Chapter 7
Biofuel: Marine Biotechnology Securing Alternative Sources of Renewable Energy

Jakir Hossain and Roksana Jahan

Contents

Abstract Due to the excess demand for fuels and the subsequent impact of global warming issues, the establishment of alternative environment-friendly energy is a prime concern to the scientific communities. Thereby, renewable energy in the form of biofuel is gaining research momentum and finding its way into the energy processing for development and consumption. Biofuel is potentially thought as one of the greatest sources of renewable energy in use currently unlike fossil fuels

---

J. Hossain · R. Jahan (✉)
Department of Marine Fisheries and Oceanography, Faculty of Fisheries, Aquaculture and Marine Science, Sher-e-Bangla Agricultural University, Dhaka, Bangladesh
e-mail: roksana.mfog@sau.edu.bd

N. R. Maddela et al. (eds.), *Advances in the Domain of Environmental Biotechnology*, Environmental and Microbial Biotechnology,
https://doi.org/10.1007/978-981-15-8999-7_7

such as natural gas, coal, and petroleum. Therefore, this chapter describes an overview of biofuel production from marine algal sources by applying biotechnological approaches meta. Algae can produce a plethora of biofuels including biodiesel, biogas, biomethane, biobutanol, bioethanol, syngas, bio-oil, etc. In that case, marine algae can be a potential and reliable biomass source because ocean has an untapped vast algal resource that could reduce land cost and efficiently synthesize organic carbon through photosynthesis. The chapter elaborates on the potential of marine algae biomass as a renewable feedstock for biofuel production. Moreover, this chapter has compiled various marine sources involved in biofuel production, along with their properties, some important biofuel production procedures, and prospects and challenges of biofuel production from marine sources and commercialization. Hence, this section could provide a baseline summarization in biofuel production from marine algal sources through biotechnological advances.

Keywords Marine bio-resources · Blue biofuels · Renewable bio-energy · Sustainable approach · Marine biotechnology

7.1 Introduction

From the beginning of civilization, the primary energy in which human is depending on is only fossil fuel. The world energy requirement is raising quickly with increasing excess consumption of fossil due to increasing population and commercial industries. But regrettably, the surges of fossil fuels and oil reserves are being exhausted rapidly. Besides, these fossil fuels contribute to negative effects in the environment like emission of harmful gases, climatic changes, rising sea levels, loss of biodiversity, etc. Due to the excess demand for fuels and the subsequent impact of global warming issues, the establishment of alternative environment-friendly energy is a prime concern to the scientific communities. Thereby, renewable energy in the form of biofuel is gaining research momentum and finding its way into the energy processing for development and consumption. Biofuel is a cost-effective and environment friendly alternative to fossil fuels especially high pricing petroleum. It is being projected that renewable energy especially biofuels would become prominent in the energy mix led by the invention of sophisticated technologies. Researchers are doing experiments continuously to produce biofuel from renewable biomass sources as an alternative effective approach to reduce the use of non-renewable fuels.

Biomasses are living or dead organisms containing carbon that is utilized for biofuel production. Biodiesel, biogas, bio-alcohol, bio-oil, syngas, etc. are some concerning biofuels for energy supply. Biofuels are produced from agricultural crops like maize, soy, rapeseed, palm, or microalgae, macroalgae, seaweeds, etc. In the recent past, a review covered by Pogson et al. (2013) focused on the long-term cost and environmental impact of biofuel production using terrestrial biomass and determined that although terrestrial energy crops are less costly and economical, the problem is an alarming risk to food security. Because the same resource (arable land) will face a tight competition between energy crops and food crops production. Conversely, the biomass which has highest production per unit area is more economical and considerable as a huge amount of biomass is needed for biofuel production commercially. In that case, marine algae can be a potential and reliable biomass source because ocean has an untapped vast algal resource that could reduce land cost and efficiently synthesize organic carbon through photosynthesis.

The bioenergy produced from marine renewable sources is being a sustainable alternative energy which received warm appreciation in many fields such as public, industries, and government policies. Moreover, biofuel produced from marine sources offers various advantages of providing good content of energy production, consumes high carbon dioxide, and provides a cheap fuel source. However, the production process and chemical transformation are being an expensive process and therefore commercial supply of biofuel on large scale is not yet successful. Hence an economic and efficient production process is essential to commercialize marine biomass-based biofuels. Many critics are paying curiosity about the prospect and the rise of a variety of biofuels because of the economic and environmental benefits. Therefore, this chapter describes an overview of biofuel production from marine algae sources by applying biotechnological approaches. This chapter has compiled various marine sources involved in biofuel production, along with their properties, some important biofuel production procedures, and prospects and challenges of biofuel production from marine sources and commercialization.

