Chapter 1 Biologically Renewable Resources of Energy: Potentials, Progress and Barriers

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1.1 Introduction

1.1.1 Energy

Energy revolves around various aspects of life and plays a major role in the survival of all living organisms. It may be defined as the capacity to do work and its unit of measurement is joule. Several types of energy exist, and these include chemical, mechanical, kinetic, potential and electrical, among others. Energy sources may be categorized as renewable and non-renewable (Shockey et al. [2010\)](#page-20-0). Non-renewable energy resources include petroleum-based fossil fuels that are diminishing at an alarming rate as a result of the increased global energy demand. In the present time, global energy requirements are primarily met by non-renewable fossil fuels such as coal, petroleum, bitumen, natural gas and tar sand (Das and Veziroglu [2001\)](#page-18-0). Dependence on conventional fossil fuels such as petroleum-based reserves has led to its depletion combined with environmental pollution (Levin et al. [2004](#page-19-0)). Thus, renewable energy production has occupied global precedence and has made the search for an efficient and sustainable energy system an imperative for sustainable socio-economic development (Barbir et al. [1990](#page-17-0); Demirbas [2009\)](#page-18-1). Renewable energy resources include solar, wind, hydro- and geothermal power (Shockey et al.

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[2010\)](#page-20-0) in addition to microbial-produced biofuels such as bioethanol, biogas and biodiesel (Naik et al. [2010\)](#page-20-1).

1.1.2 Energy Resources and Sustainable Development

Sustainable development can be defined as living, producing and consuming in a manner that meet the needs of the present without compromising the ability of the future generations to meet their own needs. Energy needs are widely regarded as a major sustainable development challenge, with close links to the climate change and global poverty agenda. It was at the Stockholm UN conference in 1972 where the relationship between the increasing energy consumption and its relation to environmental degradation was first addressed (Petford [2004\)](#page-20-2). Later in May 2002, UN secretary-general Kofi Annan identified five key areas as global critical challenges of the twenty-first century. The areas were energy, water and sanitation, health, agriculture and biodiversity. With climate change as a challenging issue to be faced, the world now focusses to tap clean and renewable energy to achieve sustainable development.

1.1.3 Current Scenario of World's Energy Usage

It will be apt to mention that the world's major energy requirement is met by fossil fuels till date. The longevity of the resources available to meet the world's energy demands is yet to be understood. The world's population is ever increasing with it presently being about 7.5 billion and is projected to reach about 9.2 billion by 2050 as per 2008 estimate [\(www.fao.org/docrep/014/i2280e/i2280e.pdf](http://www.fao.org/docrep/014/i2280e/i2280e.pdf)). With the increase in population, the energy demand is expected to increase regardless of the countries. In the International Energy Outlook (IEO) 2000, much of the growth in worldwide energy use is projected for the developing world. In particular, energy demand in developing Asia and Central and South America is projected to more than double between 1997 and 2020 ([http://www.eia.doe.Gov/oiaf/ieo/tbla1_](http://www.eia.doe.gov/oiaf/ieo/tbla1_a8.html) [a8.html](http://www.eia.doe.gov/oiaf/ieo/tbla1_a8.html)). Based on the world's energy demand, coal was estimated to last till 2080. Crude oil has been estimated to be completely exhausted by the year 2060, whereas natural gas is estimated to be exhausted by the 2050s. ([www.ecotricity.co.uk\)](http://www.ecotricity.co.uk). As per Beyond Petroleum (BP) statistical review in [2003,](#page-17-1) the proven reserves include 1000 million barrels of oil by 2001, of which 65% is reported to be with the Middle East, 165 trillion m³ of natural gas and about 800 billion tons of coal. Considering both the availability and demand, it is clear that these reserves will not last long enough to support the global future demand. In addition to its exhaustion, fossil fuels have been shown to be detrimental to the environment which has further prompted the search for alternative resources.

Fig. 1.1 Regional oil reserves to production ratio for 2016. (BP [2017\)](#page-17-2)

Oil reserves have shown to be the most exploited energy source worldwide. The annual Beyond Petroleum (BP) statistical review of world energy 2017 reported that the total proven oil reserves at the end of 2016 increased by 0.9% (BP [2017](#page-17-2)). The Middle East is the major oil supplier contributing 47.7% of the total world oil reserves. The global oil reserve-to-production ratio (Fig. [1.1](#page-2-0)) shows that the Middle East oil reserves, according to the current production rate, are sufficient to meet nearly 50.6 years of global production (BP [2017](#page-17-2)).

The *Hubbert peak theory* says that for any given geographical area, from an individual oil-producing region to the planet as a whole, the rate of petroleum production tends to follow a bell-shaped curve (Hubbert [1956](#page-19-1)). It is one of the primary theories on peak oil. The theory is based on the observation that the amount of oil under the ground in any region is finite; therefore, the rate of discovery which initially increases quickly must reach a maximum and decline. In the USA, oil extraction followed the discovery curve after a time lag of 32–35 years (Fig. [1.2\)](#page-3-0). The theory is named after American geophysicist M. King Hubbert, who created a method of modelling the production curve given an assumed ultimate recovery volume.

