consists of several hundred to tens of thousands of D-glucose monomers connected via β-(1,4)-glycosidic linkages with amorphous and crystal-like structure. It is a water-insoluble, non-branched, and the most abundant naturally

Fig. 2 Several requisite features that justify the potentialities of lignocellulosic biomass as a valuable source

occurring biopolymer on earth [10]. The individual chains of cellulose polymer are bundled together generating the independent cellulose fibrils, which are feebly joined through van der Waals forces and hydrogen bonding. Hemicellulose is a multifarious heterogeneous polymeric material composed of various monosaccharide units such as hexoses, pentoses, and sugar acids. These polysaccharides are vulnerable to hydrolysis because of the low molecular weight, amorphous, and branched structure with short adjacent chains [11]. After cellulose, lignin is the second most plenteous bio-renewable polymer with a natural occurrence on earth. From a chemical point of view, it is a complex three-dimensional structure of phenylpropane inter-units, which are extremely resistant to microbial attack, and decreases its biodegradability. It is a bulky polymer composite of non-carbohydrate polyphenolics, i.e., phenylpropane and methoxy groups, which make it difficult to break. Lignin makes approximately 20–30% of the dry-basis weight of wood; this shows that it is the most copious organic substance present on the earth [12]. Lignin is linked with hemicelluloses and cellulose and form physical seals around these two components preventing the enzymes and solutions to penetrate [13]. The weakening

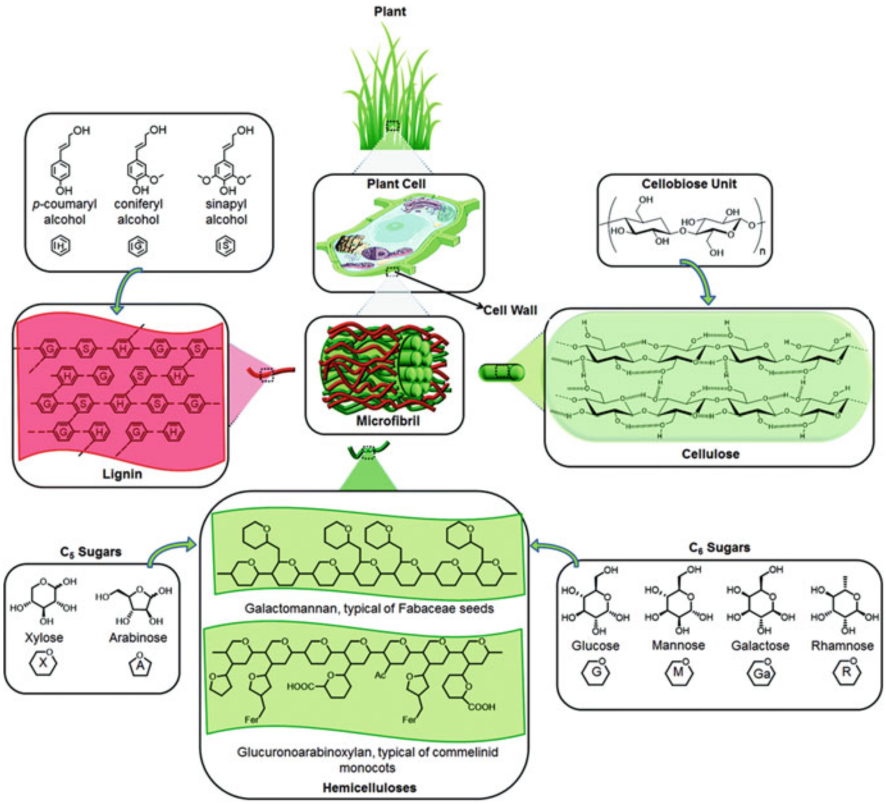

Fig. 3 The main components and structure of lignocellulose (adopted with permission from [6])

of the recalcitrant nature of renewable lignocellulosic biomass is a major obstacle for their bioconversion into useful and worthwhile products. Therefore, pretreatment is a mandatory step to modify the structural organization of lignocellulosic biomass, which enables enzymes accessibility to cellulose polymer and convert it into fermentable sugars [14]. Ligninolytic pretreatment seems a potential approach to hasten its bioconversion is highly important to harness the lignocellulosic biomasses entirely.

Despite numerous palpable advantages, the utilization of natural enzymes faces several practical difficulties like high-cost isolation and purification, activity inhibition, operational unsteadiness in organic media, and repeatability. Currently, enzyme immobilization is conceived as one of the most successful innovations in green biotechnology that could provide multiple benefits over the use of soluble enzymes such as recovery and separation, reusability of costly enzymes with less degradation rate, and durable shelf lives, and protection from proteolytic activity. Besides, enzymes in an immobilized form are more resilient to perturbed environmental conditions like pH, temperature, and acquaintance to toxic chemicals.

3 Gainful Harnessing of Lignocellulosic Waste

The rising energy crisis in the 1970s rekindled increasing interest in producing chemicals, biomaterials, and biofuels from biomass resources [15]. Recent years have witnessed a significant momentum in the effective utilization of lignocellulosic agro-waste because of the dismissing of fossil resources, economic crises, and environmental burden. Traditionally, the agricultural waste was usually burnt in crop fields besides its utilization as cooking fuel or cattle feed. This practice can still be observed in several countries. The burning of agricultural waste is uneconomical and imparts undesirable consequences on the ecosystem and health because of the generation of smoke, fumes, and gases. Some reports have demonstrated that the atmospheric smoke, in some countries, is partially due to the open crops burning in neighboring regions. Recently, the inclination in biomass exploitation has been shifting toward fossil fuel replacement with the harnessing of biomass resources. Current research impetus related to biomass utilization is focused predominantly on the production of chemicals and fuel additives, many of which possess similar properties as petroleum-based products. Valorization of biomass into fuels and chemicals is an active area of research European Union and the USA [5, 16]. In comparison to fossil carbon sources, biomass possesses an elevated O/H ratio and therefore necessitates fewer reaction steps to manufacture commodity chemicals following an easier synthetic method. Figures 4 and 5 show a simplified selective and non-selective transformation of lignocellulosic biomass, respectively.

4 Physico-chemical vs. Enzyme-Oriented Strategies

Despite an immense potential of biomass, the deconstruction and separation of primary lignocellulosic components (cellulose and lignin) is a major bottleneck step in the process of biomass bioconversion to fuels and specialty chemicals owing to their intricate chemical and rigid structural arrangement. Processing of lignocellulosic materials by conventional physico-chemical strategies received less attention because these are cumbersome, suffer from elevated production costs, and result in the generation of by-products similar to the petroleum-originated products that consequently may impart ecological, environmental, and health-related complications. In contrast to fossil carbon sources, it is easy to produce economic and eco-sustainable products from the processing of biomass resources. Hence, it is meaningful to design new, environmentally responsive, and sustainable approaches for the effective processing of complex lignocellulosic-rich agricultural biomasses. Ligninolytic enzymes assisted bio-delignification of lignocelluloses is of paramount interest and has renewed the researcher's attention due to associated drawbacks and limitations of existing pretreatments techniques.

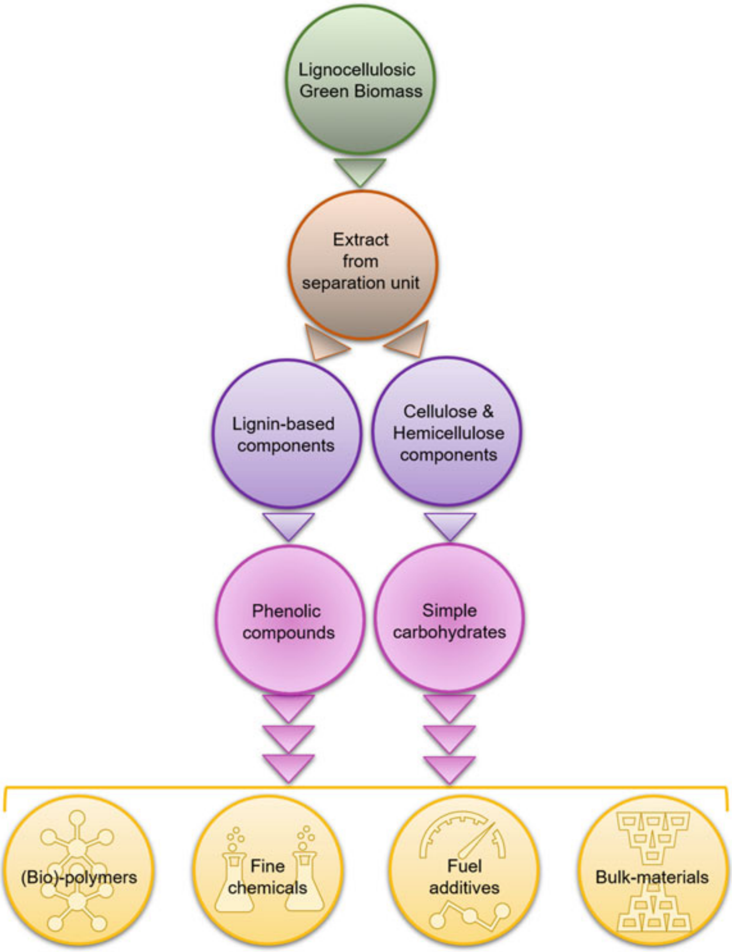

Fig. 4 A simplified selective (bio)-transformation of lignocellulosic biomass

5 White-Rot Fungi and Lignin-Modifying Enzymatic System

During the last few decades, a tremendous effort has been made on fungal biotechnology to produce a vast array of various commodities and high-value bioproducts such as liquid biofuel, chemicals, enzymes, secondary metabolites, etc. Among various wood-inhabiting microorganisms, white-rot basidiomycetous fungi are the prime microorganisms for depolymerization and deconstruction of wood lignocellulose with an incredible capability to secreting an irreplaceable set of non-specific extracellular oxidases and peroxidases including manganese peroxidase (MnP, E.C. 1.11.1.13), lignin peroxidase (LiP, E.C. 1.11.1.14), and laccase

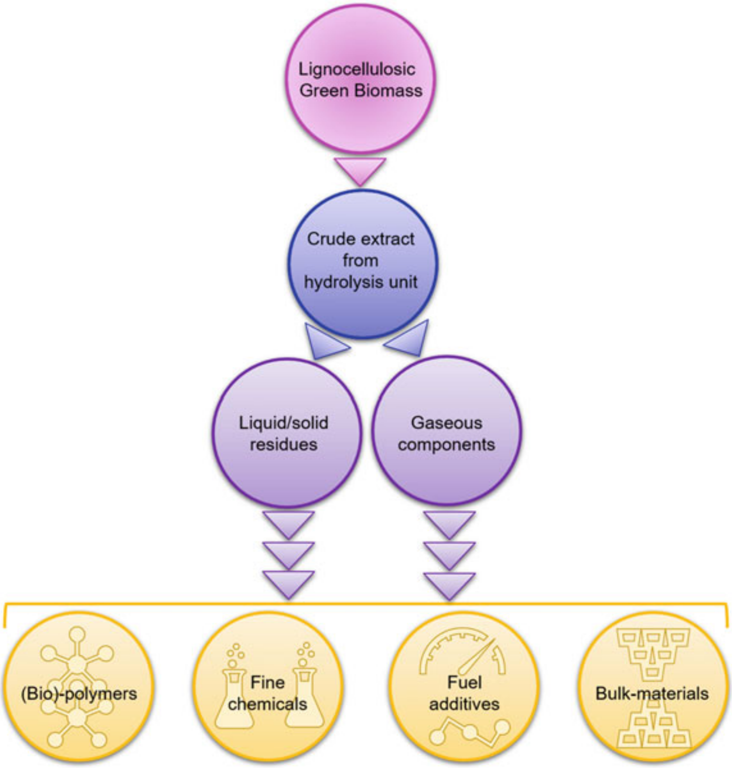

Fig. 5 A simplified non-selective (bio)-transformation of lignocellulosic biomass

(EC 1.10.3.2). Apart from this unique enzyme battery, many auxiliary enzymes such as glyoxal oxidase, aryl alcohol oxidase, versatile peroxidase, P-450 monooxygenase, and oxalate decarboxylase are also involved in lignin deconstruction. The broader substrate specificity allows this enzyme to catalyze depolymerize a wide variety of refractory xenobiotics and organ pollutants that possess structural similarity with the lignin molecule. These fungal oxidative enzymes are efficient biocatalysts, which play a major role, in not only lignin valorization but also are involved in the oxidizing a broad array of inorganic and organic contaminants such as dyes, PAHs, and chlorophenols [17, 18]. During their secondary metabolic phase, some wood-decaying fungal organisms secrete all three major kinds of lignin mineralizing enzymes, whereas only one or two enzymes are produced in the ligninolytic culture of other fungi [19]. Besides these three families of enzymes, some versatile peroxidases (VPs) with combined properties of MnP and LiP are also documented in the literature.

Lignin peroxidase discovered was the first time discovered in carbon- and nitrogen-deficient cultures *P. chrysosporium* culture in 1983 and seems a major component with the principal contribution in the ligninolytic system. It displays low pH optimum (3–4.5), high redox potential, and excellent potentiality to the catalytic decomposition of numerous compounds with aromatic structures, i.e., methoxybenzenes, and 3,4-dimethoxybenzyl [20]. MnP, a key heme-containing peroxidase associated with ligninolysis, was also first discovered in the extracellular fluid medium of *P. chrysosporium.* MnP belongs to the family of oxidoreductases and is so far one of the most common glycosylated, heme-containing lignin-mineralizing enzyme secreted by nearly all wood-decaying basidiomycetes organisms [21]. In an H_2O_2-mediated reaction, MnPs catalyzes the oxidative conversion of Mn^{2+} to reactive Mn^{3+} and thereby transform phenolic structures to phenoxy radicals [22]. However, the range of MnPs can be expanded to even non-phenolic molecules by incorporating some low molecular weight redox mediators. Furthermore, many other proteins synergistically functioning with MnPs have also amplified the roles of MnPs in fungal degradation. Laccases (EC 1.10.3.2) are N-glycosylated multicopper-containing oxidases that are versatile mineralizers of lignin and an array of several different recalcitrant compounds. In the past decade, ligninolytic enzymes find a prominent place in various industries such as in biomass debasement for biofuel synthesis, biobleaching, bio-pulping, pollutants mitigation, fruit juices stabilization, construction of biosensors, textile, beverage processing, animal feed, cosmetics, detergent manufacturing, and transformation of steroids and antibiotics.

6 Ligninolytic Enzymes Mediated Delignification

Enzyme delignification is referred to as the utilization of ligninolytic enzymes in crude, semi-purified, or purified form to catalyze lignin deconstruction. Among the ligninolytic enzymes, laccase is advocated as the most widely adopted biocatalyst for this purpose, followed by MnP and LiP. Nonetheless, some pretreatments have also implicated the consortium of two or three enzymes. In such a scenario, the synergetic collaboration among the ligninases led to the augmented debasement of lignocellulosic biomass. In contrast to chemical pretreatment, ligninolytic delignification of plant biomasses is particularly appealing because of several beneficial aspects such as mild processing conditions, pronounced biocatalytic potential, and high reaction specificity [23]. Moreover, the existence of small amounts of other additional enzymes/proteins along with redox mediators in WRF culture extracts may accelerate the lignin depolymerization by cleaving the linages involved in associating xylan chains and hence exposing the lignin structures [24]. When compared with the chemical pretreatments, the enzyme-based method generates no or negligible inhibitory compounds. It is documented that more than 35 different kinds of toxic by-products are produced during the processing of lignocellulosic biomass by acid or alkali treatments, which exhibit a significant effect on the suppression of enzyme availability and microbial growth [25]. Figure 6 illustrates the schematic representation of ligninolysis and lignin deconstruction potential of ligninolytic enzymes [23].

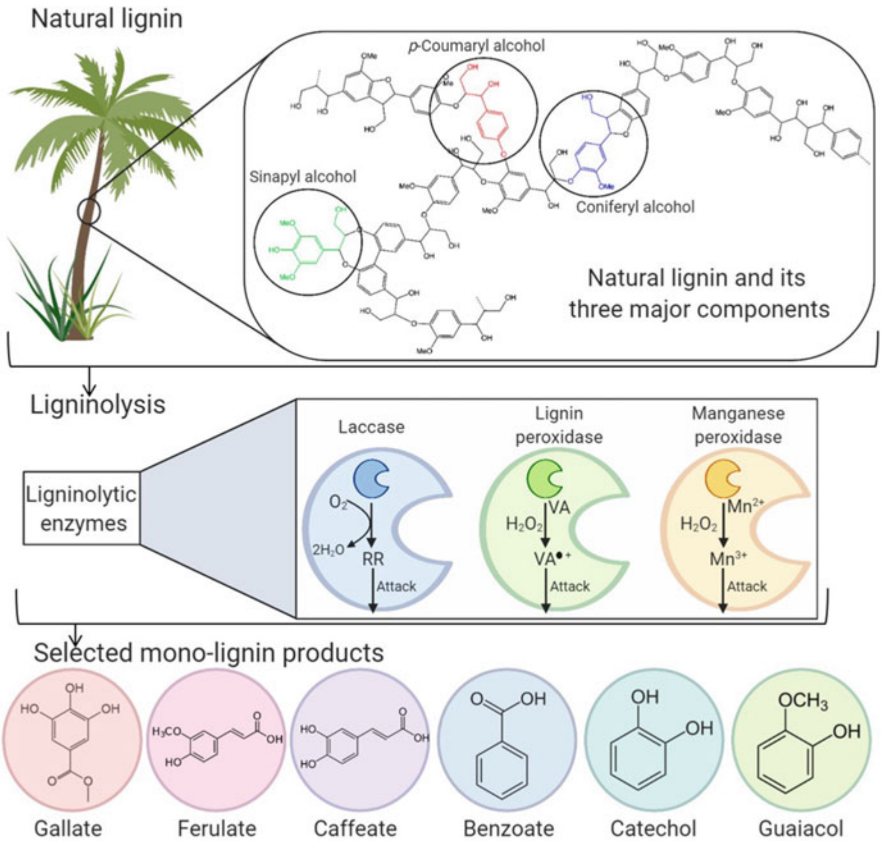

Fig. 6 Schematic representation of ligninolysis and lignin deconstruction potential of ligninolytic enzymes. The upper starting part represents the natural lignin with sinapyl alcohol, *p*-coumaryl alcohol, and coniferyl alcohol units. The middle part represents the unique action mechanisms of ligninolytic enzymes, i.e., laccase, lignin peroxidase, and manganese peroxidase as models. The last part shows various mono-lignin products that can be obtained after multiple steps involved in the ligninolysis process (adopted with permission from [23])

Though enzyme-assisted treatment processes result in an identical percentage of lignin removal as in microbial pretreatment. However, the enzyme exposure accomplishes the target delignification in less time duration of 24–96 h [26]. For example, ligninolytic enzyme extract from *G. lucidum* effectively catalyzed the lignin removal in different agro-industrial based lignocellulosic wastes. After 15 h exposure, it showed a high delignification rate of 57.3% in sorghum Stover [3, 4]. Likewise, ligninolytic consortium produced by *Pleurotus ostreatus* caused 33.6% depolymerization of lignin content in sugarcane bagasse after 48 h of contact time [26]. *P. sapidus* WC 529 derived ligninase extract catalyzed the removal of 51.08, 56.54, 57.4, and 65.81% lignin from sugarcane bagasse, rice straw, wheat straw, and corn cobs, respectively, after 48 h enzyme exposure to these substrates at 35°C

[27]. Despite the significant reduction in time duration, the enzymatic process cannot compare with the physicochemical methods with regard to costs and timespan [28].

Delignification of lignocelluloses by ligninases can be enhanced by modifying the catalytic traits of enzymes following protein-engineering approaches. Ligninolytic enzymes can be modified by using three kinds of engineering strategies including directed evolution, rational, and semi-rational protein engineering. In rational strategies, the sequence of the ligninolytic enzyme is reconstructed or modified at the molecular level by carrying out site-specific mutation. Using these approaches, the degradation ability of the laccase enzyme was remarkably increased toward non-phenolic molecules. It also presented enhanced aptitude to oxidizing large phenolic substances [29, 30]. In semi-rational approaches, saturation mutagenesis was applied for the alteration of functional "hot-spot" residues in the enzymes [31]. This strategy can lead to the production of the enzymes with three- to eightfold greater biocatalytic efficacies [32]. Directed evolution is an incredibly powerful enzyme engineering method that is widely exploited to optimize the catalytic properties of enzymes. This can be achieved by the combinatorial effect of the site-specific mutation, semi-random mutation, gene recombination, and high-throughput expression of the protein. Importantly, directed evolution does not depend on the prior structural information for enzyme engineering. It has been successfully employed to increase solvent tolerance and catalytic activities of numerous enzymes [31].

7 Conversion of Lignocellulosic Materials to Valuable Chemicals

Bioconversion of biomass is important to produce chemicals for sensitive or special application purposes like cosmetics, pharmaceuticals, and commodity products. The fundamental constituents of lignocellulosic biomass, including lignin, cellulose, and hemicellulose exhibit immense untapped potential to produce an array of various specialty chemicals [33, 34]. These polymers could be transformed into their monomeric forms. For example, hemicellulose and cellulose can be converted to sugars, while lignin is transformed into phenols [35, 36]. Additional modification of the resultant monomers enables their use in diverse applications. A wide variety of aromatic compounds can be synthesized by the effective utilization of lignin, whereas cellulose can be used to produce a list of specialty chemicals that possess various functional moieties like carboxylic acids, furans, and lactones [37, 38]. It is worth noting that the biomass processes implicate reducing the oxygen content as compared to classical chemical processes, where oxygen atoms were inserted or the O/C ratio was increased in fossil carbon sources [15]. The utilization of biomass can markedly decrease the number of chemical reaction steps and reagents used to make value-added compounds. In this way, this route can circumvent the discharge of environmental polluting agents such as acids, sulfur, metals, chlorine, and peroxides.

Increasing efforts have been directed on the bioconversion for biomass components into various industrial compounds and applications. Overall, it is not surprising to illustrate that biomass exhibit a great potential to swap the entire fossil fuel industry.

7.1 Formation of Sugars (C_5 and C_6) from Lignocellulosic Biomass

Sugar compounds are the first and important platform chemicals that can be achieved from the utilization of non-food lignocellulosic biomasses. The efficient formation of pentoses and hexoses with minimum energy consumption has profound significance in the bio-refinery because this step is critical to generate subsequent depolymerization products. The depolymerization of cellulose gives rise to glucose sugar, whereas both glucose and other six- (galactose, rhamnose, mannose,) and five (arabinose, xylose)-membered sugar monomers are formed as the degradation products of hemicellulose. Currently, concentrated acid (HCl)-driven hydrolysis constitutes the industrially proven and most potent method for lignocelluloses transformation into inexpensive fermentable sugars [39]. Nevertheless, this technology is mainly hindered due to the challenging recovery of acid recovery that is a major drawback of an acid hydrolysis reaction. Continuous research investigations are required to overcome the limitations of mineral acid separation and to improve the recovery and yield of target products.

7.2 Development of Sugar-Containing Polymers from Lignocellulosic Biomass

Lignocellulosic biomass can appear as the promising feedstock for the development of polymers by providing carbon five and carbon six monosaccharides and their derived compounds such as glucuronic acid, methyl glucoside, and glucaro-δ-lactone. The sugars and their modified derivatives either can serve as pendant moieties or can be integrated into the polymeric backbone. The polymer-incorporated derivatives are known as glycopolymers that garnered particular interest due to promising applications in emulating functional and structural properties of glycoproteins [40]. Hence, extensive efforts have been made to design glycopolymer with various architectures to develop novel gene/drug delivery systems. The contemporary investigation related to glycopolymeric drugs largely emphasis the treatment of patients with different diseases such as Alzheimer's disease, influenza, and HIV. Nonetheless, these studies are at their infancy level and thus necessitating continuous research to execute the clinical trials of the drugs [41, 42]. In addition to serving as a source of direct monosaccharides, lignocellulosic biomass-derived alditols (sorbitol, erythritol, xylitol, isosorbide, mannitol, arabinitol), aldonic acids

(2-ketogluconic acid, gluconic acid), and aldaric acids (α-ketoglutarate, xylaric acid, glucaric acid) can provide huge feedstock to synthesize numerous biopolymers. These linear carbohydrates-based biopolymers are non-toxic and biodegradable and possess improved hydrophilicity. Thus, they are useful in medical devices and food packaging related applications [6].

7.3 Synthesis of Commodity Chemicals from Lignocellulosic Biomass

A large number of platform chemicals or high-value materials such as 1,4-diacids (malic acid, fumaric acid, succinic acid), sorbitol, glycerol, aspartic acid, levulinic acid, glutamic acid, itaconic acid, 3-hydroxy propionic acid, glucaric acid, 3-hydroxybutyrolactone, xylitol/arabinitol, and 2,5-furan dicarboxylic acid can be potentially produced from lignocellulosic derived C_5 and C_6 sugars [6, 43]. Figure 7 shows a generalized scheme of lignocellulose-based integrated approach for the production of various biochemicals [44].

The US Department of Energy (DOE) recognized and listed all the high-value specialty chemicals that can be formed from lignocellulosic biomass and could be used as initial feedstocks to synthesize a wide range of bio-products through biochemical or bio-based processes [43]. Ethanol is among the most popular and well-known illustration of a bio-based fine chemical synthesized, around the world;

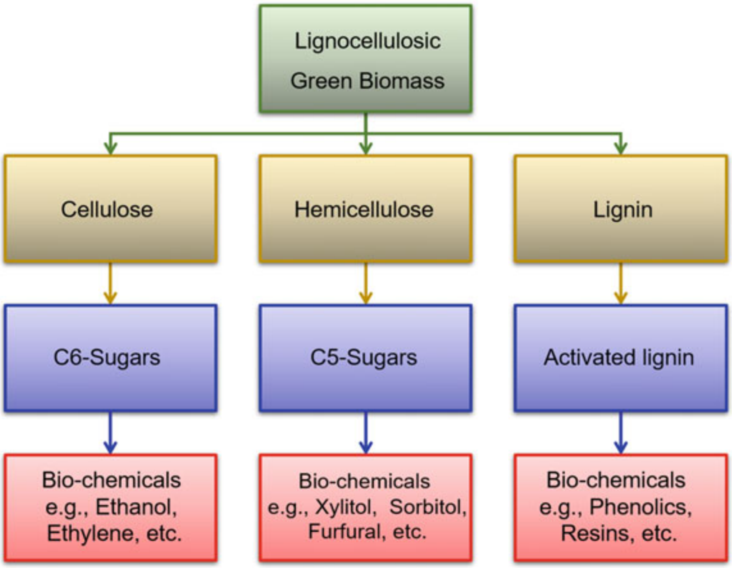

Fig. 7 A generalized scheme of lignocellulose-based integrated approach for the production of various biochemicals (adopted with permission from [44])

however, numerous other bio-based products have widespread commercial applications. The purified form of cellulose is presently employed to manufacture water-soluble gums, textile fibers, cellophane, wood-free paper, explosives, membranes, photographic film, and polymers that are widely used in varnishes and lacquers. Cellulose acetate is a major biodegradable cellulose derivative, which is utilized to form acetate rayon, photographic film, lacquers, and different thermoplastic products [45]. Enzymatic catalysis and fermentation processes are the principal routes for the production of specialty chemicals. A plethora of several different industrially relevant chemicals have already been produced for industrial level by the fermentation process, such as lysine, citric acid, and glutamic acid. Apart from these valuable chemicals, a list of commodity polymers can also be synthesized using bio-synthesized monomers by a combination of chemical and biological polymerization strategies, by either vigorously growing cells or isolated biocatalysts. Lactic acid synthesized by the fermentative processes can be chemically transformed into lactide, methyl lactate, and polylactate. The polylactate available commercially is a completely biodegradable substitution to polyethylene terephthalates [46]. Efficient processes for the synthesis of acrylic acids and methacrylic from bio-based hydroxy propionic and lactic acids are being developed. Genencor and DuPont established a lucrative and cost-efficient fermentation-based technology for the production of a key building block, 1,3-propanediol, which was not available from petro-based building blocks [47]. Succinic acid, a potential replacement to maleic anhydride has now been synthesized from butane using fermentative routes by various microbial strains [48]. In recent years, some chemical companies have commenced utilizing glycerol as an attractive and inexpensive starting feedstock material to produce value-added propylene glycol. Moreover, Solvay and Dow Chemical Company are utilizing the potential of glycerol for epichlorohydrin production, which might be useful in manufacturing epichlorohydrin elastomers and epoxy resins [49]. Owing to its cost-effectiveness, abundant availability, and high versatility, glycerol is speculated to emerge as a promising replacement to many frequently used toxic and polluting petrochemicals [50]. The contemporary scenario emphasis that the demand for commodity chemicals, food, energy, and materials will enormously increase in the coming years. It is critical to address the problems such as scarcity of raw feedstocks and deficiency of constant supply of raw material for the production of food, biofuels, energy, and materials [51].

7.4 Synthesis of Green Composites from Lignocellulosic Biomass

With the strategic technological innovations together with unique structural and excellent physicochemical properties, a special focus has been put toward the use of lignocellulosic biomass for designing novel functional composites with numerous applications. It is important to mention that biomass-derived composites are environmentally-friendly, biocompatible, and commercially feasible, thus representing a positive impact on industrial sectors and step toward global economic sustainability [3, 4]. To date, a vast number of designer bio-composites have been synthesized developed by using different polymers as building materials accompanied by various fabrication technologies [52]. Nevertheless, lignocellulosic biomass-based fibers provide a notable aptitude for easy surface functionalization via non-toxic approach with no health hazard risks [53]. Xie et al. [54] developed a new technique for the efficient exploitation of lignocellulosic biomass to synthesize highly bio-compatible thermoplastic composites of poly(propylene) and poly(styrene). Thermal characterization revealed that the as-synthesized thermoplastic wood composites presented enhanced thermal tolerance, improved melting characteristics, and were easily extruded into sheets or filaments. Recently, urea-reinforced calcium phosphate along with sugarcane bagasse and its derivatives (cellulose and lignin) were used to design novel composite materials and employed as a slow-release fertilizer. Notably, the urea release rate was observed slower in water in the case of coated fertilizer as compared with uncoated urea/HAP fertilizer [55]. Kulal et al. [56] engineered lignocellulose (lignin and cellulose)-based graphene reinforced hydrophobic spongy bio-composites for the adsorption of organic solvents and oil from wastewater. Sugarcane waste powder and graphene oxide were used to prepare cellulose-lignin modified graphene sponge by using a highly efficient and robust one-pot hydrothermal technique. The resultant biocomposite showed potential efficiency in the recovery and separation of oil from wastewater. Furthermore, it also exhibited marked sorbent ability to separate organic compounds in several repeated cycles. In addition, an array of lignocellulosic biomass-derived multifunctional composites have recently been prepared for their applications in diverse industrial domains such as environmental remediation, bio-medical, textiles, pharmaceutical, nutraceutical, drug delivery, and food packaging [57–60].

7.5 Bio-fuels from Lignocellulosic Biomass

Bio-fuels are a sustainable solution to substitute costly petroleum fuels and offer numerous economic and environmental benefits. Bio-ethanol is among the most broadly consumed bio-based fuel for transportation across the world. Synthesis of bioethanol from waste biomasses is an attractive way of reducing dependence on crude oil consumption and to alleviating ecological contamination. Production of fuel ethanol from bio-renewable lignocelluloses has immense potential to diminish petroleum dependency by reducing the emanations of greenhouse gas. Nevertheless, it is indispensable to obtain feedstocks from non-edible parts of crops to circumvent intense competition between bio-ethanol and food resources. The second-generation fuels produced from lignocellulosic waste materials such as straw, wood, and switchgrass are increasingly used because of no competition with food productions [61]. In recent years, lignocellulosic materials have, therefore, been a subject of investigation as a renewable resource for ethanol production in Sweden, Canada, and the USA [62]. Being less expensive and available in large amounts, lignocellulosic materials have great potential for bioethanol production than sucrose- (e.g., sugarcane) and starch (e.g., corn)-producing crops.

Bio-butanol is an advanced second-generation bio-fuel with lower volatility and greater energy density than that of ethanol. Butanol can be biosynthesized through fermentation technology by processing many domestic crops, including sugar beets, corn, as well as agricultural wastes and rapidly growing grasses [63]. The primary function of bio-butanol is its utilization in industrial products as a biocompatible solvent such as varnishes and lacquers. Owing to its compatibility with ethanol, it can also be employed to increase ethanol blending with gasoline [64]. In combination with fuel cell technology, butanol can be envisioned as a cleaner and safe substitute for batteries in the future. However, the fermentative production of bio-butanol mainly relies on the abundant and inexpensive openness of raw feedstock to swap the chemical process. Solventogenic Acetone Butanol Ethanol (ABE)-synthesizing Clostridia exhibit a well-known capacity to assimilate pentoses and hexoses that are obtained agricultural residues and from wood biomass following hydrolytic reactions [65]. There has been an increasing trend on butanol synthesis from agricultural-based lignocellulosic residues including barley straw, switchgrass, and corn stover. Therefore, ABE fermentation was re-examined by various strategies to reduce or eliminate the toxicity effects of butanol to the culture, and the culture was manipulated to realize high product yield and specificity by using lignocellulosic biomass [66, 67].

Similarly, all of the fermentable sugars found in cellulose and hemicellulose hydrolysates, including arabinose, glucose, galactose, mannose, xylose, and cellobiose can also be transformed into 2,3-butanediol, also known as butanediol or 2,3-butylene glycol. 2,3-butanediol is a highly important and industrially pertinent biochemical that possess application as a liquid fuel and biocompatible solvent. It also serves as a building block for synthesizing a range of resins and synthetic polymers [68]. Cheng et al. [69] utilized corncob hydrolysate as a lignocellulosic medium for the synthesis of butanediol in a fed-batch fermentation mode. After 60 h fermentation, butanediol titer reached 35.7 g/L with a corresponding yield and productivity of 0.5 g/g and 0.59 g/h/L reducing sugar. In conclusion, the effective deployment of lignocellulosic biomass as renewable feedstock integrated with advanced processing technologies ensures the socially acceptable and economically feasible production of biofuels to address the ever-increasing demand of the world.

In conclusion, given exponentially rising population growth and accelerated consumer demand, special research attention should be given on economic, ecological, environmental, and food considerations. In this regard, the utilization of agricultural waste might play a leading alternative to fossil resources. Massive research explicitly in chemical sciences and biotechnology is underway to promote structural modification of biomass, and its bioconversion into a variety of specialty chemicals and biomaterials. New or state-of-the-art bioconversion techniques adhering to the circular bio-economy based concept should be developed for effective utilization of agro-waste biomass or transformation to chemicals, materials, or biofuels adopting a multidisciplinary method. Timely and prioritized collaboration among various sectors like academia, agriculture, scientists, industries, research, and government can lead to quicker developments and improvements in the beneficial use of agricultural waste.

8 Current Challenges and Solutions

This chapter summarized the current progress on the synthesis of liquid fuels and many high-value chemicals from lignocellulosic waste biomass. Tremendous achievements have been made in the past decade in terms of efficient biocatalytic systems, multipurpose bioprocesses, and novel catalytic routes for the decomposition of lignocellulose, enabling the value-added utilization of bio-renewable biomass-based feedstocks a practicable reality. Notwithstanding incredible advancements in this arena, many insufficiencies need to be addressed for industrial exploitability.

1. A highly pure final product is necessary during the synthesis of commodity chemicals, but the complex nature and recalcitrance of lignocellulosic biomass and the poly-functionality of molecules produced from biomass result in the synthesis of a mixture of products, which in turn render the target compounds separation and purification very costly and energy-intensive.
2. Though the catalytic lignocellulose transformation offers considerable advantages of milder reaction conditions and higher selectivity over the thermochemical routes, the majority of the catalytic processes furnish low product yield in batch mode due to the non-soluble nature of lignocellulosic biomass, which makes these processes less appealing.
3. As an eco-friendly and natural bio-solvent, water is generally involved in the conversion of lignocellulose, but only a few catalysts are capable of tolerating the hydrothermal milieu for longer industrial lifespan practice.
4. The majority of the catalysts employed for biomass processing are developed only at a laboratory scale with elevated processing costs; therefore, the amplified preparation of catalysts without compromising their performance remains the biggest issue to solve.

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Waste-to-Energy: Suitable Approaches for Developing Countries

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Abstract A global estimate for the generation of solid waste is projected to be ~1.3 billion tonnes/year. This volume is supposed to further increase up to 2.2 billion tonnes/year by the mid of 2030. In this context, the effective treatment and disposal of solid waste around the globe is becoming of utmost importance. Moreover, sustainable management of solid waste is not only necessary to solve the disposal issues but also beneficial in terms of energy production. Developed countries have already adopted technologies for utilization of their solid waste in energy production, heat generation, conversion to biofuel, compost preparation and as the metal reservoir. In contrast, developing countries are still struggling to manage their solid waste as an alternative resource. Amongst all other ways of solid waste management, the waste-to-energy (WtoE) technology is better suitable for developing countries in terms of building up their energy resources. In this chapter, the status of solid waste in the developing nations along with their WtoE options is being discussed. Moreover, the cost estimation has marked as significant tool to identify suitable WtoE option for developing countries.

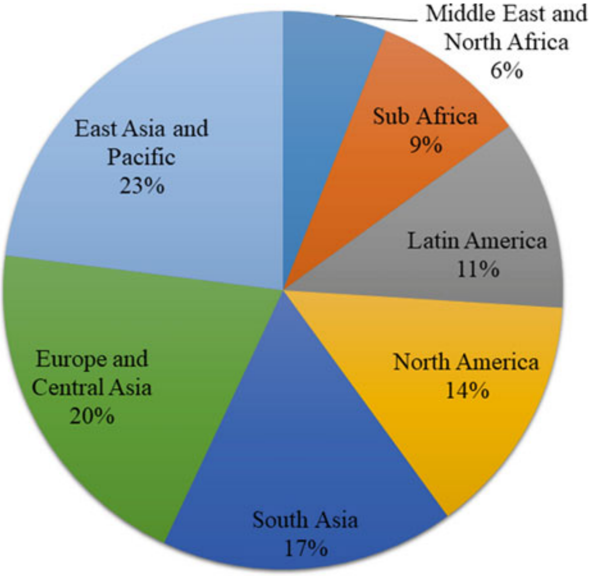
Keywords Cost estimation, Solid waste, Sustainable management, Technology, Waste-to-energy

1 Introduction

Developing nations are fastly embracing upgraded technology and a sophisticated lifestyle to ease humans' life and lead by incessant urbanization and industrialization. To support this upgradation, huge amount of energy and materials are needed which primarily comes from limited natural resources [1]; however, due to excessive demand, these resources are depleting and posing threat to sustainable development.

Rapid urbanization shows economic development but exhibits significant contribution in generation of solid waste [2]. Additionally, waste generation pattern of developed and developing nations mainly depends on the social, economical and environmental conditions of the country. It has been found that high-income-level individuals produce maximum waste as compared to low income due to advancement in technology. It upgrades the countries' economies from low to middle and high income and responsible for increase in per capita waste generation [3]. The global scenario of waste generation is shown in Fig. 1. In a nutshell, population growth, urbanization and technological development are prime factors for the waste generation [4, 5].

Fig. 1 Global scenario of waste generation



The major contributors to waste are municipal solid waste (MSW), agriculture waste, commercial and industrial waste, biomedical waste, and hazardous waste [6, 7]. The study done by Tyagi et al. [8] stated that globally MSW generation is increasing tremendously and estimated to be >2,200 million tonnes/year by 2025. Further, these wastes are collected, stored, and disposed off, but poor collection and inadequate transportation are responsible for hips of solid waste on the outskirts of the urban and rural areas [9–11]. Improper solid waste management, i.e. uncontrolled incineration, open dumping and unsanitary landfill, contributes several environmental issues such as global warming, ecosystem damage, abiotic resource and ozone depletion. Besides, it is reported that ~11% of methane gas is produced due to open dumping or unsanitary landfilling [12, 13]; whereas, 1 kg of MSW generated from refinery is able to release 1,250 g CO_{2eq} of greenhouse gases [14]. Improper waste management not only causes environmental burden but also shows negative social and economic impacts. Therefore, formal management of solid waste is recommended which includes formal collection, segregation, transportation, recycling and recovery options to convert the waste into energy/resource. Unfortunately, it has been observed that these treatment methodologies are not effectively implemented in developing nations and experiencing huge environmental and economical losses due to the release of toxic and greenhouse (methane) gases.

In connection to this, some of the developing nations including China, India, Malaysia and Vietnam infer the challenges associated with municipal solid waste management (MSWM) and implemented waste treatment methods like gasification, pyrolysis, RDF, biogasification (biomethanation) and landfilling that have the potential to utilize waste and convert it into energy shown in the Fig. 2 [15, 16]. The

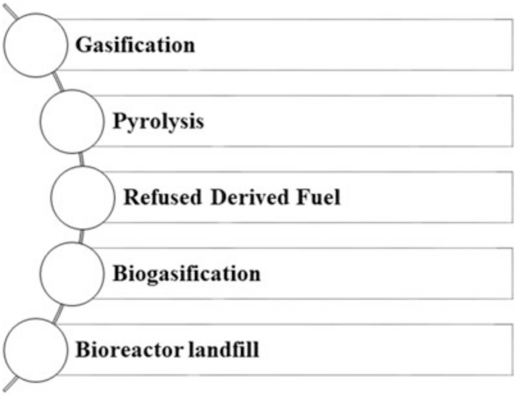


Fig. 2 Waste-to-energy processes

waste-to-energy (WtoE) option included in the solid waste management is remedy to fulfil their energy and material demands. The organic and inorganic fraction included in solid waste first segregated and further the organic waste can be either used as compost after aerobic degradation or generate notable amount of biogas through the anaerobic biomethanation process [17]. Conversely, inorganic non-recyclable papers, cardboards, plastics and combustible wastes would either undergo thermal treatment like incineration, pyrolysis and gasification process or used as refuse-derived fuel (RDF) in boilers as a source of energy [16].