7.2 Biofuels and Its Types

If any of the molecules produced during carbon fixation provides energy in a mechanical setting, it is called as fuel. Biofuels are a renewable energy source, made from organic matter or wastes, that can play a valuable role in reducing carbon dioxide emissions. Biofuel is any kind of fuel that is produced from biomasses such as plants, algal materials, animal wastes, organic matter, or any other organism and can play a starring role in lessening carbon dioxide discharges (Demirbas 2009).

Biofuel produced from biomasses of different sources can be solid, liquid, and gaseous biofuel. On the basis of nature and chemical structure of biomass, biofuels are categorized as first-generation biofuels, second-generation biofuels, third-generation biofuels and somewhat fourth-generation biofuels. Different generations of biofuel with their characteristics are shown in Table 7.1. The first-generation biofuels are being produced from oil crops, food materials, and animal fats by applying conventional technology (Nigam and Singh 2011). This can be corn, sugarcane, wheat, sugar beet, sorghum, etc. As conventional technologies are use to produce this type of biofuels, they are also known as “conventional biofuels.” Some industrial concerns like cost and inadequacy and competition with food crops led to the second-generation biofuels. Feedstocks used for second-generation are not a food crop and they are no longer used for consumption. This involves agricultural

Table 7.1 Different generations of biofuel (modified from Vaishnavi et al. 2020)

	First-generation biofuel	Second-generation biofuel	Third-generation biofuel	Fourth-generation biofuel
Biomass sources	Produced from sugar, starch, vegetable oil, or animal fats. Basic feedstocks are wheat, corn, rapeseeds and grains	Produced from a variety of non-food crops, such as lignocellulosic materials from agricultural, forestry, and industry	Produced from yeast, fungi, and algal biomass	Produced from photobiological and solar biofuels
Examples	Bioethanol, biodiesel, starch-derived biogas, vegetable oils, biomethanol, and boating fuels	FT (Fischer Tropsch) diesel from biomass and bioethanol	Hydrogen and methane gas, bioethanol, butanol, and acetone	Electrofuels, photobiological solar fuels
Technology used	Enzymation	It utilized liquid technology to produce biofuel from solid biomass	Biochemical, thermochemical, and chemical	Not highly developed yet. Basically, synthetic biology tools
Advantages	Reduced global warming emissions and fossil energy consumption	Improved land-use efficiency and environmental performances Availability of widespread and cheap raw material Allow coproduction biofuels, chemical compounds	Eco-friendly and cost-effective	Eco-friendly and resources available
Disadvantages or limitations	Compete with food and feed industries for the use of biomass and agricultural land	Biomass residues used are still at the pre-commercial stage	Usage of large volumes of water	Efficient technology needed for better usage of materials used for fuel energy production

residues, woody crops that are a little more difficult to extract and require advanced conversion technologies for their process. Therefore, second-generation biofuels are called "advanced biofuels." Lignocellulosic processing is a well-recognized second-generation technology. Increased fuel consumption upsurges the challenge of sustainable supply of feedstock and so the scientists look for an alternative resolution concerning these problems.

In the third-generation biofuel, the marine resources, seaweeds, and cyanobacteria are promising sources because they can produce higher yield with lower resources and lower production cost. Among these algae is the most capable non-food source of biofuel and can highly grow even in saltwater, adverse condition, and also in seawater (Amish et al. 2010). Depending on the technique and the part of the cell used, the algal feedstock can be transformed into different kinds of fuels. The increasing concern about the use of algae to produce biofuel is due to the accumulation of a very high level of lipid that can be then easily transesterified into biodiesel.

7.2.1 Qualities of Sustainable Biofuels

The sustainability of producing biofuels relies on the net energy gain that is fixed in the biofuels and depends on the production parameters, such as the type of land where the biomass is made, the volume of energy-intensive inputs. Sustainability also depends on the energy input for harvesting, transporting, and running the production facilities (Haye and Hardtke 2009). In addition, competition for cultivation land between biomass crops versus food production is also an important issue. The parameters like raw materials, complicating life-cycle assessments, local conditions, and preventing any valid global statement are responsible for biofuel sustainability (Davis et al. 2009; Farrell et al. 2006). If the energy balance of the biofuel is substantially positive only then the large-scale biofuel production can be considered sustainable (Haye and Hardtke 2009). The biofuel production would be certainly sustainable when it is eco-friendly (less emission of greenhouse gas, insulation of huge quantity carbon, not polluting the soil, air, water, and biodiversity, etc.), be acceptable in society and economically feasible. Lora et al. (2011) listed the basic criteria and sustainability indices for a sustainable biofuel (Table 7.2).