Human population have dwindled the natural resources of the world, be it the fossil fuels, minerals, metals, coral reefs, etc. However, as non-renewable resources are finite, different estimations were made regarding the time period these resources will last. It is found to vary between 50 and 500 years (Harris [2014](#page-18-2)). But still, certain productive ecosystems were not fully utilized by the mankind which includes the biomass.

Fig. 1.2 Comparison of actual oil production rate data with the prediction made by Hubbert in [1956](#page-19-1)

1.2 Renewable Energy Resources

Renewable energy resources include wind, tidal, solar, geothermal and biomass. Though nuclear energy is categorized as renewable, it has its own demerits of disposal of the nuclear wastes and also with respect to the problems associated with the decommissioning of such nuclear power plants. Hence for the sustainability to be ensured, renewable energy resources are to be depended upon by both the current and future generations to meet their energy needs. The National Environmental Policy Act of 1969 declared the sustainability as a national policy. It is aimed "to create and maintain conditions under which humans and nature can exist in productive harmony, that permit fulfilling the social, economic and other requirements of not only the present but also the future generations". This aspect necessitates the usage of renewable resources which are nonconventional till date.

1.2.1 Potential of Biological Energy Resources

Following an oil shock experienced in the 1970s which resulted in a rise in the prices of petroleum, the attention turned towards biomass (Klass [1998\)](#page-19-2). Biomass is a renewable energy resource, is carbon neutral and is found to have a good scope for future generation [\(http://biomasspower.gov.in/\)](http://biomasspower.gov.in/). Such biomass is the storehouse of energy as the photosynthetic fixation of $CO₂$ occurs in it resulting in the starches, lignocelluloses, etc. Such biomass has the possibility of being converted into fuels such as ethanol, methanol and hydrogen. Such biological origin renewable energy

| Biomass type | Energy generation potential | Reference |
|--|---|---|
| Lignocellulose | Abundant biomass resource suitable for direct combustion for generation of heat, power Gasification and pyrolysis for energy conversion Fermentation for ethanol production but further improvements are needed for energy conversion efficiency and economic feasibility | Wang et al. (2013) , Paz (2013) Bahng et al. (2009) Alvira et al. (2010) , Viikari et al. (2012) |
| Saccharose-rich biomass, e.g. sugarcane, sugar beet, cereal grain, potatoes and cassava | On subjecting to fermentation, ethanol can be obtained | Alvira et al. (2010) Balat et al. (2008) |
| Algal biomass | A promising feedstock for fermentation, large-scale production under development | Wei et al. (2013) |
| Vegetable oil | Could be used directly or mixed with alcohol through transesterification resulting in biodiesel | Daroch et al. (2013) |
| High moisture or wet biomass, e.g. sludge of industrial and domestic wastewater treatment, livestock manure and food residues | Suitable for biogas production which could be used in gas turbines | Tauseef et al. (2013) Weiland (2010) |

Table 1.1 Energy generation potential of different biomass

resources could be regarded as the promising sources of energy for the present and future.

Biomass refers to the wood from trees, bushes, charcoal, crop residues and animal wastes. However, it is estimated that it could provide about 7–15% of the global energy requirement (Woodward et al. [2000](#page-21-0)). It has the advantage of being grown at any place and could be utilized to meet the energy demand. Further, it could be stored and used easily for a longer time interval. The usage could be matched with the rate of growth to again ensure sustainability.

Such biomass is classified according to their origin, namely, agricultural and forest residues, residues form agro-industries and municipal waste (Paz [2013\)](#page-20-3). According to the composition of the biomass, they are classified as follows (Table [1.1](#page-4-0)):

Biomass is further less site-specific than other renewable energy resources such as wind or tidal power, as some type of vegetation can be grown anywhere. From such biomass, combustion is the immediate process of energy extraction, but other processes such as fermentation, anaerobic digestion and gasification are also possible. It is important to understand that the rate of growth of such biomass must not be exceeded by the rate of harvest. However, one major consideration is the efficiency of plant leaves which could convert only about 1% of the incident solar radiation into energy (Petford [2004\)](#page-20-2).

1.2.2 Potential and Progress of Biomass Utilization as Biofuel

The total primary production occurring on planet earth meets the demands of the human population. The demand is met through the agriculture, fisheries, forestry and other similar activities. The US Energy Information Administration's latest IEO (International Energy Outlook) 2017 projects that the world energy consumption would grow by about 28% between 2015 and 2040. Now the attention is focussed on the reduction of greenhouse gas emissions in accordance with the Kyoto Protocol. Thus, renewable biological energy resources have gained significant interest. Renewable biological energy resource, namely, biomass, includes the wastes and residues of plants and animals. It is organic, is carbon based, and undergoes combustion to release heat. Heat may be used to generate work and electricity. There are three different ways to utilize biomass: as mentioned above it can be burned to produce electricity and heat, it could be changed to gas-like fuels such as hydrogen, carbon monoxide and methane and it could be converted into liquid fuels also called biofuels such as ethanol and methanol (Demirdas [2010\)](#page-18-4).

The heat energy available after combustion equivalent to the enthalpy or net energy density ranges from 8 MJ/kg (undried green wood) and 1.5 MJ/kg (dry wood) to 40 MJ/kg (fats and oils) and 56 MJ/kg (Methane) (Twidell and Tony Weir [2006\)](#page-21-6).