The present chapter discusses the waste scenario and the status of solid waste in developing nations. It also identifies the mechanisms of WtoE recovery in plants along with its limitations. Further, WtoE processes for four developing nations based on population density, i.e. China, India, Malaysia and Vietnam, are discussed. However, economy is the key factor for developing nations; hence cost estimation of WtoE plants needs to be considered for sustainable solid waste management.

2 Status of MSWM in Developing Nation

Management of MSW is a universal issue for moving every single person in the world. It greatly affects health, productivity and cleanliness of communities, if not managed properly; therefore safe disposal and treatment options should be incorporated properly. However, the implementation of solid waste management rules in developing countries is a crucial issue where management of MSW for urban and rural areas is different which is primarily dominated by the informal sector. In urban area waste collection and segregation are often done at different places in line with socio-economic, commercial-residential and industrial space [18, 19]. Nevertheless, rural and suburb areas do not have proper collection and disposal facilities. Besides, open dumping of solid waste is a common practice that causes threat to the sustainable development. Kumar et al. [11] have reported that open dumping is preferred due to apathy of municipal authorities, lack of community involvement, dearth of technical knowledge and inadequate money resources. It evidence ambiguities associated with MSWM; owing to this, several factors/barriers based on policies, social elements, financial and technical aspects are identified by Zurbrugg et al. [20], which underpinned informal sectors. Keeping in view, five common categories of barriers with their possible intervention are classified in Table 1 by Aparcana [21] to make the formal solid waste management sustainable in the long term.

To overcome this issue, developing nations have prepared multiple laws, policies for MSW disposal by keeping in view towards air, water and soil pollution along with health aspects of waste workers [19, 22, 23]. Furthermore, waste-to-energy guidelines are formulated to utilize different treatment schemes to convert MSW into energy [24–26]. It reveals that the MSW has huge potential if managed properly; therefore, much emphasis is on the collection of MSW from waste generation site [27, 28]. Ministry of urban development [29] in India has analysed the significance of the waste collection and increased the collection from 68% to 70–90% in major cities and 50% in rural sites for the treatment of the solid wastes. A major portion of the MSW contains organic (~60%) waste which has more potential to utilize it as a resource. Henceforth, aerobic and anaerobic biological treatment are recommended to deal with such kind of biodegradable waste which produces compost and biogas energy [7, 30]; whereas other types of wastes undergo landfill disposal.

3 Different Mechanism for Waste-to-Energy (WtoE) Conversion

Energy is the prime need of every nation, whereas waste serves as an opportunity to fulfil the energy demand through WtoE plants and serving as a resource of alternative fuel. Two mechanisms mainly thermal and biological are prevailed in the WtoE conversion [16, 31]. In the beginning, thermochemical methodology was adopted where biomass along with waste was burned to convert into energy; further with time, technologies were upgraded following the same mechanisms. Incineration, gasification, pyrolysis and RDF are the thermal technologies used to convert combustible waste into energy which also reduces the mass and volume of waste [1]. On the other hand, composting, biogasification and bioreactor landfill are the biological technologies to convert organic waste into energy, and types of WtoE technologies are shown in Fig. 3.

3.1 Gasification

Gasification is a very effective economical thermal process to convert waste into energy. Unlike conventional WtoE plants, gasification plant also uses waste as

Table 1 Common barriers to formalization and enabling measures for their removal (reproduced with permission from [21])

Categories	Barriers to formalization	Common recommended measures/interventions towards formalization
Policy and legal arrangements	Absence of adequate policies, clear legislation and strong regulations; waste legislation is fragmented into different laws, causing the lack of technologies, cost-effective aspects, enforcement mechanisms	Favourable national policies, regulations, political support nationally and locally, law enforcement; eco-efficiency: reductions in packaging, producer responsibility
Economic/financial instruments	Budgetary constraints, lack of economic support from the central government, weak strategies for raising funds from residents, inappropriate economic and financial planning	Microcredit initiatives, expansion of capital basis, financial incentives; entering of new service roles and niches; increase in bargaining power; appropriate payment schemes reducing economic uncertainty
Institutional/organizational arrangements	Lack of organizational capacities and managerial skills (leadership) of local authorities; perception that environment protection conflicts with national economic goals; sharing of similar roles and responsibilities, confusion regarding their delineation and distribution. Cross-agency collaboration rare	Organization of the informal sector, formation of cooperatives/micro- and small enterprises, cooperatives and associations; collaboration and partnerships amongst stakeholders of waste management systems, good relationship with the receiving industries and the formal MSWM system, national initiative–participatory approach
Social acceptance and welfare	Lack of educational and awareness campaigns regarding the importance of a proper waste management system and the role of citizens as waste generators; social rejection: working as a recycler is associated with low status and considered undesirable. There is a general disrespect for the work, producing low working ethics of workers and poor quality of their work	Information and education campaigns, training and empowerment of the various stakeholders; acknowledgment; acceptance by authorities of benefits that informal recycling can provide, inclusion of informal recycling into waste management, political and legal recognition, acceptance by the public; change to policy makers' perceptions about informal recycling activities; occupational safety practices, social and environmental health, improvement of working conditions and equipment
Technical/operational	Unavailability of technology and/or human work force, lack of skilled personnel with technical expertise on waste management, lack of country appropriated technology, deficient waste equipment and structures (waste transfer	Assessing and documenting existing MSWM system, accurate data collection regarding waste and recycling markets, data quality; pilot projects; technical/operational requirements: access to

(continued)

Table 1 (continued)

Categories	Barriers to formalization	Common recommended measures/interventions towards formalization
	stations, storages, old waste vehicles), poor roads, unreliable data and lack of information- sharing between stakeholders	adequate sorting and storage spaces, infrastructure, topographical considerations, improved quality of secondary raw materials; appropriate technology, economic and technical assistance, technical capacity-building for waste workers

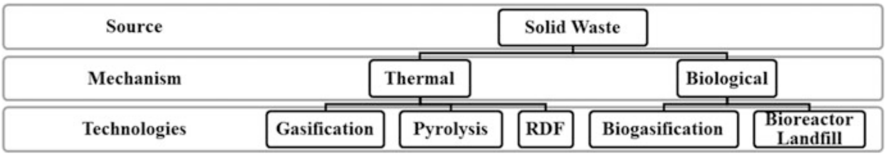


Fig. 3 Types of waste-to-energy technologies

feedstock to the reactor where the waste fraction is burned at higher temperature around 550–900°C with partial gasifying agents (viz. steam, air, oxygen or steam-air). The gasification process is shown in Fig. 4 [32]. It results in the generation of valuable syngas gases like H_2, H_2O (steam) and CH_4 [33]. All of these gases can be separated and utilized as a fuel to generate energy for various purposes such as reverse steam reforming process to obtain methane, Fischer-Tropsch (FT) reaction to produce liquid fuels, and methanol synthesis to provide methanol [34, 35].

Moreover, pre-processing of waste such as segregation of non-combustible metal waste and an inert material (sand and stones) is needed to prevent gasifier units with any kind of mechanical damage. Further, waste is shredded and ready to feed into the gasifier where various types of reactor such as fixed bed gasifier, fluidized bed gasifier, molten salt gasifier and plasma gasifier are used depending upon the need for capacity, expected energy outcomes, temperature range, need of oxidants and the economy of the system [36]. However, during the gasification process, pollutants like PM, H_2S, HCl, NH_3, HCN, CO, CO_2, tar and alkali matter emit into the atmosphere and are responsible for the air pollution [33]. The process also produces ash or char that is in molten form, but it can be utilized in cement manufacturing plants. The properties of ash depend on the various types of inlet feed (waste) like plastics, biomass, thermocol, etc., and it has to be treated before landfilling.

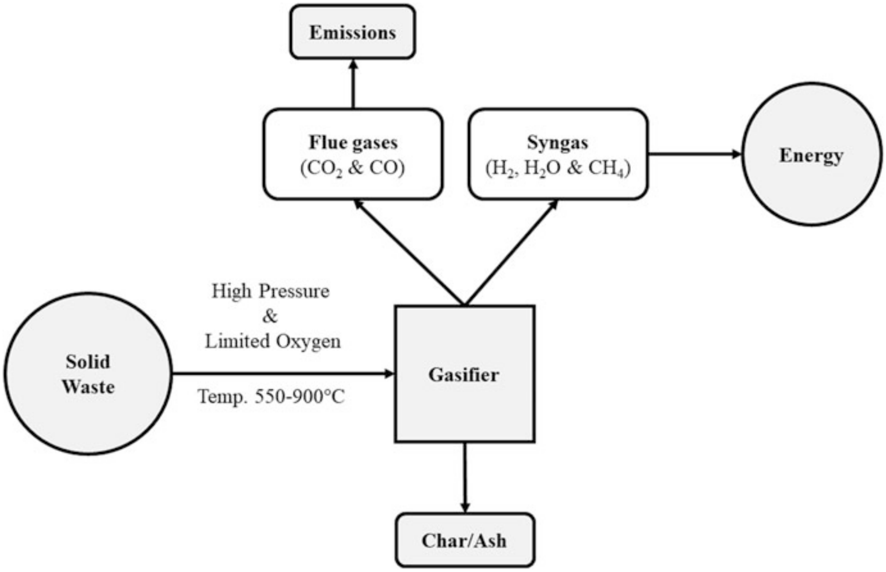


Fig. 4 The gasification process

3.2 *Pyrolysis*

Pyrolysis is defined as the thermal decomposition (500–600°C) of organic wastes under the inert oxygen-deficient environment, where the word ‘pyro’ means fire and ‘lysis’ states disintegration into integral parts [37]. The objective of pyrolysis is to yield high-value energy products char, bio-oil and gases that gradually replace non-renewable fossil fuels [14]. Pyrolysis is considered a good alternative due to the production of clean energy as compared to the incineration plants [38]. Different types of pyrolysis reactors such as fixed bed reactor, rotary kiln reactor, fluidized bed reactor, tubular reactor and fast catalytic reactor are developed based on the inlet feeds. Different types of organic matter can be used to charge the reactors such as wood, organic waste (soft and hard biomass) residues from agriculture, forestry and pulp industry as inlet feed in the pyrolysis process [39, 40]. A process flow diagram for the pyrolysis process is shown in Fig. 5. This process also emits pollutants, but in comparison to incineration, it minimizes corrosion and emissions by retaining alkali and heavy metals, sulphur and chlorine inside the process remainders. It also reduces NO_x formation because of the lower temperatures.

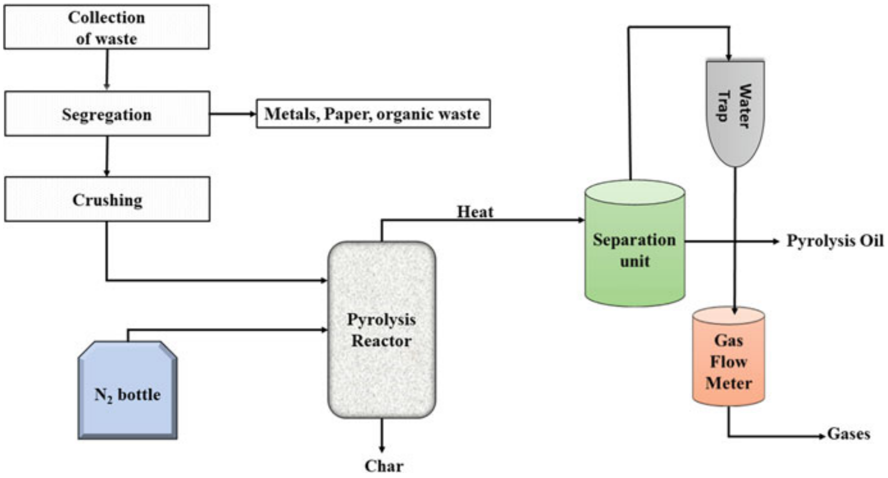


Fig. 5 A schematic diagram for pyrolysis process

3.3 *Refuse-Derived Fuel*

Refuse-derived fuel (RDF) is the high calorific non-recyclable combustible fraction of processed MSW, which is employed either as a fuel for steam and electricity generation or as an alternative fuel in industrial furnaces and boilers. The Ministry of Urban Development has given guidelines for the composition of RDF which mainly includes combustible inert materials than those present in the parent mixed MSW due to proper sorting and segregation. Accordingly, specific industrial wastes such as sewage sludge, plastics, textile waste, spent oil, scrap papers, wood cuttings and agriculture waste would be used along with RDF in the WtoE plants to increase the calorific value of the feed. Most of the developing nations include a mixture of wet and dry combustibles waste like paper, plastics, cloths, food, garden trimmings, etc. in RDF and are not directly suitable to use as raw feed for any WtoE processes. Thus, RDF process includes segregation of the non-combustible wastes like glass, stones, sand, metals, etc. and further crushing the remaining dried waste to increase its surface area. Lastly, the waste either can be directly used as feed into the boilers or can be converted into pellets if required. Synthesis of RDF from waste is shown in Fig. 6.

Moreover, RDF is classified on the basis of the state material, composition, size and shape if pelletized. Physical properties of ideal RDF should have particle size of 10–300 mm and bulk density of 120–300 kg/m^3 with 10–30% moisture contents. The optimum calorific value should be >2,000 kcal/kg and 75–80% of volatile matter followed by 10–20% ash content [41, 42]. The lower moisture content and higher calorific values are desirable for an economical and profitable WtoE RDF plant [43], but sulphur, chlorine and heavy metals are not desirable for the RDF [42]. RDF acts as sustainable fuel which reduces the environmental burden and helps

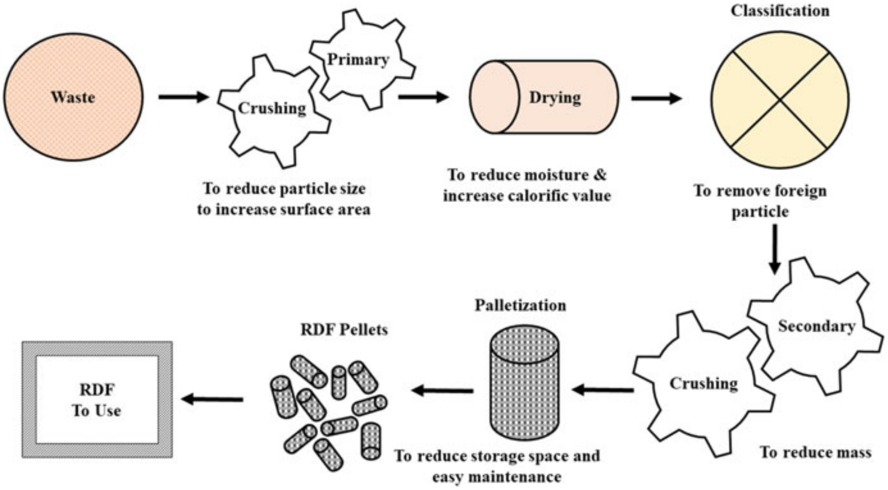


Fig. 6 Preparation of RDF from waste (http://cdwaste.co.uk/refuse-derived-fuel-rdf/. Accessed 1 May 2020)

in conservation of natural resources like coal, petroleum and natural gas. The RDF contains various types of waste including plastics that releases particulate matter, dioxins and furans gases during the combustion (temperature below 850°C); however, this issue can be minimized by increasing the temperature above 850°C and then no harmful and toxic gases would release. Therefore, RDF is preferred for co-processing in cement plants, steel industry and power generation as they operate at higher temperatures [32].

3.4 Biogasification

Biogasification refers to the generation of renewable biogas through anaerobic digestion of organic waste. This is the most efficient, economic, viable and clean technology and widely adopted in the developing nations. Generally, food waste is used as a substrate in anaerobic digestion (AD) along with organic fraction of MSW, garden waste, crop residue and sewage sludge, which is used as feed in a closed reactor. Li et al. [44] have reported that temperature and pH are the two significant parameters for the anaerobic digestion. Moreover, based on the total solid concentration in the substrate, AD is classified into three categories: (a) wet AD functioned with $TS < 15\%$, (b) dry AD functioned with $TS < 25\%$ and (c) solid state AD functioned with TS up to 40% [45].

The microbial activities prevailed to degrade organic waste in the biogasification plant and have four anaerobic digestion stages, namely, hydrolysis, acidogenesis, acetogenesis and methanogenesis. During hydrolysis process organic waste breaks

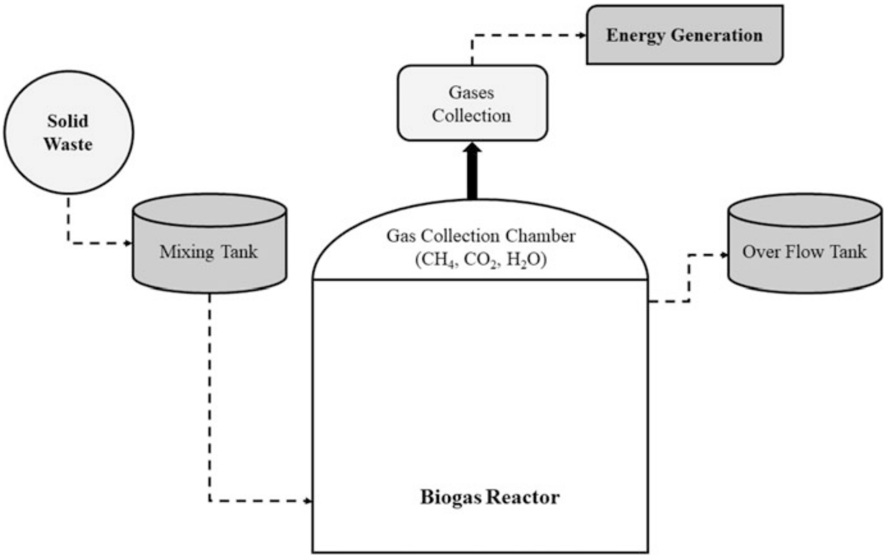


Fig. 7 A schematic diagram of biogasification plant

into protein, carbohydrates and lipids; further acidogenesis process converts them into sugars, amino acids and monosaccharides which later form volatile fatty acids and ammonia in acetogenesis stage. In the last stage methanogenesis bacteria forms methane gas that can be used as a source of energy directly for cooking purposes, running vehicles or indirectly used to generate electricity. The remaining slurry after the biogasification process can be used as manure for soil conditioning in agricultural activities. The biogasification plant is illustrated in Fig. 7.

Biogasification plants are feasible in tropical environment, but it becomes difficult to operate under temperate environment where temperature is low due to interferences in microbial kinetics and necessitates skilled person to maintain the temperature in a closed reactor.

3.5 Bioreactor Landfill

Landfilling is considered to be the least preferred option in waste management hierarchy, as it adversely affects the environment also occupying large land areas and has economic losses. As discussed previously, a major portion of MSW in developing nations is composed of organic waste that has the potential to generate biogas and can be used as a source of renewable energy. Bioreactor landfills are the upgraded version of the engineered landfills which includes recirculation of leachate to increase the microbial degradation rate and collection bags for storing the landfill gas (LFG) as presented in Fig. 8 [7].

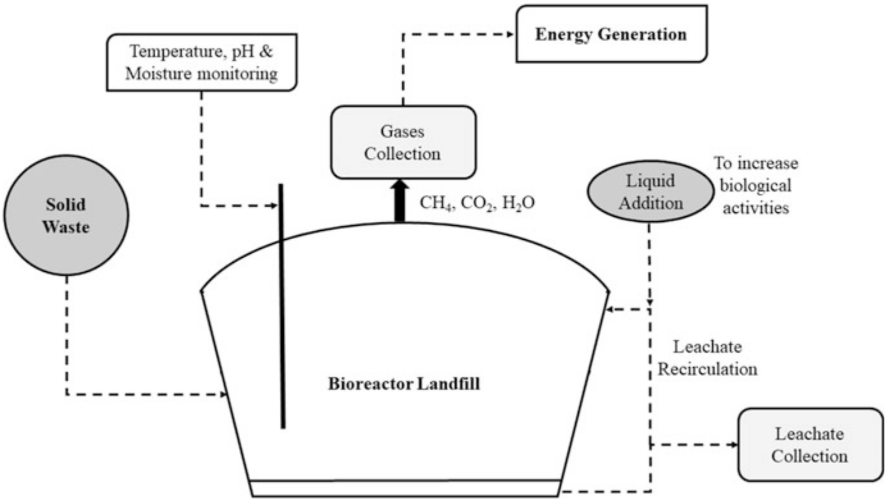


Fig. 8 Schematic view of a bioreactor landfill

USEPA [46] has classified the bioreactor landfills under three categories, namely, aerobic, anaerobic and hybrid based on the nature of waste and the geographical location of the place for installation. However, several parameters like moisture content, pH, temperature, redox conditions, biochemical kinetics and gas emissions should be monitored on a regular basis to have maximum production of LFG [47]. Due to fast degradation of organic waste, huge amount of leachate generate, which can further recirculate in bioreactor landfill to control the rate of biological activities and provide natural conditions to microbes. It also minimizes the wastewater treatment cost. A schematic diagram for a bioreactor landfill is epitomized in Fig. 8. Further, biomining is done when landfill completes its self-acquiring life. The materials obtained from biomining can be treated and further used as urban resource [48].

Bioreactor landfilling is an evolving technology for most of the developing nations but primarily practised in the developed nations. However, it can be a boon for developing nations if it plans and design to replace or modify the conventional landfills, though high initial investment and skilled operational teams are needed to maintain the bioreactor landfill. As it involves biological activities, it does not have a wider range of applications in colder regions, and odour control becomes a challenging task.

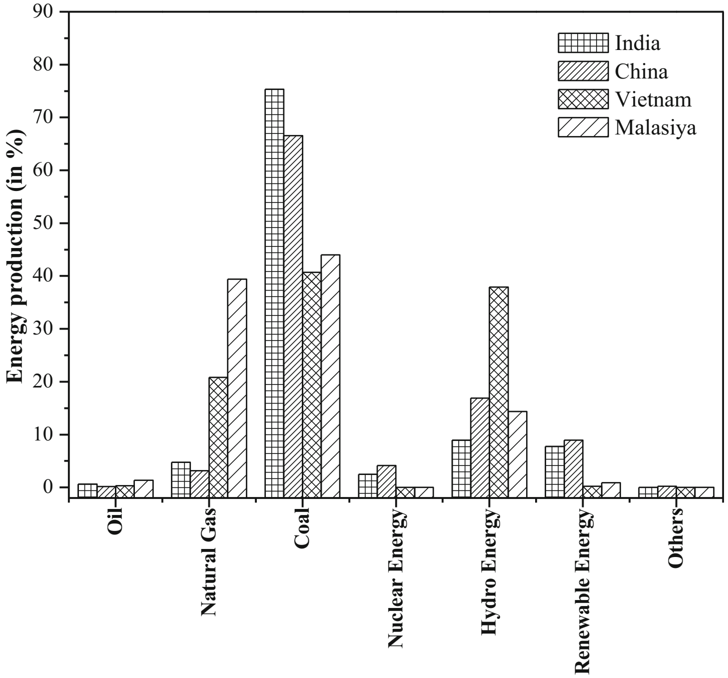


Fig. 9 Energy generation scenario in developing nations [51]

4 Waste-to-Energy Process in Developing Nations

Developing nations are struggling to meet the energy demand from conventional and nonconventional energy sources as consumptions are more as compared to energy production [49]. In this context, WtoE scenarios for four developing nations, viz. China, India, Vietnam and Malaysia, are discussed based on the population density. India and China, most populated developing nations, are primarily dependent on conventional energy resources though both the nations are blessed with a favourable geographical location that can generate notable amount of renewable energy [1, 50]. While less populated developing nations like Malaysia and Vietnam are struggling to meet energy demand through various resources and mainly dependent on non-renewable energy sources. Energy sources of China, India, Vietnam and Malaysia are represented in Fig. 9.

4.1 China

China generates maximum amount of energy from the solid waste as compared to any other developing nations. It has 300 WtoE plants in operation, and the capacity of the plant is increasing 26% annually over the past 5 years [52]. Moreover, Chinese government has set an ambitious target of utilizing one third garbage in waste-to-energy plants by 2030. To meet the target, China has constructed the world's largest WtoE plant in Shenzhen, Guangdong [53]. This city generates about 15,000 t of waste per day of which 5,000 t are processed every day with an annual increase of 7%. The plant is scheduled for operation in 2020 and estimated to be driven by 5,600 t of waste in a day and produce ~168 MW of energy. The 99% of the energy generated from plant would be utilized for producing electricity and heating, 95% of the water would recover and 90% of the metal (e.g. aluminium, copper) recovery can be done from waste. Moreover, 90–95% clean flue gas would emit from the plant. In addition to this, solar panels were installed on the rooftop of the plant to produce solar energy. This WtoE plants is one kind of integrated plant to produce energy from waste as well as solar.

4.2 India

India, the second largest populated country in the world, generates ~55 million tonnes of MSW and 38 billion litres of sewage in urban areas and expected to double in 2030, which indicates huge environmental and economic impacts. The largest WtoE plant is installed in Narela-Bawana, Delhi, and can process ~2,500 metric tonnes of waste every day and generate 24 MW of energy (https://www.indiatoday.in/mail-today/story/wte-plant-nmcd-narela-bawana-plant-haryana-border-waste-to-energy-351732-2016-11-13. Accessed 1 May 2020). Prior to this, Ghazipur WtoE plant was generating 12 MW of energy. The WtoE plant requires minimum man power, has low emissions, and has minimum operational cost.

4.3 Vietnam

Vietnam targets to reduce the import of coal and oil to curtail 5% greenhouse gas emission by 2020 and 25% by 2030. To achieve this target, the government is promoting promising renewable energy technologies. Therefore, WtoE plants along with solar and wind farm are installed in the country. Vietnam generates ~70,000 t of waste per day, where 76% of waste dumped into the landfill. However, there are few WtoE plants, and the largest plant has capacity of up to 2.4 MW. The first industrial WtoE plant is installed in Hanoi which can process 75 t of waste per day and has 1.93 MW power generation capacity [54].

4.4 Malaysia

Malaysia's first WtoE plant was scheduled to operate in 2019 in Ladang Tanah Merah, Negeri Sembilan [55]. The ministry is expecting to build SMART (Solid Waste Modular Advanced Recovery and Treatment) WtoE plant to generate green energy. The facility converts waste into electricity based on sustainable and integrated waste management options. The 600 t of segregated waste would be processed in this plant with a capacity to generate 20–25 MW of electricity and able to power about 25,000 households. This plant has waste storage and segregation facility, material recovery facility and a fully anaerobic bioreactor system with a capacity to process 1,000 t of waste in a day. Moreover, the plant is engineered to be robust and would meet the high-pitched norms of the Department of Environment (DoE), creating the most environment-friendly facility in the world.

5 Cost Approximation for Conversion of Waste to Energy

Collection, treatment and disposal of solid waste draw significant attention due to negative environmental and economic impacts, and it emanates because of inadequate waste managing system. However, WtoE is an integral part of urban mining which minimizes the environmental impact but have significant installation and operational cost [56]. Different treatment technologies such as incineration, RDF, anaerobic digestion (AD), landfill gas recovery and gasification are used to recover energy from MSW [57]. However, capital cost and operational and maintenance costs are significantly varying with technology and shown in Table 2.

It has been reported that the gasification process has the highest potential to recover energy from waste though it has highest capital and O&M cost. Amongst all energy recovery options, landfill gas (LFG) recovery and anaerobic digestion technologies are economical and feasible options. All technologies require segregation of waste either at source or before processing which also increases the operational cost and become uneconomical [56]. In developing countries, waste management plays a major role in municipal budgets, spending from 20 to 50% of their existing budget on solid waste management, in which a large portion 80–90% is used to collect and segregate the waste [31].

Table 2 Capital and O&M cost of waste-to-energy technologies [56, 57]

WtoE technologies	Capital cost (USD/TPA)	O&M cost (USD/TPA)
Incineration	155–250	85
RDF incineration	135	High as compared to incineration
Gasification	170–300	65–112
Anaerobic digestion	50	5–30
Landfill gas recovery	10	0.2–0.3

TPA tonne per annum

6 Conclusions

Waste-to-energy processes are boon to developing nation to fulfil the energy requirement. It utilizes solid waste as a raw feed and converts it as energy due to high calorific value. Therefore, formal management of solid waste is recommended but generally encountered with failures. Therefore, several barriers are identified and assessed that are responsible for informal waste management in developing nation. Based on the recommendation in support with informal collection, formal solid waste management legislation is drafted that includes WtoE technologies. Different thermochemical and biological treatment technologies are discussed that convert waste into energy. However, the economic and environmental costs of these technologies are higher and necessitate further research to minimize this issue.

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Biomass-Derived Triglyceride: A Source of Renewable Aviation Fuel and Biodiesel

Dipali P. Upare and Pravin P. Upare

Contents

Abstract Biomass-derived biofuels are receiving significant attention due to their huge potential to fulfill the world's energy demands. Significant utilization of nonrenewable fossil resources to fulfill the current fuel demand made negative impact on the environment. In this contest, biomass-derived biofuel can be a viable alternative to replace the non-eco-friendly fuel from conventional resources. The current topic is mainly focusing on the use of bio-based feedstock such as triglycerides from bio-based seed oil and animal fats for the production of biofuel. In addition, the catalytic conversion of triglyceride-related compounds into biofuel is summarized in this chapter.

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1 Introduction

Biofuel can be originated from renewable biomass resources. As per US energy information, most of the US biofuels come from vegetable oils and animal fats. At the current stage, biofuel production and their consumption have become an inherent part of regular life worldwide [1]. However, the production of biodiesel has been extensively reviewed over the past years [2]. Non-sustainable fossil resources are almost at the maturity stage, and they are moving toward their declinations, which are not only affecting the petroleum-based economy but also affecting the environments very badly [2, 3]. The use of biofuel contributes several advantages such as the reduction in greenhouse gas emissions, mitigation to the complete dependency on fossil resources, and development of forest and agricultural areas [1]. Biomass-derived carbon feedstock is the only current sustainable source of liquid fuel, which generates a very low amount of CO_2, and it can be further reduced by developing efficient biofuel production technologies [4]. The schematic representation of biomass to biofuel and biochemical conversion is presented in Fig. 1.

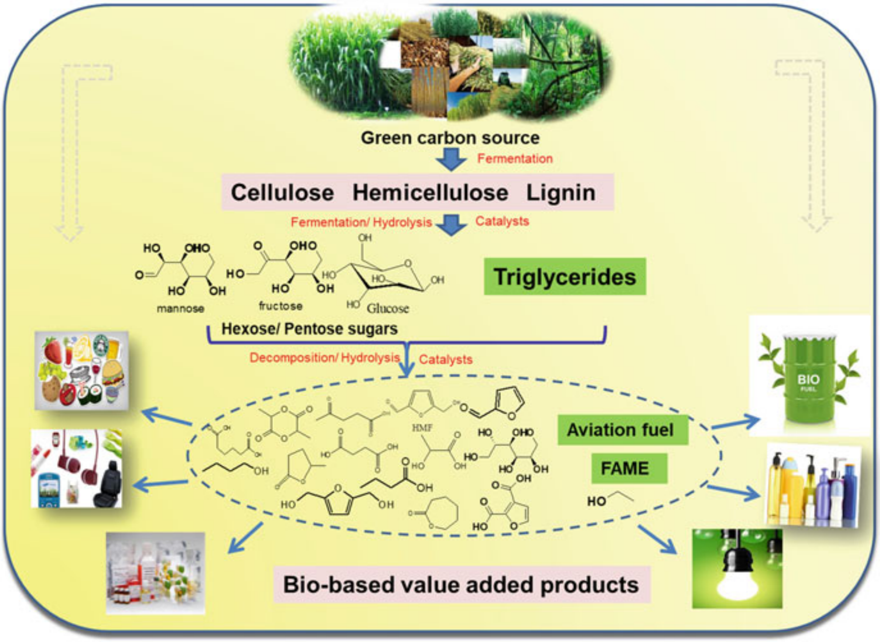


Fig. 1 Biomass to biofuel and biochemical conversion

Biomass is an abundant and sustainable source of carbon for producing a wide range of platform chemicals [5]. Among these bio-based platform chemicals, biomass-derived triglycerides are very important to produce biofuel for renewable and chemical industry. Transesterification of bio-based triglycerides with alcohol to produce alkyl esters and glycerol; these esters are referred to as biofuels [2, 6]. As per the literature, both homogeneous and heterogeneous catalysts can play a predominant role in selective conversion of triglyceride to produce biofuels [7, 8], exhibiting a significant commercial compatibility. On the other hand, the catalytic production of biofuel is also reported. Transesterification of triglyceride can produce fatty acid methyl ester (FAME) that acts as a biofuel [9, 10]. In addition, further etherification products of glycerol can also exhibit fuel properties, which can also be considered as fuel or fuel blender [11, 12]. Rapeseeds, soybean oil, palm oil, and *Jatropha* oil are the main triglyceride-rich resources. Biofuel including bioethanol is the most important and popular worldwide due to the suitable climatic conditions for the production of rapeseed and the highest share of diesel engine-driven cars. Many international bio-refineries and petroleum industries are generating green biofuels from triglyceride over the last few decades. They are considering the use of nonedible vegetable oil and animal fats as a raw material in this important production. In fact, several developed countries are significantly involved in this business [13]. Although the availability of these raw materials has remained questionable in the past due to unfavorable weather climate for their desired growth, their cultivation is no longer a serious issue by using the advanced techniques.

Another biofuel candidate, the aviation or jet fuel, has also been introduced. It is a mixture of alkanes, alkenes, aromatics, and cycloalkanes with fundamental properties of fuels for aircraft engines. Bio-based aviation fuels can be a good alternative to non-sustainable petroleum-based aviation industry [14]. Hence, their production encourages minimizing the issues caused by the use of petroleum-based fuels including the economic and environmental factors. Nonedible plant-derived aviation fuel can offer fewer carbon emissions over their life cycles with a lesser adversity to the environment and biota. Theoretically, bio-based aviation fuel can be the best alternative to the conventional petroleum-based fuel, but their efficient production from biomass in commercial scale has been highly challenging [8, 14]. The related challenges include a collection of triglyceride feedstock, development of production processes, fuel properties and their characterization, etc. Among the several bio-based feedstocks, nonedible feedstocks such as *Jatropha*, *Camelina*, algae, halophytes, society and sewage wastes, and agricultural and forest residues are highly recommended for the biofuel productions [15]. Many emerging technologies related to the thermochemical and biochemical production of bio-based aviation fuel are under development. As per reports, more than 100 trillion kg/year of renewable biomass is produced worldwide [16]. It drives a great opportunity to the development of new technologies for the future bio-based aviation fuel production and utilization. In that case, combined efforts and in-depth participation of international agencies and developed and developing countries are necessary, by which the target decided by the International Air Transport Association (IATA) to utilize more than 30% of bio-based aviation fuel by 2030 can be achieved [14].

Catalytic upgradation of bio-renewable feedstock into biofuel and value-added chemicals is considered as a major obstacle in biomass processes to compete with the existing petroleum-based processes, due to complexes in structure and the presence of multifunctionality in initial bio-based feedstock [1, 5]. However, some techniques are quite common for such types of important conversion. Among them, transesterification, cracking, and hydroprocessing of fatty acid are three of the most important conversions in the bio-based process because of its most abundant functional group in the biomass-derived vegetable and animal oil [8, 10]. In this regard, the number of heterogeneous and homogenous hydrogenation catalysts based on the transition metals, noble metals, and precious metals is reported. Most of them required a higher hydrogen pressure and batch types of reactor systems. Transition metal catalyst is highly utilized in these important conversions. In this chapter, we mainly focus on the types of triglyceride sources and their utilization in biofuel production.

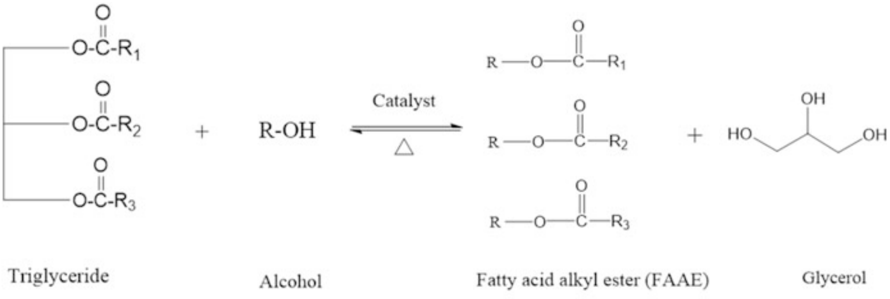
2 Types of Biofuel

Biofuels come in several forms to fulfill the different energy demands. At present, most considerable biofuels are biodiesel, bioethanol, bio-alcohol, and the aviation fuels. The current topic mainly focuses on biodiesel and aviation fuel-related topics, which are being discussed below.

2.1 *Biodiesel*

As mentioned above, the transesterification of vegetable oil can produce fatty acid alkyl ester (FAAE) that can be referred to as biodiesel (refer Fig. 2).

In other words, biodiesel is a fatty acid methyl ester (FAME) that is mainly produced from the catalytic treatment of vegetable oils (triglyceride source) with



(R_1, R_2, R_3 – C10 to C18 (saturated and unsaturated fatty ester), and R-alkyl

Fig. 2 Transesterification of triglyceride for biodiesel production methanol via transesterification process [1, 8, 10]. Notably, the highly viscous triglyceride cannot be used directly as a fuel albeit the transesterification product of triglyceride contained the same viscosity as petroleum-based diesel. The blending of FAME into diesel can significantly enhance the lubricity of diesel [3]. The triglyceride-derived biofuels can be used as additives to petro-diesel in all proportions because they have the same properties as petroleum-based diesel. Hence, it can be directly used in the conventional diesel-based motor engines. Apart from its comparative efficiency in diesel engine, it is nontoxic and biodegradable, it generates less CO_2 than petroleum diesel which can significantly reduce greenhouse gas emissions, and it was estimated that biofuel can generate more than 90% of energy than the energy required for its production [17, 18]. The biodiesel has been referred to be carbon neutral because crops for the triglyceride can recycle more CO_2 to grow themselves than the generated CO_2 in biodiesel productions and consumptions. In addition, CO_2 emission can be minimized or vary by blending them into petroleum-based diesel. Additionally, biodiesel exhibits a higher cetane number (60) than that of petroleum-based diesel (40) which is related to the engine ignition quality. Due to the high cetane number of biodiesel, it is able to ignite the engine in cold weather with creating a noise. Furthermore, its higher flash point of 150°C serves some additional advantages such as safer handling, transportation, and storage [3, 17]. These eco-friendly properties of biodiesel make it a promising alternative to petroleum-based diesel.

As estimated by Hill et al. [4], soybean-derived biodiesel serves some advantages over corn grain-derived bioethanol. Soybean biodiesel can provide significant energy than the energy needed for its productions and lesser greenhouse gas emissions compared to the relevant factors of bioethanol. As emission reductions can minimize environmental pollution, it is expected that the production of biodiesel from triglyceride will become the main priority to replace conventional petroleum-based diesel in the near future.

The comparative properties of diesel and biodiesel by the American Society of Testing and Material (ASTM) are summarized in Table 1 [3, 12, 19]. The superior properties of biodiesel allow it to be used currently in diesel engines with minor modifications that emit food smells during engine ignition, instead of the smoky smell generated by fossil diesel utilization. However, triglyceride can be produced with very less facilities as a small-scale or domestic industry, which could encourage villages and agricultural developments. No doubt, biodiesel carry some disadvantages due to its chemical properties, e.g., it has flow limitation in cold conditions, and eventually, it contains around 8% or less energy per gallon than the conventional fossil diesel. The presence of unsaturated sites in triglycerides can generate oxygenated hydrocarbons as well.

Table 1 Physicochemical properties of biodiesel

Fuel properties	Petro-based fuel	Biomass-based triglyceride and their biofuel properties					
		Soybean biodiesel	Peanut biodiesel	Sunflower biodiesel	Palm biodiesel	Babassu biodiesel	Rapeseed biodiesel
Density (at 40°C, kgL^{-1})	0.823	0.885	0.833	0.860	0.855	0.875	0.882
Viscosity (at 40°C, cST)	4.0	4.5	4.9	4.6	4.5	3.6	4.2
Flash point (°C)	98.0	178	176	86	174	127	80
Cloud point (°C)	18.0	1	5	–	16.0	–	–
Pour point (°C)	15.0	−7	–	–	16.0	–	–
Cetane number	53	43	564	49	65	63	54
Sulfur content (wt.%)	0.10	–	–	–	0.04	–	–
Carbon residue (wt.%)	0.14	–	–	–	0.02	–	–

– not known

2.2 Aviation Fuel (Jet Fuel)

Aviation fuel is a mixture of alkanes, alkenes, cycloalkanes, and aromatics (refer to Fig. 3), which has huge potential to meet the properties and workability of jet fuel [14, 20]. These ranged biofuels can be easily derived from triglyceride and other plant-based feedstocks. Different techniques including pyrolysis (thermal cracking and catalytic), hydroprocessing, and fermentation are quite well known for the production of aviation fuel from triglyceride [8]. The flowcharts for the production of jet fuel from waste oil are presented in Figs. 3 and 4. However, these aviation biofuels still need improvements in terms of their properties (as summarized in Table 2) for their efficient performance in the aviation engine. Based on their characteristics, the aviation fuels are classified into two types, kerosene range fuel and gasoline range fuel.