Table 7.2 Criteria and sustainability indicators for sustainable biofuels (Lora et al. 2011)

Criteria	Sustainability indicators
1. To be carbon neutral, considering the necessity of fossil fuel substitution and global warming mitigation 2. Not to affect the quality, quantity, and rational use of available natural resources as water and soil 3. Not to have undesirable social consequences as starvation because of high food prices 4. To contribute to the social-economic development and equity 5. Not to affect biodiversity	1. Economic indicators (cost of production) 2. Output/input relation (net energy analysis) 3. Substituted fossil fuel per hectare 4. Avoided GHG emissions (CO_2 savings) 5. Evaluation of Environmental impacts using impact categories indicators 6. Carbon emissions due to land-use changes 7. Renewability indicators (exergy or emergy accounting)

7.2.2 *Benefits of Third-Generation Biofuel over First- and Second-Generation Biofuels*

Due to some concerning issues such as reported displacement of food crops, effects on the environment and climate change, the sustainability of many first-generation biofuels has been progressively questioned over (Singh et al. 2011). Since the first-generation biofuels' sources are mainly food, oil crops, and animal fats, the increasing energy need makes the competition in food and fuel crops production for utilizing arable lands, high water, fertilizer requirements, etc. (Nigam and Singh 2011). Due to these negative criticisms about the sustainability of many first-generation biofuels, the potentiality of the so-called second-generation biofuels that have raised attention is manufactured from lignocellulosic feedstocks, agriculture residues, municipal wastes, and grasses because it emits little greenhouse gases and does not contradict with food supply needs. Still, second-generation biofuel production experiences some limitations to accomplish commercial deployment, though considerable progress continues to overcome the technical and economic challenges (Sims et al. 2010).

Conversely, algal biomass culture for biofuels production has gained much attention because algae can produce higher energy yield and need less space for growth than any conventional feedstocks. Moreover, the marine algal biomass cultivation is not limited to fertile or arable land. So that algae as a feedstock for third-generation biofuel would not compete with food for animals and it could grow within a short time at minimal inputs with a variety of nutrient and carbon sources. So, GreenFuel Technologies Corporation considered algae as the fastest growing plant in the world (Girardet and Mendonça 2009). The benefits of using marine algae as alternative sources for biofuel include: obtained from renewable resources, sustainable, cheap, reduce our reliance on foreign energy, reduce greenhouse gas emission. Moreover, this is the fourth largest energy resource available in the world (Saxena et al. 2009).

7.3 Marine Sources for Biofuel Production

Marine resources like macroalgae, microalgae, seaweeds, fungi are extensively diverse to use as renewable sources for biofuel production. But, until now maximum works are highlighted on one species of brown algae (*Laminaria japonica*), subsequently some species in *Sargassum*. Because this species is conventionally used and hence widely cultured and researched in many countries (Mazarrasa et al. 2014). In 2014, *Laminaria japonica* is produced roughly half of the total seaweed production in China, which is presently the biggest seaweed cultivating country in the world. In contrast, in the case of red and green algae, the maximum researched species are *Gracilaria* sp. (red algae) and *Ulva* sp. (green algae) which are also high production

Table 7.3 Marine resources used in biofuel production (Baskar et al. 2018)

Macroalgae	Microalgae
Acrosiphonia orientalis	*Dunaliella tertiolecta*
Ulva fasciata	*Isochrysis galbana*
Ulva lactuca	*Botryococcus braunii*
Enteromorpha compressa	*Chlamydomonas reinhardtii*
Caulerpa peltata	*Chaetoceros calcitrans*
Valoniopsis pachynema	*Euglena* sp.
Bryopsis pennata	*Spirogyra* sp.
Caulerpa racemosa	*Phormidium* sp.
Padina tetrastromatica	*Cyanobacteria*
Dictyota adnata	*Tetraselmis suecica*
Lobophora variegata	*Scenedesmus obliquus*
Sargassum wightii	*Nannochloropsis oculate*
Centroceras clavulatum	*Phaeodactylum tricornutum*

species annually in Asian countries, like Japan, Indonesia, and Philippines. The list of algae commonly used in biofuel production is summarized in Table 7.3.

7.4 Algae Harvesting Technology

Biomass harvesting tends to be the most energy-requiring process because of the algal concentration, smaller size, and surface charge. Filtration, flocculation, settling, and centrifugation are the most common approaches to harvest algae biomass. Based on the size and density of algae, target product, and the production procedure, the harvesting methods are selected to have the ultimate product.

Filtration is used as one of the best commonly methods, but it is only applicable comparatively for larger microalgal species (>70 μm) and is considered unsuitable to smaller strains (<30 μm). Mohn (1980) confirmed that the filtration process can accomplish 245 times more concentration factor than the original concentration of *Coelastrum proboscideum* to get a sludge that contains solids around 27%. To harvest the algal strain of small-sized cells membrane, it is suggested to apply microfiltration and ultrafiltration/centrifugation methods (Petrusevski et al. 1995).