Lignocellulosic biomass refers to plant material which is predominantly composed of carbohydrate polymers such as cellulose and hemicellulose bound by lignin. Cellulose is a polymer consisting of unbranched linear glucose, whereas hemicellulose is a heterogeneous polymer composed of hexose and pentose sugars (Binod and Pandey [2016\)](#page-17-6). The cellulose, hemicellulose and lignin layers usually make up approximately 30–50%, 20–40% and 10–30%, respectively, depending on the type of biomass (Sindhu et al. [2016\)](#page-20-4). Lignocellulosic biomass accounts for approximately 50% of the global biomass, with an annual production of 200 billion tons (Kabir et al. [2015](#page-19-3)). Biomass is a major contributor to both the agricultural and forestry industry and is considered a promising feedstock for biofuel production given its low cost and abundance, and it does not compete with food security (Cai et al. [2017\)](#page-18-5). The agricultural industry generates millions of tons of lignocellulosic waste which are dumped in landfill sites or burnt in the field postharvest (Moodley and Gueguim Kana [2017a\)](#page-19-4). The conventional use of lignocellulosic biomass has been mostly burning for energy, for instance, sugar-processing plants that use the sugarcane bagasse residue to power boilers (Smithers [2014\)](#page-20-5). However, this process has severe negative environmental implications. In recent times, there has been a shift towards using biomass for the production of biofuels such as hydrogen, ethanol and biogas (Brethauer and Studer [2015](#page-17-7)) as shown in Table [1.2](#page-6-0).

Prior to biofuel production, lignocellulosic biomass needs to undergo biochemical conversion to release simple sugars such as glucose and xylose either via enhanced enzymatic or chemical hydrolysis (Taherzadeh and Karimi [2008\)](#page-20-6). Various pretreatment strategies exist that can achieve efficient biochemical conversion by degrading the recalcitrant lignin layer thereby allowing either microorganisms or

| Biomass | Biofuel | Yield | Reference |
|------------------|-------------------|---------------------|---------------------------------|
| Sugarcane leaves | Biohydrogen | 248 ml/g sugar | Moodley and Gueguim kana (2015) |
| Sorghum leaves | Biohydrogen | 213.14 ml/g sugar | Rorke and Gueguim kana (2016) |
| Sorghum leaves | Bioethanol | 17.15 g/L | Rorke and Gueguim kana (2017) |
| Seaweed | Bioethanol | 14.89 g/L | Adams et al. (2011) |
| Corn cobs | Bioethanol | 24 g/L | Li et al. (2016) |
| Duckweed | Biogas | 11,620 ml | Yadav et al. (2017) |
| Pine | Biogas | 17 L/kg | Brown et al. (2012) |

Table 1.2 Biofuels produced from lignocellulosic biomass

enzymes access to the cellulose and hemicellulose fractions (Moodley and Gueguim Kana [2017b\)](#page-19-5). These pretreatments are detailed in Table [1.3](#page-7-0). Currently, acid and alkali pretreatment are being explored at a pilot scale. Kapoor et al. [\(2017](#page-19-6)) examined pilot-scale dilute acid pretreatment of rice straw, whereas Skiba et al. [\(2017](#page-20-7)) examined pilot-scale alkali pretreatment of oat hulls. New pretreatment technologies have significantly enhanced enzymatic saccharification and sugar recovery from lignocellulosic biomass. Inorganic salt has emerged as an effective and lowcost chemical for biomass pretreatment (Sewsynker-Sukai and Gueguim Kana [2017\)](#page-20-8). A previous report by Sewsynker-Sukai and Gueguim Kana ([2017\)](#page-20-8) optimized a sequential alkalic and metal salt pretreatment using corn cobs and gave a high reducing sugar yield of 1.10 g/g with 14.02% Na₃PO₄.12H₂O, 3.65% ZnCl₂ and 5% solid loading. The optimized pretreatment gave a tenfold increase in sugar yield compared to previous studies on corn cobs (Sewsynker and Gueguim Kana [2017\)](#page-20-8). Likewise, Moodley and Gueguim Kana [\(2017c\)](#page-19-7) reported on a sequential microwaveassisted salt-alkali pretreatment of sugarcane leaves that yielded 1.17 g/g reducing sugar using 1.67 M ZnCl₂ and 1.52 M NaOH at 400 W for 10 min. This pretreatment technique showed a 62% sugar yield improvement compared to previous reports (Moodley and Gueguim Kana [2017c](#page-19-7)).