Since the last decades, researchers have been focusing on the development of heterogeneous catalytic processes for the production of hydrocarbon biofuel from a variety of triglycerides. In this regard, a diverse range of catalyst systems was investigated [8]. Due to the continuous increasing prices of jet fuel, it poses challenges for the world airline industry, with real prices nearly tripling from approximately $1.30/gal in 2000 to approximately $3.00/gal in 2012 [14]. In addition, the aviation industry faces environmental concerns associated with petroleum-based aviation fuel, including CO_2 emissions. As per the report, US-based refinery industries aim for more than 10% of jet fuel production biomass out of petroleum-

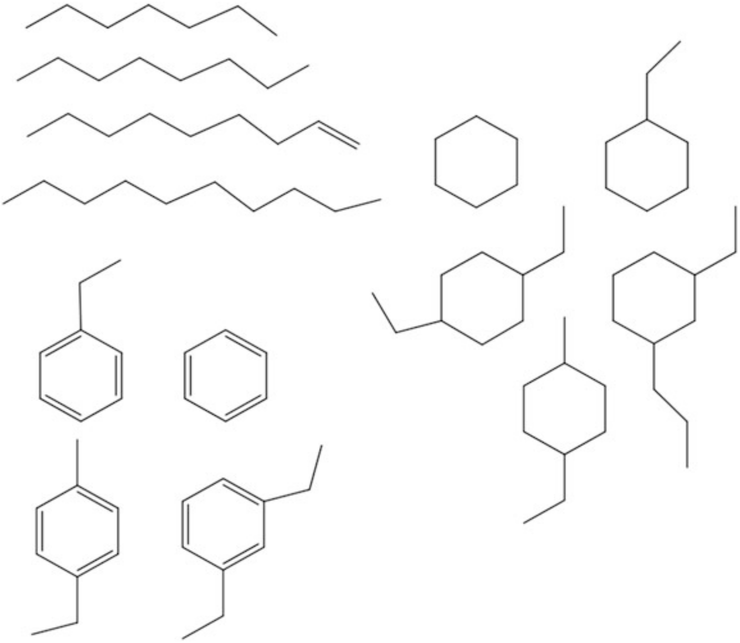


Fig. 3 Aviation fuel components

based fuel production, which are around 22 billion gallons/Annam. As per the US Energy Information Administration, jet fuel cost will gradually increase for the next few decades [21], which may cause rapid depletion of fossil resources. The use of bio-based aviation fuel can meet the huge demand for aviation fuel and somehow share the significant burden on it, which may provide several benefits including in terms of green chemistry point of view. As mentioned above, bio-based aviation fuel can satisfy the fundamental properties of petro-based fuel such as low-temperature performance, low flash point, high thermal stability, etc. In the last decades, discussion on the bio-based aviation fuel and related process development received significant interest. Many quality reviews related to this topic have been summarized in the literature [22–24]. These are related to the feasibility of bio-based aviation fuel, status and perspectives, feedstock resources and techniques for their conversions, production processes, biotechnology-based production of jet fuel, etc.

Although bio-based aviation fuel has a huge potential as an alternative to petroleum-based jet fuel, there are many challenges that must be faced and solved prior to these opportunities. This book chapter mainly focuses on the characteristic of triglyceride feedstock and the methods for the production of aviation fuels. For triglyceride conversions, a two-step treatment was suggested: triglyceride deoxygenation and hydrotreatment [8, 25–27]. Compared to biodiesel fuel properties, the hydrocarbon biofuel has high energy density with very little or no oxygen content. In addition, these biofuels can be applicable in lubrication and hydraulic operating fluid

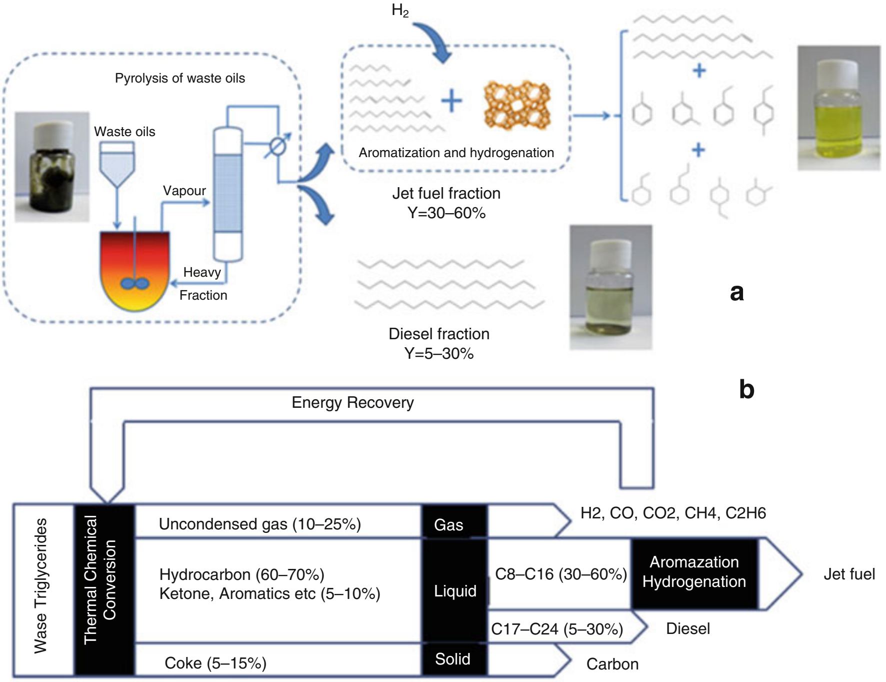


Fig. 4 Flow chart of (**a**) waste triglycerides for production of transportation fuels and (**b**) integrated process for thermal chemical conversion of waste triglycerides (adapted with permission from [20])

Table 2 Typical properties of hydrocarbon biofuel

Properties	UOM	In biofuel
Water contents	Wt.%	40–63
Carbon	Wt.%	82–86
Hydrogen	Wt.%	12–14
Oxygen	Wt.%	0–4.15
Nitrogen	Wt.%	0–0.75
Sulfur	Wt.%	Detection limit
Acidity	mg KOH/g	33.3
Viscosity	cP	1.45–4.22
Density	g/ml	0.76–0.88
HHV	MJ/kg	41–46
Freezing point	°C	5
Cloud point	°C	−5 to 30
Pour point	°C	9
Fire point	°C	145
Flash point	°C	120–138
Cetane number		70–90

due to their related properties. However, some important factors (price, average, emission) need to be considered for process development. The future development of hydrocarbon biofuel depends on a significant cost reduction. Although the feedstock supply dynamic is important to production economics, catalysts are also important in chemical processing [14].

2.3 Triglycerides and Their Feedstock

Triglycerides are primarily composed of long-chain fatty acid esters, which are the structure of bio-based vegetable oils and fats found in the environment [1, 6, 28]. The structural image of the triglyceride is displayed in Fig. 5. Triglycerides are saturated either monounsaturated or polyunsaturated. They are classified by the length and saturation degree of their side chains. Usually, a fatty acid in ester linkage consists of a linear chain of 10–24 carbons, where some of the acid chains are either unsaturated [9]. The saturation degree in the carbon chain, their isomeric presence, and their location on glycerol can classify their properties and states. For example, fats are solid at room temperature and oil is in a liquid state. Most of the vegetable oil contains saturated triglyceride, in which oxidation sites are absent, and they are less reactive so that they can be stable at higher temperatures compared to unsaturated triglyceride derived from fats.

The most common plant-based feedstocks for triglyceride productions are soybean, cottonseed, palm, peanut, rapeseed, sunflower, *Jatropha*, rubber seed, *Brassica carinata*, *Camelina*, *Calophyllum inophyllum*, mahua, Ratnajyot, etc., whereas fish oil, chicken fats, and other edible animal fats are also considered as the sources of triglyceride [12, 20, 29]. No doubt, huge utilization of these feedstocks can create some unusual food crises, which can somehow solve by reutilization of waste food oil. As per the literature, more than 46 million ton/pear of waste oil can be recovered for reutilization [29]. These zero value triglycerides can exhibit different physical and chemicals properties which can be further pretreated to make it a desirable triglyceride feedstock for biodiesel productions. In this contest, algae can be considered as one of the best triglyceride sources, because it is non-editable and it can grow very fast in all seasons and in most of the places in the world [30, 31]. Algae contain more than 50% of triglyceride, and their properties can be variable with different algae species [32]. Their huge availability in all climate conditions and lower processing cost make it an attractive triglyceride resource candidate alternative to oil- and animal-based feedstocks. In addition to the rapid growth of microalgae, triglyceride production from algae per unit area is significantly higher compared to crops for triglycerides [30].

Most of the crop and algae-derived oil contains saturated fatty acid and unsaturated fatty acids; they are mostly built with triglyceride structure together with their isolated acid portions [1, 28, 30, 32]. The common saturated acid is stearic acid (C18), palmitic acid (C16), myristic acid (C14), lauric acid (C12), arachidic acid (C20), docosanoic acid (C22), etc., whereas unsaturated acids contain oleic acid

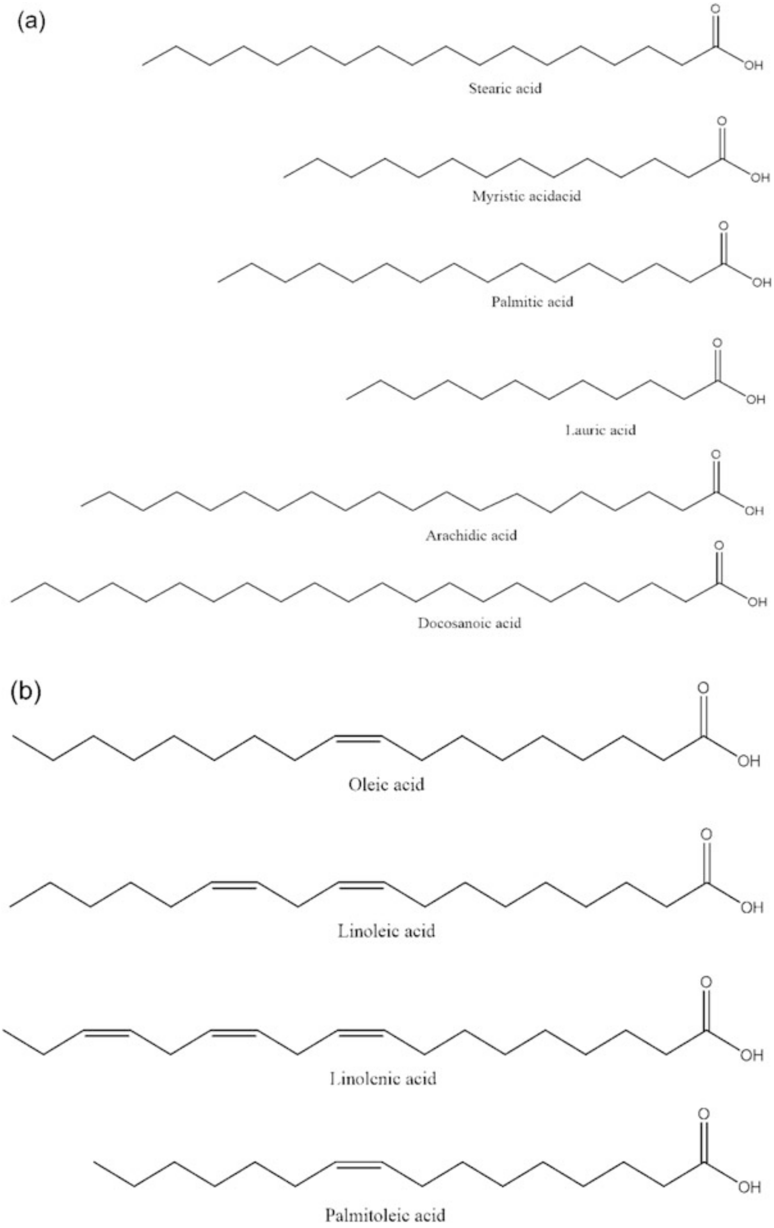


Fig. 5 (**a**) Saturated and (**b**) unsaturated fatty acids in triglyceride

Table 3 Fatty acid composition in vegetable oil

	Fatty acid carbon chain (%)				
Triglyceride	C14	C16	C18	C20	C22
Brassica carinata	–	7.74	41.7	–	48.0
Camelina	5–7	2–3	12–40	1–2	0.1–3
Flax	6.58	4.43	89	–	–
Canola	–	4.0	92	1.6	2.4
Soybean	–	14.0	82	–	–
Sunflower	0.09	6.33	89.4	0.55	0.2
Terminalia belerica	–	32.8	66.5	0.2	–
Rubber seed	–	10.2	89.2	–	–
Palm	–	35.0	65	–	–
Rapeseed	–	18.9	78.6	–	–
Crambe	0.1	2.0	31.3	4.8	59.4
Sesame	–	13.1	83.0	–	–
Cottonseed	–	28.0	72	–	–
Karanja	–	11.7	80.0	2.8	4.45
Safflower	–	9.0	91	–	–
Mustard	–	22.3	72.7	–	–

(C18) and linoleic acid (C18). The structures of these acids are depicted in Fig. 5 [7, 9, 33], while different fatty acid compositions in various vegetable oil are summarized in Table 3 [8].

In addition, it has been suggested that pretreatment of free fatty acid by reesterification and hydrogenation unsaturated site in a triglyceride can serve additional advantages such as biodiesel yield, and stability-related properties could be regained by this catalytic pretreatment [34]. The structure of bio-oil is more complicated than vegetable oil due to the presence of mixed organic components including ketones, aldehydes, ethers, phenols, furans, alcohols, water, and acids. Hence, bio-oil cannot be considered as a good resource of triglyceride for biodiesel productions [8]. It requires several pretreatment steps prior to its utilizations.

Nonedible triglyceride sources such as *Camelina*, wastes, *Jatropha*, halophytes, Karanja, algae, etc. are renewable and sustainable feedstocks, which exhibit great potential for the production of biofuels. *Camelina* crops are a good source of triglyceride (>35%); it can cultivate in any infertile land with a lesser amount of fertilizer [35, 36]. Most importantly, it can grow in a very short time and provide additional benefits in terms of profit to the landowner; also, the same land can be used for cultivation of multi-rotational crops such as wheat, cereals, soybean, etc. [35]. Similarly, *Jatropha* crop also exhibits the same advantages as *Camelina* plants. In addition, it can grow in any marginal land with less moisture [37, 38]. South Africa, South and Central America, and a few Asian countries are mainly cultivating *Jatropha* [39]. Halophyte plants are categorized as grass plants, which can grow in salty water, marshes, coastal seashores, desert areas, etc. [40]. The most important potential sources of triglyceride are wastes, which can be obtained from animals, plants, woods, sewages, industries, agricultures, municipal wastes, society, etc. [14, 41].

2.3.1 Triglyceride and Their Fuel Properties

Physical and chemical properties of triglyceride (derived from crops, algae, and animals) such as viscosity, density, iodine value, specific gravity, peroxide value, percentage of free fatty acids, acid value, saponification value, water contents, higher heating value, and pH value are the important factors for the suitability of triglyceride in biodiesel production [8, 12, 14]. The properties of triglyceride derived from different feedstocks are summarized in Table 4.

It is well known that triglyceride and free fatty acid are highly dense and highly viscous, which resulted in them into lower heating value, lower volatility, and higher cetane number with lots of flow limitation at a lower temperature. Hence, transesterification and esterification pretreatments become required to get diesel quality biodiesel [3, 42, 43]. In the case of highly viscous *Jatropha* triglyceride, a variety of pretreatments like preheating, blending, supercritical esterification, and transesterification are necessary to avoid problems, viz., coke depositions, chocking of oil rings, gel formation, etc. [44, 45]. The nonpolarity of triglyceride makes it immiscible in water, while a bio-oil may contain significant amount of water up to

Table 4 Triglyceride derived from different sources and their properties

Triglycerides from different sources	Water content (wt %)	Acidity (mg KOH/g)	Viscosity (at 20–40°C)	Density (g/mL)	HHV (MJ/kg)
Brassica carinata	0.05	4.5	87.5 cP	0.88	40.3
Camelina	0.08	1–5	59.4 cP	0.89	39.4
Flax	0.07	0.80	50.3 cP	0.91	39.1
Canola	0.05	1.8	87.2 cP	0.91	38.9
Soybean	0.06	0.20	32.6 mm^2/s	0.84	39.5
Sunflower	0.09	6.33	89.4 cP	0.55	0.2
Terminalia belerica	0.06	3.36	77.3 cP	0.92	39.5
Rubber seed	1.50	25.1	57.9 mm^2/s	0.93	37.1
Palm	0.47	4.80	48.1 mm^2/s	0.90	39.0
Rapeseed	0.03–0.04	1.14	35.2 mm^2/s	0.91	39.5
Crambe	–	0.33	6.64 mm^2/s	0.89	40.6
Sesame	–	0.55	25.8 mm^2/s	0.90	39.5
Cottonseed	0.03	0.30	58.2 cP	0.92	39.4
Karanja	–	1.23	25.0 cP	0.97	38.4
Safflower	0.04	0.97–9.24	31.3 mm^2/s	0.93	39.5
Mustard	0.03	0.55	73.0 mm^2/s	0.92	39.0
Jatropha	3.28	27.2	46.8 mm^2/s	0.92	39.6

30% [3, 46, 47]. Nevertheless, the presence of moisture can make a negative impact on the biodiesel production efficiency in the transesterification reactions. The acid number and their chemical composition are highly important to produce quality biodiesel [3]. In this regard, soybean-, sunflower-, canola-, rapeseed-, *Jatropha*-, sesame-, Karanja-, and safflower-derived oils are found are to be acid-rich, which is highly desired for quality biodiesel productions [1, 10, 44]. However, free fatty acids are highly important in triglyceride, which can improve biodiesel production process efficiency during transesterification reaction with alcohol by esterifying themselves. Perhaps, reaction conditions should be acid-catalyzed. In the case of base-catalyzed esterification, there are huge chances for the soap formation during transesterification that can significantly affect the quality of diesel and separation cost [7, 9, 48, 49].

Notably, the unsaturated sites in triglyceride should be very limited, because unsaturated double bond in triglycerides is highly reactive, they can either oxidize or polymerize at higher heating value. These unwanted side reactions can often lead to the formation of coke and polymer deposited on engine parts, by which the efficiency of the engine can be decreased within a short period of time [3, 12]. As mentioned above, the cetane number and flashpoints are very important factors for high-quality diesel. These cetane numbers are related to the ignition and combustion properties of the fuel. Low cetane number of fuel can produce a lot of noise during engine start-up and exhaust undesired gas emissions [43, 50–52]. Generally, triglyceride with small chain acid contains a lower cetane number, and they are not considered as a deserving candidate for biodiesel productions. Hence, selection of triglyceride for biodiesel production was always made based on the length of fatty acid and their cetane number [43, 52–54]. Nevertheless, the cetane number of fatty acids can be improved by their transesterification with alcohol. From a green environment point of view, nitrogen and sulfur contents should be negligible, by which toxic NO_x and SO_x emissions will be controlled during the fuel burning process, which is favorable to crop-derived triglycerides as they carry very less concentration of nitrogen and sulfur.

2.3.2 Algae

The main barriers in biodiesel production from crops are discussed above. These barriers are related to the economic and technological developments, their availability, storage, transportations, and safety concerns. As per the experimental data, crop-based triglyceride is the best feedstock for biofuel productions. Currently, the crude oil is much cheaper than the cost of vegetable oil, and their extensive utilization can create another serious issue including food crises and land crises. Hence, these triglycerides can be considered as future feedstock for biodiesel productions. In this contest, algae/microalgae exhibit similar potential for biodiesel production [18, 30, 31]. Importantly, they can grow rapidly in any weather conditions without any maintenance and the need of fertile land, and largely the growth is dependent on the availability of CO_2 and sunshine [30, 31, 33]. It is likely that algae can consume

Table 5 Concentration of triglyceride oil in algae

Microalgae	Oil concentration (%)
Botryococcus braunii	25–75
Chlorella sp.	28–32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16–37
Dunaliella primolecta	23
Isochrysis sp.	25–33
Monallanthus salina	>20
Nannochloris sp.	20–35
Nannochloropsis sp.	31–68
Neochloris oleoabundans	35–54
Nitzschia sp.	45–47
Phaeodactylum tricornutum	20–30
Schizochytrium sp.	50–77
Tetraselmis suecica	15–23
Achnanthes sp.	44.5
Ankistrodesmus sp.	24–31
Botryococcus braunii	25–75
Chaetoceros calcitrans	39.8
Chaetoceros muelleri	33.6
Chlorella sorokiniana	19.3
Chlorella vulgaris	19.2
Chlorococcum sp.	19.3
Chlamydomonas sp.	18.4
Ellipsoidion sp.	27.4
Heterosigma sp.	39.9
Nannochloropsis oculata	22–29
Pavlova lutheri	35–40
Pavlova salina	30.9–49.4
Skeletonema sp.	31.8
Thalassioria pseudonana	20.6

solar energy in the everyday growth cycle and convert it into another form of fuel energy [55]. Oil production per acre from microalgae is significant in number (200 times) compared to the vegetable oil from crops [32]. For example, the best fertile crop is palm, and it can generate 6,000 L/hector oils, whereas algae can generate around 90,000 L/hector of oil. As mentioned above, algae can consume CO_2 for its regular growth, and 50% of dry microalgae is carbon. It means 1.0 ton of algae can fix around 1.83 tons of CO_2 every easily.

All algae are composed of carbohydrates, proteins, lipids, and nucleic acid in different concentrations, and these proportions can be varied with algae types. However, some algae consist of more than 40% of fatty acids, which can generate more yields for biodiesel [56]. The oil content in some microalgae is summarized in Table 5.

Theoretically, around 310,000 L/hector oil can be produced annually to derive biodiesel [57–59]. However, fertilizers and water are required for their cultivation. In addition, oil extraction from algae is the most difficult process and required lots of energy. Theoretically, algae are the most promising feedstock for biodiesel productions, most of the algae mainly composed of polyunsaturated fatty acids. No doubt, lower melting points and unsaturated sites of polyunsaturated fatty acid in oil derived from algae can create biodiesel stability and engine ignition problems. As reported, lipids (a diverse group of organic compounds including fats, oil, and hormones) and unsaturated fatty acids are the main components, which can create challenges in converting them into biodiesel [60].

However, lipid and fatty acid can vary with different cultivation conditions, and their compositions are entirely independent on the types of algae; triglyceride and their chemical compositions are completely dependent on the types of crop-based feedstock [60]. Green algae (*Chlorophyceae*) and diatom algae are the most promising feedstock for biodiesel productions [30, 32, 61]. Polyunsaturated fatty acids such as eicosapentaenoic acid and docosahexaenoic acid are presented in certain algae, and these fatty acids are mainly found in fish oil and sea animal's oils [62–64]. The major advantage of green algae is that it can enhance its growth rate two times by optimization in cultivation conditions, which can directly double the lipid production and their potential required for biodiesel. These attractive properties of green algae can make it ideal for biodiesel production. Algae-derived oil and triglyceride undergo transesterification to produce biodiesel. Interestingly, algae-derived biodiesel can exhibit almost similar energy content (41.0 MJ/kg) as the energy estimated for petroleum-based diesel (42.7 MJ/kg) and crop-based biodiesel (39.5 MJ/kg) [65, 66]. These important fuel properties make it a desirable fuel candidate alternative to conventional petroleum-based fuel. It was estimated more than 0.53 billion m^3 of biodiesel need to replace the petroleum-based fuels as per US transportation consumptions [67, 68]. Hence, biomass can be a productive source of biodiesel for this important replacement. In addition to biodiesel production from microalgae, aviation biofuels can be produced very efficiently. Usually, triglyceride for biofuel productions has been obtained by the extraction and transformation of the lipid material. However, as diverse range of treatments is investigated for the production of biofuel from lignocellulose biomass, similar techniques can be utilized for the pretreatment of algae for biofuel productions. Here also, significant factors such as algae types, availability, conversion processes, process economy factors, and energy factors can influence the cost of biofuel from triglyceride or algae-derived bio-oil. The flow diagrams for the transformation of microalgae into biofuel are presented in Figs. 6 and 7.

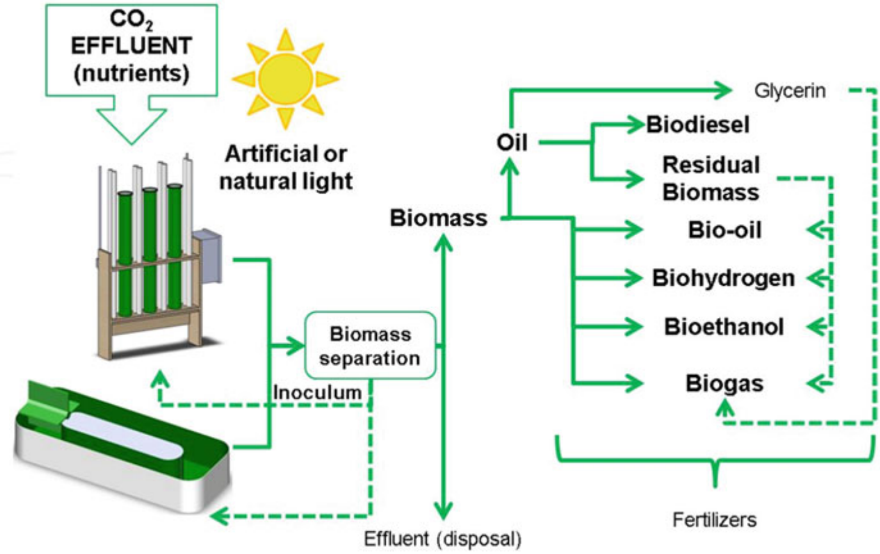


Fig. 6 Microalgae production and its utilization for biofuel productions (adapted with permission from [31])

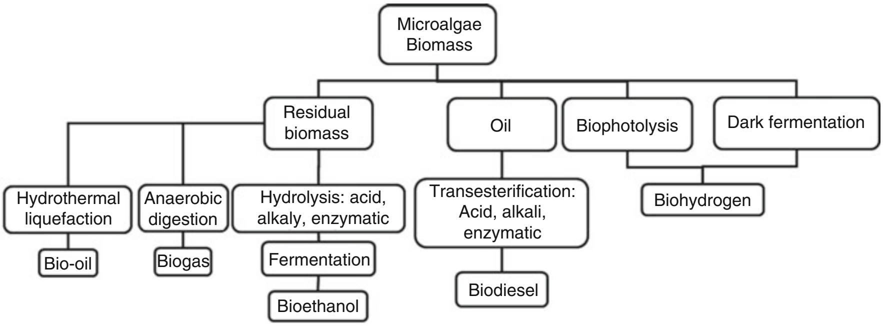


Fig. 7 Flow diagram for transformation of microalgae biomass into biofuel production (adapted with permission from [31])

3 Biofuel Production Processes

Several techniques are discussed in the literature for the upgradation of viscous triglyceride into less viscous biodiesel. These common techniques include mainly transesterification, thermal cracking, catalytic cracking, hydroprocessing, and fermentation. In this chapter, we are mainly focusing on the transesterification, catalytic cracking, and hydroprocessing technologies.

3.1 Transesterification of Triglyceride

Schematic representation for transesterification of triglyceride into biodiesel (FAME) is presented in Fig. 2. It is a chemical reaction between triglyceride and alcohols using catalyst system; the catalytic system will be either heterogeneous or homogenous systems. In this alcoholysis reaction, resultant esters (FAME) and glycerol are the main products. However, these reactions are reversible; hence, excess amount of alcohol (above the stoichiometry) is necessary to obtain the higher yield for desired biodiesel products [69]. As per reports, base catalysts are found to be more effective in the biodiesel production to get higher yield [70–72]. However, utilization of homogenous bases in transesterification can come up with major disadvantages such as soap formation through saponification with fatty acids [73]. The soap formation and miscibility of homogeneous bases can significantly affect the purification cost of biodiesel. In these contests, heterogeneous bases and solid acid catalysts are considered suitable candidates for biodiesel productions. In literature, several catalyst systems have been investigated for this important reaction, most of them able to produce good yield for FAME. In most of the studies, methanol was utilized in biodiesel production because it is highly reactive than any other alcohol under less critical conditions. However, more energy and critical conditions are necessary to achieve great yield when other alcohols are used in this reversible reaction. The diverse list of catalyst and their catalytic activities in transesterification have been summarized in many reviews [3, 8, 10, 20]. Mostly, base catalyst systems, including basic zeolites (NaX, ETS-10, La-beta zeolite, Na-Y, etc.) [12, 72, 74, 75], hydrotalcite (Mg-Al, Mg-Zn), alkaline and earth metal catalysts (Mg-, Ca-, Sr-, Ba-, Na-, La-based catalysts), and alkali metal-supported catalysts (Al_2O_3 modified with K_2CO_3, KF, $LiNO_3$, and NaOH) [66, 75–77], are extensively investigated to achieve higher yield (>90%) for biodiesel [7, 9, 12]. It is likely that Lewis basic properties in solid catalysts are a more suitable candidate for biodiesel productions. However, some reports are related to the use of a solid acid catalyst (zeolite, heteropoly acids, WO_x, ZrO_2-SO_4, resin catalysts, etc.), which have also shown a higher yield for FAME [78–80].

As per the extensive survey of existing reports, solid bases are found to be more efficient in biodiesel production compared to solid acid catalysts and enzymes [1, 9, 10, 79]. In order to process industrialization, catalysts should provide better activity below 150°C and ambient pressure conditions. However, solid acid catalysts, enzymes, and non-catalytic supercritical transesterification are less investigated due to pessimistic expectations in terms of reaction rates, undesirable side reactions, and high costs. In this regard, extensive research is necessary to get more catalyst candidates and process options in these important topics. In addition, issues concerning their constraints should also be addressed continuously so that the limitations can be overcome and they evolve as viable alternatives in the near future.

In the last decade, biodiesel has been produced by using NaOH and $NaOCH_3$ homogenous catalyst systems, which are yielding glycerol-related side products [66, 75–77, 81]. As mentioned above, triglyceride with less concentration of free fatty acid is a good candidate for biodiesel formation, which helps to avoid soap formation and emulsion formations [48, 49]. In base-catalyzed (homogenous) biodiesel production, bases should be neutralized throughout workup of the reactions, by which mixture of glycerol and salt can be separated out from the resultant biodiesel (FAME). However, the quality of the resultant crude glycerol from this process is not good; it always requires significant purification. Noteworthy, due to the development of biodiesel productions, glycerol became an important building block for the production of value-added chemicals like acrolein, acrylic acid, 1,3-propanediol, epichlorohydrin, etc. [82–85]. In order to achieve good-quality biodiesel and glycerol from low-quality fats and oil (with higher FFA level), heterogeneous catalysts with basic sites are highly recommended. Prior to the utilization of low-quality triglyceride, FAA in triglyceride should be pre-esterified by treating them with methanol using solid acid catalyst systems; it helps to get more FAME. The transesterification process using heterogeneous catalysts (Al_2O_3/$ZnAl_2O_4$/ZnO) was developed by the Institut Francais du Petrole (IFP) which was commercialized by Axens as the EsterFip-H process [86, 87]. A Europe-based company, Diester Ind. Ltd. developed a plant with a capacity of 360,000 ton/year biodiesel [88]. In this process, glycerol was recovered as a side product with more than 98% purity. No doubt, development in heterogeneous catalysts systems for transesterification processes received great interest in recent years. Over a decade, many studies are found based on alkali and alkaline earth metal for biodiesel productions from oil and fats [24, 89–92]. Where most of the basic catalysts showed soap formation due to the presence of FFA in triglyceride, which can be avoided by simultaneous esterification of FFA together with triglyceride etherification, in this regard, a combination of acid and basic catalysts can be a hybrid choice to solve this important issue.

In transesterification, glycerol is the main side product; it can be recovered with $>98\%$ purity [69]. This triglyceride-derived glycerol can be further etherified with alcohols or alkanes to produce diesel blender. Among the synthesized ethers of glycerol (mono-ether, di-ether, tri-ether), tri-ether of glycerol is the most desired blender for diesel due to their similar fuel properties with petroleum fuel [8, 12, 93, 94]. In these consecutive conversions, the solid base catalyst is highly recommended to obtain trialkyl ether of glycerol with very high yield (as depicted in Fig. 8).

3.2 Catalytic Cracking of Triglyceride to Produce Hydrocarbon Fuel

There are two main techniques for converting triglyceride into hydrocarbon fuel (jet fuel range): catalytic cracking and hydroprocessing. Catalytic cracking is a cost-effective technology for hydrocarbon production from triglyceride at a relatively lower reaction temperature [8, 96, 97]. The schematic representation for the catalytic cracking of triglycerides is displayed in Fig. 9. Hydroprocessing is a widely known

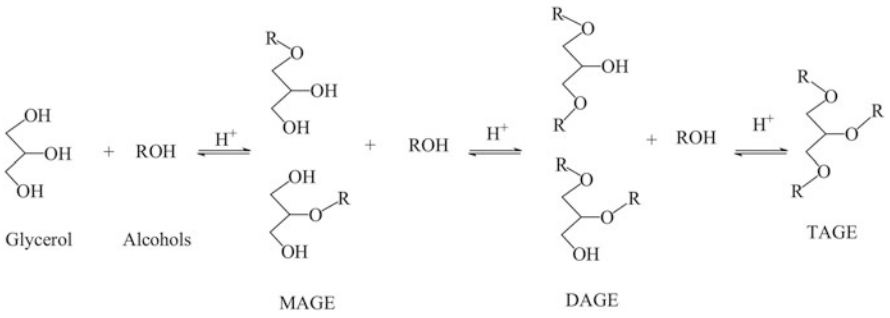


Fig. 8 Etherification of glycerol with alcohol by following the dehydration pathways (adapted with permission from [95])

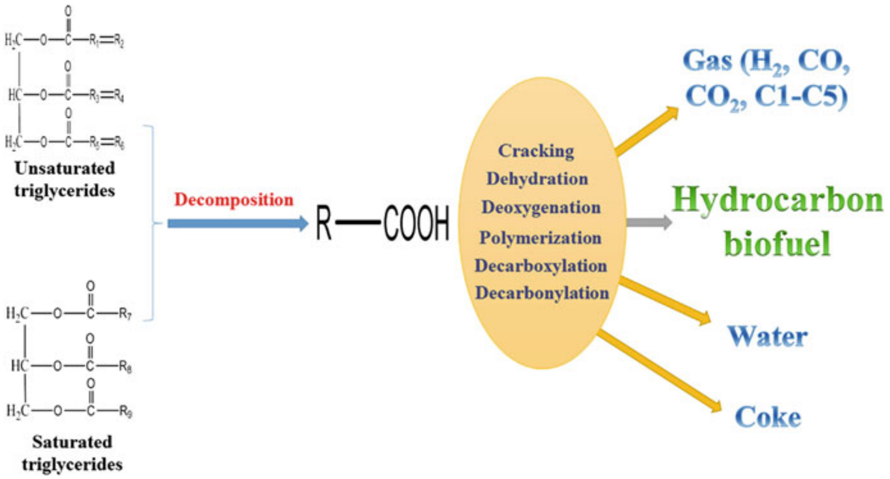


Fig. 9 Catalytic cracking of triglycerides into hydrocarbon fuel (adapted with permission from [8])

technique in the chemical refineries, in which oxygen in triglyceride or acids can be selective and removed by their treatment with hydrogen [8, 98]. Hydrocarbon biofuel (jet fuel) from triglyceride should possess some important characteristics including high flash point (>140°C), high energy density (37–46 MJ/kg), and low freezing point (<5°C), and it should be less toxic and immiscible in water and should have higher lubricity, higher cetane number (70–90), higher thermal stability, and cold weather operability for the safe operation of current fuel systems [8, 98]. Nevertheless, these properties can be varied with the triglyceride source for hydrocarbon biofuels; hence, some hydrocarbon cannot be suitable with the requirement of transportation liquid fuel. Therefore, these hydrocarbon biofuels need to be further refined using techniques such as distillation and isomerization.

For catalytic thermal cracking of triglyceride, temperature range between 380 and 530°C is required because thermally stable triglyceride cannot be cracked at a lower temperature range [25–27, 29]. However, higher temperatures significantly affect the liquid yield of products and produce a higher amount of gaseous products. To solve this issue, higher-pressure conditions are recommended. Generally, catalytic cracking of triglyceride was carried out in continuous flow system, by which liquid product yield can be varied very easily by changing the reaction parameters. In catalytic cracking, oxygen can be removed from triglyceride by decarboxylation, decarbonylation, reoxidation, etc., and these reactions or paths are completely dependent on the catalytic sites and reaction parameters [8]. However, in these reactions, coke formation was observed quite frequently. It was reported that quality and yield of hydrocarbon biofuel from vegetable oil are better than bio-oil [8, 99, 100]. In addition, the simultaneous catalytic pyrolysis and catalytic cracking of triglyceride could improve the quality as well as the yield of hydrocarbon biofuel yield compared to the traditional catalytic cracking process. Zeolites are one of best catalyst systems to achieve good yield of desired hydrocarbons in this particular cracking of triglyceride, because zeolites are well defined with shape, size, Brønsted acid sites, and higher surface areas [96, 101, 102]. However, some zeolite-based catalyst system suffers serious deactivation. The catalytic activities of different catalysts for particular feedstock are presented in Table 6.

Catalytic pyrolysis and cracking are highly applicable for the waste triglyceride instead of transesterification because these waste triglyceride mixtures contain higher concentrations of FFA in different carbon ranges with triglyceride of different fatty acids [20, 29, 81]. Disposal of these waste oils can be a headache for oil refinery industries. Hence, their simple pretreatment without any expensive reactant (e.g., hydrogen) to remove oxygen from waste triglyceride comes up with advantages and more opportunities to reduce the overall cost of the process. This process can obtain jet fuel range hydrocarbon obtained with very high yield (60–70%) from waste triglyceride [20, 29, 81]. This approach also generates an alternative 30% of the yield of diesel products by catalyst system and optimized reaction parameters. These types of integrated catalytic systems provide a cost-efficient processing strategy for transportation fuel production. Multiple aim products for this approach will improve the flexibility of product selling strategies for the industry. As per energy calculations, the energy generate from pyrolysis of gas (during catalytic cracking) can be recyclable energy for utilization, thereby realizing the whole process without the need for additional energy.