On the contrary, flocculation and settling are thought to be low-costing methods which need short time energy only for mixture of the cells with a coagulant. Flocculants decrease the negative charge of the algal surface and avoid them from sticking to the suspension (Molina et al. 1999). Algae responses vary expressively with some flocculants. The effectiveness and dosage of a particular flocculant differed immensely from one species to another. Some algae get accumulated and settled down when pH increases that is regulated by CO_2 aeration or lime addition (Demirbas 2011a). Brennan and Owende (2010) found multivalent metal salts such as $FeCl_3$, $Al_2(SO_4)_3$, and $Fe_2(SO_4)_3$ as suitable flocculants.

Lastly, only the centrifugation method is found reasonable for high-value products (Molina Grima et al. 1999). Because this is a highly energy consuming technique, though the nonstop centrifugation method has been discovered that is more profitable if the systems are assembled on a larger volume (Briggs 2004). Ultrasound induced aggregation with increased sedimentation can also be considered to collect microalgal biomass (Brennan and Owende 2010) and this approach is effectively applied in a study conducted by Bosma et al. (2003) which found 92% segregation proficiency and a heavy concentration factor with 20 times more than the original concentration.

7.5 Algal Oil Extraction for Biofuels Production

The sustainability of algae-based biofuel is established by the process of algal oil extraction as it is an expensive approach. All algae cell contains a sturdy cell wall that causes oil extraction more convoluted. The algae need to get dried before the oil extraction process (Heger 2009). Widjaja et al. (2009) uncovered that during the lipid extraction process from algal biomass, the drying temperature could influence the lipid composition and its content. Freeze drier process can hold the original lipid composition while drying at higher temperature reduced the TAG content. Still drying at 60 °C can cause a slight decrease in the lipid composition. Ultrasonication process does not have any considerable impact during the extraction of lipid but appropriate pulverization facilitates extracting the lipid content from the algal cells. Using proper harvesting technology, the algae is segregated from the growth medium, and oil is obtained by any of the mechanical or chemical methods.

The chemical method includes: (1) hexane solvent method, (2) Soxhlet method, and (3) supercritical fluid extraction. The use of chemical solvents may result in safety issues, health problems, and environmental pollution. The supercritical extraction is both costly and energy-intensive as it requires a high-pressure device. For convenient and effective oil extraction, a combination of mechanical pressing and chemical solvents can be used by many manufacturers. The other method is enzymatic extraction in which enzymes are utilized to damage the cell walls and this improves the extraction process. But, in this case, the cost is highly exclusive in contrast to chemical extraction. The solvent extraction method is not only a rapid but also an effective method that is used on dried biomass directly (Mata et al. 2010). In this method, oil is extracted from microalgae by cleaning or washing repeatedly using organic solvents. Several solvents like ethanol, hexane, or mixture of hexane–ethanol, cyclohexane, benzene, etc. are applied and these are successful to extract fatty acids up to 98% (Becker 2004). Supercritical fluid extraction method uses those substances that have both liquid and gaseous properties (i.e. CO_2) while exposing to rising temperatures and pressures. This quality helps to be used as an extracting solvent and there are no residues left behind after the system is taken back to normal atmospheric pressure and standard room temperature (Mercer and Armenta 2011).

The mechanical method includes: (1) expression press and (2) ultrasonic assisted extraction. In both the methods dry algae can only be used which is energy exhaustive. Cravotto et al. (2008) used UAE (ultrasound-assisted extraction) and MAE (microwave-assisted extraction) methods to isolate lipids from plant sources. They also used a cultivated marine microalga containing much DHA (docosahexaenoic acid) and revealed that either single or mixed methods can significantly upgrade the extraction of the bioactive substances with greater proficiency and lower reaction periods with moderate costs and minimum toxicity. Widjaja et al. (2009) showed that algae grown in nitrogen lacking culture media result in higher lipid content and gradually change the lipid composition from FFA-rich lipid (free fatty acid) to mostly TAG contained lipid. Consequently, cooperating between increasing lipid accumulation and time of harvesting is essential to attain better lipid percentage and higher productivity. Moreover, the osmotic shock treatment can be used to crack the cells in solution to release cellular components and oil. This requires low-energy input but it gives the lowest efficiency. In a project by the US Department of Energy's Aquatic Species Program (ASP), solvent extraction costs are found three times higher for algal oil than for soybean oil. It is possibly due to the higher moisture percentage of the paste in the experiment (Sheehan et al. 1998). Pressing and filtration (mechanical dewatering) can be more inexpensive than heating but the real key is having a few steps and simple scalable extraction (Molina Grima et al. 1999).

7.6 Biofuels Production

The algae are transformed into many kinds of renewable biofuels like biodiesel, biogas, bioethanol, biomethane, biohydrogen, bio-oil, and syngas. Algae can be converted into different biofuels depending on technique and part of the cell used in the process. There are many steps followed for producing liquid biofuels from algae like microalgae, macroalgae, seaweeds, fungi. The lipid obtained from algal biomass is converted into biodiesel and following the extraction of lipid, the carbohydrate contents of algae are fermented into bioethanol and butanol fuel and so on.