1.2.3 Production of Ethanol from Biomass

Present-day energy security coupled with environmental concerns has skewed research towards alternative energy sources that are renewable and sustainable, lowcost and environmentally friendly (Zabed et al. [2016\)](#page-21-7). Ethanol has gained significant interest as a potential replacement for fossil fuel-derived sources (Aguilar-Reynosa et al. [2017](#page-17-8)). This is largely due to its several advantages over fossil fuels such as gasoline which include its renewable and sustainable nature, ease of storage, higher oxygen content and higher octane number, among others (Zabed et al. 2016). In the present time, countries such as the United States of America (USA), Brazil, China, Canada and several European Union (EU) member states have publicized their commitment to bioethanol development programmes in an attempt to reduce the reliance on conventional fossil fuels. The annual global

| Pretreatment | Mode of action | Advantage (s) | Disadvantage (s) | Reference |
|-----------------------|---|--|---|---|
| Steam explosion | Mechanical shearing and defibrillation of fibres Amorphous cellulose potentially depolymerized | Cost effective No toxic chemicals required | Partial degradation of lignocellulosic matrix Produces toxic inhibitor compounds | Wang et al. (2015) |
| Irradiation | Cellulose is degraded into fragile fibres and oligosaccharides | Improves enzymatic hydrolysis | High cost Challenges with scale-up | Akhtar et al. (2015) |
| Pyrolysis | High temperature causes cellulose to decompose | Less volatile compounds are produced | Process is slow | Akhtar et al. (2015) |
| Alkaline | Cleaves linkages in lignin and glycosidic bonds of polysaccharides | Requires low temperature and pressure Low inhibitors generated Produces highly digestible substrate | High cost Generation of irrecoverable salts | Sindhu et al. (2015) |
| Acid | Hydrolyses hemicellulose to xylose Modifies lignin structure | Simple method. Thermal energy not required | High cost Produces toxic inhibitor compounds | Jung and Kim (2015) |
| Microwave chemical | Dipolar polarization achieves heating Rapid oscillation causes molecules to vibrate | Uniform heating Improves pretreatment speed Decreased energy input | Dependent on properties of the material Formation of hot spots Challenges with scale-up | Xu(2015) |
| Inorganic salt | Act as Lewis acids Dissociate into complex ions and rupture glycosidic linkages | Low cost Low toxicity | Partial degradation of lignocellulosic matrix | Sewsykner- Sukai and Gueguim kana (2017) |

Table 1.3 Commonly employed pretreatment technologies

bioethanol production has stealthily increased over the last 10 years and is depicted in Fig. [1.3.](#page-8-0) The USA contributed to the highest ethanol production and has been projected to be more than 50% of the total global ethanol produced in 2016 (RFA [2017\)](#page-20-11). More specifically, second-generation lignocellulosic bioethanol production has received much attention as a suitable process for bioethanol production without raising food security concerns (Aguilar-Reynosa et al. [2017](#page-17-8); Zabed et al. [2016](#page-21-7)). The annual global production of lignocellulosic biomass has been estimated at 200 billion t/year, of which nearly 8–20 billion t can be used for biofuel production (Saini

Fig. 1.3 Global ethanol production by country in the last 10 years. (RFA [2016](#page-20-15))

et al. [2014\)](#page-20-13). The majority of agricultural waste residues are derived from corn, sugarcane, rice and wheat. Corn stover has shown to be one of the most promising agro-residues for lignocellulosic bioethanol production and consists of stalks, leaves, cobs and husks. The global average annual production rate of corn stover is estimated at 4 t/acre (Kim and Dale. [2004\)](#page-19-11). Another major agro-residue for bioethanol production is sugarcane bagasse which consists of stalks, leaves and tops and is the leftover waste from sugarcane processing at approximately 317–380 million t/ year (Sánchez [2009](#page-20-14)). Other biomasses that show bioethanol potential include wheat straw (1–3 t/acre annually) and rice straw (731 million t/year) (Saini et al. [2014\)](#page-20-13). Both rice and wheat straws are majorly produced in Asian countries, whereas corn stover and sugarcane bagasse are generated in large quantities in North and South America, respectively. Bioconversion of these agro-residues to ethanol involves three crucial steps: biomass pretreatment, enzymatic hydrolysis of sugar polymers to fermentable sugar monomers and fermentation of sugar monomers to bioethanol (Zhao et al. [2015\)](#page-21-11). The biomass pretreatment step is necessary for the improvement of enzymatic accessibility to the structural matrix. A previous report on corn stover, corn cobs and wheat straw gave yields of 450, 510 and 490 L/t, respectively (Kreith and Krumdieck [2013](#page-19-12)). Presently, corn, wheat, rice and sugarcane lignocellulosic wastes display significant potential feedstocks for bioethanol production and require further exploration to maximize several key technological issues. These include cost-effective biomass pretreatment regimes that result in high sugar yields, efficient utilization of feedstock and fermentation processes that result in high ethanol yields with shorter fermentation times (Aguilar-Reynosa et al. [2017](#page-17-8); Zhao et al. [2015;](#page-21-11) www. 〈http://ethanolrfa.org/resources/industry/statistics/#1454099788442-e 48b2782-ea53〉; [2016](#page-21-12).

1.2.4 Production of Biodiesel from Biomass

The biodiesel is scientifically defined as alkyl esters of especially long-chain fatty acids. Such acids are derived from either animal fats or vegetable oils. This biodiesel has higher energy density, facilitates favourable combustion and has an enhanced lubricating property. Biomass is an energy resource which could facilitate the production of such biodiesel. Various reports explain the possibility of utilizing agricultural residues such as tea waste, bagasse of sugarcane and hazelnut, cotton waste, corn cobs and residues of olive seeds for the production of different valuable products including biofuels (Conesa et al. [2009;](#page-18-6) Blanco et al. [2002;](#page-17-12) Demiral and Sensoz [2008\)](#page-18-7).