3.3 Hydroprocessing of Triglyceride

In hydroprocessing of triglyceride, triglyceride was treated with hydrogen at a higher temperature range above 300°C and higher hydrogen pressure using suitable catalyst systems [100]. Generally, metal-supported catalysts in flow reactor systems have been used in this technique. In hydroprocessing, hydrogen pressure and temperature

Table 6 Catalytic cracking of triglyceride into hydrocarbon biofuel

Triglyceride	Catalyst	Main products	Product yield (%)	References
Brassica carinata	Zn/Na-ZSM-5	Hydrocarbon fuel	40–63	[102]
Sunflower	V_2O_5	Organic liquid product	88–92	[103, 104]
	Metal oxides (Co_3O_4, KOH, MoO_3, NiO, V_2O_5, ZnO)		55–87	
	Pt-Ni/Al_2O_3 and Pd/C	Hydrocarbon fuel	22–49	
Soybean	Mesoporous HY zeolite	Gasoline (C5-C11)	>26	[105]
	CaO, Na_2CO_3, K_2CO_3, NaOH	Hydrocarbon fuel	25–50	[20, 29]
Rapeseed	Fluid catalytic cracking equilibrium catalyst (FCC-ECAT)	Organic liquid product	50–53	[104, 106]
	Fluid catalytic cracking ZSM-5 (FCC-ZSM-5)		47–53	
Rubber seed	MNC-13 (mesoporous molecular sieves)	Hydrocarbon fuel	75	[107]
Palm	Fe-Zn-Cu-ZSM-5	Hydrocarbon fuel	59	[96, 108]
	Na_2CO_3	Hydrocarbon fuel	65.9	
Camelina	ZSM-5-Zn	Hydrocarbon fuel	15–19	[102]
Jatropha	CaO	Hydrocarbon fuel	83	[109]
Vegetable	HZSM-5	Hydrocarbon fuel	45	[110]
Waste oil	Base	Hydrocarbon fuel	52	[20, 29]
Pyrolytic oil	Ni-ZSM-5, Raney nickel, ZSM-5	Aromatization products	>90	

Hydrocarbon fuel (C8-C18 hydrocarbons), organic liquid product (gasoline, kerosene, diesel, gasoline), aromatization products (alkanes, alkenes, aromatics, cycloalkane)

are the resultant factors to minimize the coke formation and yield the higher liquid hydrogen fuel [8]. The schematic representation is displayed in Fig. 10. During the hydroprocessing of triglyceride, multiple reactions are taking place such as hydrogenolysis, hydrogenation, hydrodeoxygenation, decarbonylation, decarboxylation, hydrocracking, polymerization, etc. Noteworthy, hydroprocessing usually used to remove oxygen, sulfur, nitrogen, and metals from the triglyceride mixtures, and it could help to remove the organic impurities, which contains oxygen atom [8, 100, 111]. Hence, the hydroprocessed triglyceride contains less or no saturated sites, which could become desirable feedstock for the good-quality aviation fuel and biodiesel productions. However, the use of huge hydrogen can affect the cost of the process. Hydroprocessing of crop-derived triglyceride can produce higher yield

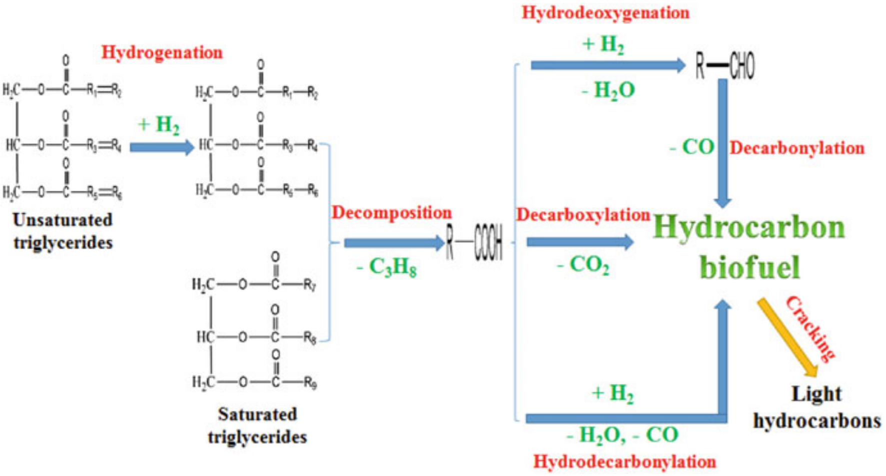


Fig. 10 Catalytic hydroprocessing of triglycerides into hydrocarbon fuel (adapted with permission from [8])

(>90%) for biofuel including green diesel, jet fuel, hydrogenated fuel, and organic products [8, 100, 111].

The list of catalysts and their activities in hydroprocessing of triglyceride derived from the different crops are presented in Table 7. Most of them showed excellent catalytic activity. Of course, the catalyst and reactor system should be optimized; otherwise, it may significantly affect the desired hydrocarbon yield, by producing several side products of fatty acid, undesired coke, and tar. These coke depositions can cause serious catalyst poisoning. Hence, the suitable catalyst and reactor systems need to more advance for this particular treatment for triglyceride.

4 Biofuel Productions and Economical Concerns

At present stage, triglycerides are more expensive than crude oil, which could affect the cost of biodiesel. However, crude oil is almost at the maturity stage, and these resources are already moving toward their declinations. Hence, the significant research on triglyceride conversion into biofuel is necessary for future biofuel productions to fulfill the world's energy needs. As discussed above, biodiesel has lots of potentials to replace the petro-based diesel. In addition, it is easy to burn eco-friendly fuel, and it can be more economically viable if the advanced technologies are developed. No doubt, commercial biodiesel productions directly raised the agriculture economy, and it will significantly benefit the regular employments and developments in ruler and forest areas. Biofuel production from sustainable and renewable resources can always manage the economic, health, and environmental development by reducing the cost of eco-management, which is caused by greenhouse and toxic

Table 7 Catalytic hydroprocessing of triglyceride to hydrocarbon biofuel

Triglyceride	Catalyst	Main products	Product yield (%)	References
Brassica carinata	Mo-Zn/Al_2O_3	Hydrocarbon fuel	93	[112]
Sunflower	Co-Mo/Al_2O_3	Hydrocarbon fuel	>93	[113]
	Pt-Ni/Al_2O_3 and Pd/C		>95	[114]
Soybean	NiMo/ZSM-5 carbide, NiMo/ZSM-5	Hydrocarbon fuel	50	[115]
		Hydrocarbon fuel		
Canola	NiMo/SiO_2-Al_2O_3	Diesel	81.4	[116]
	Pd/C	Hydrocarbon fuel	>90	[117]
Palm	Ni/mesoporous-Y	Hydrocarbon fuel	31	[118]
Camelina	ZSM-5-Zn	Hydrocarbon fuel	15–19	[102]
Jatropha	Ni-H_3PW_{12}/nanohydroxyapatite	Liquid products	83.5	[119]
Karanja	Ni/Al_2O_3	Green diesel	80	[120]
Waste oil	Ni-ZSM-5	Hydrocarbon fuel	>90	[20, 29]
Pyrolytic oil	Ni-ZSM-5	Hydrocarbon fuel	>90	

Hydrocarbon fuel (C8-C18 hydrocarbons), organic liquid product (gasoline, kerosene, diesel, gasoline), aromatization products (alkanes, alkenes, aromatics, cycloalkane)

gas emission form petro-refinery industries and petro-based vehicles and machines. These eco-friendly benefits from biofuel production can be achieved by its simple blending with petroleum diesel. The biofuel blending can re-drop the petroleum prices and depletions significantly, which would be somehow able to reduce the huge burden on fossil resources. However, there are some challenges that can be solved in replacing petroleum-based fuel including related food crises, availability of lands, cost and availability of raw materials, less production of crop oil, and their sustainability. Although biofuel has become more attractive to environmental benefits, the cost of biofuel remains the main obstacle for commercialization of the product since the cost of biodiesel is higher than diesel fuel. The cost of biodiesel can be reduced by developing the hydride transesterification process, which could be compliable for producing petroleum quality biodiesel and their easy separation from side products including glycerol.

5 Perspectives

Looking at the need of the hour for shifting toward the energy produced by alternative resources, biofuel productions using the upgraded triglyceride techniques that include transesterification, catalytic cracking, and hydroprocessing are imperative to be investigated in the coming time. Utilization of stable heterogeneous catalysts can be a great choice to upgrade the triglyceride in terms of biofuel yielding, quality, and minimal operational costs during the separation and purification process. The posttreatment of biodiesel or hydrocarbon biofuels like distillation can be utilized for refining the hydrocarbon biofuel that could meet the requirement of transportation fuel. In line with reducing the operational cost, cutting of production cost is also important to encourage the triglyceride use for biofuel production. The by-product obtained during the triglyceride treatment can be recycled to improve the production economics. Most importantly, economic evaluation and plant scale investigation on triglyceride upgradation should be investigated more thoroughly. Such an investigation will give a direct idea on the viability of triglyceride as alternative to fossil source of energy.

6 Conclusions

In order to fulfill the soaring energy demand for transport fuels, the replacement of conventional fuels by renewables/alternatives that do not harm the environment and do not compete with food resources is a vital need of the present time. In this context, the biofuels produced from the nonedible triglyceride crops have been paid much attention by the energy researchers. Triglyceride is one of such prime candidates which can be derived from nonedible sources including algae, *Jatropha*, Karanja, rubber, manhua, palm, rapeseed, etc. for biodiesel production. Algae are very important as other bio-based sources; some of the algae species may be better suited for different types of fuels. A variety of nonedible triglyceride seeds with suitable properties has been explored for improving the yield and quality of biofuels. In the near future, the new researches recommended in this area will decide the fate of this infant technology in the coming years.

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Microbial Electrochemical Systems (MESs): Promising Alternatives for Energy Sustainability

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Contents

Abstract Over dependence on energy sources of fossil fuel origin to meet the ever-increasing global energy demand not only leads to depletion of nonrenewable energy sources but also results in greenhouse gas emission mediated climatic crisis.

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Therefore, the renewed research interests in the quest of alternate sources of sustainable and clean energy research are being prioritized in recent times. Microbial electrochemical systems (MESs) are engineered electrochemical systems that facilitate the direct transformation for organic wastes into bioenergy through microbial catalyzed reactions. MESs hold great potential as green bioenergy conversion technologies and related laboratory-scale research have reached unprecedented success in the past 5–10 years. Despite the advantages of this technology, the widespread commercial application of the technology was restrained by limitations of slow microbial kinetics, low efficiency, and high cost. In the last few years, significant advancements have been attempted in the reactor configurations, electrode materials, substrate types, diversity of electrogenic microorganisms, etc., thereby increasing the performance efficiency to several folds. However, further improvements are highly desired for the MESs to be economically viable. This chapter offers an inclusive review of all the recent developments that have been made in MESs emphasizing on bioenergy perspective. In particular, it highlights novel anodes, bio-cathodes, engineered microbes, and xenobiotics of diverse classes that can be exploited for bioenergy production. Besides that, this chapter discusses the scale-up and practical implementation in large-scale settings as pioneering attempts of commercialization.

Keywords Bio-cathodes, Bioenergy, Electrogenic microorganisms, Microbial electrochemical systems, Practical implementation

1 Introduction

With ever-increasing population growth, energy crunch, water scarcity, environmental contamination, climate change, etc. continued to be major global issues. Depleting fossil fuel energy appears to be the greatest challenge in the twenty-first century. As the quality and prosperity of a society is heavily dependent on the magnitude of energy usage, population influx along with rapid urbanization, industrialization, technological advancement, and higher living standard of the contemporary society has led to an unprecedented increase in energy demand. The global energy consumption is growing at an alarming speed, and this is likely to worsen with the projected annual global energy demand of 23 terawatts (TW) by 2050 against the current demand of around 13 TW [1]. Fossil fuels, coals, in particular, have catered to the sizable portion of the total global energy requirements. Being a nonrenewable source, over dependence on fossil fuel for energy triggers a global crisis of fossil fuel reserves. Furthermore, carbon dioxide, a potential greenhouse gas emitted during fossil fuel combustion, has global warming-like harmful consequences on the environment. Owing to the gradual widening of the gap between supply and demand of fossil fuel and concern about its fair share of greenhouse gas contribution, there is a growing interest worldwide to exploit alternate renewable energy resources with a minimal negative impact on the environment. Contextually, biomass, particularly organic waste, is being considered as a preferred renewable energy resource in recent years. Similarly, it is anticipated that half of the global population may face severe water shortage by 2030; therefore, maintaining an adequate supply of water for human consumption is another significant challenge in the twenty-first century since freshwater is a finite natural resource [2]. Therefore, finding alternative water resources is a major focus of recent times to minimize the widening gap between water supply and unprecedented demand. On the other hand, annual global wastewater production as high as 1,000 billion m^3 has been reported by Qureshi et al. [3]; therefore, the reuse of treated wastewater as an alternative source would be beneficial in minimizing the over dependence on freshwater. As a matter of fact, proper wastewater treatment technologies to achieve desirable wastewater reusability standards are of high importance. Significant fossil fuel consumption by conventional aerobic wastewater treatment processes has diverted the research focus on energy efficient anaerobic treatment technologies [4, 5]. But, dissolved gases produced in the anaerobic treatment process are a major hindrance to the practical applications of these technologies [6]. Contextually, advanced treatment systems that enable simultaneous energy recovery and wastewater treatment are gaining research attention. Consequently, there has been considerable research interest in microbial electrochemical systems (MESs) as a promising alternative for clean energy production (electricity) by harvesting energy from waste substrates (wastewater) through microbial metabolisms [7].

In conventional electrochemical systems, an oxidation reaction takes place at anode and reduction reaction at the cathode. Driven by the potential differences of oxidation and reduction reactions, electrons drift from a low to high potential, freely. The electrochemical systems in which the oxidation or reduction or both reactions are catalyzed biologically (by microorganisms or enzymes) are termed broadly as bioelectrochemical systems (BES) or microbial electrochemical systems (MXC) where X symbolizes the main function of the electrochemical systems. As BES term is used frequently to exemplify cell free enzyme based electrochemical systems, this chapter uses the terminology microbial electrochemical systems (MESs) to denote the systems where the microorganisms are involved in carrying out anodic and/or cathodic reactions [8–10]. If anodic reactions are catalyzed by microorganisms, they are classified as bioanodes, and if cathodic reactions are catalyzed by microbes, they are categorized as bio-cathodes. Like conventional electrochemical systems, the MESs can be operated as galvanic cells, when the redox reactions are spontaneous and as electrolytic cells when the redox reactions are non-spontaneous in nature and necessitate additional electrical energy to proceed [10]. The electromotive force, that is, the potential difference between the anodic and cathodic reaction is mainly responsible for driving the electron move from a low potential to high potential. In both the galvanic cell and electrolytic cell mode, oxidation of the substrate takes place at the anode. However, in galvanic cells, the thermodynamically favorable cathodic reactions result in spontaneous reaction (electron drift from anode to cathode), whereas in electrolytic cells, to attain a thermodynamically favorable cathodic reaction, the anodic potential generated through substrate oxidation is enhanced with an external power supply that drives electrons from anode to cathode [11]. The microbial fuel cell (MFC) is the first and most studied MESs prototypes operated in the galvanic mode for simultaneous wastewater treatment and electricity generation. On the other hand, when the MESs is operated in the electrolytic mode to generate hydrogen and other valuable chemicals, they are usually denoted as microbial electrolysis cells (MEC). So, from the early examples of MFC, this microbial-derived electrochemistry leaped into MESs that rely on the process of bioelectrochemical utilization of organic substance, to produce bioelectricity, value-added by-products, remediate contaminants, and desalinate water [12, 13]. The outline of different types of MESs, their basic working principles, and selective applications are discussed in the following sections.

Michael C. Potter, for the first time in 1911, confirmed the generation of electricity (voltage range of 0.3–0.5 V) by employing microbial cultures like *Saccharomyces cerevisiae* and *Escherichia coli* [13]. Using the concept, the practical development of MFC was undertaken by Cohen in 1931 with his 35 unit setup and MFC was subsequently patented by Davis in 1967 [14]. A conventional fuel cell (FC) has electrodes and generates electricity by electrolysis reaction of chemicals. However, MFCs use microorganisms as biocatalysts to catalyze electrochemical reactions for bioelectricity production. Microorganisms present in the anode compartment, upon provided with suitable substrates (electron donors), metabolize them anaerobically and generate electron, proton, and carbon dioxide as oxidation products. The generated electrons are then moved from the bacterial cell membrane to the anode either directly through membrane bound structures like pili or indirectly by exogenous electron carrier compounds like potassium ferricyanide (mediator) [7]. Subsequently, the electrons are transferred from the anode to the cathode via an external electric circuit. The protons, on the other hand, migrate to the cathode through the proton exchange membrane. These electrons and protons react in the cathode through the process of reduction of dissolved oxygen (electron acceptor) to make water. Electric current is generated by placing an external load between the two electrode chambers. As the microbes transform the chemical energy of the substrate into electrical energy, they are termed as exoelectrogens (microbes generating electricity) or electricigens or electrochemically active bacteria (EAB) [8, 9]. The microbes are also called as anode respiring bacteria (ARB) since the anode first accepts the electron from the anaerobic respiration (anaerobic degradation of substrates) [1]. The general reaction is shown in Eq. (1) and (2) by considering acetate as the organic substrate.

$$\text{Anodic reaction}: CH_3COO^- + 2H_2O - 2CO_2 + 7H^+ + 8e^- \tag{1}$$

$$\text{Cathodic reaction}: O_2 + 4H^+ + 4e^- - 2H_2O \tag{2}$$

Based on the design, MFC can be of dual-chambered and single-chambered, as shown in Fig. 1a, b. The conventional types enclosing distinct cathodic and anodic compartments are dual-chambered MFCs. Single-chambered MFC is devoid of a

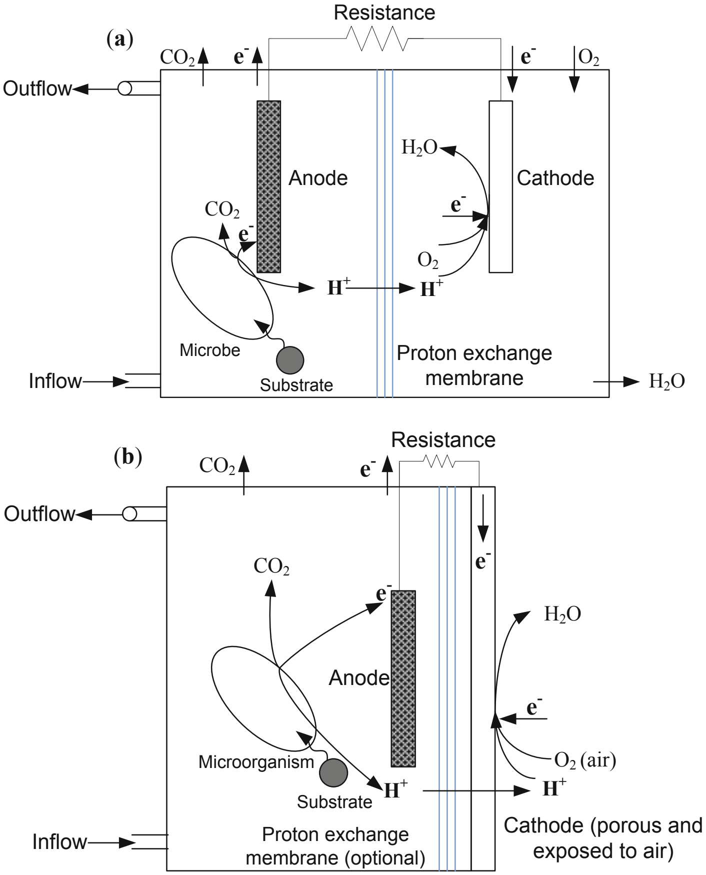


Fig. 1 Design and working principles of (**a**) dual-chambered MFC and (**b**) single-chambered MFC

definite cathode chamber. A porous cathode is fixed on the outer side of the wall of the anodic compartment and is exposed directly to the air, otherwise called as air cathode. The porous cathode allows proton transfer through it and utilizes atmospheric oxygen as the electron acceptor [15, 16]. Likewise, the MFCs that use mediators for electron transport from the microbes to the anode are classified as mediator MFCs, whereas the MFCs that do not depend on mediated extracellular electron transport are called mediator-less MFCs. In a similar manner, membrane MFCs are those that use proton exchange membrane or cation exchange membrane for proton transfer from anode to cathode chambers, whereas the MFCs that eliminate the use of membranes are termed as membrane-less MFCs [7, 17]. Besides these common designs, several designs and structural modifications have been made in MFCs based on the desired end objectives, and some significant developments in conception, design, and targeted multifaceted applications of MFCs are elaborated in the following sections.

2 Structural Configurations and Classifications of MESs

Invariably all the MESs are configured with similar basic constituents, such as an anode, a cathode, electrolytes (anolyte and catholyte), and an electrical circuit. Practically all MESs are based on similar oxidation reaction driven by microorganisms in the anode chamber, in which inorganic or organic substrates are oxidized and the generated electrons are transported first to the anode and then to the cathode. Systematic utilization of these electrons on the cathode side for the realization of a multitude of reduction-based reactions is the key determinant of the versatility of the system with numerous application possibilities. For example, direct capturing of the electrons through an external circuit generates electricity in one instance, whereas in other, the electrons are used in the cathode chamber for the synthesis of organic compounds. Several MESs have been evolved to date, and they are classified based on their application and functionality aspect, as displayed in Fig. 2. When the potential difference across the electrodes (low reduction potential for organics oxidation at the cathode and high redox potential for oxygen reduction at the cathode) is used for electricity generation, the MESs is specified as MFC. When an external voltage is applied to reduce the cathode potential for hydrogen and other product generation, MESs are termed as MEC. Likewise, when the objective is to synthesize useful products via cathodic reductions catalyzed by microorganisms, the MESs are named as microbial electrosynthesis (MES), to reduce oxidized contaminants; microbial remediation cell (MRC), to desalinate water; and microbial desalination cell (MDC) [1, 8, 9]. Therefore, MESs are generally categorized as electrohydrogenesis systems, electrogenesis systems, electrosynthesis systems, and bioelectrochemical treatment systems [1]. There are also some other sub-systems of classifications like enzymatic fuel cells (EFCs) that use particular enzymes for the catalytic oxidation of the substrate, microbial solar cells (MSC) that integrate photosynthetic organisms to supply substrate for microbial electricity generation, the microbial reverse electrodialysis electrolysis cell (MREC) to synthesize hydrogen without external voltage application by connecting reverse electrodialysis (RED) with MEC, and microbial capacitive desalination cell (MCDC) for improved desalination by integrating capacitive deionization (CDI) with MDC [1, 18–20]. Detail discussions of the major types of MESs that have been reported so far are beyond the scope of this chapter. Therefore, only the energy sustainability aspects of the MESs are primarily emphasized, and some new-fangled perspectives of MESs have been highlighted in the following sections.

2.1 *Microbial Electrolysis Cell (MEC)*

The idea of microbial electrolysis cell (MEC) was firstly introduced in 2005 [21]. MEC needs an external supply of electricity to enable hydrogen generation at the cathode through electrolysis of water, followed by the reduction of protons.

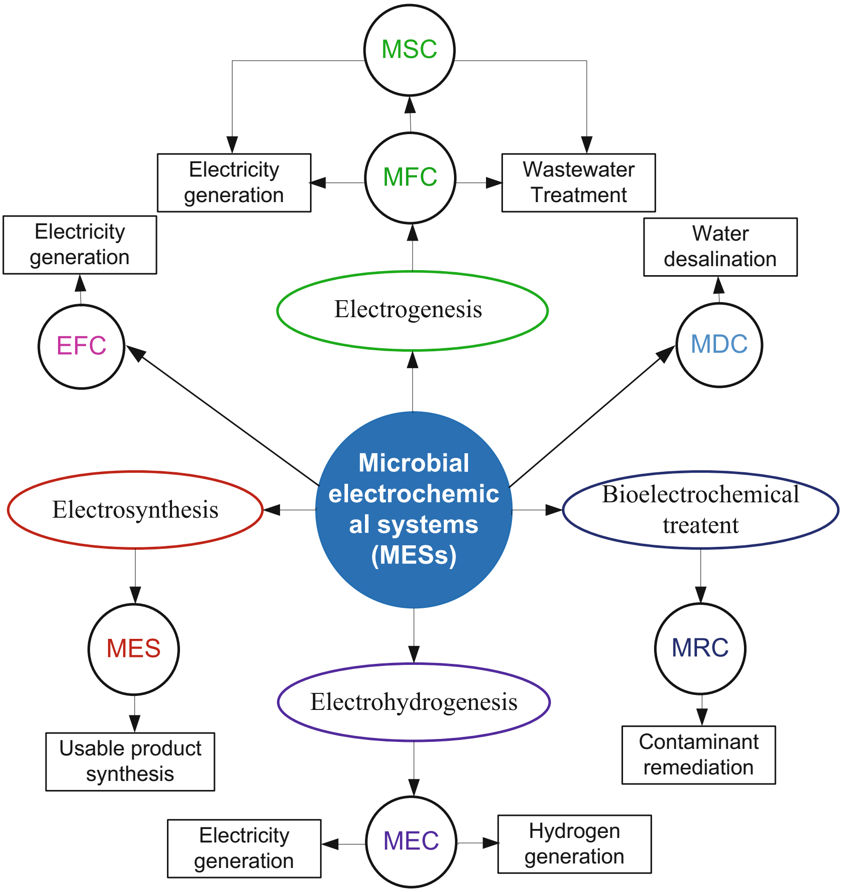


Fig. 2 Overview of different types of microbial electrochemical systems (MESs)

Unlike MFC, the anaerobic condition was maintained in the MEC cathode chamber to facilitate hydrogen production. The basic working principle of the MEC is depicted in Fig. 3a, and as shown in the figure, the supplied external power facilitates the electron movement from anode to cathode. However, most of the energy for this process comes from the microbial substrate oxidation (chemical energy) at the anode; energy requirement from the external source is of a small amount. The power supply in the range of 0.6–1 V reported in the literature was much lesser than the conventional water electrolysis energy requirements (1.8–2 V) [21, 22]. Moreover, due to additional applied voltage, higher electric currents than MFC are generated. One more advantage is that MECs can rely on waste materials as substrates, thereby making the approach more sustainable.

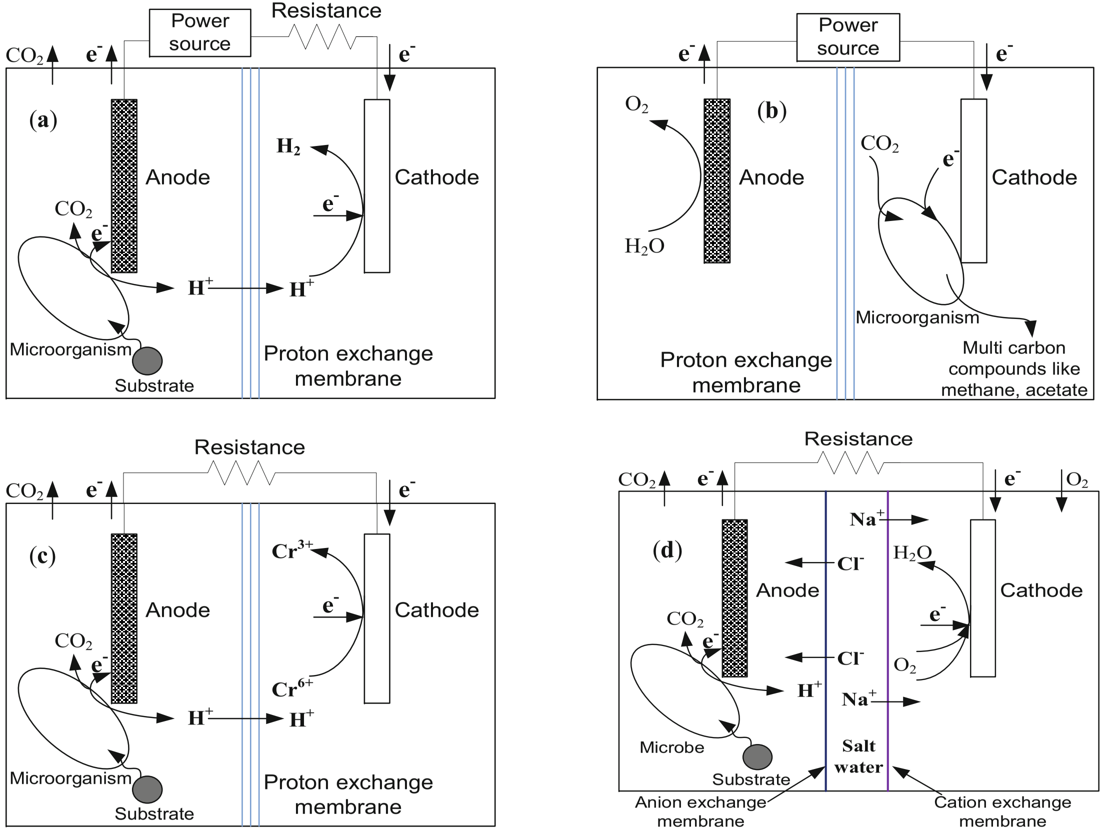


Fig. 3 Structural configuration of different types of microbial electrochemical systems (MESs) (**a**) microbial electrolysis cells (MEC), (**b**) microbial electrosynthesis (MES), (**c**) microbial remediation cells (MRC), and (**d**) microbial desalination cells (MDC)

2.2 Microbial Electrosynthesis (MES)

Microbial electrosynthesis (MES), also named as bioelectrosynthesis, is an emerging domain of microbial electrochemical systems. The concept of MES was introduced hardly a decade ago with the demonstration of methane synthesis using a bio-cathode and an abiotic anode immobilized with *Methanobacterium palustre* [23]. MES utilizes the reducing power generated from the anodic oxidation to reduce carbon dioxide and other compounds into a variety of value-added products. As per the displayed working principle in Fig. 3b, the microbes present in cathodic chamber reduce the available terminal electron acceptor like CO_2, specifically to multicarbon compounds like acetate, ethanol, butyrate, etc., which are precursors of many desirable products like liquid transportation fuels [1, 24]. The MES offers twofold profits of organic production and carbon sequestration, and in addition to that, the possible utilization of renewable energy (the electrons can be from any renewable sources) attracts high research attention toward this emerging domain of microbial electrochemical systems.

2.3 Microbial Remediation Cell (MRC)

Microbial remediation cell (MRC) is one more evolving application of the MESs where contaminants can be applied as cathodic electron acceptor that subsequently undergoes reduction by accepting the electron generated in the anodic chamber (Fig. 3c). Through the process of reduction, the toxicity of the contaminant is either reduced or wiped out. For example, chromium exists in trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) form in aqueous solution, and hexavalent chromium is more hazardous than trivalent one. Using Cr^{6+} as a final electron acceptor, it is reduced to nontoxic Cr^{3+} as per the following cathodic reaction:

$$\mathrm{Cr_2O_7}^{2-} + 14\mathrm{H}^+ + 6\mathrm{e}^- - 2\,\mathrm{Cr}^{3+} + 7\mathrm{H_2O} \tag{3}$$

The above reaction with a redox potential of 1.33 V was thermodynamically favorable for electricity production [25]. In a similar manner, so many oxidized contaminants like uranium, perchlorate, selenite, etc., can be reduced to nontoxic forms in MRCs, thereby remediating the contaminants [8, 9]. MRC also has dual advantages of contaminant remediation and power generation; it is considered sustainable as it uses waste resources as substrates [26].

2.4 Microbial Desalination Cell (MDC)

Microbial desalination cell (MDC) is one more interesting and progressing research area of MESs. MDC uses the electric potential difference among the electrodes to simultaneously perform desalination, electricity generation, and wastewater treatment. It was originally familiarized by Cao et al. [27] as an integrated technology of MFC. As shown in Fig. 3d, it has a supplementary compartment between the anode and cathode compartments to carry out the in situ desalination process. The middle compartment houses a cation exchange membrane (CEM) toward the cathode and an anion exchange membrane (AEM) toward the anode. When the electrons from the anodic compartment migrated to the cathodic compartment, the anions (Cl^-, SO_4^{2-}), and cations (K^+, Na^+) of the desalination compartment transfer to anode chamber and cathode chamber, respectively, to maintain charge balance. In this process of ion movement, the saline solution of the middle chamber is desalinated. Ion migration-mediated increased conductivity resulted in higher electricity generation in MDC as compare to MFC [1, 8, 9].

2.5 Microbial Solar Cells (MSCs)

Microbial solar cells (MSCs) are types of MESs that augment microbial electricity generation with photosynthetic reactions. Unlike other MESs, organic compounds synthesized by the photosynthesis process are used as substrates by anodic electro-active microbes for electron generation. The basic working principles of MSCs include (1) production of organic matter using solar energy by photosynthetic organisms, (2) transportation of the synthesized organic substance to the anode chamber, (3) oxidation of organic substance by anodic electro-active microorganisms, and (4) cathodic reduction of oxygen (or other electron acceptors) to produce water and electricity or compounds like hydrogen, methane, ethanol, etc., based on final electron acceptor [20]. While the anodic microbes in MSCs are essentially same as that of other MESs, based on the photosynthetic organisms used, MSCs are of different types such as plant MSC or plant microbial fuel cell (PMFC) when higher plant cells or plant's root systems are incorporated into MFC anode for photosynthesis, phototrophic MSC when photoautotrophic bacteria is used, and algae MSC when algae is used as photosynthetic organism. MSCs are the sole MESs that do not depend on external organic substrates but harness solar radiation by transforming it into chemicals for further generation of electricity in a clean and effective way [1, 8, 9].

3 Applications of MESs from Bioenergy Prospective

MFC, the first reported MESs, was conceptualized for converting chemical energy to electrical energy accompanied by wastewater treatment employing microorganisms as biocatalysts. However, the application potential of the MESs has broadened dramatically in recent decades due to the diversity of employed microbial biocatalysts. To date, MESs offer a range of applications that includes but not limited to biohydrogen production, synthesis of valuable chemicals, desalination of saline water, bioremediation of contaminants, nutrient recovery from wastewater, etc. This chapter elaborates on some of the application opportunities of MESs pertinent to bioenergy generation for energy sustainability in the following sections.

3.1 Bioelectricity Generation

MFC is the most widely used MESs that uses a diverse group of electro-active microorganisms as biocatalysts to transform chemical energy stored in substrates to electrical energy, and as the generated electricity is the outcome of biological reaction (bio-oxidation of substrate in anode), it is termed as bioelectricity. The basic mechanism of bioelectricity generation is already discussed in Sect. 1. As the power generation in MFCs is generally low, their applications are restricted to small electrical devices like wireless sensors and telemetry systems that have lesser power necessities [15]. Essentially, an MFC has its fuel source or substrate (e.g., wastewater), which on oxidation at the substrate-anode interface generates electron for electricity production [28]. Therefore, the electricity production efficiency of MFCs is governed by the degree of substrate biodegradation and electron recovery, which means the higher the biodegradation and electron recovery, the higher the bioelectricity generation. For example, MFCs fed with synthetic wastewater containing simple and easily degradable organic substrates like glucose and acetate generate approximately ten times more power densities than the MFCs supplied with actual wastewater containing complex carbon sources [21, 29, 30]. Bioelectricity generation efficiency is also dependent on the electron transfer efficiency of the employed microorganism. Ideally, a single *Escherichia coli* cell with a doubling time of half an hour and a volume of 0.491 μm^3 has the potential to yield 16,000 kWm^{-3} power densities [31]. However, practically a voltage between 0.3–0.5 V is obtained considering the energy gain by microorganism and energy loss at the cathode while using glucose or acetate as a fuel source [31]. Continuous improvisation in the bioelectricity generation efficiency of MFCs has been witnessed in recent times by adopting architectural changes in MFCs, electrode modifications, exploring efficient electro-active microbes, etc. Some of these strategies include tubular design to increase electrode surface area and decrease system resistance, internal resistance reduction by using proton exchange membrane with the larger surface area than electrodes, increasing electrolyte conductivity, moving anode closer to the cathode, using mixed microbial culture instead of pure culture, using of air cathode for reduced internal resistance, etc. [1, 8, 9, 15]. Though theoretical maximum power density has yet to be achieved, power density in modern MFCs rose from 0.1 to 6.9 W/m^2 during the period 1999–2008 [32]. Further improved power densities, as reported in recent literature, are mostly achieved by connecting multiple MFC modules or by using large-scale configurations as discussed in detail later in Sect. 5 [33]. For example, a power generation efficacy of 51 W/m^3 was reported when 5 units of 72 L MFCs were integrated [34]. Likewise, power densities more than 120 W/m^3 was achieved in cassette-electrode MFCs using starch, peptone, and fish extracts containing model organic wastewater [35, 36]. In recent studies, power densities of 31.6 and 12 W/m^2 were reported using clarified cashew apple juice and mustard tuber wastewater as feedstock in MFCs, respectively [37, 38]. It can be mentioned here that power densities are typically reported in W/m^2 (meter square of the electrode surface area) or W/m^3 (meter cube of the anode compartment volume); conversely, in the case of devices connecting several units, it is preferable to express power densities in terms of watts per MFC unit [33]. Most of the modern MFCs' ability to generate electricity by using wastewater as fuel sources might play a vital role in renewable energy production. Therefore, from practical aspect of bioelectricity generation, pilot MFCs with adequate energy output should be encouraged [28, 39]. A summary review of bioelectricity potential of different MFCs is presented in Table 1, and further details can be obtained from Kumar et al. [33], Bhatia et al. [54], and Bajracharya et al. [1].

3.2 *Bioelectrohydrogenesis*

MECs are the designated MESs to produce hydrogen instead of electricity. As discussed in Sect. 2.1, MECs offer attractive alternatives to hydrogen production at comparatively low electric power requirement (0.6–1 V) than conventional water electrolysis (1.8–2 V). Hydrogen generation by MEC is otherwise known as bioelectrochemically assisted microbial reactor process (BEAMR) or biocatalyzed electrolysis or bioelectrohydrogenesis [33]. Kreysa et al. [55] first attempted hydrogen production using MECs. Unlike electricity generation in MFC, the synthesis of hydrogen from the protons and the electrons generated in the anode by microbial metabolism (substrate oxidation) is thermodynamically unfavorable [15]. Therefore, the external power supply is essential to overcome the thermodynamic barrier to reduce H$^+$ to hydrogen at the cathode. The overall reactions of hydrogen generation in MEC considering acetate as substrate are as follows:

$$\text{Anodic reaction}: \mathrm{CH_3COO^-} + 4\mathrm{H_2O} - 2\mathrm{HCO_3}^- + 9\mathrm{H^+} + 8\mathrm{e^-} \tag{4}$$

$$\text{Cathodic reaction}: 8\mathrm{H^+} + 8\mathrm{e^-} - 4\mathrm{H_2} \tag{5}$$

Table 1 Summary of bioenergy potential of some reported MESs

MESs employed	Substrate types	Bioelectricity generation	Bioelectrohydrogenesis	Bioelectrochemical methane production	References
MEC-MFC coupled system	Acetate	CD- 9–78 mA/m^2	0.2–2.9 mL/Ld	NR	[40]
Pilot-scale continuous flow electrolytic cell	Winery effluent	CD- 0.25 A/m^2	13.8 L/dm^2	30.2 L/dm^2	[41]
Single and two-chamber MECs	Waste activated sludge	CD- 8–129 A/m^3	0.056–0.91 m^3-H_2/m^3d	NR	[42]
Pilot-scale microbial electrolysis cell	Domestic wastewater	CD- 0.3 A/m^2	3.6 L/dm^2	0.06 L/dm^2	[43]
Semi-pilot tubular MEC	Domestic wastewater	CD- 0.22 A/m^2	2.1 L/dm^2	0.4 L/dm^2	[44]
A 19 L microbial electrolysis cells	Synthetic wastewater	CD- 0.1 A/m^2	0.45 L/dm^2	0.82 L/dm^2	[45]
H-type reactor	Spent yeast and ethanol	CD- 222 A/m^3	2.18 m^3-H_2/m^3d	NR	[46]
Pilot-scale MEC	Urban wastewater	CD- 0.3 A/m^2	2.52 L/dm^2	<5% of total gas volume	[47]
Single-chamber MEC	Glycerol, milk and starch feed	CD- 150 A/m^3	0.94 m^3-H_2/m^3d	NR	[48]
Stacked MEC	Activated sludge	CD- 0.01 A/m^2	0 m^3-H_2/m^3d	0.08 L/dm^2	[49]
Single-chamber photosynthetic biohydrogen reactors	Glucose, acetate, propionate, butyrate, etc.	PD- 1451–3,351 mW/m^3	0.44 mmol L/h	NR	[50]
Single-chamber MEC	Swine wastewater	CD- 112 A/m^3	0.9–1.0 m^3-H_2/m^3d	13% of total gas volume	[51]
Single-chamber MEC	Starch processing wastewater	CD- 135–158 A/m^3	1.41–1.52 m^3-H_2/m^3d	NR	[52]
Single-chamber MEC	Sodium acetate	CD- 292 A/m^3 PD- 0.0145 W/m^2	3.12 m^3-H_2/m^3d	28% of total gas volume	[53]

CD current density, *PD* power density, *NR* not reported

Theoretically, the endothermic barrier is of −0.414 V (versus the standard hydrogen electrode); the anodic oxidation reaction can supply potential of −0.274 V, so, applying only the small voltage difference of 0.14 hydrogen formation can be possible [22]. Due to the contribution of microbial metabolism for hydrogen production, this technology is termed as bioelectrohydrogenesis. MECs can generate about two times more hydrogen (8–9 mol) than conventional fermentation (4 mol) from 1 mole glucose [21, 29]. However, the hydrogen evolution reactions (HER) are slow in nature, and the practical applications necessitate high hydrogen generation rates. The operational and design criteria, such as the use of electrocatalysts like platinum, nickel, etc., use of exclusive organic materials as substrates, increased electrode surface area, low space between electrodes, etc., are being practiced to achieve up to 11 mol H_2/mol glucose that is three times more as compare to dark fermentation [22]. For example, Sun et al. [40] managed a hydrogen generation rate of up to 17.8 m^3 H_2/m^3d through low electrode space. Likewise, through the increase of the specific surface area of Ni cathode, hydrogen generation rate as high as 50 m^3/m^2 MEC/d was achieved [56]. Superior hydrogen generation in the range of 5.67–15.02 mg-H_2/g-VSS was accomplished from waste activated sludge in a two-chamber MECs [42]. Sosa-Hernández et al. [46] highlighted a hydrogen generation rate of 2.18 m^3 H_2/m^3d from spent yeast feedstock in a single-chamber MEC using stainless steel mesh cathode and graphite fiber brush anode. With an energy yield 2.57 times higher than that of methane, hydrogen is viewed as the promising energy carrier of the forthcoming global economy [57]. Hydrogen finds extensive applications both as fuel and chemical in numerous industrial practices, such as saturating fats and upgrading fossil fuels. Therefore, MEC-mediated biohydrogen production can add significantly to the global hydrogen demand in a hydrogen economy. Excessive hydrogen generated can even be stored for future applications. Moreover, as bioelectrohydrogenesis relies on renewable and waste materials as substrates, it may appear as a promising renewable hydrogen/energy source in the future. A brief overview of hydrogen production efficiencies of different MECs is summarized in Table 1, and for further details, Rousseau et al. [58], Kumar et al. [33], and Bajracharya et al. [1] can be referred.