7.6.1 Biodiesels Production

Biodiesel is a combination of fatty acid methyl/ethyl esters produced from the transesterification of algae oil, vegetable oil, or any animal fats. These feedstocks contain 90–98% triglycerides (TAGs) and a small amount of monoglycerides and diglycerides, FFAs (free fatty acids, 1–5%), and little amounts of other by-products like phosphatides, phospholipids, carotenes, tocopherols, and sulfur compounds and some water (Bozbas 2008). Biodiesel is thought to be one of the most demanding alternatives of fossil fuels because of its similarity in physical and chemical properties with commercial petroleum diesels. Besides, biodiesel performs like commercial fossil diesel by emitting lower emissions. Moreover, biodiesel has some environmental advantages, for instance, highly biodegradable, lower emissions of toxic and carcinogenic gases (Sheehan et al. 1998). Biodiesel is used up more effectively and reduces the emissions of carbon monoxide, unburned hydrocarbons, and particulate things such as smut, sludge, and so on (Kumar et al. 2015).

The most common feedstocks used for biodiesel production are lipids of vegetable seeds, organic wastes, and marine biomass of algae and other organic matter. Yet, the most reported potential feedstock to produce lipid is marine microalgae. Some prominent marine microalgae and its chemical composition are summarized in Table 7.4. As macroalgae do not contain triglycerides, they are not widely used for biodiesel production. To date, biodiesel from macroalgae is sparingly reported and yields very low compared to microalgae (Huihui et al. 2015). Moreover, marine algal feedstocks do not compete with others animals' foodstuffs and resources. The marine algal feedstocks are available in larger quantities and are considered sustainable by increasing commercial cultivation without any negative impact on the environment.

7.6.1.1 Methods of Biodiesel Production

There are many kinds of oils from different sources that are used to produce biodiesel through transesterification or esterification process. Algal biodiesel production includes harvesting biomass, drying, oil extraction, purification, and further transesterification of oil. Balat (2011) has illustrated the processes of biodiesel production and Lin et al. (2011) have discussed the pros and cons of all these processes of biodiesel production. Both studies found transesterification as the most auspicious solution to the high viscosity problem and biodiesel produced from the transesterification with methanol is almost similar to the conventional diesel in its main characteristics and compatibility. Presently, transesterification is the most recognized method to produce biodiesel from biobased oils because of its better conversion efficacy and low costing.

Transesterification

Transesterification (alkali catalysis) is a common process for most of the biodiesel production systems for lipid conversion. The alkali process is more efficient and lower corrosive than the acid process. That is why it a favorable catalysis process to be used in maximum commercial biodiesel production. Generally, KOH, NaOH, or CH_3ONa are very much popular catalysts that are used with any alcohols (methanol or ethanol) and any oils. The transesterification performs well when the free fatty acids and moisture of the lipid are less than 0.1% and the amount of phosphorus is less than 10 ppm. Nevertheless, base catalysts are very much sensitive to free fatty acids and moisture content. But oil feedstock contains high FFAs that cause soap

Table 7.4 Chemical composition of microalgal biofuel sources (% of dry matter) (modified from Zabed et al. 2019)

Microalgae species	Lipid (%)	Protein (%)	Carbohydrate (%)
Euglena gracilis	4–20	39–61	14–18
Chlorella protothecoides	55	10–52	10–15
Chlamydomonas reinhardtii	21	48	17
Chlorella vulgaris	14–22	51–58	12–17
Dunaliella salina	6	57	32
Dunaliella bioculata	8	49	4
Scenedesmus dimorphus	16–40	8–18	21–52
Scenedesmus obliquus	35–55	50–56	10–17
Spirogyra sp.	11–21	6–20	33–64
Anabaena cylindrical	4–7	43–56	25–30
Spirulina maxima	6–7	60–71	13–16
Spirulina platensis	4-9	46–63	8-14
Synechococcus sp.	11	63	15
Chaetoceros calcitrans	39	58	10
Chaetoceros muelleri	33	44–65	11–19
Porphyridium cruentum	9–14	28–39	40–57

formation. The soap formation has adverse effects on the production process and decreases the production of biodiesel. Moreover, NaOH and KOH also cause water and soap formation that reduce the reaction rate. Therefore, sodium methylate or sodium methoxide is pretty good to use as a catalyst than NaOH or KOH, but it is more costly in fact. Sodium methoxide is used as 30–50% solution with methanol for safe uses and added around 0.3–0.5% of the oil biomass. Anyway, according to Barnwal and Sharma (2005), the concentration of the catalyst differs from 0.5% to 1% of oil content (w/w). Reaction temperature is another critical variable in the transesterification process. The recommended optimum reaction temperature is 60 °C though it can vary depending on the catalyst types and different conversion rates. In general, the temperature should be within 25–120 °C (Barnwal and Sharma 2005; Marchetti et al. 2007).