1.2.4.1 Production of Biodiesel from Microalgae

Microalgae are a large group of unicellular autotrophic microorganisms that carry out photosynthesis. These microorganisms can convert solar energy into chemical energy with a greater efficiency than plants due to their unicellular structure (Harun et al. [2010](#page-18-8)). This group of microorganisms has received significant attention as a promising biodiesel feedstock due to their widespread availability, ability to grow on nonarable land and being cultivable on wastewater or saltwater (Brennan and Owende [2010](#page-17-13); Mata et al. [2010\)](#page-19-13). Microalgae have higher growth rates and oil yields compared to crop plants with a productivity unit per area of $13,69$ l/m² oil yield which is higher than the 0,6 $1/m2$ oil yield obtained from feedstocks such as soybean, coconut and palm oil (Chisti [2007\)](#page-18-9). Microalgae are also a source of different value-added products such as carotenoids, β-carotene and chlorophyll which all have uses in food and pharmaceutical industries thereby increasing the economic potential of microalgal bio-refineries (Mata et al. [2010;](#page-19-13) Harun et al. [2010](#page-18-8)).

As seen in Table [1.4,](#page-10-0) microalgae can produce much higher amounts of biodiesel as compared to plant crops. Under optimal growth conditions, microalgae are capable of producing and accumulating hydrocarbons of between 30% and 70% of their dry weight (Kong et al. [2007\)](#page-19-14); most commonly reported oil yields are between 20% and 50% of the biomass dry weight (Spolaore et al. [2006](#page-20-16)). Parameters that are important for microalgal cultivation include light, $CO₂$, temperature and pH (Faried et al. [2017\)](#page-18-10).

Microalgal fatty acids can be divided in two groups based on the polarity of the molecular headgroup: polar and neutral lipids. Polar fatty acids consist of phospholipids and glycolipids. The neutral fatty acids consist of free fatty acids and acylglycerols, which are of interest in terms of biodiesel production (Cuellar-Bermudez et al. [2015](#page-18-11)). Acylglycerols are fatty acid esters that have been bonded onto a glycerol backbone and according to the number of fatty acid chains can be classified as triacylglycerols, diacylglycerols or monoacylglycerols (Halim et al. [2011\)](#page-18-12). The content and lipid profile of microalgae are species dependent but can also be affected by culture conditions such as light intensity periods, nitrogen depletion, salinity

| | Oil yield | Land area needed | |
|-------------------------|-----------|------------------|--------------------------------------|
| Crop | (L/ha) | $(M ha)^a$ | Percent of existing US cropping area |
| Corn | 172 | 1540 | 846 |
| Soybean | 446 | 594 | 326 |
| Canola | 1190 | 223 | 122 |
| Jatropha | 1892 | 140 | 77 |
| Coconut | 2689 | 99 | 54 |
| Oil palm | 5950 | 45 | 24 |
| Microalgaeb | 136,900 | $\overline{2}$ | 1,1 |
| Microalgae ^c | 58,700 | 4,5 | 2.5 |

Table 1.4 Comparison of some sources of biodiesel

Chisti [\(2007](#page-18-9))

a For meeting 50% of all transport fuel needs of the USA b 70% oil (by wt) in biomass

c 30% oil (by wt) in biomass

stress, temperature change and pH (Richmond. [2008;](#page-20-17) Guschina & Harwood. [2006\)](#page-18-13). Nitrogen limitation is a commonly used strategy in the increase of lipid and triacylglycerols in microalgae to produce biodiesel (Cuellar-Bermudez et al. [2015](#page-18-11); Xin et al. [2010\)](#page-21-13).

The ASTM definition of biodiesel is a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils and animal fats (Hoekman et al. [2012\)](#page-18-14). It can serve as alternative to diesel fuel that could be used in diesel engines, only if its physical and chemical properties conform to the international standard specification. The relevant standard in the USA is the ASTM Biodiesel Standard D 6571 (Knothe [2006](#page-19-15)). The European Union uses separate standards for biodiesel used in vehicles (standard EN 14214) and biodiesel used as heating oil (standard EN 14213) (Knothe [2006](#page-19-15)). In South Africa, the SANS 342:2016 is used to specify automotive diesel fuel blended with 5% of biodiesel.

Microalgae are rich in polyunsaturated fatty acids with four or more double bonds; for example, eicosapentaenoic acid which has five double bonds and docosahexaenoic acid which has six double bonds occur very commonly in microalgal oils; unfortunately such fatty acids and fatty acid methyl esters (FAMEs) are susceptible to oxidation during storage which reduces their acceptability for use as biodiesel (Chisti [2007\)](#page-18-9). Triglycerides consist of three chains of fatty acids joined to a glycerol backbone (Halim et al. [2011](#page-18-12)); the process of transesterification replaces the glycerol molecule with methanol forming fatty acid methyl esters (Harun et al. [2010\)](#page-18-8). The fatty acid profiles of microalgae are influenced by specific growth conditions such as nutrient levels, temperatures and light intensities; this can make it difficult to define a compositional profile for algal biodiesel (Hoekman et al. [2012\)](#page-18-14). Ashokkumar et al. ([2014\)](#page-17-14) showed that the major fatty acids found in *Botryococcus braunii* were methyl palmitate and methyl oleate and the acid number of 0.49 mg KOH/g and a cetane number of 55.4 were both within the ASTM standards, whereas a study done by De Alva et al. [\(2013](#page-18-15)) using *Scenedesmus acutus* showed that the biodiesel produced from this microalgal species did not meet ASTM standards and