3.3 Bioelectrochemical Methane Production

Microbial electrosynthesis (MES) carries great potential to convert carbon dioxide to methane. In MES, methanogenic microorganisms in the cathode compartment use the electrons derived from the cathode (bio-cathode) to generate methane by reducing CO_2, and the basic mechanism is explained in Sect. 2.2. As MES exploits the microbial metabolism for methane generation, the process is also known as bioelectromethanogenesis. Theoretically, a cathodic potential of −0.244 V (against standard hydrogen electrode) is required to overcome the thermodynamic unaffordability of methane generation from CO_2 reduction; therefore, applied cathode potentials in the range of −0.5 to 1 V have been suggested bioelectromethanogenesis [59, 60]. Though the methane production efficiency through MES is usually low, a significant increase in production rate has been witnessed from 4.5 to 30.3 L CH_4/m^2 of cathode/d with respective efficiencies of 80 and 100% [61]. The advantage of bioelectrosynthesis as compared to conventional methanogenesis is the physical isolation of the substrate oxidation from methane synthesis process, thereby protecting the methanogens from the inhibitory chemical compounds [1]. CO_2 produced from different biological methods can be combined into MES for improved sustainability of methane production. MES is adjudged as a clean technology since it uses a contaminant (CO_2) to generate a product (CH_4), which is a fuel with little harmful impact on the environment with respect to other fossil fuels. Moreover, methane produced through MES process are in pure form (contrast to biogas generated from anaerobic digestion with 30–40% CO_2 content) which can be directly used in different applications without a further purification step; hence additional cost for purification can be avoided [10]. Another advantage of MES mediated electromethanogenesis is that using wastewater as substrates, wastewater treatment and methane production can be achieved simultaneously. The results of bioelectromethanogenesis are quite encouraging, despite many techno-economic challenges like low reaction kinetics, product separation from the solution, etc. [13]. Therefore the prevalent challenges of bioelectromethanogenesis need to be overcome before large-scale implementations.

4 Strategies for Enhanced Efficiency and Cost-Effectiveness

Despite continuous expansion in the application scope of MESs beyond electricity generation and wastewater treatment, this early-stage technology has never been considered a serious contender in any of its promising application fields, mainly because of high operating costs and low performance efficiencies. The high capital costs of MESs are associated with the use of expensive electrodes materials, like platinum and palladium; commercially available proton exchange membrane, like Nafion 117; and use of pure carbon sources as substrates, whereas efficiency issues are mostly linked to the competencies of employed biocatalysts or microorganisms and electrode materials. In the past few years, plentiful strategies have been attempted by many researchers to improve the performance efficiencies of the MESs and make them more cost-effective. Some of the recent advancements in electrodes, microbial biocatalysts, and waste material based substrates are highlighted in the following sections.

4.1 Alternative Anode Materials

The anode is a vital constituent of MESs that facilitates the electron transfer process, so it is critically important for the performance efficiency of the diversified electrochemical systems. Therefore, the anode materials and its architecture play a major role in determining the performance efficiency of the MESs since anode regulates important mechanisms like electron transfer, microbial immobilization/biofilm formation, and substrate oxidation [62]. Key features of anode materials for enhanced performance include (1) biocompatibility, (2) low electrical resistance, (3) resistance to corrosion, (4) high electrical conductivity, (5) high mechanical strength, (6) large surface area, (7) environmental friendly, and (8) low cost [13, 28, 62]. The anode must exhibit sufficient longevity when exposed to diverse wastewaters containing various contaminants that can possibly react with the anode materials, thereby deteriorating anode and declining efficiency [63]. While most of the past studies emphasized on the use of materials of carbon origin like carbon cloth, graphite rod, activated carbon, etc., in the last few years, the use of a new class of anode materials, like graphene, carbon nanotubes, stainless steel, etc., is on the rise. The earlier anode materials are mostly two-dimensional in nature with many limitations, like low surface area, high activation overpotential, high internal resistance, etc., which result in lower efficiency [62].

In recent times, with the help of nanotechnology, three-dimensional anode materials are being developed that offer high surface areas for microbial colonization, ease in substrate accessibility, reduced mass transfer limitations, and high electron transfer efficiency, subsequently resulting in higher efficiency [64]. The anode surface modification for accelerated biofilm development also plays an important role in performance efficiency improvisation through superior electron transmission from bacteria to anode surface. For example, surface modified with a conducting polymer (polyaniline (PANI)) coating and carbon nanotubes was found to be effective in improving biocompatibility and attaining high surface areas, favoring electron transfer kinetics [65]. Composite anodes where two or more materials are used to realize the synergistic effects of all the constituent materials have attracted considerable interest in recent years for their improved anodic kinetics performances. Similarly, the use of many metals like stainless steel, copper, etc. as anode materials is also on rise in recent times [62]. The modern anode materials are broadly classified into four different categories, such as composite, metal-based, carbon-based, and surface-modified anodes [62]. Some of these advanced anode materials, their classifications, examples, advantages, and disadvantages are highlighted in Table 2.

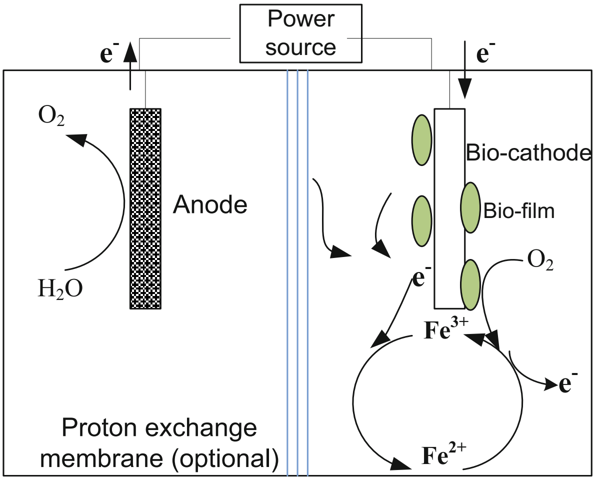
4.2 Bio-Cathodes

The cathode is the electrode where oxygen reduction reaction takes place, which is often the limiting reaction of most of the MESs. Therefore, cathode materials also play a vital role in the performance efficiencies of MESs. Most of the materials that are used as anodes, such as carbon cloth, graphite, etc., can be also used as cathodes. But the slow oxygen reduction kinetics nature of theses cathode necessitates the usage of catalysts like platinum (Pt-coated carbon electrode) to reduce the cathodic reaction

Table 2 A brief lists of reported advanced anode materials

Category	Sub-category	Examples	Advantages	Disadvantages	References
Carbon-based	Natural materials	Bamboo charcoal, corn stem charcoal, mushroom carbon, etc.	High surface area, low cost, biocompatibility, high electrical conductivity, high chemical stability, etc.	Low mechanical strength, high resistance, prone to clogging, etc.	[62, 66–68]
	Synthetic materials	Electrospun carbon fiber, interlacing carbon yarn, graphite fiber brush, etc.			
Composite	Graphene-based	Reduced graphene oxide-nickel (R-GO-Ni) foam, graphene modified stainless steel mesh (GMS)	Large specific surface area, better kinetic activity, high mechanical strength, tolerance to high substrate concentration, etc.	Relatively expensive	[8, 9, 69–71]
	Carbon nanotube-based	Carbon nanotube-textile (CNT-textile), CNT coating on macroporous sponge (CNT-sponge)			
Surface-modified	Polymer coating	Polyaniline (PANI)-mesoporous tungsten trioxide (m-WO_3), PANI coated glassy carbon anode	High conductivity, enriched biofilm formation, high biocompatibility, low overpotential, lower ohmic loss, lower start-up time, etc.	Occasional reduced porosity, interchangeability of hydrophobic-hydrophilic property, etc.	[8, 9, 72–74]
	Carbon surface treatment	TiO_2 nanosheet modified carbon paper, activated carbon (AC) with SSM (AcM)			
Metal-based	–	Stainless steel, planar gold	Cost-effective, high mechanical strength, high conductivity, reasonable biofilm formation, etc.	Corrosive in nature, surface area limitation, etc.	[75, 76]

Fig. 4 Abiotic iron reduction and biotic reoxidation in a bio-cathode reaction process



activation energy for improved performance efficiency. Platinum is an expensive material, and the use of catalysts itself is often expensive and not a sustainable option due to the persistent need to replace the exhausted materials [28]. To overcome the catalyst requirement, research interest is currently directed toward bio-cathode application, in which microorganisms are employed to catalyze the cathodic reaction by accepting electrons from the cathode [77]. In bio-cathodes, many materials including transition metal compounds (Fe(II), Mn(II)), oxygen, inorganic salts (nitrate, sulfate), carbon dioxide, etc. can be used as the final electron acceptor [78, 79]. Depending on the final electron acceptors, bio-cathodes can be of aerobic type when final electron acceptor is oxygen and anaerobic types when nitrate, sulfate, etc. are used as the final electron acceptors. In aerobic bio-cathodes, the oxygen can be used as a direct electron acceptor or as an indirect electron acceptor where under aerobic conditions, transition metals such as iron and manganese mediate the oxygen transfer process. The transition metal compounds are first reduced abiotically by the cathode and subsequently reoxidized by the cathodic bacteria. For example, ammonia oxidation to nitrate (nitrification) and successive reduction of nitrate to dinitrogen gas (denitrification) by *Geobacter metallireducens* in MESs is an example of anaerobic bio-cathode reaction [80–82]. Similarly, an example of an aerobic bio-cathode is the abiotic reduction of ferric ion to ferrous ion by accepting electrons from the cathode and subsequent regeneration of ferric ions (oxidation of ferrous) that have been utilized as electron mediators in the cathodic chamber by *Thiobacillus ferrooxidans*, as demonstrated in Fig. 4 [79, 80]. Bio-cathodes have several advantages over abiotic ones, including less expensive (no catalyst use), reduced internal resistance, sustainable (no electron mediator use), elimination of Pt-catalyst-mediated sulfur poisoning, microbial metabolism mediated usable product generation in cathodic reaction, etc. However, further research is needed to address some issues like inefficient proton transport-mediated pH fluctuations in anode and cathode chamber and possible inhibition of microbial activities within the cathode chamber due to metabolite accumulations [78, 79].

4.3 Improved Microbial Electrogenesis

The anodic electron transfer mechanism is a crucial step involved in governing MESs performance efficiency. In earlier times, redox-active compounds, mediators (exogenous mediators) were used to transport the electrons generated through the microbial degradation of substrates to the electrodes. Subsequently, from cost-effectiveness and practical application point of view, microbial transfer of electrons either through the mediators produced by the microorganism (endogenous mediators) or by direct transfer via respiratory enzymes like cytochromes on the outer plasma membrane or via pili to the anode is being focused by many researchers [7, 15]. Many microorganisms have the inherent feature of electron donation, and they are called exoelectrogens or electrochemically active bacteria, as discussed in Sect. 1, whereas the microorganisms capable of accepting electrons are termed as exoelectrotrophs [28]. As per literature, approximately 35 pure culture strains have been used in MESs as exoelectrogens till 2018, and some of the widely used ones include *Geobacter*, *Pseudomonas*, *Shewanella*, *Rhodoferax*, *Clostridium*, *Escherichia*, *Saccharomyces*, *Klebsiella*, etc., belonging to diverse microbial phyla such as *Proteobacteria*, *Actinobacteria*, *Firmicutes*, *Eumycota*, *Acidobacteria*, *Chlorophyta*, etc.; for detail classification, Li et al. [7] can be referred. Low electron transfer rate is a major bottleneck that hinders practical applications of MESs; therefore, many ongoing researches are focusing on improvisation of the electron transfer mechanism or electrogenicity of the microorganisms to achieve enhanced performance efficiency for possible practical applications. Several techniques have been used to improve electrogenicity features of certain microbes such as chemical modification of microbial cells, genetic modifications of microbial cells, synthetic biology approach, etc.; however, based on the wider application, former two aspects are discussed in this section [7]. In the case of some exoelectrogens, endogenous mediators are abundant in the cytoplasm to mediate electron transfer operation. But, very often, due to the presence of non-lipopolysaccharide outside the plasma membrane (gram-negative bacteria), the mediators cannot transport to the outer membrane for further transfer to electrode surfaces. Chemical treatment (polyethyleneimine (PEI) treatment) of the microbial cells induces large pore and channel formation on the cell membrane, which ultimately facilitates the diffusion of mediators for enhanced electron transfer. Moreover, the alteration of the cell membrane (increased roughness) by chemical treatment assists the bacterial cell in adhering to the electrode surface more easily, thereby enhancing electron transfer rates [83]. Similarly, Xu et al. [84] recommended the addition of trace heavy metals (Cu^{2+} or Cd^{2+}) to the anodic chamber as a viable strategy to improve the performance efficiency of MESs by improving mediator accumulation and the anodic bacterial attachment for a higher rate of electron transfer. Like chemical modification, genetic modification of exoelectrogens is one more effective method to increase the microbial electrogenicity. Genetic modifications can be done by modification of endogenous mediator synthesis pathways, electron transfer pathways, cofactor manipulation, etc. For example, pyocyanin (PYO) in *Pseudomonas aeruginosa* mediates electron transfer between sessile cells in anodic biofilms and the anode surfaces. The electron transfer rate was increased significantly by inoculating *Pseudomonas aeruginosa* with a genetically modified PYO synthesis pathway [85]. The same researchers achieved fourfold increase in power output, 1.6-fold increase in PYO production and onefold decrease in internal resistance in MESs by using *Pseudomonas aeruginosa* strains with overexpressed methyltransferase encoding gene, *phzM* as compared to wild-type strains [85]. Therefore, strategic genetic modification is an effective approach to improve microbial electrogenicty, provided, the genetic manipulation should not trigger the virulence factors of the microbial strain.

4.4 Waste/Xenobiotics as Substrates

The substrate is a critical factor affecting the performance efficiency and economic viability of MESs as it serves as a source of electron and energy for the microbial biomass of MESs. A varied range of substrates including pure compounds (glucose, acetate), lignocellulosic biomass, organic and inorganic wastes, landfill leachates, wastewater of diverse origin, etc., have been utilized in MESs till date [16]. However, exploiting natural or synthetic (xenobiotics) waste materials as substrates is considered as a sustainable and environmental friendly approach with dual advantages of bioenergy production and pollution prevention. Though it has been observed that the performance efficiencies of the MESs are relatively low when complex waste materials are used as substrates than the usage of simple and pure substrates, it is anticipated that with progresses in technology, the improved performance efficiency can be achieved [16, 17]. In this section, the use of some uncommon wastes in MESs has been highlighted. The waste materials of diverse origins are usually complex and consist of a mixture of oxidizable and non-oxidizable compounds. Based on the fraction of oxidizable constituents, waste materials can either be used as an electron acceptor or electron donor. The contaminants like azo dyes, organochlorine, nitro aromatic compounds, metal ions, etc., with a dominant fraction of non-oxidizable components, cannot be oxidized at anode due to their high redox potentials [26]. However, these compounds can be used as terminal electron acceptors at the cathode, and considering chromium (metal ion) reduction process, the detailed mechanism is already discussed under microbial remediation cell heading. On the other hand, the waste materials like agro wastes, wastewaters, etc., with higher oxidizable fractions can be easily degraded by oxidation, thus can be used as substrates (electron donors) at the anode. For example, the agro wastes (the waste materials from agricultural activities like poultry processing, farming, slaughter houses, fisheries, agro industries, etc.) generated during the production of starch from cassava are rich in organic matters. The starch-rich wastewater is also rich in cyanoglycosides, which on hydrolysis forms cyanide, the common contaminant of cassava wastewater that necessitates proper treatment prior to the discharge of the wastewater to the environment [86]. So, employing the cassava processing wastewater as a substrate in MESs, both wastewater treatment (COD and cyanide removal) and bioenergy generation can be achieved. Kaewkannetra et al. [86] reported the utilization of sludge from a wastewater treatment plant of a cassava mill factory (16,000 mg/L organic content) as a substrate in MFC. They achieved 88% COD removal and 1,771 mW/m^2 power generation within 120 h of operation. Similarly, for detailed use of lingo cellulosic biomass, poultry processing wastes, brewery wastewater, textile wastewater, etc., in MESs from treatment and bioenergy recovery prospective, Chaturvedi and Verma [26], and Pant et al. [16] can be referred.

5 Scale-up and Summary of Large-Scale Practical Implementations of MESs

Even though in recent years the functional aspects of MESs have extended noticeably and the performance efficiencies have upgraded exponentially, the scale-up and commercialization of MESs are still facing enormous challenges. The successful implementation of these technologies is limited to laboratories, and achieving the rigor of laboratory testing in field conditions is essential to take these technologies forward. Moreover, the scaling-up of MESs from laboratory-scale to pilot-scale systems is necessary to figure out the suitability of the technologies in real-world applications. The major drawbacks MESs is facing during scaling-up are reduced performance efficiency. This is because of process complexity in terms of mixing in the anodic chamber, aeration in the cathodic chamber, membrane fouling mediated increase in the internal resistance, the distance between the electrodes, influent fluctuation, leaking unfavorable products, etc. [8, 9, 12]. Another factor hindering scaling-up is the cost associated with the electrodes, membranes, and pure substrates used in the MESs and the accessibility of the components (electrodes, membranes, etc.) in large quantities for pilot-scale assembly [12, 26]. However, continuous attempts are being made to overcome the existing limitations in MESs. For example, miniaturization of MFCs and stacking up the number of MFCs and multiple electrodes in individual modules, hydraulic isolation of these modules, and connection of multiple modules (series/parallel) resulted in increased power densities by overcoming internal resistance [87]. Similarly, low-cost alternatives, like substituting platinized cathodes with non-platinized ones, ion exchange membranes with cheap battery separators, use of nickel and stainless steel alloys as inexpensive alternative cathodes in MECs, utilization of waste materials as potential substrates etc., have dramatically reduced the operational costs of MESs [10, 16]. A few pilot-scale studies of MESs are discussed hereunder.

The initial large-scale MES-based application was an MFC developed by the University of Queensland that comprised of 12 individual, summing up to a total volume of approximately 1 m^3. The power production was inadequate due to the low conductivity of the wastewater used and cathodic biomass proliferation on the cathode [88]. Another implementation of a 200 L modular MFC for the treatment of primary effluent as reported by Ge and He [89] achieved 75% chemical oxygen demand (COD) removal and power generation of 200 mW, which was sufficient to drive the catholyte recirculation pump of the plant. Another large-scale MFC of 1,000 L capacity consisting of 50 modules exhibited approximately 90% of COD removal and around 60 W/m^3 power densities on treating real municipal wastewater for a period of 1 year [90].

The first pilot-scale 1,000 L capacity single-chambered MEC was operated in a continuous mode for a period of 100 days in treating winery wastewater at a hydraulic retention time (HRT) of 1 day, 31°C temperature, and 760 ± 50 mg/L soluble COD. The COD removal rate was 62%, methane production was 85%, and hydrogen production was limited since methanogenesis was dominated by consuming the generated hydrogens in the single-chamber design [41]. Heidrich et al. [91] reported the operation of a continuous flow 120 L MEC with cassette design of electrodes for the treatment of raw domestic wastewater at an HRT of 1 day, the temperature in the range of 1–20°C, and 125–4,500 mg/L of COD, for a period of 12 months. The COD removal rate was 30%, pure hydrogen (100 ± 6.4%) production rate was 0.015–0.007 L_{H2}/L/d, and 41–55% columbic efficiency was observed. However, energy recovery was inadequate to achieve energy neutrality of the system [91]. In another study, Baeza et al. [47] used a 130 L MEC with cassette-style electrodes to treat primary domestic wastewater for 5 months at an HRT of 2 days and temperature range of 18–22°C. COD removal was 25%; almost pure hydrogen (95%) was produced at a rate of 0.032 L-H_2/L/d, with the high energy recovery of 121% and cathodic gas recovery of 82% (with respect to electrical energy input). Though this is one of the most successful implementations of MESs in terms of energy production, difficulties were there related to the application of electric potentials [47]. Even though the up-scaling of MESs provided promising results so far, some associated issues like overpotential, long-term stability of electrode materials in pilot-scale application, etc. need to be addressed.

As discussed in earlier sections, MESs has exhibited noteworthy efficiency in treating diversified wastewaters of municipal, industrial, and agricultural origins. The ability of MESs to concurrently treat wastewater and generate clean energy in the form of electricity and fuels such as methane and hydrogen makes it a promising implementary technology of the future. On the other hand, as discussed in the Introduction section, anaerobic treatment technologies with advantages of low energy demand and renewable energy recovery from the produced biogas are extensively practiced as energy positive processes in recent times [92]. Therefore, both MESs and anaerobic technologies are energy positive processes that generate clean energy through wastewater treatment. Both these technologies have their own advantages and limitations. In Table 3, a comparison is presented between MESs and anaerobic technologies by considering bioenergy aspects as reported by Pham et al. [93] and Do et al. [15].

Table 3 Comparison of MESs and anaerobic treatment technologies

Category	MES	Anaerobic technology
Application scope	Appropriate for low-strength wastewater containing simple carbon sources like glucose or acetate. Satisfactory performance even at temperatures below 20°C	Suitable for both high- and low-strength wastewater with complex carbon sources. Performs best at hig + her temperature of about 30°C
Inoculum	Pure or mixed cultures of aerobic or anaerobic microorganisms	Usually a mixed microbial consortium of anaerobic microorganisms
Form of bioenergy	Direct electric current and other energy rich chemicals like biohydrogen, biomethanol, etc. Low level of energy is produced	Mostly as methane or hydrogen from biogas. Produced biogas can be converted to high energy sources for heating or electricity generation
Bioenergy equivalence	4 kWh of electrical energy can be obtained from1 kg of COD Typical power density of MFCs is around 40 W/m^3 which can be enhanced up to 200 W/m^3 in stacked MFCs	1 kWh energy equivalent can be achieved from 1 kg of COD digestion 400 W/m^3 power density can be obtained on digesting 5–25 kg of COD/m^{3}d
Advantages	High organic removal, low energy demanding, less sludge production, no aeration requirement, efficient pathogen removal, etc.	High removal of nutrients and xenobiotic wastes, less sludge production compared to anaerobic technology, extensive application with limited electrical infrastructure
Disadvantages	Treatment/removal of dissolved gases like H_2S and CH_4, inefficient nutrient removal, difficulty in recovering CH_4 from biogas	Low organic removal efficiency, sometimes require aeration, low bioenergy generation efficiency, high cost of proton exchange membrane and electrode materials

6 Future Prospects

MESs are a group of advanced technologies capable of exhibiting electricity-driven chemical and fuel production to chemical energy-driven electricity production and are more recently termed as a platform technology, that is, the technology with numerous application possibilities. However, there are certain shortcomings like low efficiency, high operational and constructional costs, low power density, limited long-term stability of electrodes, etc. that hinder the scale-up and practical applications of these technologies. Therefore, forthcoming research activities should emphasize on the following few issues for the prospective commercialization and real-world applications of these technologies. As the electron transfer mechanism is the key determinant of diverse functionalities of MESs, it is critical to understand the microbial metabolism in light of the electron transfer efficiency, mechanisms involved, the biochemistry of microorganisms while serving as electron donors (anode), or electron acceptors (cathode). Instead of pure cultures, the mixed microbial consortium could effectively carry out electron transfer operations. Future research should emphasize in terms of materials (sustainable, low cost, high performance), cots, and substrates materials that can be helpful in bringing these systems at a level where they can be commercially viable. MFC stacking is an important approach of increasing the net power to the level necessary for large-scale operation; for efficient MFC stacks, further consideration must be given to minimizing ionic short circuiting and kinetic losses. Future research should also focus on the possible synergism of MES with other technologies for further versatility in MESs application. The combination of MESs and fermentation technology known as electro-fermentation (EF) can use electrical energy for microbial fermentation and can supply electrons for the synthesis of the desirable products. This approach is forecasted as prospective applications to overcome challenges associated with the microbial electrosynthesis of value-added products.

7 Conclusions

MESs have the potential to play a central role in energy sustainability by producing bioenergy in the form of electricity, biofuels (methane and hydrogen), etc., from renewable and waste biomass. It is reported that MES-based chemical production is techno-economically more feasible process than electricity generation in MFCs, due to the cost of chemicals and simple collection processes of synthesized chemicals. But MESs are relatively new with a limited assessment of their life cycles and efficiency comparisons with the established technologies. Still, keeping the research progress and encouraging results in view, it has been anticipated that the application of MESs will contribute significantly to transitioning dependency from fossil fuel based resources (grid electricity) to renewable resources (bioelectricity, biofuel). However, the environmental footprints and bioenergy potential of different MESs have to be systematically quantified before the implementation of pilot-scale applications. Therefore, though the MESs are in their nascent stage of development, it is through focused research these technologies can be effective with wider acceptance as sustainable solutions to simultaneously address global environmental and energy issues.

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Generation of Osmotic Power from Membrane Technology

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Contents

Abstract The whole world is facing challenges for energy supply due to the economic developments, increasing population because of the decrease in oil/gas reserves. Therefore, in current decades, alternative energy sources are in focus to fulfil the energy gap between energy demand and supply. Wind, solar, and biomass are good and sustainable energy sources but – have high installation costs. Henceforth, to find out the cheap, clean, safe, and adequate energy sources is still a prime challenge for the researchers. Power generation by using membrane technology is the new achievement in this list. From the last few decades, pressure-retarded osmosis (PRO) is involved to generate the power, and it offers the opportunity for utilizing osmotic pressure gradients for a wide range of applications. Generating power from the PRO is an emerging platform technology that produces high electric power. In this research area, the membrane science community has expanded huge attention, currently, polymer composite, and nanocomposite membranes are involved in osmosis power generation application. In this chapter, we discuss the treasured insights and tactics for the fabrication and design of highly active anti-fouling materials and membranes for pressure-retarded osmotic power generation.

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1 Introduction

Nowadays energy demand is increasing day by day in human life due to economic growth and rising populations [1–3]. As predicted by US energy information administration, the total energy consumption will increase up to 240 British thermal units (Btu) in 2040 [4]. The world primary demand for energy has been increased more than doubled in the next two decades. Day by day oil and gas reservoirs are going to reduce and because of that whole world is facing lots of energy problems [5]. There are lots of challenges on how to fulfil the increasing demand by our society [6]. To provide the sufficient energy, we need to find out various resources. Currently, we are using safe and sustainable energy sources like coal, wind, hydro, tidal wave, and biomass for providing energy to our societies for the use of their daily life. However, these all energy sources required high energy costs, and even though, also there is a problem of uneven distribution of energy. Providing affordable clean, safe, and satisfactory energy sources is the biggest world challenge. For the generation of affordable energy sources, alternate energy sources are needed to find out [7]. Polymer-based membranes can become one of the preeminent alternatives for the generation of energy, and researchers are working very hard for the large-scale commercialization of it.

PRO is one of the best alternatives, to fulfil our energy demand in the future [1–3]. More than five decades ago, Norman and Loeb et al. find out the concept and viability of PRO for the osmotic power generation [8–10]. PRO has a low environmental impact to fulfil energy demand because no chemical or hazardous gas can be generated throughout the process [5, 11–13]. In this process through the polymer membranes, osmotic energy can be generated. In PRO the energy is generated while mixing two different salinity water called osmotic pressure gradient energy [14]. For PRO electrospun nanofibers prepared by a postcosolvent treatment were used by Park et al. and generated power density [15]. In PRO process water impulsively permeated through the semipermeable membrane from the feed side into pressurized salty water due to chemical potential gradient across the membrane. It is found that global osmotic generation per year is 1,750–2,000 TWh, and additional energy also predictable when concentrated brine and brackish water are taken into consideration [16, 17]. The development of the PRO process was postponed from the last several years due to the privation of the development of active membrane and incentive to find alternative sources of energy. In 2009 first plant was successfully demonstrated by Norway-based company Statkraft. The osmotic power is generated by mixing river water and seawater across a semipermeable membrane by mixing river ([18];

http://www.statkraft.com; [19]). After the PRO the RO-PRO hybrid type of prototype is developed by the researchers, and on the basis of this, the plant called "Megaton water system" was installed at Fukuoka, Japan, in 2010 [20]. As per Statkraft analysis for the commercial viability of PRO plant through flat sheet membrane 5 W/m^2 and through hollow fiber 3 W/Kh, power densities are required [16, 18, 21]. For the commercialization of PRO, there are several challenges when compare with fossil fuel because of privation of effective PRO membranes [22]. Current work is going on to reduce the price of the membrane-based PRO process and improve the power density by reducing fouling, scaling, and the concentration polarization. Increase the durability of the membrane is also one of the great challenges. Thin-film composite (TFC) membranes are the best membranes for the PRO process. Kim et al. [23] studied the PRO for energy production very well along with the detailed study of membrane materials and operating conditions.

The study of Yip et al. [24] on TFC membranes for PRO exhibits quite high power density, i.e., 10.0 W/m^2, with taking river water as a feed solution and seawater as a draw solution. The same group was also demonstrated that the PRO has a high prospective to exploit the free energy of mixing when freshwater flows into the seawater for clean and renewable energy/power generation. Using PRO with taking river water as a feed solution and seawater as a draw solution at constant operating pressure produce power density of 0.75 kW h/m^3 [25, 26]. Prof. Menachem Elimelech at Yale University with his group and co-workers has done tremendous work by using TFC as a major membrane material for the PRO process. His one of concept, he studied about reverse electrodialysis (RED) and justified, when Gibbs free energy of mixing when fresh river water flows into the seawater can become the source of sustainable power generation [27, 28]. Ingole et al. [1–3] developed several thin-film nanocomposite (TFN) membranes for power generations with various modification using polysulfone and polyethersulfone hollow fibers as a substrate material [29]. As reported by Han et al. first time in the laboratory reported data, the PRO power generation tests produced 14 W/m^2 power density with 1.0 M NaCl as a draw solution and deionized water as the feed solution using the TFC membrane developed on the surface of hollow fiber membrane substrates [11, 12]. Furthermore, Han and Chung constructed the robust hollow fiber membrane support having high strength exhibits 16.5 W/m^2 as a power density withdraw solution 1.0 M NaCl and deionized water as a feed solution at hydraulic pressure 15 bar [30]. The thin-film nanofiber composite pressure-retarded osmosis (TNC-PRO) membranes are also one of the best alternatives for the production of high power density. TNC-PRO membranes at hydraulic pressure 3.92 bar with 80 mM NaCl feed and 1.06 M NaCl, $\pi = 51.8$ bar draw solution produce 15.2 W/m^2 power density and same TNC-PRO membrane when changing feed solution as 0.9 mM NaCl, $\pi = 0.045$ bar achieved 21.3 W/m^2 power density [31]. Superhydrophilic water the soluble zwitterionic random copolymer was synthesized via single-step free-radical polymerization in between 2-methacryloyloxyethyl phosphorylcholine (MPC) and 2-aminoethyl methacrylate hydrochloride (AEMA) for the preparation of antifouling membrane to generate high power density by Han et al. Their study achieved 13.5 W/m^2 power density and also provides appreciated insights and strategies for the fabrication and design of the antifouling membrane materials for energy generation through the PRO process [32]. Currently thin-film nanocomposite (TFN) membranes are developed by several types of research for the generation of clean and affordable power generation. Nanoparticles-based membranes have the capability to provide a high surface area for the application along with to reduce the fouling and concentration polarization [33–35]. Metal-organic framework (MOF)-based TFN membranes are also the best choice for to developed TFN membranes producing high power density as studied by Gonzales et al. [36]. Carbon nanotubes incorporated TFN membranes show high hydrophilicity along with chemical etching of the active layer gives 1.7 W/m^2 power density by using 0.5 M NaCl solution as draw and deionized water was used as feed solutions, respectively [37]. Carbon quantum dots (CQDs) having an average size 3.4 nm has been prepared by Zhao et al. and immobilized onto the polydopamine (PDA) layer grafted on PES substrate via covalently bonding and tested for PRO at 15 bar exhibited 11 W/m^2 power density [38].

By considering above points the thin-film nanocomposite (TFN), membranes are more effective for the PRO process. In this chapter, we explain the mechanism and generation of the power capacity of various kinds of membranes. Also in this chapter, special focus is given on thin-film composite and thin-film nanocomposite membranes for the osmotic power generation. In addition, in this chapter, the current research focus of researchers for the development of the PRO membrane has been summarized.

2 Polymeric Membranes for Energy Generation

2.1 Thin-Film Composite (TFC) Membranes for Energy Generation

The TFC membranes are one of the best choices for the generation of energy through PRO process as it is considered as a substitute and renewable technology for the production of energy from mixing two different salinities solutions. For the production of energy in the PRO process, most widely used setup is used as mentioned in Fig. 1 [39]. In this process, the high concentration solution called as a “draw solution” arrives in prepared membrane module after passing it through a pressure exchanger, which enhanced the operational pressure in the stream to as already fixed pressure ΔP. In the opposite side of membrane module, the low concentration solution called as “feed solution” is pumped out. The water molecules are allowed from the feed stream to draw stream with enhancing flow rate due to osmotic pressure difference across the membrane is higher than the hydraulic pressure difference. Due to increase flow rate, it’s diluted the pressurized draw stream and while reducing the flow rate, concentrating the feed stream. The departing pressurized draw stream formerly divided into a stream that flows through the pressure

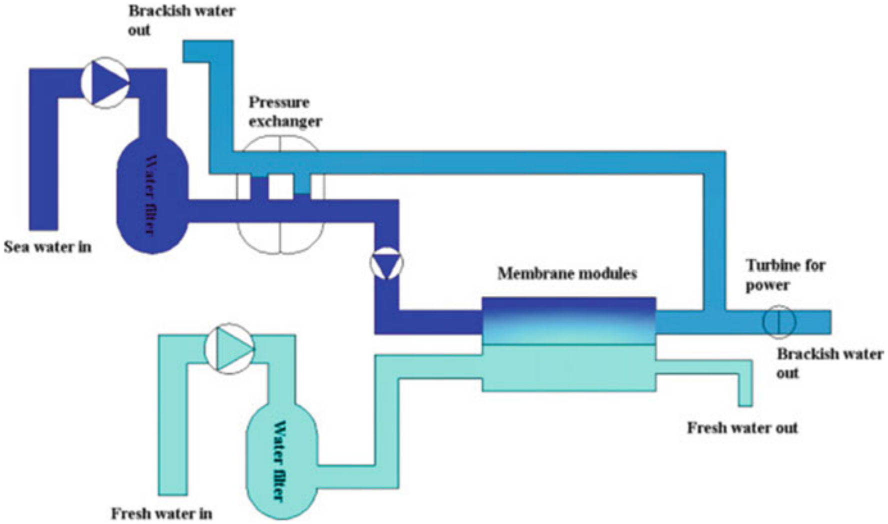

Fig. 1 Basic process layout setup for a typical osmotic power plant (adapted with permission from [39])

exchanger where it transfers pressure in the incoming draw stream and a stream that flows through the turbine to generate power. The detail about how the PRO testing unit work is mentioned in Fig. 2 [1–3].

Sun et al. [40] have developed the TFC membranes achieving high-flux and robust reinforced aliphatic polyketone for osmotic power generation. Their study shows the prepared TFC membrane produced a 6.1 W/m^2 power density with 0.6 M/L NaCl as a draw solution [40]. Fouling is the main issue, while operating the membrane modules for PRO, due to fouling, flux becomes reduce, and power generation efficiency has been decreased. To reduce the fouling, Zhang et al. developed the antifouling hollow fiber membranes by using poly(vinyl alcohol) as the modifying agent. Here TFC membrane has been prepared followed by PDA coating, PVA is coated, and cross-linked it with glutaraldehyde solution shows the antifouling characteristics [41]. The polymer made by hyperbranched polyglycerol grafted PES hollow fiber membranes also exhibit antifouling nature [42].

Arena et al. [43] have suggested, in PRO the membrane revealed compaction which improved structural parameters. The membrane has been tested with 0.5 M NaCl as a draw solute concentration against deionized water as a feed with 0.25 m/s cross-flow velocities for both (draw and feed) solutions. In this system, while experiment negligible pressure drop was found within the draw solution channel [43]. Various experimental conditions have been checked by Straub et al., and they found that in PRO will meaningfully reduce the accessible net energy, emphasizing significant new challenges for the development of systems exploiting hypersaline draw solutions [44]. Their study focused, at different pressure, the membrane compaction depends on applied hydraulic pressure as shown in Fig. 3. They also

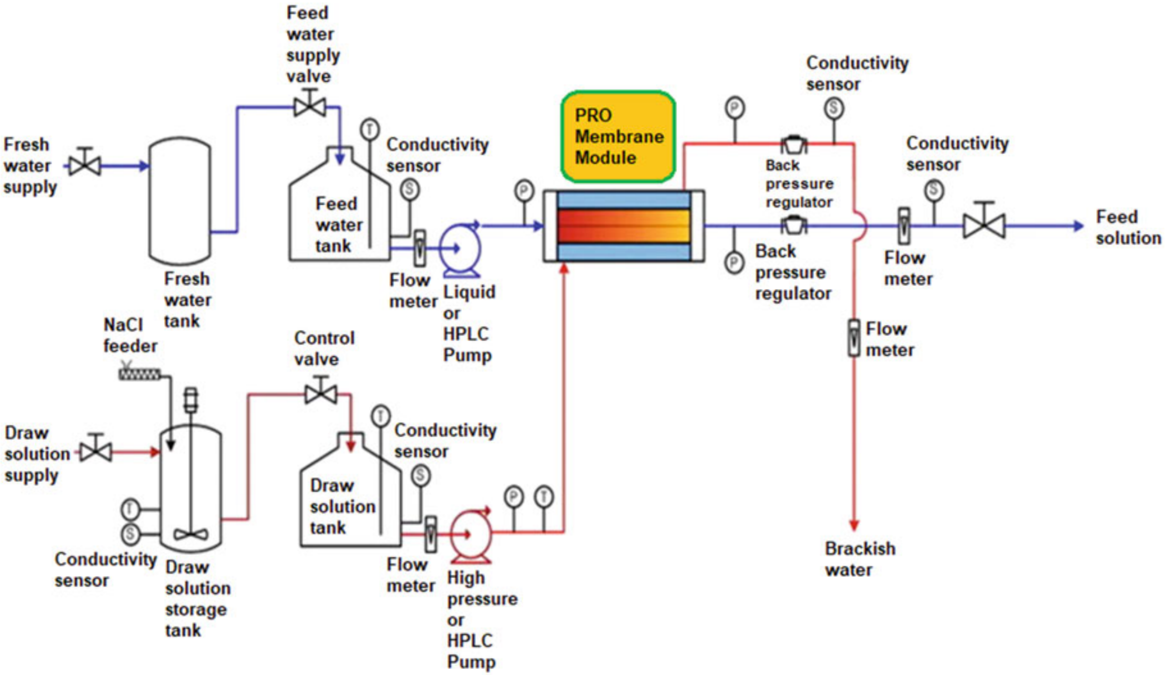

Fig. 2 Pressure-retarded osmosis (PRO) testing unit (adapted with permission from [2])

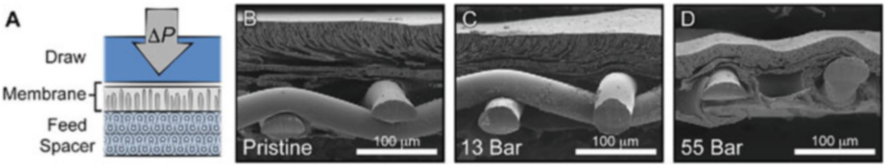

Fig. 3 (**a**) Schematic representation along with (**b–d**) SEM images of HTI-TFC membrane before and after applied different hydraulic pressure for PRO (Adapted with permission from [44])

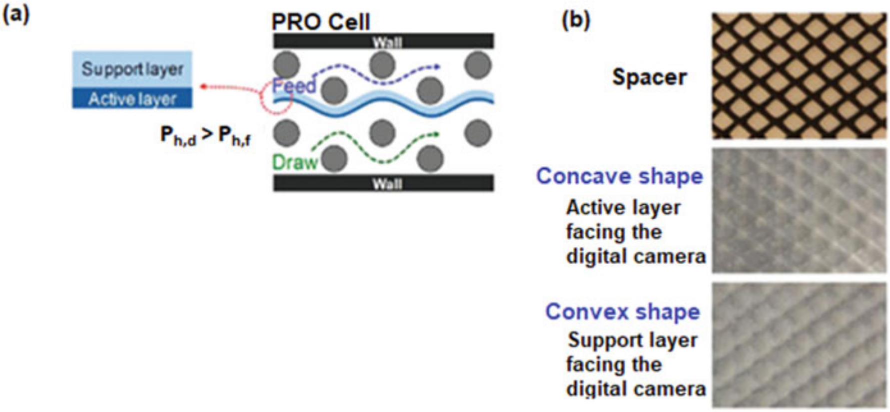

Fig. 4 (**a**) Lab scale PRO membrane test unit with (**b**) effect of spacer on membrane after experiment at 12.5 bar pressure (adapted with permission from [49])

examine the performance of PRO at the module scale, accounting for the harmful effects of reverse salt flux along with external and internal concentration polarization [45].