Esterification

Alkali catalysis performs better if the FFAs content in the feedstock is less than 1% of the content of the oil. Before transesterification, chemical neutralization is done to remove FFAs with a base compound, for example, NaOH or physical deacidification is done with a vacuum. Anyway, it is not recommended because some oil is lost during this pretreatment. Fats and lipids containing high FFAs are used to produce biodiesel by acid esterification process. In that case, the formation of soap is not a challenge as no alkali metals are in the reaction medium. Besides FFAs, triglycerides are also transesterified by acid catalysts, but it must take a couple of days to complete that is why it is not considered suitable for industrial esterification. Yet, the entire process can take around one hour at 60 °C. So, the process of esterification of FFAs to alcohol is comparatively quick. An issue to remember is that the produced water should be removed continuously from the reaction medium by phase separation for better reaction rates.

In acid esterification, more acid around 5–25% and higher alcohol:FFAs ratio (20:1 to 40:1) are necessary. Like the alkali esterification, extra alcohol enhances the triglyceride conversion but regaining of glycerol is far critical. According to Marchetti et al. (2007), alcohol and raw material ratio should be optimum. When the conversion of the FAs (fatty acids) to alcoholic esters has been completed, then the water, alcohol, and acid mixture is removed by settling or centrifugation. After that, clean alcohols and basic catalysts are incorporated to the remaining transesterification reaction process. Therefore, esterification should be run after transesterification to get better results and full oil conversion.

Enzymatic Conversion

Enzymes act as catalyst to produce biodiesel from oils. Currently, lipase has gained attention as one of the most used catalysts for enzymatic catalysis of oils into biodiesel. Lipases are a common group of enzymes that are generally used to catalyze the reactions, for instance, hydrolysis, acidolysis, and alcoholysis. Besides these, lipases also catalyze the transesterification and esterification reactions (Marchetti et al. 2007). The reactions are run at 35–45 °C for 4–40 h. Still, there is no single standardized enzyme that can be used with different feedstocks for biodiesel production. Still now, there is a far difference between the cost of existing techniques and the industrial application, although reuse of the immobilized enzymes reduces the cost relatively. Unfortunately, considering the economic perspective this process is not cost-effective for biodiesel production from microalgae.

Non-Catalytic Conversion

Non-catalytic conversion can be considered to some extent like to enhance the reaction of lipids with alcohol or to improve the miscibility of the oil–alcohol step and to reduce the drawbacks of the mentioned methods. Some commonly used non-catalytic methods are supercritical conversion, microwave-assisted conversion, or ultrasound-assisted conversion (Bharathiraja et al. 2014).

Supercritical Alcohol Conversion It is a relatively advanced and more appropriate method (Warabi et al. 2004), but it is not sure that this process is more efficient and faster than transesterification and esterification to convert oil into biodiesel (Marchetti et al. 2007). This is a very simple process and can be completed within a very short time (2–4 min). Since there is no need for catalyst, biodiesel purification is more simple, easy, and eco-friendly (Demirbas 2005). Reaction time and temperature, catalyst loading, stirring rate, and alcohol/oil molar ratio are considered to identify the optimum conditions for the conversion process (Meher et al. 2006).

Microwave-Assisted Conversion Microwave-assisted conversion works under microwaves and the reaction is completed within a short time by a huge reduction of by-product quantity (Hernando et al. 2007). Furthermore, this process produces a high quantity and quality of the products quickly which helps to reduce the production cost significantly (Nüchter et al. 2000).

Ultrasound-Assisted Conversion It is a good method that secures maximum mixing and increases liquid–liquid mass transfer (Ji et al. 2006). This process also enhances the surface area for interacting between alcohol and oil (Stavarache et al. 2006). Ultrasound supplies the activation energy needed for initiating the reaction that increases the mass and heat transfer of the solution and causes up the reaction rate and better production (Adewuyi 2001).

7.6.1.2 Biodiesel Separation and Purification

After finishing the process, biodiesel is found in a mixture of extra methanol, glycerin, and catalyst. Self-phase separation happens due to the specific gravity of the compounds in the mixture like the rules of thumb. Gravity separation is helpful to separate the biodiesel from the by-products (glycerin and methanol). Yet, emulsion formation is induced if the feedstock is not purified that causes the separation far tough. So, to face this difficulty, saturated salt (sodium chloride) or centrifugation is used to segregate the emulsion that intensifies the phase separation process. Further, the concentration of methanol in the reaction is reduced for good phase separation. Distillation, glycerin, and methanol used in the process could be purified generally. When phase separation is completed, the remaining methanol in the process is eliminated through evaporation. In the end, the remaining of the microalgal biomass after biodiesel production process can be used further to get other biofuels like biobutanol, bioethanol, or bio-oil (liquids) (Gouveia and Oliveira 2009; Miranda et al. 2012) or gaseous biofuels like biomethane, syngas, and biohydrogen (Ferreira et al. 2013). If that could be done, then the overall cost would be reduced significantly.