Fig. 1.4 Aerial view of an open raceway pond. (Adapted from: Brennan and Owende [2010](#page-17-13))

the dominant fatty acids being palmitic acid, hexadecadienoic acid and linoleic acid were over the ASTM limit and the 1.08 mg KOH/g acid value did not comply with both ASTM D6751 and EN14214 standards (de Alva et al. [2013\)](#page-18-15), highlighting the different fatty acid compositions found in different microalgal species.

The production of microalgal biomass is generally more expensive than crop cultivation since microalgal cultivation requires light, carbon dioxide, water and inorganic salts. Therefore, to minimize costs, cultivation should rely solely on freely available sunlight (Chisti [2007](#page-18-9)). Cultivation of algae is most commonly carried out in raceway ponds or photo bioreactors.

Raceway ponds are open circular ponds and can be in the form of natural waters such as lakes and lagoons or artificial ponds and containers. The configuration of raceway ponds is a closed loop oval recirculation channel that is typically 0.2–0.5 m deep, the depth is limited due to the penetration limit of light and an increase in depth would result in a decrease in the efficiency of the pond (Brennan and Owende [2010\)](#page-17-13). A paddlewheel provides mixing and circulation in the pond, and cooling is achieved only by evaporation which often results in significant water losses; also there is no temperature control as temperature fluctuates seasonally (Chisti [2007](#page-18-9)) (Fig. [1.4](#page-11-0)). Carbon dioxide can be sparged at the bottom of the pond as a carbon source for autotrophic cultivation as the atmosphere only contains about 0.03– 0.06% CO₂; therefore, it is expected that the mass transfer limitation could slow down the growth of the microalgae (Mata et al. [2010\)](#page-19-13). Ashokkumar et al. [\(2014](#page-17-14)) used a 25m² open raceway pond in semi-continuous mode for the cultivation of *B. braunii*-TN101 resulting in a biomass productivity of 33.8 g m⁻³ day⁻¹ (Ashokkumar et al. [2014\)](#page-17-14). Raceway ponds are less expensive cultivation method but

Fig. 1.5 Photo bioreactor schematic with horizontal tubular solar array. (Adapted from: Chisti [2007\)](#page-18-9)

have several limitations such as high risks of contamination that cannot be completely prevented especially in open outdoor raceway ponds, and this can greatly affect the productivity of the algae. Poor mixing in the pond can also affect biomass concentration (Chisti [2007\)](#page-18-9). Raceway ponds are currently used in research and in industry in the form of shallow big ponds, circular pond tanks and closed ponds; these are usually operated in continuous mode to prevent sedimentation (Harun et al. [2010\)](#page-18-8).

The algal culture is introduced into the pond at a point after the paddlewheels and follows the shape of the pond with mechanical aeration from $CO₂$ spargers; culture is harvested before the paddlewheel point.

There are several types of photo bioreactors such as airlift, tubular, flat plate and vertical column photo bioreactors. The main advantage of photo bioreactors is that it allows for the maintenance of optimum growth conditions allowing for consistency in biomass and lipid productivity (Lam and Lee [2012](#page-19-16)). Sunlight or artificial light is captured in an array of transparent tubes that are made of plastic or glass, less than 0.1 m in diameter (Chisti [2007\)](#page-18-9). These tubular arrays can be aligned horizontally, vertically, inclined or as a helix (Brennan and Owende [2010](#page-17-13)) (Fig. [1.5\)](#page-12-0). The tubing configurations can influence a number of parameters in energy usage; horizontal tubing is more scalable but requires large areas of land (Halim et al. [2011\)](#page-18-12). A degassing column functions in circulating the culture medium to the tubes and back (Chisti [2007](#page-18-9)). Zhu et al. ([2010\)](#page-21-14) cultivated *Chlorella zofingiensis* on piggery wastewater in tubular bubble column photo bioreactor resulting in a net biomass productivity of 1.314 g l⁻¹ day⁻¹. *Scenedesmus acutus* was cultivated in a tubular photo bioreactor with six vertical cylinders housed in a greenhouse illuminated by solar light. A biomass of 113.7 g dry weight was obtained from 123.1 l of wastewater (de Alva et al. [2013\)](#page-18-15). Feng et al. ([2011\)](#page-18-16) used four 2.2 L column aeration photo bioreactors for the cultivation of *Chlorella vulgaris* in artificial wastewater resulting in a cell concentration of 0.28 g/l (Feng et al. [2011](#page-18-16)).

Microalgal broth is circulated from the degassing column into the solar array of horizontal tubes and back to the degassing column.

1.2.4.2 Current Progress in Biodiesel Production

The most pressing and urgent need for biodiesel production is high lipid accumulation in microalgal strains. Naturally, microalgae produce different amounts of proteins and lipids, and these amounts vary strain to strain, but physiological stress has been used as a technique for driving metabolic fluxes towards biosynthesis of the target products.