Considering all aspects for the commercialization of PRO membranes the mathematical modelling in detail was studied by Anissimov [46]. The mathematical modelling is very important and plays a vital role to set up the experimental analysis, optimization of the system, and development of membranes for PRO energy generation system. To find out the concentration polarization effect yet more modelling work is needed. The hybrid osmotic heat engine system produces sustainable energy by combining PRO as energy generation stage and membrane distillation (MD) as a separation stage [47]. Experiment investigation of PRO using spiral-wound (SW) membrane modules was studied by Kim et al. and investigates the relationship between two relating flow streams. The addition of tricot fabric spacer inside the membrane changes the PRO membrane module performance because the addition of tricot fabric spacer caused a pressure drop [48]. The contrary influence of feed channel spacers on PRO performance was also studied by Kim and Elimelech. The effect of spacers is always an important parameter because PRO membranes work on hydraulic pressure, and it is found that membrane deformation under the high hydraulic pressure on the feed channel a spacer as shown in Fig. 4 [49].

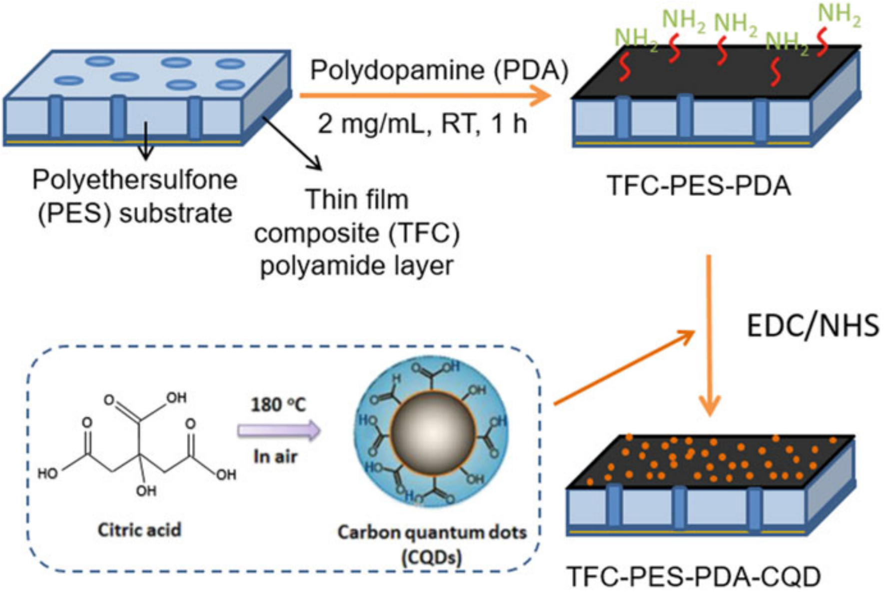

Fig. 5 Route for the synthesis of carbon quantum dots (CQDs) using citric acid to modify surface substrate of CQDs (adapted with permission from [38])

The outer surface-modified hollow fiber TFC membranes prepared to produce 7.63 W/m^2 as a power density at pressure 20 bar by vacuum-assisted interfacial polymerization technique [50]. Vermaas et al. [51] captured the renewable energy from the mixing of salt and freshwater in reverse electrodialysis. Their study shows that the transportation of ions equivalent to the gained energy and the electromotive force equally encourage each other. Due to this, it is enabled to capture 50% of the theoretical energy. Using interfacial polymerization and surface modification various zwitterionic polymers have been used for the PRO membranes development [38, 52]. As studied by Zhao et al. for the PRO processes, the carbon quantum dots grafted antifouling membranes were produced osmotic power generation. Their study in PRO taking 15 bar pressure, the prepared membranes will exhibit 8.8 W/m^2 power density. As shown in Fig. 5, this developed membrane opens up a new path for the PRO processes for high osmotic power generation [38].

There is another salinity gradient energy source found out by Tan and Zhu [53]; they mixed entropy battery on the base of a pair of cationic and anionic electrodes. They use bismuth oxychloride (BiOCl) as anionic and hexacyanoferrate (CuHCF) as a cationic electrode for the production of the energy density of 8.0 J m^{-2} with a 59.0 mW/m^2 as an average power density. TFC membranes with high power density were developed by Park et al. [54]. They developed the mixed-matrix PES/graphene oxide (GO) hollow fiber support membrane and achieved 14.6 W/m^2 power density with 0.2 wt% added graphene oxide. A comparative review of forward osmosis (FO) and PRO was done by Klaysom et al. [6] in detail and suggest probable

Table 1 Comparison between forward osmosis (FO), and pressure-restarted osmosis (PRO) (adapted with permission from [6])

Factors	FO	PRO
Driving force	Osmotic pressure	Osmotic pressure
Main application	Water purification process Desalination	Power production
Operating condition	• P – atmospheric • Brackish, seawater, or some synthetic draw solutions, such as aqueous NH_3 • Impaired water, seawater, or other feed solution • pH 6–11	• P – 10–15 bar • River, brackish, seawater, and brine solution • pH 6–7
Desirable membrane property		
(1) Physical morphology	• Thin membranes with dense active layer on porous, low torturous sub-layer	• Thin membranes with dense active layer on porous, low torturous sub-layer
(2) Chemical property	• Very hydrophilic • Good chemical stability to chloride solution and synthetic draw solution	• Very hydrophilic
(3) Membrane requirement	• High water permeability • High solute retention • Stable in synthetic draw solution	• High water permeability • Good solute retention to maintain osmotic pressure driving force • Strong enough for the external applied pressure
Target performance	• High flux and good water recovery	• High power density (>5 W m^{-2})
Challenges	• Internal concentration polarization • Suitable draw solution • Draw solution recovery and reconcentration	• Internal concentration polarization • Module design • Membrane cleaning • Feed stream pre-treatment

solutions for worldwide challenges in energy and water supply. The comparative study about the desirable membrane property, operating condition, main application, driving force, targeted performance, and challenges are discussed in Table 1.

Osmotic power generation using 2D materials are also once of the good choice, to make thin layer by incorporating 2D materials, while interfacial polymerization, the membranes produce clean blue energy. In it possible due to materials' unique properties and novel transport mechanisms occurring at the nano and sub-nanometer length scale [55]. Two different polyethylene glycol (PET) of molecular weight 4,000 and 6,000 g/mol were used for the development of CA membranes by Sharma et al. [56]. The effect of these two PEG additives was checked for PRO process, and it is found that using 4,000 g/mol PEG added CA membranes exhibit 2.7 W/m^2 and 6,000 g/mol PEG added CA membranes exhibit 3.1 W/m^2 power densities. The mathematical model-based assessment was done by Jalili et al. [57] to assess power densities and competence and to address the inspiration on the performance of factors such as residence time and temperature. Salamanca et al. demonstrated the osmotic power plant in the Magdalena River mount in Colombia on the basis of their experimental field data. In the case study, the plant is operated through the controlled mix of two different flows having different salinities. Their obtained energy net production is 6 MW with above 5 W/m^2 membrane density [58]. They use the Lee model for the study of internal concentration polarization [59] and Achilli model for external concentration polarization [60]. Both the model equations are mentioned as below:

Lee model Eq. (1):

$$J_W = A\left[\pi_{D,m}\frac{1-\frac{C_{F,b}}{C_{D,m}}\exp\left(J_W K\right)}{1+\frac{B}{J_W}\exp\left(J_W K-1\right)} - \Delta P\right] \tag{1}$$

Achilli model Eq. (2):

$$J_W = A\left[\pi_{D,b}\exp\left(-\frac{J_W}{k}\right)\frac{1-\frac{\pi_{F,b}}{\pi_{D,b}}\exp\left(J_W K\right)\exp\left(\frac{J_W}{k}\right)}{1+\frac{B}{J_W}\exp\left(J_W K-1\right)} - \Delta P\right] \tag{2}$$

where $C_{F,b}$ is the feed side bulk salt concentration, $C_{D,m}/C_{D,b}$ the draw side salinity at the membrane-fluid interface, the solute resistivity is mentioned as K and B the salt permeability of the membrane.

2.2 Thin-Film Nanocomposite (TFN) Membranes for Energy Generation

The progress of new PRO membranes depends on the development of new design strategies of the materials. Membrane modification materials are very important for membrane performance enhancement. The use of nanoparticles is the best choice, and nowadays to increase the performance of membrane for PRO, functional nanoparticles incorporated membranes are exhibiting enhanced performance. The functional nanoparticles embedded in structure are one of the best strategies to enhance the performance of the membrane for PRO. There are several nanoparticles were used by researchers to develop the TFN membranes in the PRO process for saline power production.

TFN membranes are one of the recent sources find out by the researchers for the osmotic power generation. TFN membrane also one of the several issues solvable sources for energy generation. For example, as explained above the drawback of TFC membranes like concentration polarization, the TFN membranes resolve this problem, and due to this, high-energy production has been possible. The use of low-cost nanomaterials for the development of TFN membranes is one of the best options for a commercial point of view. Figure 6 depicts that the TFN membranes

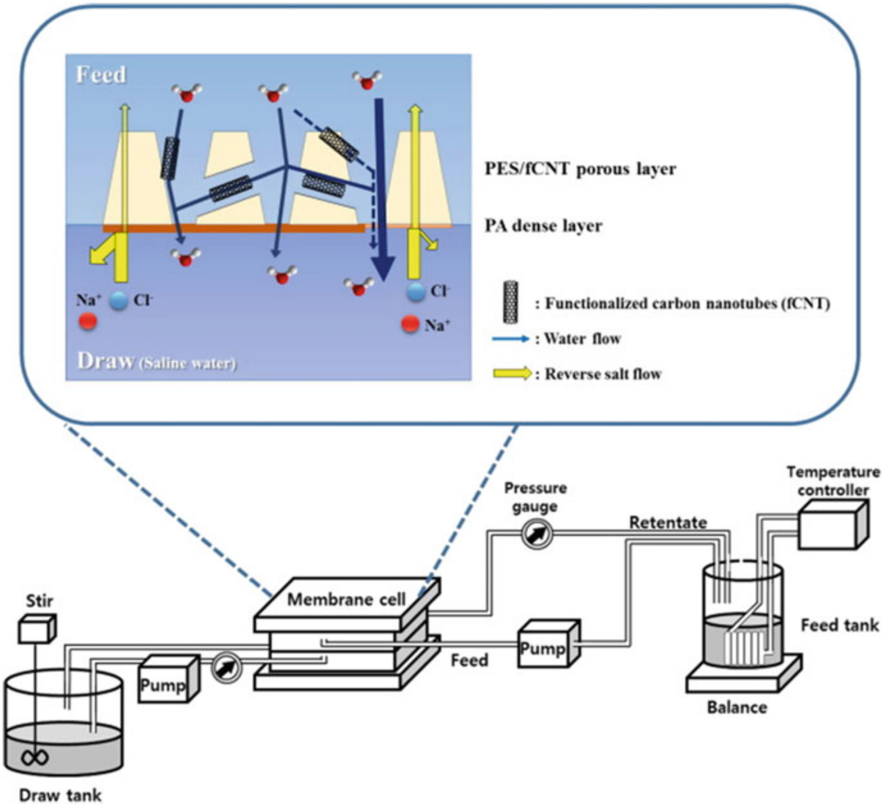

Fig. 6 Thin-film nanocomposite membrane for the production of blue energy via PRO process (adapted with permission from [37])

prepared by incorporating carbon nanotubes (CNT), while interfacial polymerization to harvest the energy is the best way in a PRO process [37].

Chen et al. [61] found the steadfast source of renewable energy with negligible everyday inconsistency by using bioinspired nanocomposite membranes. They used the layer-by-layer composite membranes that are made by aramid nanofibers and boron nitrate nanosheets as shown in Fig. 7 and concluded that these materials made nanocomposite shows extraordinary toughness and fast ion transport, which is responsible for the high osmotic energy harvesting. Also, their study shows the future directions in aramid-boron nitride (ABN) composite membranes expansion may contain simulation and theory base development of the ion selectivity of ABN nanochannels.

Nanocomposite membranes have one of the great potentials to apply in any application. The PRO process also came as the best choice for the osmotic power generation using TFN membranes. Minimizing the fouling tendency and growing the separation properties ultrasmooth and the ultrathin selective layer is one of the

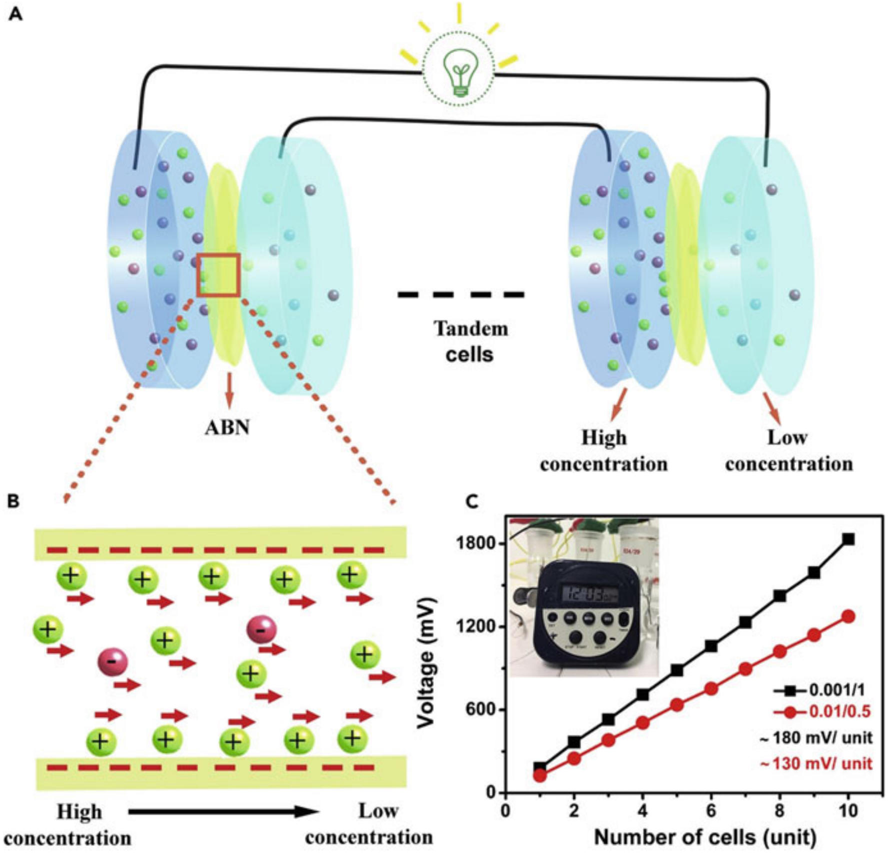

Fig. 7 Aramid-boron nitride (ABN) composite membranes for osmotic energy harvesting/ powering electronic devices (adapted with permission from [61])

best supreme goals in the PRO processes. The first time using this type of TFN membranes shows the remarkable performance to produce high energy density. Agboola et al. [62] nicely explain the development of PRO membranes and their working mechanism. Also highlighted that for power generation the PRO concept is the energy mixing that offers a countless valuation of the non-expansion work which could be generated from mixing; however, for the development of effective PRO membranes with suitable planning and performance is required for the power generation. To take the care of fouling in PRO extenuation efforts need to focus on the support layer in the feed side [63]. Whenever there are no foulants in the feed always flux and power density are differ, if the foulants are present in the freed and draw, the membranes give similar power density values. For the sustainable energy production, the osmotic power energy can be recovered from hypersaline waters from gas and oil reservoirs and concentrated brine [64].

Covalent organic framework (COF) nanomaterials are one of the best choices for the development of TFN membranes. Gonzales et al. synthesized the melamine-based COF nanomaterials, Schiff base network-1 (SNW-1) added TFN membranes for the PRO process [36]. Their study impact shows that after adding SNW-1 nanoparticles while interfacial polymerization to make a thin selective polyamide layer influence the osmotic power density. The TFN membranes prepared by interfacial polymerization in between 1,3,5-benzenetricarbonyl trichloride (commonly called trimesoyl chloride, TMC) and 1,3-phenylenediamine (MPD). It is also found that the secondary amine groups of SNW-1 make bonding with carbonyl groups of TMC as a result high potential active layers are formed as shown in Fig. 8. The prepared TFN membranes with 0.02 wt.% SNW-1 nanoparticles tested withdraw solution concentration 1.0 M NaCl at 24 bar hydraulic pressure exhibits 12.1 W/m^2 power density. Their study is promising in the field of fabrication of PRO membranes for the improvement of osmotic energy production performance abilities of the PRO processes.

Tian et al. [65] developed the TFN membranes for PRO application by incorporating functionalized CNTs which gives the additional mechanical strength to the tiered polyetherimide nanofibers. In this study, it is found that incorporation of functionalized CNTs reduced the ICP problem and shows high mechanical strength at operating pressure 24 bar. Here membranes performance also found ten times greater than commercial HTI-CTA membranes, and as a result, this prepared TFN PRO membranes exhibit 17.3 W/m^2, high power density using 1.0 M NaCl solution as the draw and deionized water as the feed solution. Antibiofouling membranes are also prepared by Liu et al. [66] using silver nanoparticles for the PRO. This TFN membrane shows enhanced water permeability with high power density. Developed TFN membranes are more hydrophilic in nature having excellent antibacterial properties exhibited by silver nanoparticles against the Gram-negative *E. coli* and Gram-positive *B. subtilis*. The detailed study about the synthesis of nanoparticles incorporated TFN for PRO to generate the energy is well explained and reviewed by Arar et al. [67]. Free-standing graphene oxide membranes (GOMs) were prepared for the PRO process to generate salinity gradient power by Tong et al. [68]. These membranes have excellent mechanical strength and high water permeability coefficient. The schematic of PRO system is shown in Fig. 9. The prepared membranes with the help of theoretical and experimental calculations exhibit very high power density, i.e., 24.62 W/m^2 at 6.9 bar withdraw solution 3 M NaCl and feed solution of NaCl 0.017 M.

These abovementioned all membranes have the great potential for the PRO process to produce high osmotic power. In particular, TFN membranes have great potential and capability to generate high osmotic power.

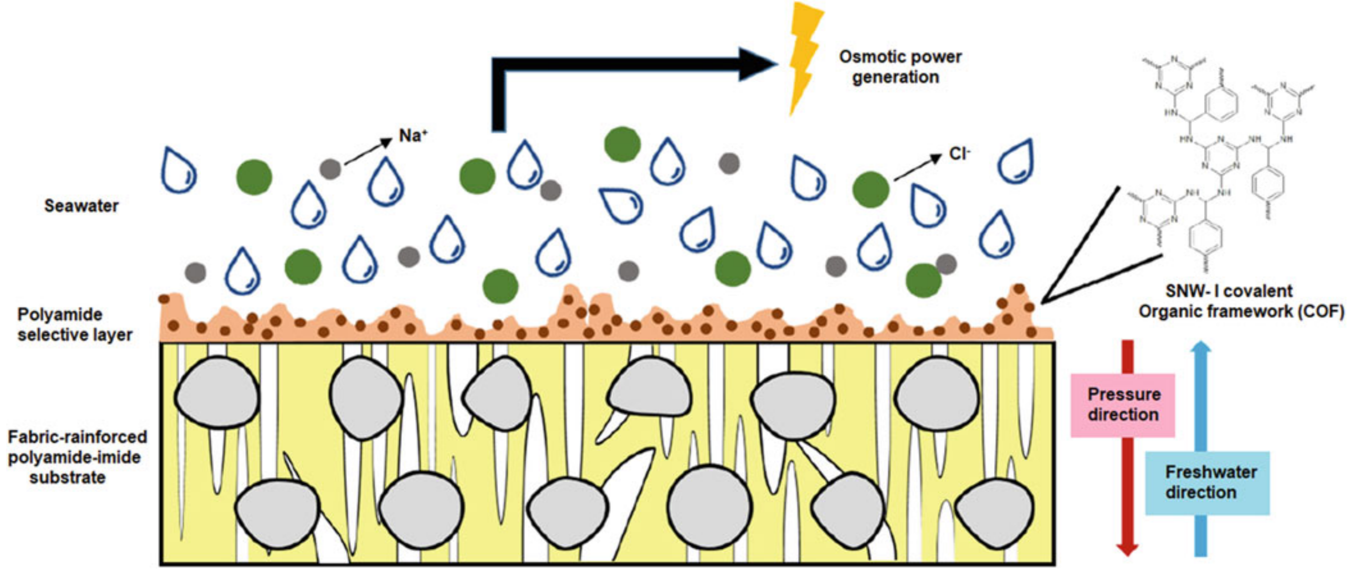

Fig. 8 Schematic of melamine-based covalent organic framework SNW-1 nanoparticles incorporated TFN membrane for the enhanced osmotic power generation (adapted with permission from [36])

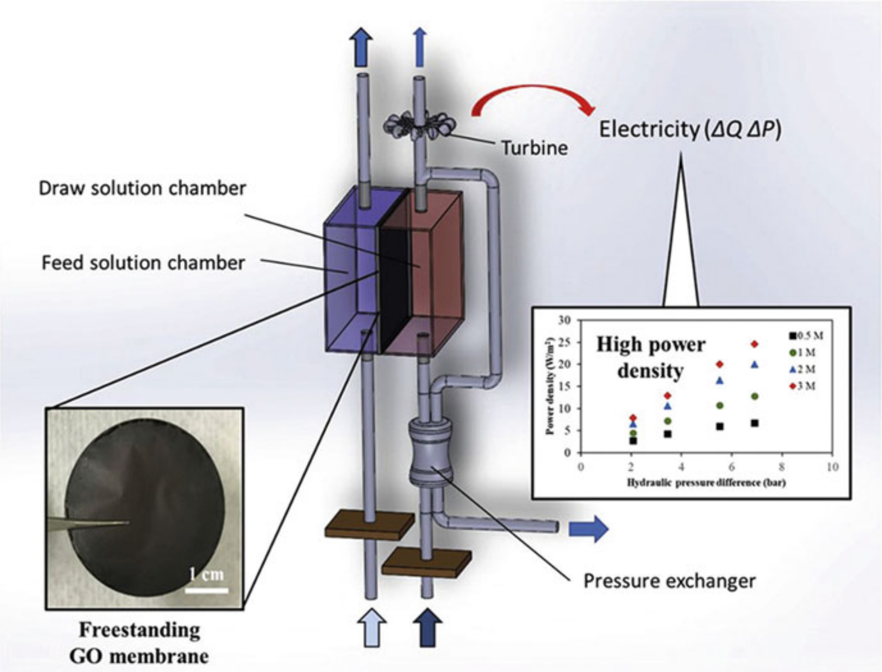

Fig. 9 PRO system for the production of salinity gradient power using GO membranes (adapted with permission from [68])

3 Concluding Remarks and Future Prospective

Pressure-retarded osmosis (PRO) is one of the high potential methods to use for the generation of osmotic power. For the harvesting of clean energy, highly efficient TFC and TFN membranes are the best choice. It has been found that the involved effect of support and active layer properties of PRO are more important for the enhancement of power generation. Looking at the viability of the technical PRO process, the energy generation at higher scale is already in practice. For the generation of maximum energy, a PRO power generation plant should harvest extreme power from river/seawater at low cost (operational and investment). However, in order to determine the feasibility of these power plants, a number of pilot runs are needed to be study in details. The sustainability and reproducibility of the modified membranes have been observed to be vital important which tells the necessity of a detailed study on a large scale before going to the real site. For industrial application cost reduction is imperative to make the PRO viable which is still costing high about \$6.79/kW h. Hence, new developments are much required in materials point of view. Nanocomposite material can be a futuristic alternative albeit cost reduction is again required to establish this technique of energy generation. Given that the nanoparticles with high surface area are highly recommended.

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Environmental Impact and Challenges Associated with Bio-Based Energy

Jaanvi Garg and Susmita Sharma

Contents

Abstract The growth of global economy and industry along with population explosion has led to an exponential enhancement in the consumption of energy in the past few decades. With this escalation in demand for energy, the utilization of renewable/sustainable energy sources, to provide long-term sustainable benefits to society, has also spiralled on a massive scale. Approximately 85% of the world energy consumption is primarily reliant on fossil fuels, a non-renewable source of energy. Thus, bio-based energy, a sustainable source of carbon-based energy, is considered as a substitute for the depleting non-renewable energy sources. Owing to

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the decreased carbon emissions, in comparison to fossil fuels and associated government support policies, the global demand for biomass-based energy plants is increasing rapidly. Though, the utilization of biomass in the form of food crops like maize, wheat, sugarcane and soybeans for the generation of biofuel is unlikely a sustainable approach. Further, the thermochemical processes of generation of biofuels from biomass have its associated environmental concerns such as generation of detrimental toxins and its accidental release into the atmosphere, during thermal decay and chemical reformation procedure. The chapter thus takes into account the various types of biomass and its promising techniques for generating energy, in addition to highlighting the environmental impacts along with Greenhouse Gas (GHG) emission for bio-based energy generation/utilization alternatives.

Keywords Biomass, Climate change, Renewable energy, Resources, Sustainable development

1 Introduction

The augmented use of fossil fuels has led to a continuous escalation in the earth temperature due to upsurge of Greenhouse Gas (GHG) emissions such as CO_2, N_2O and CH_4 into the earth's atmosphere ensuing in 'Global Warming' [1, 2]. The total anthropogenic emissions contributed from the energy sector is approximately 35%, which has increased since 1.7% per year in 1990–2000 to 3.1% per year in 2000–2010 as per Intergovernmental Panel on Climate Change report [3]. To reduce and limit the GHG emissions, primary protocols which have been constituted included (a) 1992 Kyoto protocol [first commitment stage 2008–2012] and (b) 2012 Doha amendment [second commitment stage 2013–2020] to keep the rise in global temperatures well below 2°C [1]. Under the light of these protocols, countries are urged to meet their goal of GHG emissions mainly through national measures exploiting renewable resources of energy, in addition to the market-based mechanisms such as (a) International Emissions Trading (IET), (b) Clean Development Mechanism (CDM) and (c) Joint Implementation (JI) to mitigate GHG emissions. With this in view, the European Union (EU) renewable energy announcement 2009/28/EC postulated an agenda for reducing GHG emissions [4, 5]. By fulfilling 20% of its total energy needs with sustainable resources by 2020, later revising it to 32% by 2030 [EU dedicated to lessen GHG emissions to 5% against 1990 levels] [4, 5]. The major countries wrt to their renewable energy power capacity or electricity generation are shown in Fig. 1. Likewise, US biofuel statistics have also shown steady growth in renewable (mostly biomass bioliquid) fuels production [7]. Since 2010, the creation of biofuel increased from 14.1 billion gal in 2012 to 16.6 billion gal in 2016. In the year 2017, the USA has provided about 5% of its total primary energy by contributions from

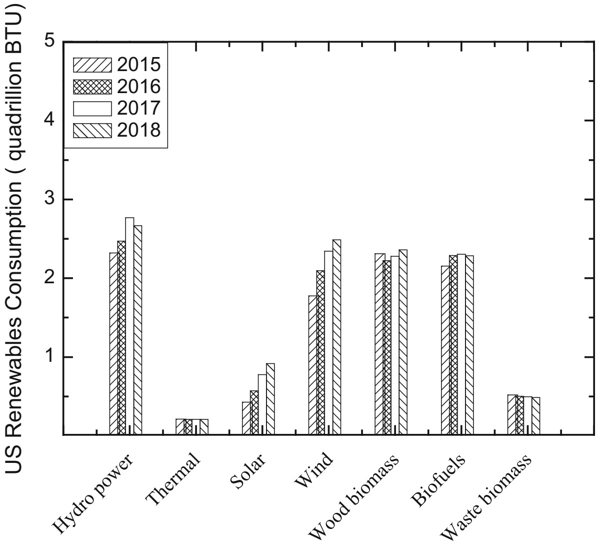

Fig. 1 Total consumption of different renewable sources in gross final consumption of energy in the USA [6]

1. Biofuel (mainly ethanol) ~ 47%
2. Wood biomass ~ 44%
3. Waste biomass ~ 10% (also highlighted in Fig. 1) by biomass renewable

Interestingly, Fig. 2a, b demonstrates that the production and consumption of total renewable energy are outpacing nuclear power in the USA (very similar to the scenario, as confirmed in China). This transition may be due to the insecurities, complexities and cost linked with radioactive waste management policies and impact during the process of mining and other operations associated with nuclear power. However, it is opined that for efficient decarbonization and restoring the dwindling supplies of fossil fuels, the contribution from renewable energy together with nuclear energy is useful in the long run.

The global biofuel marketplace has been managed by the top three renewable producers of the world, namely, the USA, Brazil and China, nearly generating up to 80% of biofuel, mainly in the form of bioethanol from food crops like maize and sugarcane [8, 9]. Owing to the chemical similarities wrt petroleum-based fuels and ease in distribution through current infrastructural facilities, biofuel can be upgraded to play a vital role in the motor vehicle, as transportation fuels [10].

International Energy Agency (IEA) has clarified that with the expansion of worldwide economic and fast-growing population; in the next few decades, global demand for transport fuel is expected to rise significantly by 55% in 2030 [4, 5]. Thus, biofuels have the potential to generate a noteworthy contribution to meet future energy requirements of humanity [11]. However, for developing economies like India, sourcewise allocated installed power generation capacity from total renewable energy, constitutes 21.95% [as on 31st march 2019], with an announced target of 175 GW as growing renewable power by 2022. Due to noteworthy

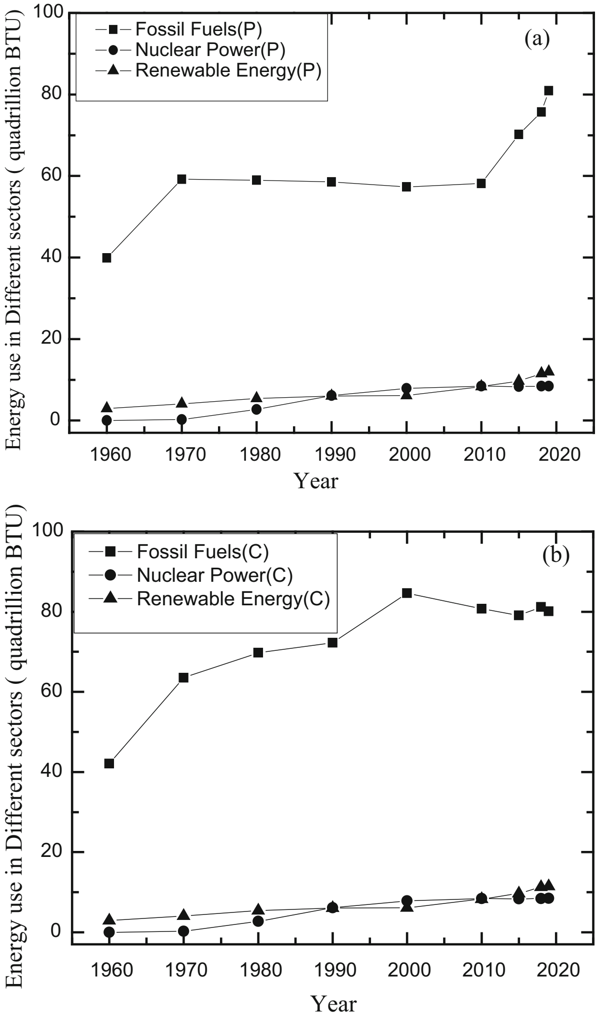

Fig. 2 (**a**) Rate of production (P) and (**b**) rate of consumption (C) of renewable energy outpacing nuclear energy in the USA

dissemination of commercial energy in India, in the last few decades, biomass only maintains to govern energy supplies in traditional and rural sectors, mostly to support the cooking energy demands in households [12]. But, the recent improvements in biomass technology associated economic benefits of commercial biomass production and rural employment, the saving of foreign exchange for oil imports has provided an additional scope for the creation of a new market for biomass energy in developing economies like India [13]. Ministry of New and Renewable Energy (MNRE) has articulated that India has a bioenergy potential of 25 GW. '*Biomass Power and Bagasse Co-Generation Programme'* promoted by MNRE aims in recovering energy from biomass including bagasse, agricultural remains and timber, thus assisting for the transition to a low-carbon nation in addition to climate change mitigation [14]. Further, with the environmental complication, such as global climate change, acid rain and deterioration in local air quality, etc., associated with the extensive use of fossil fuels, the share of biomass in the total energy sector, which has declined progressively over the century, has again caught the attention of policymakers, as a sustainable and environmentally benign energy source. However, the increase in demand associated with food, feed and fuel have added pressure on the ecosystem through the land-use change patterns in the bioenergy sector [15]. This chapter thus tends to provide a basis for broad assessments of biofuel production under the following categories: (1) extent of impacts associated with the sustainable production of a different generation of biofuel, Food versus Fuel scenario; (2) prospect of feedstock growth, change in land-use pattern, cultivation and management practices; and (3) ensuring environmentally sustainable bioenergy production and climate mitigation.

2 Constituents of Biomass and Associated Bioenergy

Biomass is a non-fossilized and complex biogenic solid product generated from the natural and anthropogenic process. The natural process involves biomass produced by (a) cultivating water-based and land-based flora via the processes of photosynthesis or (b) animal and human excretion. Whereas, biomass-derived products obtained after processing of above are the anthropogenic processes. All biomass is a multifaceted heterogeneous mixture of organic and inorganic material, containing intimately associated phases of various solid, fluid or minerals [13, 16]. The solid, non-crystalline constituents of organic matter include cellulose (anhydrous glucose units), hemicellulose (500–3,000 sugar units), lignin and extractives such as polymers like protein [15, 17]. The mineral species of inorganic matter constitutes carbonates, phosphates, sulphates, silicates, chlorides, hydroxides, oxy-hydroxides and nitrates [17]. The fluid constituents include moisture, gas and moisture-gas inclusions related to organic and inorganic fractions [18]. The necessary molecules in hemicellulose are covalently bonded to cellulose fibres, keeping cellulose fibres intact and thus increase in its amount is highly unfavourable in biomass [15, 17]. Lignin, on the other hand, is hydrophobic but also acts as reinforcing material, providing the structural rigidity to cellulosic material [19, 20]. The thermal putrefaction characteristic of lignin is also diverse compared to the composition and structure of cellulose, hemicellulose [15, 17]. Usually, hemicellulose, cellulose and lignin content of biomass are 20–40 wt%, 40–50 wt% and 10–40 wt%, respectively in biomass. The other significant elements in biomass commonly include C, N, H, O, K and Ca, while the minor elements usually include Si, Al, S Mg, Fe, Cl, P and N.

Natural biomass is a renewable/sustainable source of energy, whereas bioenergy/biofuel is still an incomplete renewable energy resource. Different sources of biomass are available for energy production. These sources are categorized as (a) organic wastes, (b) residues from cultivation and forestry and (c) additional forestry and energy crops [20, 21]. But depending on technological approaches, bioenergy is classified into ‘traditional’ and ‘modern’ methods. The traditional approach refers to the incineration of biomass such as timber, animal waste, cooking, drying and charcoal production, whereas modern methods include the production of liquid biofuels, gas substitutes or biogas [12, 20–23]. The technological advancement in the field of biofuels (from crops, lignocellulosic material) is done to meet the growing demand for oil stocks obtained from fossil fuels which are on a gradual depleting trend due to its continuous use in the preceding generations. As the name suggests, biofuels are generated from organic material having renewable sources of carbon. The use of biofuels, such as ethanol as cooking and lamp oil, has been prevalent since ages. Its use as a fuel for the transport sector in the internal combustion engine was introduced only in the early nineteenth century by Samuel Mforey, the success of which led to its utilization in both the automobile market and for farm machinery. However, in the early twentieth century, ethanol was replaced by oil-derived products, only to be introduced again in the 1970s during the Arab oil impediment when the price of petroleum and petroleum-based derivatives soared.

3 Aspects of Biomass Investigations for Biofuel Generation

Biomass investigations for biofuel generation from crops and its substitutes is governed by the influence of the stakeholder’s (i.e. the producers, provider, transmission and distribution operators, regulatory bodies and mediators) attitudes in the market-based nation. Each type of biofuel obtained from different biomass, has its own socioeconomic and environmental implications. The feedstock generation, the process of production, distribution networks and markets are different, in different nations. About one quarter of the globe’s renewable energy use involves bioenergy, 50% of the same utilizes traditional biomass, i.e. crops. But, in a world searching solutions for food security and energy, biofuel created with very less or no contest with food production is anticipated [22]. This is where it becomes mandatory to distinguish between different types of biofuel based on its potential race with food and effectiveness in carbon balance. Thus, based on the basis of generation of feedstock, biomass is distinguished into three types: first, second and third generation biofuels.

3.1 First Generation Biofuels: Biomass Contesting with Food Production

The first generation biofuel are mainly derived from starch, sugars, oil from vegetable, animal fats or biodegradable agriculture, forestry, industry and household wastes using conventional technologies. They are derivative from edibles such as maize, sugarcane, wheat palm oil, etc. These different forms of feedstock and

Table 1 Types of feedstock and associated first generation bioenergy

Feedstock	Bioenergy type	Reference
Sugarcane, corn, sugar beet, wheat, plant oil	Bioethanol	[11, 16, 23–25]
Rice straw, wheat straw, corn fibre, other crop and grass residues	Biobutanol	[20, 23, 25, 26]
Palm oil, soybean oil, sunflower oil, peanut oil, rapeseed oil, corn oil	Biodiesel	[9, 27–31]

Quantity/hectare for biodiesel production (400–2,400 L) is highly dependent on the type of feedstock

associated types of bioenergy are listed in Table 1. The technical advantage of first generation biofuel is that the biofuels can be blended with petroleum-based fuels, combusted in IC (internal combustion) engines and is in commercial production for nearly 50 billion litres annually [4, 32].

Despite the increased use of water, fertilizers and pesticides for improving farmer productivity of the first generation feedstock, the technique of cultivation allows diverse group of the underprivileged (like employment for agricultural labourers and rural patrons) to share the benefits along with the farmers/producers, both at farm and factory levels. Around 15–20% of biofuel demand can be satisfied if the use of arable crops is aggressively expanded. However, the barrier to the expansion of this feedstock market is limited to the non-availability of additional suitable land to cultivate traditional plants. The first generation feedstocks are primarily used as a food source for the global population, and its use as resource/feed in energy sectors can threaten food security by affecting the food supply and price chain. The demand for fuel in the international market has led to diverse attitude: (a) stakeholder in small tropical countries with less arable lands could use the available land for biofuel creation and create a competition with food production, and (b) stakeholder in large tropic countries could grow biofuels instead of food crops (as the infrastructure for planting, processing and harvesting of the crops already exists) thereby changing their land-use patterns. The examples of these scenarios were demonstrated in the markets of the USA, where the demand for bioethanol led to an increase in maize price by 33% in 2007–2008 [27]. Similar market observations were recorded in China where 3.5–4% of the total maize cultivation was utilized for bioethanol production [33] leading to a scarcity of the product in the food market. The growing scarcity of food crop may reflect demographic shifts of improved diets in the population. In developed nations, the dietary preferences may change from staple crops to products like meat and dairy. However, for underdeveloped nations, the shock on agriculture markets and higher food costs would in turn result in increased undernourishment. Higher food prices will lead to rise in fuel prices and thereby increasing the pressure on the fragile natural energy resources, which will further threaten the economic stability and overall growth of the nation.

Furthermore, lifecycle estimation of the emissions from the production and transport of first generation biofuels opined that emissions for these biofuels frequently exceed those of traditional fossil fuels. First generation biofuels can offer CO_2 benefits and assist to improve security in domestic energy sector, but its impact on the biodiversity, land use and competition with food crops calls for global concern. Thus, scepticism surrounds the future prospect of production of first generation biofuel and deem it as a not so economically efficient emission abatement technology. This resulted in the study of lignocellulosic biomass from which after technological advancements the second generation biofuels could be obtained [30, 34]. The problems and limitations appearing from first generation fuels can be solved at a more extensive extent with the implication of second generation biofuels which will pave to supply fuel in a sustainable, affordable consequences to a larger quantity, with significant environmental benefits [28, 30, 33, 34].

3.2 Second Generation Biofuels: Biomass Not Contesting with Food Production

The second generation biofuels, also recognized as advanced biofuels, comprise of the residual non-food parts, viz., stems, leaves and husks of edible crops, switchgrass, cereals which have less grain and more fibres and lignocellulosic feedstocks such as energy crops, industrial and forest residues [24]. The industrial waste such as timber chips, skins and pulp from fruit pressing, etc. are other promising sources of second generation biofuels [35]. In comparison to first generation biofuels, the production of second generation biofuel is less but has better return values, environmental friendly and is cost-effective in comparison to first generation biofuel. This feedstock produces non-oxygenated, pure hydrocarbon fuels through complex biochemical and thermochemical approaches. When compared total production of second generation biofuels, production rate was ~500 million gallons, against 15.5 billion gal for first generation biofuels, in 2014 [36]. However, there is a burgeoning industry building up around second generation biofuels, for production of 3,600 GGE of CNG per day using local food and biosolids waste in Ohio [36]. The second generation biofuels directly may not affect food security, but seed crops may compete for fertile soil with food crops [8, 33, 35, 37]. There are also concerns about land-use changes that might create ecological harm for second generation feedstocks. The water and land requirements for these biofuels procurement are less compared to first generation biofuels [8, 33, 35–37]. The fuel acquired is said to be a call on replacement on the extensive use of fossil fuels, paving a much required alternative solution. However, there exist some significant disadvantages of second generation biofuels. Due to its high production costs, it is yet to be produced on a commercial scale. For the processing and distribution of biomass at a greater extent, the available harvesting, storage and transportation systems are inadequate. Further, with the expansion of agricultural frontier, if large-scale land conversions are commenced on forested/marginal lands, related losses in biodiversity and increases in carbon dioxide emissions are likely to occur [26, 38].