7.6.1.3 Some Issues Considered During Biodiesel Production

In order to increase the yield, new techniques like ultrasound irradiation assisted transesterification were used to form emulsion of oil and alcohol and the cavitation formed during this process accelerates the rate of the reaction. It was also observed that biodiesel from wet biomass is ten times lower from dry biomass and it implies the negative effect of water on transesterification (Huihui et al. 2015). Thus, the dehydration process is necessary to achieve high yield. As these steps increase the total production cost, direct transesterification or in situ extraction is carried out in which the oil-bearing material directly contacts with alcohol instead of reacting with extracted oil and thus eliminates the two-stage process of biodiesel production.

Microalgae can accumulate a significant number of triglycerides amounting to 20–50% of its cellular weight (Chen et al. 2015), though it depends on the type of strain and cultivation condition. The microalgae selected for biofuel production is firstly grown under optimal growth condition. Then they are put on a restricted diet nutrient growth media resulting in increased oil production. TAGs synthesis in these species can be improved by some conditions subjected to the growing microalgae, for instance, causing stress to the microalgae with temperature, pH, salinity, nutrient starvation, and age of cultured algae. Increased TAG content enhances the production and effectiveness of biodiesel.

In order to enhance the economics of biodiesel production using microalgae, genetic modification and molecular level engineering receive keen focus to increase its photosynthetic efficiency, biomass growth rate, oil content, and reduces photoinhibition. To attain a consistent annual yield of oil, photobioreactors should be used that provides a controlled environment to increase the microalgal biomass required for making biodiesel.

7.6.2 Bioethanol Production

Bioethanol is one of the highest utilized alcoholic biofuels and is a vital promising biofuel worldwide (Chia et al. 2018). Ethanol is thought as a booster of octane for gasoline. 40% ethanol mixing with gasoline can cause 3.0–4.4% less gasoline consumption, induce the efficacy of internal combusting of engines, and also reduce the emissions of CO_2 around 19 to 35 metric tons annually.

Bioethanol from macroalgal feedstock is also a liquid algal transportation fuel. As macroalgae are rich in carbohydrates and contain only little lignin, they are considered suitable for the fermentation process for producing bioethanol (Hamelinck et al. 2005). Some prominent marine algae sources for bioethanol production are reported that include brown algae: *Laminaria hyperborean* (Adams et al. 2009), *Alaria crassifolia Kjellman* (Yanagisawa et al. 2011), *Laminaria japonica* (Kim et al. 2011), *Sargassum* spp. (Lee et al. 2011); Red algae: *Gracilaria verrucose* (Kumar et al. 2013), *Kappaphycus alvarezii* (Khambhaty et al. 2012); Green algae: *Ulva* spp. (van der Wal et al. 2013), *Chaetomorpha linum* (Schultz-Jensen et al. 2013). As these organisms are grown in an aquatic environment, the buoyancy helps its upright growth without lignin crosslinking and so they contain hardly the same type lignin crosslinking compounds in their cellulose. Due to the lower amount of lignin, it contains enough sugars (not less than 50%) that can be applied for the fermentation of bioethanol.

7.6.2.1 Marine Algae-Based Bioethanol Production Process

The process of bioethanol production is similar to the technological process of common ethanol production. The bioethanol production from marine biomass includes a series of sequential steps that are algae drying, crushing, pulverization, liquefaction, saccharification, ethanol fermentation, and refinement. Among them, some major steps are discussed below.

Liquefaction

After the algal ingredients being extracted, liquefaction is needed for enzyme treatment or microbial fermentation. The methods of this liquefaction are extracting sugars from dried powder, using enzymes on live algae to break the polysaccharides in cells or cell walls, and then liquefying live algae in intense heat and pressure.

The extraction of sugars from dried powder reduces the energy balance because it requires a large amount of energy for drying and pulverization. The enzyme treatment method involves the liquefaction of algal structural polysaccharides through the treatment of cellulase or the digestive enzymes of algivorous mollusks. Liquefaction is achieved by treating the dried, powdered form of kelp or other brown algae using enzymes. The enzymes break the fibrin in the cell wall or alginic acid and reduce the molecular weight of the mucopolysaccharides (alginic acid) between cells to decrease their viscosity. The red algae such as *Gelidium amansii* is treated with sodium chloride for removing the lignin. After that, b-galactosidase and xylanase are used for liquefaction and saccharification. To reduce the molecular weight of proteins and other polymer compounds, the intense temperatures and pressure are used in liquefaction. However, this method faces difficulties to treat a high amount of algae because of its capacity issues with the internal pressure vessels (Huang et al. 2011).