Nitrogen limitation/deficiency has been found to be the most efficient stimulant for high lipid production in several different microalgal species (Mallick et al. [2016\)](#page-19-17). A lipid content increase of 33% dry cell weight (dcw) in *Choricystis minor* was achieved under simultaneous nitrate and phosphate deficiencies (Sobczuk and Chisti [2010](#page-20-18)). Mallick et al. ([2016\)](#page-19-17) observed an increase in lipid content from 8% to 57% (dcw) under simultaneous nitrate, phosphate and iron limitations in the microalgae *Chlorella vulgaris*. A high light intensity together with nitrogen-depleted conditions has also been found to increase lipid contents to 54% (dcw) in *Nannochloropsis oceanica* IMET1 (Xiao et al. [2015](#page-21-15)). Nitrogen limitations can also be applied to municipal wastewater mediums; Robles-Heredia et al. ([2015\)](#page-20-19) achieved a 63% (dcw) lipid content in *Chlorella vulgaris* (Robles-Heredia et al. [2015](#page-20-19)).

Other methods that may be used to increase the accumulation of lipids in algae include metabolic engineering. In order to achieve optimal metabolic engineering for optimal lipid production, an in-depth knowledge and understanding of the microalgal lipid biosynthesis is required. This has not been extensively examined till this date (Mallick et al. [2016\)](#page-19-17). Mass cultivation of microalgae in raceway ponds or enclosed photo bioreactors is another technique to increase the feasibility of microalgal biodiesel by producing algae biomass at a large scale for various other products including biodiesel (Mallick et al. [2016\)](#page-19-17).

The cultivation of microalgae at a laboratory scale differs when compared to common cultivation methods at large scale. This poses a problem with scale-up studies concerning microalgae production. A miniature parallel raceway pond was developed in our laboratory to bridge the gap between laboratory-scale and commercial-scale production. The similar cultivation methods will be similar in the important configurational structures and therefore allow for easy translation of laboratory results to commercial results.

1.2.4.3 Challenges with the Commercialization of Biodiesel

The cost of microalgal biodiesel production at a commercial scale is one of the major drawbacks to the commercialization of this product. Factors that contribute to these costs are harvesting, drying and oil extraction and transesterification.

Harvesting

The solid-liquid separation is a critical step in the production of microalgal biodiesel. Though, it is most commonly achieved by centrifugation, this is an extremely cost-intensive step. Research has shifted to finding less energy and cost-intensive methods to separate microalgae from their growth liquid. The use of chemical flocculants such as FeCl₃ and AlCl₃ increases the speed of the sedimentation process but is not environmentally friendly; therefore, less toxic and cheaper flocculants need to be investigated (Mallick et al. [2016\)](#page-19-17). In a study carried out by Knuckey et al. ([2006\)](#page-19-18), chitosan was found to be an excellent flocculant for freshwater microalgae such as *Chlorella* sp. and the marine alga *Isochrysis galbana*. Electro-coagulationflocculation (ECF) is an effective method for microalgal flocculation resulting in faster flocculation at higher current densities; when using an aluminium node, the ECF method is effective at laboratory scale, but at large scale the use of much more power due to the higher current densities required is not feasible (Vandamme et al. [2011\)](#page-21-16). Magnetic separation is a simple, easy, low energy consuming and low-cost separation technique that can be applied to separation of microalgae from growth medium (Yavuz et al. [2009](#page-21-17)). The separation is based on the movement of magnetically tagged particles in response to a magnetic field (Yavuz et al. [2009;](#page-21-17) Borlido et al. [2013\)](#page-17-15). Fe3O4 particles have been successful in the separation of *Botryococcus braunii*, *Chlorella ellipsoidea* and *Nannochloropsis maritima* (Hu et al. [2013](#page-18-17); Xu et al. [2011](#page-21-18)). Iron oxides are preferred due to their biocompatibility, strong paramagnetic behaviour, low toxicity and easy synthesis (Reddy and Lee [2013](#page-20-20)).

Drying

The drying of algal cells after harvesting is necessary for the storage of the feedstock as well as for downstream processing. The drying step can account for up to 30% of the total production costs of algal fuel therefore making this a big hurdle in the commercialization of algal biofuel (Grima et al. [2003](#page-18-18)). Generally, heat is used to dry algal biomass, but due to the high moisture content of microalgae, more heat is required to dry larger quantities of biomass relating to higher energy costs, and the high moisture content of microalgae makes sun drying very low in efficiency. Several artificial drying methods have been used in food industries such as drum, freeze, spray, oven and vacuum drying to name a few (Mallick et al. [2016](#page-19-17)). Solar drying is the most feasible drying method that can be employed at large scale but poses problems relating to large areas of land required for the drying of large amounts of biomass. There is a pressing need for the development of solar dryers that can overcome the issues of feasibility at a commercial scale.