3.3 Third Generation Biofuels: Prospect Fuel

Third generation biofuels are the fuels obtained from algal biomass, which has an outstanding growth yield as compared with first and second generation biofuel [39]. The third generation biofuels produce 30 times extra energy per acre than the terrestrial/land crops [40]. In terms of quantity or diversity, algae feedstock has a higher potential to produce fuel. Genetically modified algae, in addition to environmentally available algae, are also used to produce fuel from algae; however, the characteristics of the finished product depend on the attributes of the organism [41]. The developments of algae ranch happen in open ponds, closed-loop systems and photobioreactors and do not require any farmland [31]. The socioeconomic risks associated with algal feedstock, unlike the first and second generation biofuels, is also very minimal. The major drawback in the production of algae is that it requires a huge quantity of nitrogen fertilizer and can pollute the water and soil significantly, creating environmental issues. The capacity of algae to fix CO_2 can also be a new technique of reducing gases from the atmosphere. However, the applied fertilizers generate higher GHG emissions in the production, which exceeds the quantity saved by using algae-based biofuel. Algae can be developed in wastewater, offering secondary benefits by digesting municipal waste in MSW lagoons and avoiding taking up of extra land [9]. The primary sludge has low-quality fat and grease, thus third generation biodiesel produced will be of low quality, while the biodiesel produced from secondary sludge is of a high quality due to high organic loading in the sludge [29]. Such plants can grow throughout the year, and the rate of consumption of water is also very less. They, being biodegradable, are entirely safe for the surroundings in comparison to their counterparts. As algal biofuels have high oil content and high productivity, they make a possible substitute for liquid petroleum fuel. All of the factors thus make algal cultivation less intricate in comparison to cultivate than traditional biofuels. However, its significant drawbacks include requirement of more energy input for harvesting.

4 Biofuel Production Technologies and Associated Complexities

Various technological alternatives are available for acquiring the same biofuel from multiple feedstocks [32]. Anaerobic digestion (AD) process for the production of biogas from first generation feedstock is a fermentation process, which takes place in a closed airtight digester (at temperature $30°C < T < 45°C$ or more) where the complex organic raw materials (for about 55%) are broken down into complex organic matter, in the presence of microorganisms [42]. The other process associated with AD includes hydrolysis, acidogenesis, acetogenesis and methanogenesis, which ensures that methane constitutes ~50–75% in the produced biogas. For increase production of CH_4 pretreatment techniques such as removable of inorganic

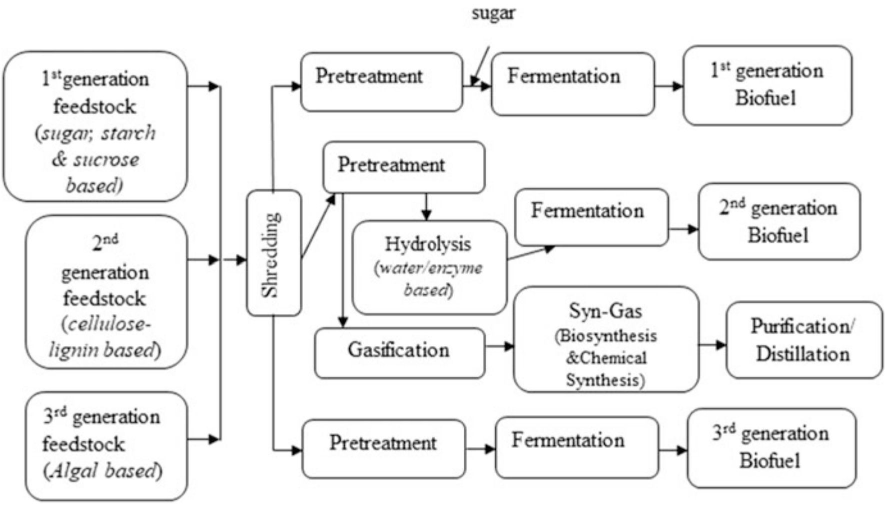

Fig. 3 Schematic representation of first, second and third generation biofuel production process

fractions, uniform particle size, co-digestion with other waste (which are readily fermentable and nutrient-rich substrates, e.g. rice, wheat straws, MSW wastes) are adopted [11, 25, 43]. However, environmental implication concerning the disposal of the waste (residuals from the distillation process has BOD~17–50 g/L) after the generation of the biogas is a considerable concern. The production of bioethanol via alcoholic fermentation of sugar feedstocks is an ancient and well-recognized process. However, the challenges associated with sustainable production of bioethanol lies in the preface of new/novel feedstocks, the assortment of efficient yeast strains for enzyme-based hydrolysis, fuel production from bagasse (second generation fuel), modification of processes for evading contamination in fermentation chamber, and reduction of residuals from the distillation process (refer Fig. 3). The challenges related to feedstock generally comprise of reproducing new varieties by improving the techniques of planting and harvesting (by monitoring the rainfall events), and reduction of aconitic and phenolic compounds undesirable for industrial processing. For second generation fuel, conversion of cellulose lignin-based materials into biofuel, i.e. ethanol can occur via two diverse pathways:

(a) Fermentation, wherein sugar pathway utilizes enzymes/microorganisms to alter pretreated lignocellulosic biomass into sugars
(b) Syngas platform, wherein gasification of feedstock to produce syngas occurs under a catalyzed biological or chemical process, and the pretested feedstock is transformed into ethanol (refer to Fig. 3)

For third generation fuel, algal-based feedstock for biobutanol production via fermentation (refer Fig. 3) is considered as an ideal contender for feedstock due to the high amount of carbohydrates (>40%) content. The infrastructural and economic constraints associated with algal-based feedstock stands as a significant obstacle in the use of microalgae. Further, third generation fuel requires high capital investment and cost of operation for cultivation (400 EJ/ton biomass) [43]. Large volume of water and nutrient (N, P and K) requirements during the growth algae renders these production technologies ineffective. These technological hiccups have resulted in the harvesting of microalgae in contaminated water to lower techno-process costs. However, the quality of the monoculture species may not be consistent. It may yield varying carbohydrate content of harvest algae, but suiting industrial applications two ways, in treating the polluted water and at the same time generate energy out of waste.

5 Biofuels and the Environment

Fossil fuels power the transportation sectors all over the world. This sector accounts for a large share of emissions, such as CO_2, SO_X, NO_X and particulate matter. Owing to the diminishing of the fossil fuels, the costs of the production of fuels are also increasing. The transportation sector needs 5.6×10^{20} J/year (560 EJ/year) of energy, which accounts for a maximum of 30% of the total annual worldwide energy demand (refer Fig. 4) [44]. To meet the steadily increasing demand for energy in the transportation sector exclusively by conventional generation technologies may put unacceptably high stress on the environment.

5.1 *Climate Change and CO_2 Generation*

Renewable energy sources have played a vital role in providing energy to humankind in a sustainable manner, mitigating climate change. With increasing concern regarding energy security and high oil prices, the demand for alternate methods of energy production to satisfy the transportation sector is increasing at a continuing pace. This direct combustion of the large amount of fossil fuel (coal, natural gas and

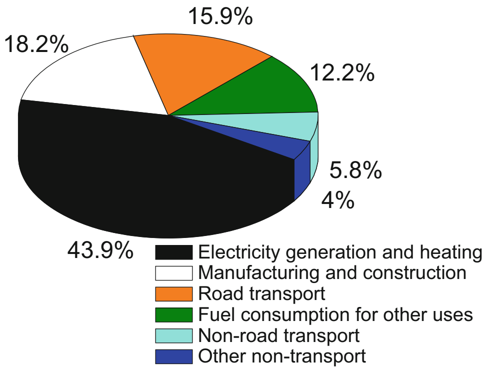

Fig. 4 Percentage emissions of CO_2 from various sources [44]

oil) to cater to the increasing need of the evergrowing population has resulted in accumulation of 15 billion tonnes of CO_2 per year [7, 22]. The percentage distribution of CO_2, a major GHG generated from the various sector, is presented in Fig. 4, as highlighted in the International Organization of Motor Vehicle Manufacturers [44]. GHG emissions associated with energy are a major source of climate change. Also, the pressing need to stop GHG emissions has resulted in considering the use of nuclear energy, in slowing climate destabilization. GHG emissions in the twenty-first century have led to the irreversible change in climatic conditions worldwide both in short and long time scales. The ecological and physical of climate change includes extreme weather events like floods, droughts, permafrost melt, heatwaves, hurricanes, sea-level rise, altered crop growth, etc. The total anthropogenic GHG emission from an energy sector having coal, hydroelectric, natural gas, nuclear energy and some non-hydro renewable energy sources is about 695 g CO_2-eq./kW-hr [1, 45]. The increased temperature has caused an increased atmospheric water vapour concentration and changes in transport of water vapour and hydrologic cycle [46, 47]. The evaluation of Atmosphere-Ocean General Circulation (AOGC) models also characterizes the changes in precipitation levels [47]. The changes in precipitation levels are linearly related to the increasing warming of the globe [48]. These adversely affect human water supplies, agriculture pattern changes, increased frequency of fire, change in ecosystem and desertification [49, 50]. By replacing the use of conventional fossil fuels, the anthropogenic GHG emissions can be avoided, and the CO_2 existing of fossil fuels can be stored within itself.

5.2 Alteration of Land Use/Land Cover (LU/LC)

Large-scale biomass energy production has the potential to change the land-use pattern and may impact the carbon ecosystem both directly and indirectly [51]. The most noticeable impacts, as highlighted in the existing literature and identified as necessary in discussion with stakeholders, are enlisted as below.

5.2.1 Cultivation of Bioenergy Crops and Associated Land Use/Land Cover

In the terrestrial ecosystem, both soil and plant biomass are the largest biological stores of carbon. In the global scale, the arable land is a finite and vulnerable resource. The average amount of arable land of 0.45 ha per capita is unevenly distributed among the globe. China, the world largest populous nation has only 7% of the global arable land. Human establishment such as buildings, roads, parking, etc. for would claim amount 50 ha per 1,000 person reducing the amount of land availability by 3% by 2050 [52]. Since the arable lands could not be displaced from the production of food and fodder; this would imply that natural, semi-natural and forest grasslands would be utilized for bioenergy crops cultivation, leading to a change in Land use-Land cover (LU-LC) pattern [53]. This change will lead to the rapid oxidation of the carbon stored in soil and biomass, with CO_2 emissions overshadowing the emission avoided by biofuel [51, 54]. This process of land conversion and recultivation introduces carbon debt in the environment, i.e. the quantity of CO_2 released by incinerating and decomposition of organic carbon stored in the plant biomass and soil [54]. The bioenergy projects have contributed to both Direct LU (dLUC) and Indirect LU Change (iLUC); dLUC is attributed as the direct conversion of land use for a particular biofuel feedstock production for economic recovery. This also included change from crop rotation patterns, conversion of grazing land, natural ecosystems and degradation of forest resources. The emissions caused by this process of transformation can be directly related to the biofuel load and associated carbon balance. Whereas iLUC is related to the production of biofuel in the land of agricultural efficiency, as a consequence of the bioenergy project and has a market effect linked to it. iLUC leads to a reduction in the cultivable area available for food and feed production, thereby affecting the supply on the world market [55]. Fortunately, less than 1% of the agriculture done globally utilizes land for cultivation of biofuel crops. Thus LUC associated with bioenergy holds a small share in overall changes in the area uses, at present. However owing to the higher assesses potential use of bioenergy in the future, policymakers and other stakeholders are highly dedicated to understanding the impact of LUC emissions on climate change behaviour due to increasing levels of bioenergy. Both dLUC and iLUC causes a loss of carbon stocks in the environment.

5.2.2 Soil Quality and Organic Carbon

The global environmental consequences of cultivating biofuel crops are critically demonstrated. The most significant impact of biofuel development is sequestration, i.e. storage or release of soil organic carbon (SOC) [56–58]. The increase in SOC increases the crop quality and productivity decrease in the rate of run-off and increased soil microbial diversity. The quality and quantity of carbon contributed to stable SOM, from root biomass is 1.5–3 times more as compared to carbon obtained from above-ground biomass, i.e. stem, branch and leaves. The organic C present in the soil is twice that of atmosphere and 2.3 times in biota [56–58] and responsible for soil productivity and ecosystem function. The improvement in the quality of the soil strongly depends on soil carbon content. The other positive aspects of increasing SOC include soil stabilization, binding of soil aggregates and an increase of fertility soil water capacity [56–58].

On the other hand, the conversion of complex ecosystems such as natural forests, lowland, peatlands (high potential for carbon sequestration) into arable lands can cause biodiversity losses [58–60]. However, to maintain the soil quality with increased bioenergy feedstock production would require: identifying crop species (dedicated perennial biomass), which as high productivity, low carbon capture, low fertilizer requirement and preserving the landscape with minimal environmental impact. Thus, soil quality refers to the capability of soil to function within the

Table 2 Classification of the type of land and the limiting factors based on Agronomic Interpretations [59]

	Soil potential for cultivation		
Classification	Type of land	Agriculture efficiency	Reckoning limit factors
Class 1	Prime agricultural land	High field crop production	None
Class 2		Slight limits that might restrict the growth of crop	Climate conditions such as moisture, temperature
Class 3		Moderate limits that might restrict the growth of crop	Soil conditions such as soil composition, salinity, organic matter, depth of top soil
Class 4	Marginal for arable agriculture	Severe limits that restrict the growth of crop	Drainage conditions such as groundwater table and hydraulic conductivity
Class 5		Very severe limits for sustained production	Landscape conditions such as pattern and flooding history
Class 6	Land has no potential for agriculture		Not applicable

LSRS Manual, 1995 under Food and Agricultural Organization (FAO) of the United Nations

boundaries of the ecosystem and facilitate good plant-animal sustainability, augment water and air quality and maintain human health and habitation [59, 61–64]. Unfortunately, long-term field studies have indicated that land competition has caused direct and indirect land-use change (LUC and iLUC), thereby affecting soil properties. The conversion of undisturbed ecosystems as natural forests, lowlands and peat lands into agricultural land for food production and/or biofuels leads to carbon debts (high CO_2 emissions from the soil). This results in SOM mineralization leading losses in carbon; 75% in tropical soils and 60% in temperate areas [58, 61–64].

In a broader sense, soil can be changed from carbon source to carbon sink resorting to accurate agronomic and land management practices. Needless to say, the estimation of the soil quality is significantly challenging, as it is dependent on the nature of argoecosystem and climatic conditions, which is severely affected by the rise in anthropogenic GHG [65]. The argoecosystem does not require the rich nutrient potential for energy crop production. In this scenario, marginal land (as designated in Land Suitability Rating System, LARS) can be considered as a potential solution to address the Food versus Fuel competition, without changing the LU/LC [66, 67].

Table 2 classifies the type of land and the limiting factors based on Agronomic Interpretations. Class 4–6 identifies marginal landscape left after excluding the Class 1–3 types of soil, forest, urban area, desert, ice, glacier, environmentally sensitive or protected areas and wetlands coming under the national land cover map of a place. Until recently the marginal land cover (i.e. the grassland and the shrubland) was utilized only for livestock grazing; however, now such landscapes are utilized for the production of switchgrass and coppice hybrid poplar, a deep-rooted perennial grass, having high cellulosic value and an ideal candidate for ethanol production [65, 66].

5.3 Impact of Biofuel on Air Quality

Considering the complexities and intricacies involved with (a) biofuel production/supply chains, (b) wide-range of biofuel practices, (c) emission of air pollutants and (d) the changing local meteorological situations, no specific trends can be recognized regarding biofuels' effect on air quality. However, [67–69] have identified that the replacement of conventional fuels with biofuel will reduce the emissions of some pollutants but may result in secondary emissions.

During the production of biofuels, the main toxic pollutants emitted into the air include carbon dioxide (CO_2), carbon monoxide (CO), oxides of nitrogen (NOx), sulphur dioxide (SO_2), volatile organic compounds (VOC), ammonia (NH_3) and particulate matter [70]. The emitted pollutants also include highly toxic substance, for example, formaldehyde and polyaromatic hydrocarbons and acts as the precursor to high level ozone. Further NOx emissions result in the increase of acid rain which is associated with various health hazards, including a decline in lung function, lung tissue damages and premature health [70–72]. The source of air population related to the production of corn ethanol was investigated in the USA [71]. Researchers also identified that ethanol blends (E85) will decrease emissions of NOx ~ 14% and CO ~ 13% but remains unaffected to VOC emissions when compared with conventional gasoline [71]. CO emissions will get reduced from 6.7 to 7.5%, when E10 blends are implemented providing modest air quality improvement but remain unaffected to NOx and VOC release [71, 73]. Identified bulk emission in the midwestern "Corn Belt corn production area". The practice of using air, stream and hexane to extract oil from seeds and plants in biodiesel processing plants also generates direct emission. Most of the hexane is recovered and reused, but some fractions are emitted into the environment creating pollution. Researchers evaluated that the average US Soybean compressing system discharges around 10 Kg of hexane per ton of oil produced, although alternatives replace hexane; but these options are not economical [74].

Further, short- and long-term exposure to agrochemicals, corrupt application practices and water/soil contamination with excessive nutrients has exposed workers to numerous acute and chronic health symptoms [70, 72]. The applications of agrochemical use in soybean production lead to cancer, fatal abnormalities and respiratory illnesses in the locality of rural communities in Argentina [70, 73, 75]. On the other hand, certain positive health benefits associated with biofuels over traditional methods have also been reported at the household level. For example, cooking from conventional biomass stoves that use of charcoal, dung and wood caused indoor air pollution, which is a major health threat in Africa due to the emission of hazardous indoor pollutants mostly CO and PM [75]. Thus implementation of specific biofuel practices would help in considerable decrease in indoor air pollutant level.

5.4 *Impact of Biofuel on Water Quality*

The processing of biofuel feedstock required large volume of water for evaporative cooling and washing plants and seeds [76, 77]. The quantity of water depends on the types of feedstocks used. A typical US soybean crusher need around 19 Kg water for every ton of produced oil [78]. For each ton of soybeans in refining/pretreatment process, around 17% of crude degummed soybeans oil, 76% of soy meal and remaining 7% of air and solid and liquid waste [78] are generated. The contaminant in such liquid wastewater is nutrient-rich and high in organic content [78]. This can result in eutrophication (due to excessive use of fertilizers during production stage) of neighbouring streams and rivers by affecting the water's dissolved oxygen content, if discharged untreated into the waterbodies [79]. Use of such water from eutrophic zones for production of biofuel might lead to unsatisfactory results. As such, feedstocks are cultivated observing the rainfall geographic and pattern. About three quarters of sugarcane and maize production in Brazil and the USA are rainfed [77]. Crops such as sugarcane, maize and oil palm are very water-intensive, thus requiring high content of water, mostly suited for high rainfall areas, unless they can be flooded/irrigated. Thus the possibility for expansion of irrigated areas for higher productivity may solely be dependent on the availability of good land and water resources free from anthropogenic contamination [79]. Water contamination due to excessive use of agrochemicals and fertilizers associated with biofuel production can create major environmental concerns.

6 Concluding Remarks

With the massive use of fossil fuels and its associated environmental concerns, the share of biomass in global total energy which has waned steadily over a century has again caught the attention of policymakers, as a renewable, sustainable and environmentally benign energy source. In the gigantic energy sector, it is seen that the production of biofuel is small yet significant. The increasing demand of biofuel has created apprehensions within agricultural sectors between delivering for the food and fuel marketplace. Herein, the diversification in the feedstock, i.e. consideration of cellulosic feedstocks over direct food resources may be favourable to the continuous production of biofuel, with the use of best practice technology. The most positive environmental aspect of bioenergy crops is that it can reduce/offset GHG emissions by removing CO_2 from the atmosphere and stockpiling in crop biomass and soil. Thus, the utilization of marginal lands and waste lands unsuitable for food agriculture can serve as a better prospect for second and third or advanced generation biofuels. Such a scenario will lead to environmental benefits such as sequestering carbon into the soil and create prospects for job opportunities and generation of income, thereby creating a positive social impact in a region. But, the socioeconomic impacts will be exceedingly dependent on the choice and mode of feedstock production and implications of various adopted agricultural practices, the region of biofuel production and use (i.e. environmental and socioeconomic context) and various governing policies framed for production and trading arenas. Until recently many policymakers believed that the alternative solution to the widespread use of fossil fuels is bio-based energy fuels; as these fuels will impart a significant and optimistic climate change effects by producing lower levels of GHG, thereby lowering the impacts of global warming. However, studies have revealed that distinct biofuel varies extensively in their GHG balances and has certain side effects on land, water and biodiversity. There is prospect that the intensification of feedstock production through the use of new technologies can severely impact the quality of soil, air and quality of water and has the potential to create even scarcity of water in non-monsoon periods.

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Role of Chemistry in Alternative Energy: The Thermodynamics and Electrochemical Approach

Sadia Ilyas, Hyunjung Kim, and Rajiv Ranjan Srivastava

Contents

Abstract Energy can simply be taken as the ability to do the work. In the specific context of chemistry, energy is an attribute of a substance as a consequence of its atomic, molecular, or aggregate structure that changes by undergoing a chemical reaction. Moreover, the first law of thermodynamics states that energy can neither be created nor be destroyed, only its transformation from one to another takes place.

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This transformation of energy in various forms, heat/work/electricity, occurs as a result of the chemistry involved in it, driving the chemical reaction into forward/backward direction. Although the chemistry of conventional energy like coal burning in the presence of air/O_2 is well known, the crucial role of chemistry continued to play in the case of alternative energy not commonly discussed in simple terms. Therefore, this chapter discusses the important and basic role of chemistry with some examples in the field of alternative energy. The approach route of thermodynamics and electrochemistry is also discussed in the present chapter.

Keywords Alternative energy, Chemical reactions, Electrochemistry, Fuel cells, Rechargeable batteries, Thermodynamics

1 Introduction

Chemistry is involved in every aspect of our life that affects the physical and chemical characteristics of most of the existing objects of this world. The law which governs such characteristics is known as thermodynamics. In the context of energy, the involvement of chemistry and the role of thermodynamics can be clearly understood in terms of efficiency like how much efficiency a photovoltaic (PV) cell has, or can any other process be viable to replace the PV cell by comparing the overall energy value [1]. Commonly, the energy change accompanying a chemical reaction is more significant than the reaction itself. For instance, the energy liberation in the form of heat by coal burning is more significant than CO_2 production after the combustion. The change in energy not only appears in the form of heat energy but also as work, electricity, and radiant energy (Fig. 1). It can be understood by the following examples [2]:

Coal burning in air:

$$C + O_2 \rightarrow CO_2 + \text{Heat energy} \tag{1}$$

Magnesium burning in oxygen:

$$2Mg + O_2 \rightarrow 2MgO + \text{Heat} + \text{Light} \tag{2}$$

Combustion of phosphorus in dark:

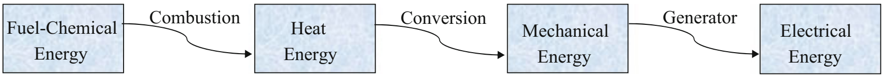

Fig. 1 A typical representation of the multiple conversions of energy required to electricity generation

$$P_4 + 5O_2 \rightarrow 2P_2O_5 + \text{Light energy} \tag{3}$$

Internal combustion of petroleum:

$$C_{10}H_{22} + 15.5(O_2) \rightarrow 10CO_2 + 11H_2O + \text{Mechanical energy} + \text{Heat} \tag{4}$$

Galvanic cell reaction:

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)} + \text{Electrical energy} \tag{5}$$

2 Chemical Reactions and Thermodynamics

Chemical reactions are usually driven by changes in energy that appears in different forms. The energy changes occur while chemical reactions are proceeding, and certain bonds are cleaved and new bonds appeared to form. In general, energy is utilized during the cleavage of bonds, while energy gets liberated during the emergence of bonds [2, 3]. As the bond energy varies from one to another, the chemical reactions are always accompanied by energy adsorption and/or release. Nowadays, thermodynamics is much widely used to deal with almost all forms of energies rather than the traditional, referring to the movement of heat. Henceforth, thermodynamics can be associated with sharing out the quantitative relationship between heat and various forms of energies. Thermodynamics is primarily based upon three fundamental laws as follows:

First Law Deals with the equivalence of different forms of energies

Second Law Deals with the direction of chemical changes

Third Law Evaluates the thermodynamic parameters like entropy

The importance of thermodynamics lies in its ability to [3] (1) provide an explanation of the macroscopic (i.e., bulk) properties of matter in terms of the concepts which are supported by the microscopic views of our material world; (2) predict the feasibility of the chemical reaction under the given set of conditions; and (3) predict the extent to which the chemical reaction can occur before the equilibrium is attained. On the other hand, the limitations of thermodynamics can be stated as follows: (1) it does not tell about the rate or kinetics of the reaction; (2) it does not reveal about the mechanism or reaction pathways; and (3) it cannot be applied to a microscopic system like individual atoms or molecular level.

3 System and Surroundings

The entire thermodynamics moves around the terms universe, system, and surroundings, where Universe = System + Surroundings. A system is defined as the part of the universe which is under investigation. It is partitioned off from the rest of the universe, i.e., surroundings. Notably, the entire universe, except the system, is not affected by the changes accompanied by the system. Therefore, a surrounding represents the portion of the remaining universe that interacts with the system [2, 3]. The wall which separates the system from the surroundings is called a *boundary*. A system can be open (such a system which can exchange mass as well as energy with the surroundings, e.g., expanding the piston via heating) or closed (such a system which can exchange energy with the surroundings but not the mass, e.g., heating a liquid in a beaker).

Not only does the system but the state is also important to define which refers to the conditions of existence of a system when its macroscopic properties have definite values. The thermodynamic properties whose values depend only on the initial and final states of the system are called state functions. Internal energy (U), enthalpy (H), entropy (S), Gibbs free energy (G), pressure (P), temperature (T), and volume (V) are some common state function [2, 3]. Further, the operation which brings about the changes in the state of the system is termed as a thermodynamic process. It can be divided into three types depending upon the conditions under which the changes are brought about. They are pointed as below and shown in Fig. 2.

1. Isothermal process which is carried out at constant temperature ($\Delta T = 0$)
2. Adiabatic process which has no heat exchange between the system and the surroundings ($\delta q = 0$)
3. Isobaric process which is carried out at constant pressure ($\Delta P = 0$)
4. Isochoric process which is carried out at constant volume ($\Delta V = 0$)

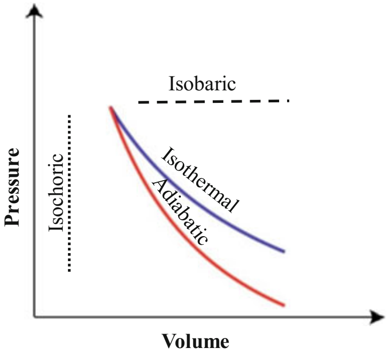

Fig. 2 A typical representation of various thermodynamic processes

4 Various Forms of Energy

In general, heat and work are two main forms of energy. The transfer of energy in terms of temperature difference between a system and the surrounding can be termed as heat. At the molecular level, it can be taken as the energy transfer to be used to stimulate the molecular motion in the surroundings. The energy transfer continues until the system and the surroundings attain a thermal equilibrium. On the other side, work is the exchange of energy between the system and the surroundings by various means like mechanical, pressure-volume, or electrical work [2, 3]. The exchange of energy as pressure-volume work can occur if the system consists of gaseous substance and there is a pressure difference between the system and the surroundings. The work done on the system is positive work ($q > 0$), and work done by the system is negative work ($q < 0$).

In order to clearly describe the direct role of chemistry in sustainable energy, some typical examples of renewable energy are being discussed in terms of chemistry (including electro-chemistry) and thermodynamics.

5 Fuel Cells

In a *fuel cell* operation, fuel and oxidant undergo into the cell to produce electricity, while waste heat and depleted oxidant are removed out (as the schematic shown in Fig. 3). Inside the cell house, the fuel in the form of an electron-rich compound is

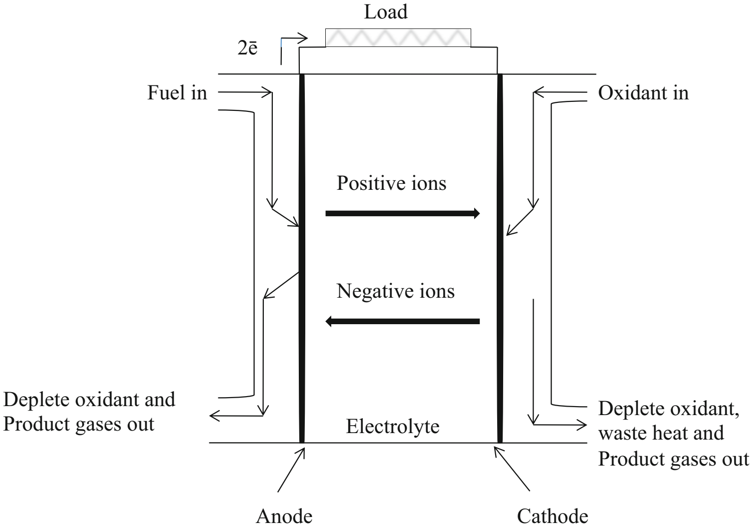

Fig. 3 A typical representation of fuel cell (adapted with permission from Carpenter, N.E., 2014. *Chemistry of Sustainable Energy*. New York: Taylor & Francis)

Table 1 A summary of few important half-cell reduction potentials

Half-cell reactions	E° (V)
$F_{2(g)} + 2e^{-} \rightarrow 2F^{-}_{(aq)}$	2.87
$O_{3(g)} + 2H^{+}_{(aq)} + 2e^{-} \rightarrow O_{2(g)} + H_2O$	2.07
$Cl_{2(g)} + 2e^{-} \rightarrow 2Cl^{-}_{(aq)}$	1.36
$O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \rightarrow 2H_2O$	1.23
$NO^{-}_{3(aq)} + 4H^{+}_{(aq)} + 3e^{-} \rightarrow NO_{(g)} + 2H_2O$	0.96
$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag^{0}_{(s)}$	0.08
$I^{+}_{3(aq)} + 2e^{-} \rightarrow 3I^{-}_{(aq)}$	0.53
$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$	0.000
$Zn^{++}_{(aq)} + 2e^{-} \rightarrow Zn^{\circ}_{(s)}$	−0.763
$2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)}$	−0.83
$Li^{+}_{(aq)} + e^{-} \rightarrow Li^{\circ}_{(s)}$	−3.05

anodically oxidized, while the oxidant having a high electrode potential value gets reduced at the cathodic surface [4]. The pairing of both reactions occurs as an overall electrochemical reaction. For a typical hydrogen fuel cell, the *half-cell* reactions can be written as:

At the anode:

$$H_2O \rightarrow 2H^{+} + \frac{1}{2}O_{2(g)} + 2e^{-} \tag{6}$$

At the cathode:

$$2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_{2(g)} \tag{7}$$

The *cell potential* (E_{cell}) or *cell voltage* or *electromotive force* (*EMF*) represents the force (1 V ~ 1 joule/coulomb) applied to electrical current moving through the circuit. The magnitude of E_{cell} usually represents the difference between the *reduction potentials* of the participant reactants in the process. In order to reduce a compound, it must have a higher positive value of the reduction potential, whereas the compound having a highly negative reduction potential value is strongly prone to oxidation. Table 1 shows some important representative values of standard reduction potentials for some selected *half-cell* reactions. It can be seen that fluorine gas has the highest positive reduction potential value (2.87 V) and hence can be easily reduced, while lithium has the highest negative value (−3.05 V), and hence it acts as the strongest reducing agent.

The output energy of a cell is often low (0.7–0.8 V); hence, *fuel cells* are usually linked to electrically conducting bipolar plates, called the *stack*, wherein the assembly like the anode of one cell remains connected to the next cell at the cathode end, which is designed to ensure the flow of fuel and oxidant supply via each of the cells in series. Therefore, an overall voltage of the stack becomes a function of the total number of cells connected in the series. In this way, solid oxide fuel cell can produce power as high as multi-100 MW. Again for a better understanding of how the *fuel cells* work and with what efficiency, it can be referred to thermodynamics involved in the process.

The calculation of *cell potential* E°_{cell} (referring to the standard cell potential at 1 atm. pressure, 298 K temperature, and 1 M concentrations) is simple using the half-cell potential values in Table 1. For example, a redox pair of H_2 and O_2:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 1.23 - 0.00 = 1.23\ \text{V} \tag{8}$$

This value ($E_{\text{cell}} = 1.23$ V) is the highest amount of energy possibly can be yielded by the particular fuel cell under the standard conditions when the operational condition is maintained to be reversible. Further, the Gibbs free energy for a given redox couple belongs to the net energy produced by the redox couple. The relation between thermodynamic factors and cell potential can be written as:

$$\Delta G = -\text{nF}E_{\text{cell}} \tag{9}$$

where F = Faraday constant (9.65×10^4 C/mol) and n = electrons transferred (in mole) in an electrochemical reaction. The value of E_{cell} must be positive to spontaneously drive the reaction (a negative ΔG). As the electrochemical reaction refers to the transfer of electrons, ΔG also relates to the amount of charge, q. As we know that $q = nF$, Eq. (9) can be written as:

$$\Delta G = -\text{nF}E_{\text{cell}} = qE_{\text{cell}}\ (\text{work done relates to heat given out; q} < 0) \tag{10}$$

Therefore, ΔG relates to E_{cell} in joules to hold the charge (in molar). Here it is noteworthy to mention that the correct use of thermodynamic data with respect to the states of reactant and product is very important. For instance, the state of water (H_2O) molecules produced in a cell (either liquid or gas) depends on the conditions. Accordingly, the E_{cell} varies: 1.23 V for liquid state and 1.18 V for the gaseous state. A lower value of gaseous water indicates the loss of energy during the vaporization of liquid water.

ΔG in terms of enthalpy (ΔG) and entropy (ΔG) is given as:

$$\Delta G = \Delta H - \text{T}\Delta S \tag{11}$$

Henceforth, considering ΔG relates to E_{cell} from Eq. (10), the temperature may play an influential role in operating potential of a fuel cell with respect to the entropic changes into the system. In general, a negative change in entropy is usually observed in all fuel cell reactions indicating that an increase in temperature results in a decreased E_{cell} value (in a hydrogen fuel cell, it decreases to ~0.3 V over a temperature range of 300–1,300 K [5]). Further, the pressure of the system significantly influences E_{cell} value for those having gaseous reactants/products, depending upon the change in the number of gaseous species (in mole). A lower gaseous

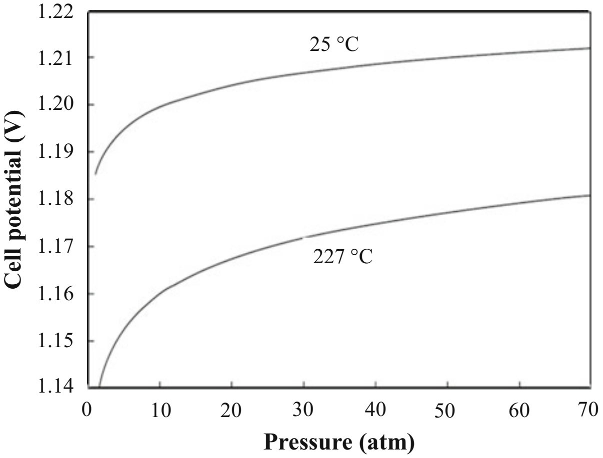

Fig. 4 Effect of temperature and pressure on cell potential (adapted with permission from Carpenter, N.E., 2014. *Chemistry of Sustainable Energy*. New York: Taylor & Francis)

species is obtained while an increase in E_{cell} value but at a lower level than that of the temperature impact, as shown in Fig. 4 [5].

The efficacy of a fuel cell in terms of energy production through an electrochemical reaction that operates under the thermodynamically reversible conditions can be obtained using the following equation:

$$h_{\text{rev}} = \frac{\text{Electricity produced}}{\text{Heating value of fuel}} = \frac{W_{\max}}{\Delta H} = \frac{\Delta G}{\Delta H} = \frac{E_{\text{rev}}}{E_{\text{tn}}} \times 100\% \tag{12}$$

where E_{rev} denotes the reversible cell potential and E_{tn} denotes the thermoneutral cell potential. The value of E_{tn} for a redox pair of H_2/O_2 is 1.48 V, and comparing this value to the $E^{\circ}{}_{\text{cell}}$ of liquid water, i.e., 1.23 V, gives a reversible efficacy of 83% for a H_2/O_2 fuel cell [5].

To determine the cell performance, the following relationship can be applied:

$$\text{Current (amps)} = \frac{\text{Potential (V)}}{\text{Resistance (ohms)}} \tag{13}$$

$$\text{Power (watts} \equiv \text{J/s)} = \text{Current (amps)} \times \text{Potential(V)} \tag{14}$$

The two extreme conditions in electrical circuits can be defined as (1) an *open circuit* (a zero current, maximum voltage) and (2) a *short circuit* (maximum current, a zero voltage). An *open-circuit voltage* is the actual measurement of voltage when the circuit is open without connecting the cathode and the anode and essentially without any electricity flow; thus, the voltage comes at its maximum. In a perfect fuel cell at the standard conditions of temperature and pressure, the *open-circuit voltage* could, in theory, match the value of E°*cell*. In a real system, it always measured to be

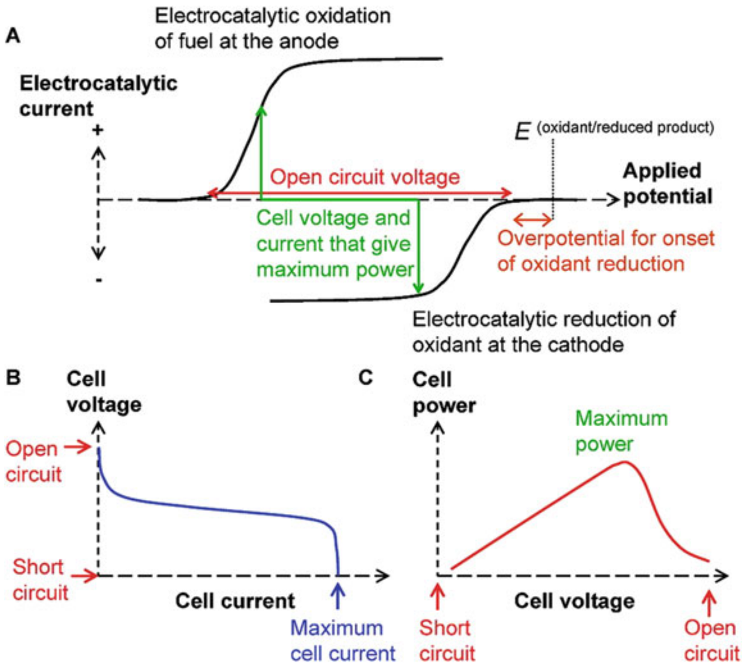

Fig. 5 A typical relation between power and voltage (adapted with permission from Cracknell, J. A., K.A. Vincent, and F.A. Armstrong. 2008. Enzymes as working or inspirational electrocatalysts for fuel cells and electrolysis. *Chem. Rev.* 108:2439–2461. Copyright 2008, American Chemical Society)

less than E_{cell}. Clearly, the closer the *open-circuit voltage*, the greater the integrity of the cell. On the contrary, a closed circuit without any load results in a maximum current value, which represents the *short-circuit current*. Therefore, a greater output for a given cell comes in between the open circuit and short circuit, as observed by Cracknell et al. [6] in Fig. 5.

Moreover, in a reversible cell, voltage vs. current should give a straight line albeit Li [5] observed that E_{cell} typically decreases nonlinearly. The relationship shown in Fig. 6 indicates that E_{tn} is the absolute and perfect amount of the maximum potential which is achievable only on a theoretical basis. $E_{\text{cell(reversible)}}$ represents the maximum potential (theoretically), accounting to the inevitable losses due to entropy which follows the thermodynamics (second law). In this manner, the actual cell potential is diminished from E_{rev} by irreversible losses which is usually referred to either *polarization* or *overpotential* or *overvoltage*. It falls into the area of a voltage/current curve of *activation*, *ohmic*, and *concentration polarization*.