1.2.5 Production of Biogas from Biomass

Currently, approximately 80% of the world's energy is supplied from fossil fuels which will eventually become exhausted, thus leading to rising fuel prices (Zabed et al. [2016](#page-21-7)). The combustion of these finite fuel sources also contributes to the emission of greenhouse gases (GHGs) which have negative effects on the environment (Taherzadeh and Karimi [2008](#page-20-6)). For this reason, renewable and sustainable sources of energy are being investigated. Biogas through anaerobic digestion has been identified as a biofuel to meet global demand; thus, efforts are being channelled towards developing technologies to enable the scale-up of biogas production (Kabir et al. [2015\)](#page-19-3). Anaerobic digestion allows for the significant reduction of waste and can generate bio-fertilizer or soil conditioner from undigested material (Lettinga [2005\)](#page-19-19).

Biogas is generated during the multistep anaerobic digestion process which involves various diverse groups of microorganisms. In the first stage, hydrolytic bacteria degrade insoluble complex molecules such as carbohydrates, proteins and fats into simpler molecules such as sugars, fatty acids and amino acids. This is followed by acidogenesis where fermentative bacteria convert sugars and other compounds into acids, alcohols, carbon dioxide, hydrogen and ammonia. The third stage involves hydrogen-producing microorganisms synergistically converting volatile fatty acids to acetate. The final stage involves methanogens using the products of acidogenesis (Jha and Schmidt [2017](#page-19-20)).

These microorganisms are able to degrade a wide range of organic matter such as food waste, municipal waste and animal manure (Kabir et al. [2015](#page-19-3)). Lignocellulosic biomass, however, is gaining much attention as a feedstock for biogas production given its renewable and sustainable nature (Brown et al. [2012](#page-17-10)). Since lignocellulosic material is high in lignin, a pretreatment is required prior to anaerobic digestion. For instance, untreated wheat straw generated $0.189 \text{ m}^3/\text{kg VS}$ methane, whereas steam-exploded wheat straw gave $0.275 \text{ m}^3/\text{kg}$ VS methane, a 45% improvement (Bauer et al. [2009](#page-17-16)). Similarly, untreated straw produced 0.165 m³/kg VS methane compared to extruded straw which produced 0.281 m³/kg VS methane (Hjorth et al. [2011\)](#page-18-19).

1.3 Barriers of Utilization of Renewable Biological Energy Resources for Fuel Production

When compared with the cost invested for refinement of available fossil fuels facilitating their commercialization, the production cost of bioethanol and biodiesel from renewable biological energy resources is expected to be more expensive. Maybe governments could encourage the usage of such bio-based fuels with a lesser tax levied for the same in order to promote their usage. Another method of encouraging the usage of fuels of biological origin is to provide subsidies for the same. However, the usage of biofuels needs certain changes in the design of the engines employed for the same. Presently, the major drawback for lignocellulosic biogas is the relatively low-methane yield; therefore, research is focussing on investigating key parameters affecting anaerobic digestion (Seppala et al. [2007\)](#page-20-21).

1.4 Future Possibilities of Utilization of Renewable Biological Energy Resources for Fuel Production

Based on the current energy reserves, it becomes mandatory to depend on the biological energy resources in the future. However, the release of $CO₂$, CH₄ and H₂S from such energy resources should be investigated to understand the possibility of gaseous emissions during the biofuel production. Much scope exists for the usage of biofuels as the greenhouse gas emissions are expected to be comparatively lesser than that is obtained from the combustion of the fossil fuels. The probable reason is that the combustion of the biofuels is complete which guarantees lesser GHG emissions including SO_2 and even particulates (Twidell and Tonyweir [2006\)](#page-21-6). The authors suggest the possible reason for the same to be the lesser amount of sulphur present in the biofuels when compared with the fossil fuels. Shifting the focus from the fossil fuels to fuels of renewable ethanol, hydrogen and biodiesel would be a boon to the mankind. However, the technologies must be framed to meet the demand of the population in the days to come.

1.5 Concluding Remarks

Environmentally, substituting biofuels for fossil fuels would reduce greenhouse gas emissions thereby reducing urban air pollution. However complete combustion of such biofuels in engines, turbines, etc. needs much sophistication. Similarly, when biomass is either burnt off or completely processed, there may be a net loss of nitrogen as the crops or the plantation does not reach nature, hence necessitating the addition of artificial manure. However, a more sustainable energy system has to evolve to meet the ever-increasing energy demand of the exploding population. Of all the renewable energy resources, biological renewable energy resources occupy a prime position to meet the global energy demand in a clean way in time to come.

 As biomass is a widely available resource unlike the area-specific nature of wind, hydro- and solar power, it has the largest potential. New concept of biorefineries is being developed to optimize the utilization of biomass after being converted into energy, food and feed (Caldeira-Pires et al. [2013](#page-18-20), Cherubini [2010a](#page-18-21), [b](#page-18-22)).

However, life cycle analysis has highlighted that some bioenergy systems could have relatively more carbon emissions than the fossil fuels which are to be replaced. Hence, it is essential to perform accurate analysis before choosing the system (Gnansoumou et al. [2009](#page-18-23), Lapola et al. [2010](#page-19-21)). The positive aspects to be considered include the employability, utilization of resources, sustainability and above all meeting the energy demand in the coming centuries.

For the future, a tie-up between the researchers, educational institutions, government, NGOs and stakeholder partnership could definitely play an important role for the sustenance of life.

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