The actual cell potential of an electrochemical cell essentially incorporates the real concentration of the reacting species in actual rather than following the theoretical or generalized concept. For instance, in a typical hydrogen fuel cell, the often used oxidant is air and not the pure oxygen. One of the well-known thermodynamic

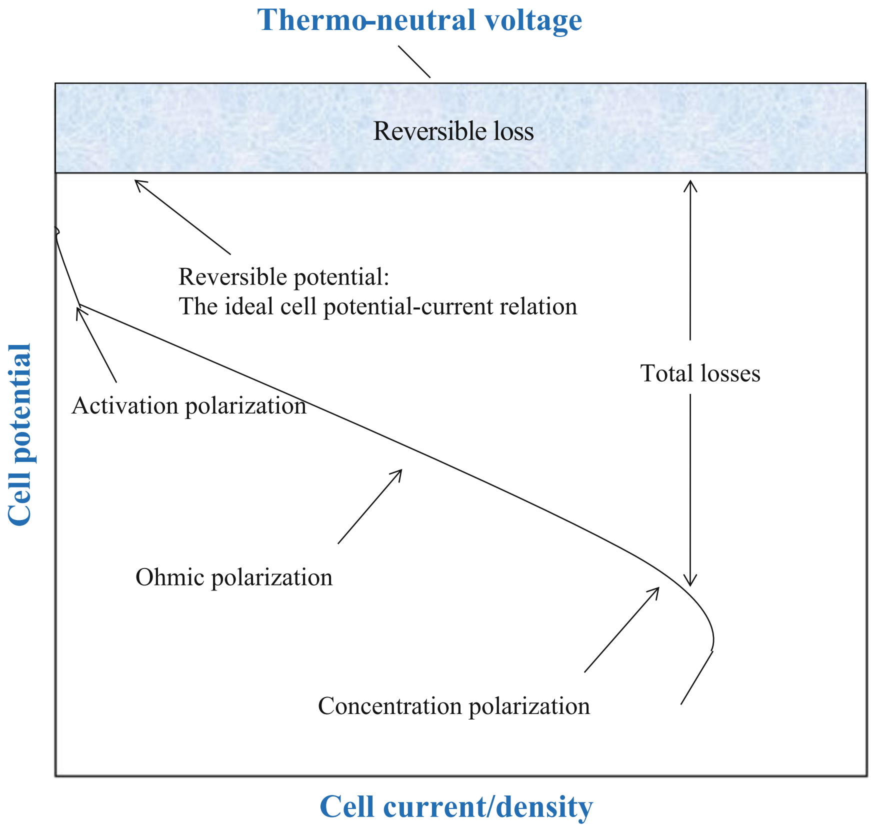

Fig. 6 A typical representation of fuel cell polarization curve (adapted with permission from Li, X. 2006. *Principles of Fuel Cells*. New York: Taylor & Francis)

equations in terms of relating the reduction potential to the standard electrode potential, temperature, and activities (approximated by concentrations) of the chemical species undergoing the redox reaction is the Nernst equation. It is given as follows:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{\text{RT}}{nF} \ln Q \tag{15}$$

By accounting concentration in the form of reaction quotient, Eq. 15 comes as:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{\text{RT}}{nF} \ln \left(\frac{{n_{H_2}}/{V_{H_2}}}{{n_{O_2}}/{V_{O_2}}} \right) \tag{16}$$

6 Electrochemistry of Lithium-Ion Batteries

The prominent role of electrochemistry can be understood by the reversible reactions in a rechargeable battery, in which the battery is discharging in one direction and getting charged by a power supply with reaction going in the opposite direction. When the cell undergoes charging-discharging cycles, ions shuttle between the cathode (positive terminal) and the anode (negative terminal). On discharge, the anode undergoes oxidation, while at the same time, the cathode undergoes reduction—vice versa movement during the charging. All the constituent materials in a battery possess a theoretical specific energy, and the key factors like the high storage capacity and greater power supply lie primarily in the cathode.

6.1 General Chemistry of LIBs

In current days, lithium-ion batteries (LIBs) are the most commonly used rechargeable battery. Lithium has a low density (0.534 g/cm^3) and is the lightest metal with very high electrochemical potential (-3.05 V), making it unmatchable in comparison to others. Like any other battery, LIBs are made of one or more power-generating compartments called cells. Each of the cells essentially consists of a positive and negative electrode, and an electrolyte is kept in between them. Typically, the positive electrode is kept to the Li metal oxides and graphite is used as the negative electrode, while electrolytes vary from one to another type of batteries. The modern LIBs are made of layered materials that can store (intercalate) Li-ions in the gaps between their layers (as shown in Fig. 7).

At the initial stage, Li-ions remain intercalated within the cathode having no charge. In order to use the LIBs, it needs to be charged first (Fig. 8a) which leads to an oxidation reaction at the cathode by losing electrons. To maintain the charge balance, an equal number of Li^+ gets desorbed from cathode to the electrolyte. These Li^+ travels to the anode and gets stored within the graphite. The intercalation at anode also deposits electrons into the graphite to tie up the Li^+-ions. The E_{cell} value of 3.7 V can generate power more than 200 W/kg [7–9]. While utilizing the stored charge of the battery, Li^+ are desorbed back from anode to cathode through the electrolyte (Fig. 8b). This also releases those electrons tying Li^+ to the anode. The flow of electrons is given via an external wire to provide the electric current to be utilized and make the electrochemical reaction to proceed. The charging-discharging reactions can be written as Eqs. (17)–(18). The battery becomes flat when all the Li^+ return back to cathode and reaction stops; again charging the battery by external electric supply is needed [41].

$$\mathrm{LiCoO_2} \rightarrow \mathrm{Li_{1-\mathit{x}}CoO_2} + x\mathrm{Li}^+ + xe^- \tag{17}$$

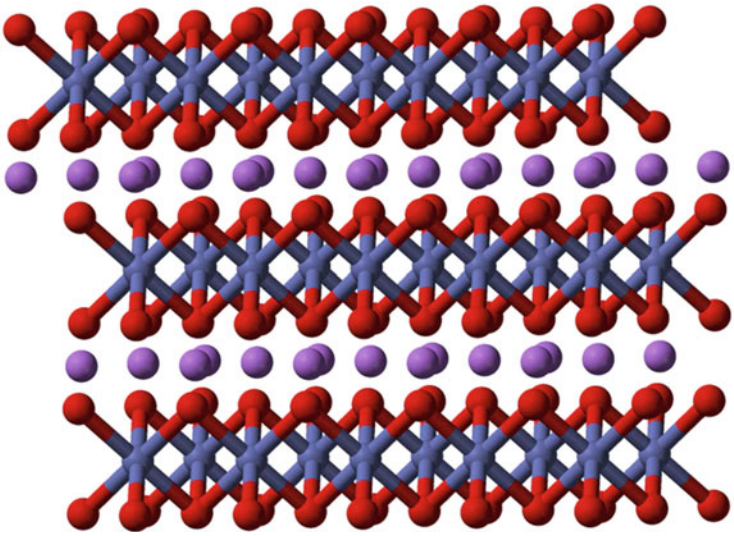

Fig. 7 A typical representation of the structure of $LiCoO_2$-type cathode material containing Li-ions intercalated within the structure of CoO_2 caging

$$x\mathrm{Li}^+ + xe^- + \mathrm{C}_6 \rightarrow \mathrm{Li}_x\mathrm{C}_6 \tag{18}$$

The use of mixtures in cathode and anode materials allows to strengthen intrinsic properties, and hence, usually mixtures are being used to obtain enhanced physical, chemical, and thermal properties of the battery. Below some important types of LIBs are discussed, more particularly as per the chemistry of the cathode material used in the battery. Depending upon the chemistry of cathode material used therein the battery [42], the properties of battery alters with each other (as summarized in Table 2).

6.2 Types of LIBs and Their Chemistry

6.2.1 Lithium Cobalt Oxide ($LiCoO_2$)

This is the most common type of LIBs that contains the cathode of $LiCoO_2$ and an anode of carbon (C) [40]. It was the first-generation LIBs developed by the Novel winners, R Yazami and J Goodenough (2019). The octahedral layers of CoO_2 holds Li^+ in between their layers, wherein cobalt also changes as $Co^{+3} \leftrightarrow Co^{+4}$ (by lose and gain of electrons) during charging-discharging cycles. Although $LiCoO_2$ has the greatest energy density, thermal instability is the major drawback, because the anodes can overheat, and at high temperatures, the cobalt oxide cathode can

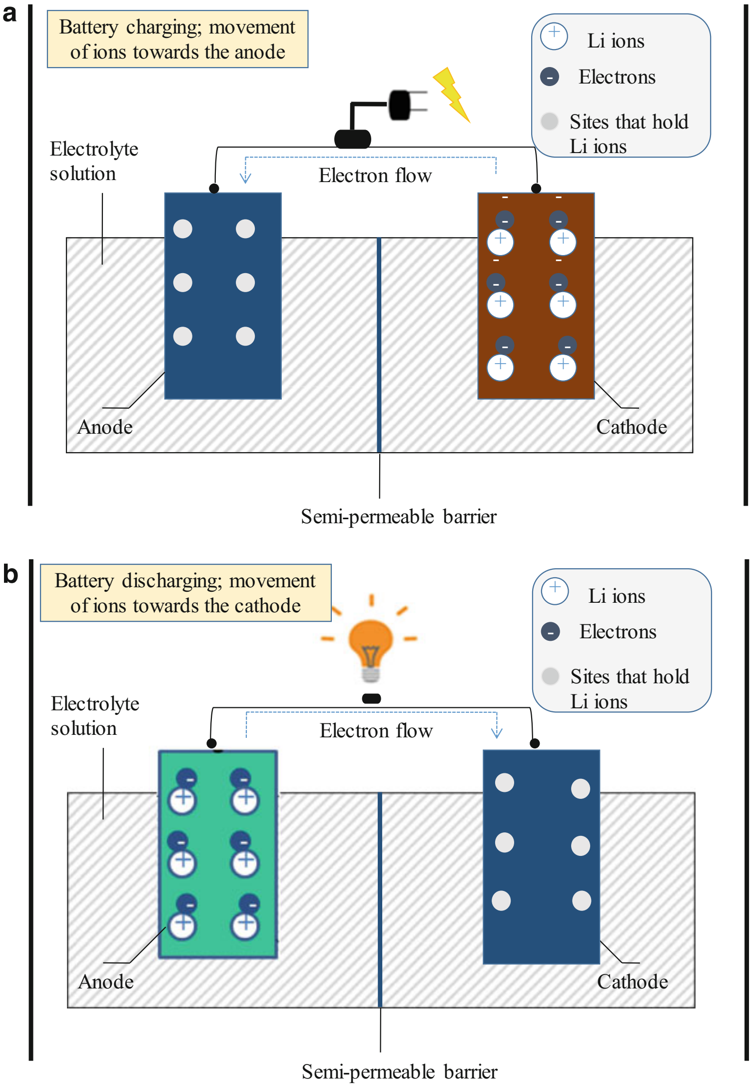

Fig. 8 (**a**) A typical representation of the charging process of a Li-ion battery. (**b**) A typical representation of the discharging process of a Li-ion battery

decompose to produce oxygen which may create fire by getting heat in the presence of electrolytes like diethyl carbonate. The reaction occurs during discharging as:

At anode:

Table 2 Main properties of commonly used Li-ion batteries depending on the chemistry of the cathode material

Specifications	$LiCoO_2$	$LiMnO_2$	$LiFePO_4$	$LiNi_xMn_yCo_zO_2$
Voltage	3.6 V	3.7 V	3.3 V	3.6/3.7 V
Charge limit	4.2 V	4.2 V	3.6 V	4.2 V
Cycle life	500	500–1,000	1,000–2,000	1,000–2,000
Operating temperature	Average	Average	Good	Good
Specific energy	150–190 Wh/kg	100–135 Wh/kg	90–120 Wh/kg	140 Wh/kg
Specific power	1 C	10 C, 40 C pulse	35 C continuous	10 C
Safety	Average, requires protection circuit and cell balancing of multi-cell pack. Requirements for small formats with one or two cells can be relaxed		Very good, needs cell balancing and voltage protection	Very good, needs cell balancing and voltage protection
Thermal runway	150°C (302°F)	250°C (482°F)	270°C (518°F)	210°C (410°F)
Raw materials' costing	High	30% cheaper than $LiCoO_2$	High	High
Specific energy	Very high	Average to high	Average	Very high
Main application	Mobile phones, laptops	Power tools, medical	Electric vehicles	High power tools, medical, electric vehicles

$$LiC_6 \rightarrow x\mathrm{Li}^+ + xe^- + C_6 \tag{19}$$

At cathode:

$$\mathrm{Li}_{1-x}\mathrm{CoO}_2 + x\mathrm{Li}^+ + xe^- \rightarrow \mathrm{LiCoO}_2 \tag{20}$$

Overall reaction:

$$C_6 + \mathrm{LiCoO}_2 \leftrightarrow \mathrm{Li}_x\mathrm{C}_6 + \mathrm{Li}_{1-x}\mathrm{CoO}_2 \tag{21}$$

The diffusivity of lithium in $LiCoO_2$ (5×10^{-9} cm^2/s) is consistent with the cycle of 4 mA/cm^2 [10]; its conductivity remains a challenge due to variation with compositions [11]. The energy density of LIBs has almost doubled from 250 Wh/L to over 400 Wh/L, since they were introduced in 1991. Using the carbonate salt of lithium into the cathode was introduced to provide a safety valve due to decomposition and the release of CO_2 which breaks the electrical flow when charging exceeds to 4.8 V. The excess of lithium in cathode material can be better represented as $Li_{1+x}Co_{1-x}O_2$. Several researches have shown that the capacity of cathode could be improved to 170 mAh/g by a metal oxide/phosphate coating onto $LiCoO_2$ surface [12–15]. The surface coating minimizes the reactivity of cobalt during charge with in situ acidic HF generated by the interaction of moisture and the electrolyte salt, $LiPF_6$. Later on a complete drying of $LiCoO_2$ at 550°C could also improve the capacity retention at 180 mAh/g at 4.5 V [16]. Although $LiCoO_2$ dominates the cathode of rechargeable LIBs, the limited availability and high cost of cobalt and hence the combination of transition metals are engineered.

6.2.2 Lithium Iron Phosphate ($LiFePO_4$)

A $LiFePO_4$ cell is similar to $LiCoO_2$, wherein the anode and electrolyte materials are also the same. The main variance relies in the cathode material by replacing $LiCoO_2$ with more stable $LiFePO_4$. In fact, neither lithium nor iron remains in $LiFePO_4$ cathode of an entirely charged cell; Li^+ intercalates around the cathode through the tunneling structure without doing any alteration to the structural frame of $FePO_4$. The negatively charged cathode containing phosphate anions remain bonded with the cationic iron in a structure that exhibits good capabilities to store Li^+ within the $FePO_4$ molecules. In the arrangement, O-atoms remain tightly bonded into the structure giving chemical stability to the cathode material. High discharge rate and better thermal stability along with lower cost than $LiCoO_2$ batteries due to phosphate (PO_4) can cope with high temperatures and elimination of cobalt with cheaper transition metal iron. Such characteristics make it a good choice where high energy is required by combining more number of batteries in series. Although $LiFePO_4$ batteries have a long life span, a lower energy density than a $LiCoO_2$ cell and a higher self-discharge rate are the disadvantages of these types of batteries.

The reaction occurs during discharging as:

At anode:

$$LiC_6 \rightarrow Li^+ + e^- + C_6 \tag{22}$$

At cathode:

$$LiFe(III)PO_4 + xLi^+ + xe^- \rightarrow LiFe(II)PO_4 \tag{23}$$

Overall reaction:

$$LiFe(II)PO_4 + 6C \leftrightarrow LiC_6 + FePO_4 \tag{24}$$

$LiFePO_4$ can be synthesized by high-temperature reactions [17], under hydrothermal conditions [18], or by sol-gel methods [19]. The olivine phase is quite easy

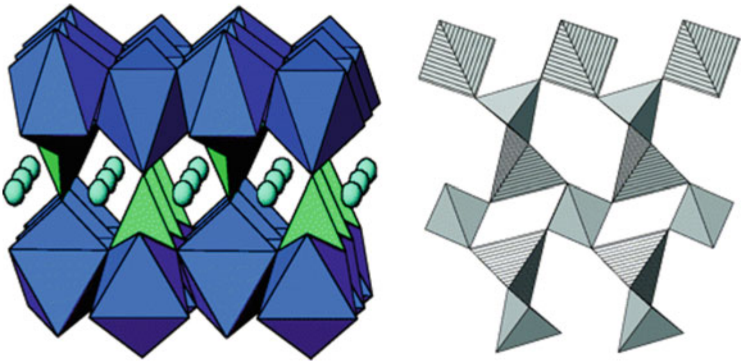

Fig. 9 Structures of orthorhombic $LiFePO_4$ and trigonal quartz-like $FePO_4$ (adapted with permission from Whittingham M.S. (2004) Lithium batteries and cathode materials. *Chem Rev* 104:4271–4301. Copyright 2004, American Chemical Society)

to synthesize hydrothermally but exhibits poor electrochemical properties. The structure of hydrothermally prepared $LiFePO_4$ showed ~7% iron atoms with lithium site along with the lattice parameters of (*a*) 10.381 Å, (*b*) 6.013 Å, and (*c*) 4.716 Å as compared to the ordered $LiFePO_4$ of (*a*) 10.333 Å, (*b*) 6.011 Å, and (*c*) 4.696 Å [23]. Diffusivity of lithium in $LiFePO_4$ is blocked by the iron atoms, since the diffusion rate is fast only along the tunnel rather in between them [28]. In order to ensure the ordering of lithium and iron atoms, the firing of hydrothermally synthesized material at 700°C, or surface prevention through the addition of ascorbic acid, could resolve the disorder [44].

Very low conductivity of $LiFePO_4$ at room temperature exhibits the low lithium diffusion [17], and hence, the theoretical capacity can be achieved either at a low current density [20] or at the elevated temperatures [21]. A carbon coating is suggested often to significantly improve the electrochemical performance of $LiFePO_4$ [22]. The samples prepared using reagent-grade carbon-containing materials have shown a conductivity of around 10^{-5}–10^{-6} S/cm [23], against the electrical conductivity of very pure $LiFePO_4$ to be 10^{-9} S/cm [24]. On the other hand, the samples synthesized with carbon-gel exhibited the capacity approaching 100% at a cathode loading of only 5 mg/cm^2 rather than high carbon contents of 20% along with 800 cycles at ~120 mAh/g [25]. Doping of niobium (certain ppm) has also shown excellent electrochemical behavior with increased conductivity by eightfold [24]. Further, the increased conductivity could be related to the formation of a highly conductive surface film of Fe_2P at high temperature, in particular the presence of carbon as a reducing agent [26].

The olivine structure of $LiFePO_4$ and $FePO_4$ (after lithium removal) is shown in Fig. 9 [44]. It can be seen that $FePO_4$ is isostructural with heterosite, $Fe_{0.65}Mn_{0.35}PO_4$. The alike two-phase system with $LiFePO_4$ in equilibrium with $FePO_4$ as the cyclic plot is also shown in Fig. 10 [23]. It depicts a 100% capacity of lithium to be cycled at 1 mA/cm^2 at 60°C and an electrode loading of 80 mg/cm^2 which is nearly 70% at room temperature [43, 44].

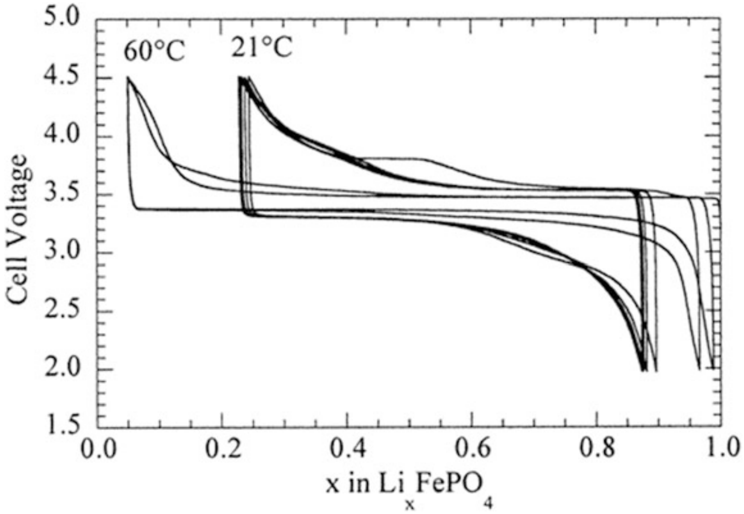

Fig. 10 Electrochemical behavior of $LiFePO_4$ cycling at 1 mA/cm^2 at two different temperatures of 21°C and 60°C (adapted with permission from Yang et al. [23] Performance of $LiFePO_4$ as lithium battery cathode and comparison with manganese and vanadium oxides. *J Power Sources* 119:239–246. Copyright 2003, Elsevier)

To ensure the batteries extended life, the long-term stability of electrode material is essential; hence, understanding the reactivity of both $FePO_4$ and $LiFePO_4$ is imperative. The iron phosphates react with an excess of *n*-butyllithium, destroying the phosphate lattices at low lithium potentials, where *n*-butyllithium is approximately 1.0 V vs. pure Li. It has been confirmed by Yang et al. [27] that Li reacts with the lattice destruction of $LiFePO_4$ lattice and considerable loss of capacity, declining a capacity by 80% after five cycles. Hence, $LiFePO_4$ cells require over-discharge protection in commercial applications. On the contrary, no evidence has been found for the conversion of the metastable orthorhombic $FePO_4$ phase to the quartz-like trigonal phase under normal electrochemical conditions. Moreover, no loss of oxygen on Li removal from the lattice is observed. The open-circuit voltage is 3.5 V for $LiFePO_4$ with a very high bandgap calculated to be 3.7 eV consistent with color and diffuse reflectance spectra and suggests that bandgap difference does not explain the electrochemical behavior; the conductivity is likely due to a polaron mechanism [28].

6.2.3 Lithium Nickel Manganese Cobalt Oxide ($LiNiMnCoO_2$)

The $LiNiMnCoO_2$ or commonly named as NMC batteries are relatively new in the family of LIBs and currently in widespread use in electric vehicles, laptops, and smartphones [29]. A NMC cell is similar to the $LiCoO_2$, wherein the anode and electrolyte materials are also the same. The main variance is the cathode material, a mixture of nickel and manganese with a lower amount of more critical element cobalt. The addition of nickel in the cathode mix provides a high specific energy, which in addition to the stable structure of the manganese spinel results in a battery with low internal resistance, high charging rate, and a better stability and safety. NMC batteries are usually made with a cathode containing equal ratio of one-third nickel, one-third manganese, and one-third cobalt, though the ratio can vary according to the manufacturing companies' own formula. The reaction occurs during discharging as below, where M denotes the equal proportion of Ni-Mn-Co:

At anode:

$$\mathrm{LiC_6} \rightarrow x\mathrm{Li^+} + xe^- + \mathrm{C_6} \tag{25}$$

At cathode:

$$\mathrm{Li_{1-x}MO_2} + x\mathrm{Li^+} + xe^- \rightarrow \mathrm{LiMO_2} \tag{26}$$

Overall reaction:

$$\mathrm{C_6} + \mathrm{LiMO_2} \leftrightarrow \mathrm{Li_xC_6} + \mathrm{Li_{1-x}MO_2} \tag{27}$$

The addition of three potential transition metals, cobalt, nickel, and manganese, was firstly coined by Liu et al. [30], while Yoshio et al. [31] hypothesized that cobalt can stabilize the structure of cathode material in a strictly two-dimensional fashion (along with $LiMn_{1-y}Ni_yO_2$). The transition metal contents in the lithium layer were observed to fell from 7.2% (for a $LiMn_{0.2}Ni_{0.8}O_2$ material) to 2.4% (for a $LiMn_{0.2}Ni_{0.5}Co_{0.3}O_2$ type material) along with the exceeded capacity of Li insertion to 150 mAh/g. Further, Ohzuku and Makimura [32] studied the symmetric compound of $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ that was synthesized at 1,000°C with almost the same capacity (150 mAh/g) cycling between 2.5 V and 4.2 V at 0.17 mA/cm^2 at room temperature (~30°C). However, a raised charge cutoff potential to 5.0 V could increase the capacity to >220 mAh/g. Later this compound is also known as *333* cathode material. Liu et al. [30] synthesized the $LiNi_{1-y-z}Mn_yCo_zO_2$ using a mixed-hydroxide approach by reacting $Ni_{1-y-z}Mn_yCo_z(OH)_2$ with a Li-salt in air/O_2 at 750°C, albeit the optimal temperature has been modified to be 800–900°C [33], resulting in a single-phase layered O3 structure. Whittingham [44] has analyzed that the cell parameters of *333* compounds depend on the mixture of transition metals as shown in Fig. 11. It can be depicted that both the in-plane *a* parameter and the interlayer spacing *c* increase with respect to nickel and decrease with the cobalt content for constant manganese [31, 33]. For a compound $LiNi_yMn_yCo_{1-2y}O_2$, the parameters of *a* and *c* obey Vegard's law, decreasing linearly with respect to the increased Co content [34]. For a constant Ni content, the parameter of *a* is directly proportional to manganese and inversely proportional to cobalt, indicating for a larger Mn ion than the Co ion.

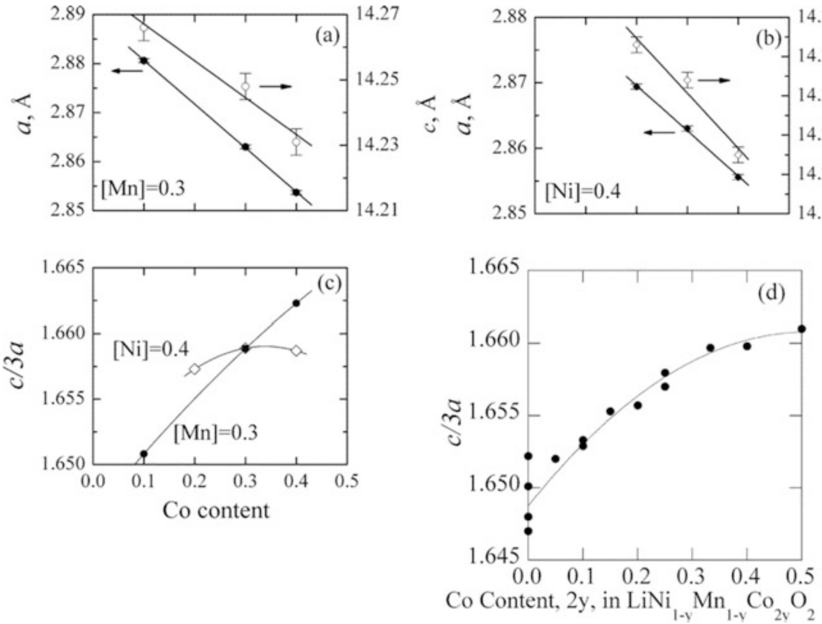

Fig. 11 Cell parameters and $c/3a$ ratio of layered $LiNi_yMn_zCo_{1-y-z}O_2$ and $c/3a$ ratio of the symmetric $LiNi_{1-y}Mn_{1-y}Co_{2y}O_2$ (adapted with permission from Ngala et al. [33] The synthesis, characterization and electrochemical behaviour of the layered $LiNi_{0.4}Mn_{0.4}Co_{0.4}O_2$ compound. J Mater Chem 14:214–220. Copyright 2004, The Royal Society of Chemistry)

Figure 12 depicts the occupancy on Li sites as a function of overall cathode composition at different temperatures [44]. It shows that the disorders of transition metal are suppressed by increasing the Co content but not to the same extent as in $LiNi_{1-y}Co_yO_2$ materials, where the disorders of nickel are only observed for $y \leq 0.3$, and increased with a higher Ni content. The temperature has also shown a profound effect as composition. As can be seen in Fig. 12, the $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ material synthesized at 1,000°C gives about 10% nickel occupancy in the lithium layer after the rapid cooling at ambient temperature. Kim and Chung [35] have also observed a high Ni content of 5.9% on the lithium site with the *333* samples synthesized at 950°C. Only at 800°C with increasing Co contents, the disorders of nickel drop to zero; on the contrary, even with more cobalt at 900°C more disorders of nickel are shown. The disorders can be reduced by slow cooling of synthesized material under the oxidizing environment that allows the partial reordering of ions [36].

6.2.4 Lithium Sulfur (Li_2S)

The aforementioned $LiCoO_2$ and NMC batteries contain high-cost, critical, and scarce elements in the cathode materials. Therefore, new material is in continuous search. Li_2S battery is possibly a suitable alternate to metal oxide batteries. A

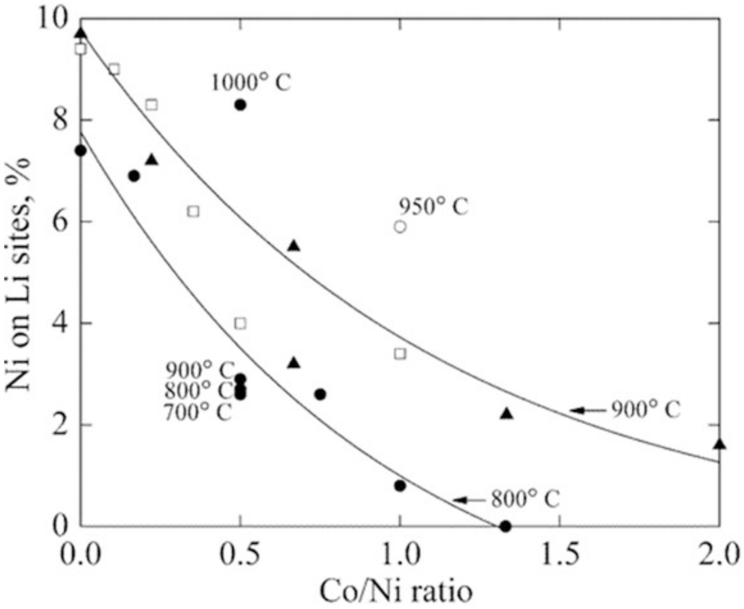

Fig. 12 Lattice disorder, percent of lithium sites occupied by nickel ions in $LiNi_yMn_zCo_{1-y-z}O_2$ (adapted from Whittingham M.S. (2004) Lithium batteries and cathode materials. *Chem Rev* 104:4271–4301. Copyright 2004, American Chemical Society)

relatively abundant and environmentally benign element, sulfur, is used as the cathode in it. During cell discharging, the S_8 allotrope of sulfur gets reduced by Li^0, leading to cleaving the ring to the final product, Li_2S [37]. The theoretical energy density of the Li_2S cell is as high as 2,500 Wh/kg; on the contrary, sulfur conducts neither ions nor electrons. Hence, novel approaches are in search to overcome the unfavorable property of Li_2S cell so that the diffusion of Li^+ and electrons is more feasible. Sulfur impregnation onto the carbon nanospheres leads to achieve a higher and stable capacity of up to 1,000 Ah/kg [37]. The main problem existing to a Li–S battery is a short life span for its charging-discharging cycles and a low efficacy that can be attributed to the use of liquid electrolytes, resulting in detrimental side reactions. Lithium polysulfidophosphates (LPSP) are compounds of the general formula Li_3PS_{4+n} $(0 < n < 9)$ that are formed from the reaction of sulfur with lithium thiophosphate ($LiPS_4$), yielding eight times higher conductivity than Li_2S at the standard room temperature, 25°C [38]. The electrochemical reaction can be written as follows:

$$S_6 + 16Li \leftrightarrow 8Li_2S \tag{28}$$

6.2.5 Lithium Air (Li_2O_2)

Li_2O_2 is another new attractive technology in the area of battery research. Air is plenty available and environmentally friendly reactant to participate in any redox reaction. Moreover, the theoretical gravimetric energy density for the Li_2O_2 battery in comparison to other battery makes it favorable to be utilized in battery technology [39]. Because oxygen is not remained stored in the battery, the safety risk is its minimum that is also limiting the potential to a thermal runaway. Inside the battery in a charging-discharging cycle, air/O_2 acts as the oxidizing agent in the Li_2O_2 battery and Li as the reducing agent. The electrochemical reactions for a Li_2O_2 battery can be written as follows:

At anode:

$$2\mathrm{Li} \rightarrow 2\mathrm{Li}^+ + 2e^- \tag{29}$$

At cathode:

$$2\mathrm{Li}^+ + \mathrm{O}_2 + 2e^- \rightarrow \mathrm{Li}_2\mathrm{O}_2 \tag{30}$$

Overall reaction:

$$2\mathrm{Li} + \mathrm{O}_2 \leftrightarrow \mathrm{Li}_2\mathrm{O}_2 \tag{31}$$

7 Summary

Energy is one of the vitally critical factors which have significant contribution to our daily life. It is a fact that almost all the chemical reactions are associated with energy changes, more significant than the reaction itself. The chemical thermodynamics plays a crucial role to being able to progress in any area of energy via the chemistry involved in it. As the thermodynamics deals with heat and/or work, both are manifestations of energy. Using thermodynamics, we can directly calculate the energy change or energy efficiency, whereas the chemistry can directly provide the explanations to such changes. In the field of fuel cells and batteries, the electrochemical reactions can better be described by reaction thermodynamics. At the same time, the materials involved in the reactions as reactants/oxidants/reductants must be understood by their chemistry. All the charging-discharging properties of the battery are directly dependent upon the material chemistry of the anode and cathode; hence, it must be studied first before their application to energy storage and/or production.

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Renewable Energy as a Sustainable Alternative: A Way Forward

Pankaj Pathak

Contents

Abstract Coal, oil, and natural gas are major conventional energy sources in the world but limited in amount. However, these sources create several environmental and health impacts during energy extraction processes. Coal mining and exploration, transportation, energy/electricity generation processes cause negative environmental externalities. Notably, electricity generation from coal alone emits approximately 60% of the global CO_2, which has been projected as 36.4 $GtCO_2$ in 2016. This scenario would be more challenging for developing nations to balance the increasing economic and industrial growth along with climate change issue. Therefore, alternative energy resources are recommended for the sustainable modern society to fulfill global energy demand with minimum environmental impacts.

Keywords Biomass, Greenhouse gases, Hydropower, Renewable energy, Sustainable energy

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1 Need of Sustainable Alternative

Conventionally, coal, oil, and natural gas have remained as the major sources of energy, however, carrying severe environmental and health concerns. Firstly, coal and petroleum mining and exploration processes are itself not very eco-friendly and resulting in a wider change in demography and ecology. After the mining exploitation, their usages in the energy/electricity generation process cause negative environmental externalities. Notably, electricity generation via coal-burning power plants (including fugitive emissions from solid fuels, oil, and gas as well) is the highest emitter of greenhouse gases (GHGs) along with other gases such as CO and SO_x [1, 2]. This sector alone emits approximately 60% of the global CO_2, which has been projected as 36.4 $GtCO_2$ in 2016. Surprisingly, among all means of energy, ~25% of the global GHGs emissions significantly contributed to the electricity generation process. This scenario has come out in a more visible manner in the United Nation's report for global CO_2 emissions with respect to different sectors. The quantification of summary can be depicted from Fig. 1. It shows the contribution of different sectors (such as energy, transportation, buildings, industries, agriculture, and land use) in global emissions of GHGs for a period of recent three decades; whereby, the prime culprit of maximum CO_2 emissions is found to be the energy sector.

This situation is more complicated to the developing countries, who have a necessity to high energy generation to fulfill their demand for maintaining their industrial and economic growth. It becomes more challenging when the factor of high population density gets clubbed with the energy poverty and a large population of the lower-middle and middle-income group with energy starvation, escalating pressures on environmental impact to curb their emissions to the atmosphere [4]. The

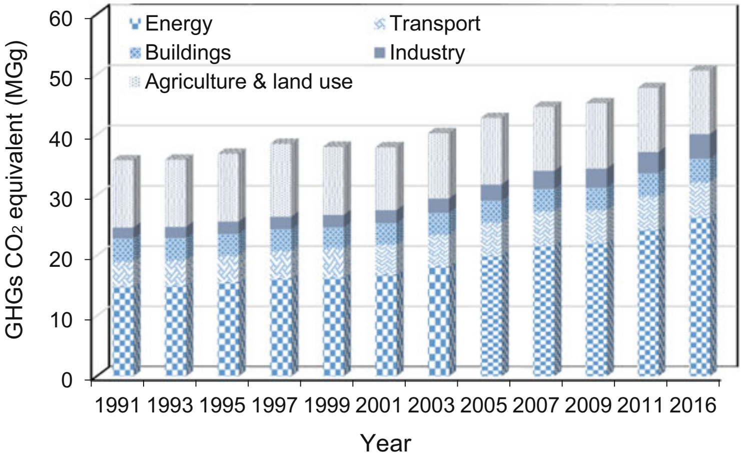

Fig. 1 The contribution of different sectors emitting the GHGs as CO_2 equivalent (adopted from [3])

developing countries are more susceptible to climate change adversity than the developed ones due to their economic and societal confinement [5]. It creates a dilemma in developing countries, because of any diversion of technological and financial resources to cope with climate change may undermine their overall growth. Making a choice or the balance between environmental concerns and economic growth is crucial to the developing countries. In contrast to the abundance of coal, oil and natural gas are not distributed widely and limited to some geographic boundaries where finite availability is estimated for the next few decades only; hence, it cannot be taken as a sustainable alternative source of energy.

In this context, the advent of renewable sectors does not only fulfill the energy demands but also shift the world toward cleaner energy alternatives with a controlled/lesser emission. A paradigm shifts toward the renewable sectors are safeguarding the limited natural resources, viz., coal and petroleum resources, and minimizing the global temperature below 1.5°C in accord to the Paris Agreement, COP21 [6]. Nevertheless, the utilization of renewable energy which would be a sustainable alternative for modern society is a debatable question among the research fraternity due to the pros and cons associated with each potential source of renewable energy as listed in Table 1.

Table 1 Advantages, disadvantages, and potential environmental impacts of each renewable energy sources (adapted with permission from [7])

Renewable source	Advantages	Disadvantages	Negative environmental impacts
Solar	Infinite supply No air/water pollution (excluding the background material production works)	May not be cost effective Back-up and storage are required Dependent on sunny days	Soil erosion Landscape change Generation of hazardous waste
Wind	Abundantly and freely available No air/water pollution (excluding the background material production works) Less expensive than solar farm	Constant and significant flow of wind is required Back-up and storage are required Significant amount of land is required	Soil erosion Landscape change Killing of birds due to collision with turbine blades
Biomass	Abundantly available Waste volume reduction after burning of biomass	Causes air pollution May not be cost effective due to high energy-intensive process	Emissions of greenhouse gases Landscape change Generation of hazardous waste
Small-scale hydroelectric	Abundantly available, clean, and safe Easily storable in reservoirs Relatively inexpensive	Dams can be built in the limited area of water flow Causes floods and landscapes in the nearby area of dams	Ecological change is possible due to controlling the flow of water Change in weather systems Change in groundwater patterns

Keeping in view, United Nations Sustainable Development Goals has emphasized to use sustainable and affordable clean energy with minimum social and environmental impacts.

2 Renewable Energy: A Way Forward

Renewable energy is a panacea to fulfill the global energy demand with minimum environmental impacts and maximum resource excavation. Sources of renewable energy such as solar, wind, small-scale hydro and biomass are freely available in our surroundings; however, the conversion of these primary sources of energy into secondary energy generation (electricity) necessitates advanced technology albeit the cost is higher to be bearable for developing and underdeveloping countries. This makes a necessity for a quick and effective energy transformation toward the alternatives and energy-mix instead of relying alone on the conventional source of high-emission fossil fuels or renewable energy. Therefore, upgradation in technology is a need of the hour to minimize the economic and environmental costs and clean energy access to all.

Keeping in view, this book emphasizes the significance of sustainable alternatives in developed and developing nations. The first chapter reported that the energy consumption is significantly varying with a different class of individuals (based on their income); higher-class individuals require more energy as compared to middle and low class, which shows the huge disparity in energy distribution. Though, the energy extraction cost can bear by higher class individuals but environmental cost-shared by the individuals of all income classes. It exhibits worrisome situation and motivating us to shift toward sustainable alternative means of energy. Further, solar and wind energy are boon for developing nations due to its available abundance resources, and hence its conversion mechanism from the primary source to secondary energy has been thoroughly discussed in the chapters “Mechanism of Photoanodes for Dye-Sensitized and Perovskites Solar Cells”, “Grid Integration of Wind Energy Conversion Systems”, and “Offshore Wind Energy: Resource Assessment”. It is concluded that dye-sensitized solar cell (DSSC) and organic photovoltaic cells (PSC) are having higher energy efficiency as compared to the other solar cells; however, still much research is needed to make it more durable and sustainable technologies. Further, onshore and offshore wind energy conversion systems came in limelight due to the ability to harness wind potential and generation of high-power green energy. Subsequently, hydropower resource is discussed in chapter “Hydropower: A Renewable Energy Resource for Sustainability in Terms of Climatic Change and Environmental Protection”, which is economic and has less impact on the environment. Chapters “Biomass Energy Sources and Conversion Technologies for Production of Biofuel”, “Renewable Energy from Woody Biomass of Poplar and Willow SRC Coupled to Biochar Production”, “Ligninolysis Potential of Ligninolytic Enzymes: A Green and Sustainable Approach to Bio-Transform Lignocellulosic Biomass into High-Value Entities”, and “Waste-to-Energy: Suitable

Approaches for Developing Countries" discussed the different mechanisms that extract energy from biomass and waste matters. Manufacturing of biofuels and biochar shows significant technological upgradation in the energy sectors. Further, the potential of waste materials is shown to utilize it as energy resources, highlighting the lignocellulosic biomass and solid waste. Further assessment was done in chapters "Biomass-Derived Triglyceride: A Source of Renewable Aviation Fuel and Biodiesel", "Microbial Electrochemical Systems: Promising Alternatives for Energy Sustainability", "Generation of Osmotic Power from Membrane Technology", and "Environmental Impact and Challenges Associated with Bio-Based Energy" to extract sustainable alternative energy/fuels from waste resources and its associated impacts. Chapter "Role of Chemistry in Alternative Energy: The Thermodynamics and Electrochemical Approach" shows the chemistry behind the green and sustainable energy.

In line with this, it is concluded that the renewable/alternative resources precedent to attain the energy need where energy mix or hybrid technology is highly recommended.

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