Saccharification

Saccharification processes are acid hydrolysis, degradation under high temperature and pressure, and enzymolysis. Acid hydrolysis method can be done by treating with 3% H_2SO_4 for 60 min at 120 °C. Polysaccharides are broken into monosugars by acid hydrolysis, but the retention of monosugar can also be decreased by extreme degradation. Besides, too much breakdown reduces monosugars' recovery rate ultimately lowering the recovery rate of ethanol. Sulfuric acid should be removed after hydrolysis. Thereby, alkali neutralization can be used to remove sulfuric acid. The type of enzyme used in enzyme-based saccharification process depends on the components and bonding of the algal sugar (Demirbas 2009).

Ethanol Fermentation

Fermentation is the conversion of monosugars into ethanol where at first, complex components must be reduced to low molecular weight. The sugars (glucose and mannitol in brown algae, and glucose, galactose, and xylose in green and red algae) is the main component in ethanol fermentation. Microorganisms like yeasts and bacteria have a major role during the fermentation of ethanol. The common enzymes found available in these microorganisms are not so reliable in fermentation. Recently, a growing concern in genetically improved yeasts with a wider range of substrate specificity has gained a new hope for the future. Anyway, some yeasts which are used to produce ethanol from glucose can be *Saccharomyces cerevisiae*, *Pachysolen tannophilus*, and *Pichia angophorae* and bacteria like *Zymomonas mobilis*. Ethanol is synthesized from galactose too. The high amount of galactose can be found in red algae. The sugar present in maximum brown algae can entirely be converted into ethanol and this is a remarkable advancement in ethanol production from marine algal biomass because the brown algae are one of the most abundant resources (Takeda et al. 2011; Wang et al. 2011; Lee and Lee 2012).

7.6.2.2 Other Issues Related to Bioethanol Production

In the production of bioethanol from macroalgae, pretreatment has a vital role in saccharification and fermentation processes. This is because as the carbohydrates in the macroalgae are not freely available and so mechanical or acid pretreatment could enhance the reaction surface and helps locked sugars in the structural polysaccharides to be more available for hydrolytic enzymes. The acid hydrolysis pretreatment is reported to be highly cost-effective but suffers from a drawback of glucose decomposition that occurs during hydrolysis (Horn et al. 2000). Thus, saccharification is enhanced by a combination of acid and enzymatic pretreatment but it is highly necessary to use suitable enzymes to obtain high efficiency in hydrolysis and enzyme recovery (Demirbas 2009). Therefore, the high efficient hydrolysis process and efficient fermentation are the two major issues in using macroalgae as the feedstock for bioethanol production. The red alga, *Gelidium amansii* consists of cellulose, glucan, and galactan and can be an efficient feedstock for bioethanol production (Horn et al. 2000). The other brown algal species such as *Alarie*, *Saccorhiza,* and *Laminaria* consists of laminarian and mannitol as main energy-storing materials and so they are widely used in bioethanol production using mannitol and laminarian as substrates (Horn et al. 2000).

Microalgae also synthesize large amounts of carbohydrates in different combinations in each species that can be fermented to produce bioethanol. Besides lipids, carbohydrates are the main components that store energy. The microalgal biomass also needs to be pretreated for the efficient extraction of fermentable sugars. For this, easily handling energy method and cost-effective hydrolysis method can be used. Enzymes or diluted or concentrated acids are commonly used for hydrolysis of algal biomass. Acid concentration, temperature, and algal loading are the important parameters to be considered for the efficient release of fermentable sugars from the biomass (Harun and Danquah 2011). High levels of polysaccharides accumulate in the complex cell wall in green algae such as *Spirogyra sp.* and *Chlorococum sp.* and this starch accumulation can be used in the production of bioethanol (Harun and Danquah 2011). It is reported that the *Chlorococum sp.* could produce 60% more bioethanol concentrations for the sample. Therefore, these suggest that same biomass source (microalgae) could be used to produce both lipid-based biofuel and ethanol biofuel at the same time increasing economic benefits (Harun and Danquah 2011).

In order to enhance the production of bioethanol, several attempts have been reported in the development of genetically modified microalgae by introducing ethanol-producing genes (Ross et al. 2008). Some private company describes the ability of microalgae in bioethanol production photosynthetically and introduced photosynthetic bioethanol production protocol. However, the technology is under development and investigated for the commercial application of microalgae-based bioethanol production. Another advantage of using microalgae is they are good producers of hydrogen; therefore, biohydrogen can be produced as a pollution-free renewable green fuel.

7.6.3 Biobutanol

Butanol is being consumed as a transportation fuel for around 100 years. So biobutanol can be a potential biofuel and even it can replace ethanol as a gasoline additive due to its low vapor pressure and higher energy density (Potts et al. 2012). The production of butanol from algal biomass could also be more energy-efficient than ethanol (Huesemann et al. 2010). It is nonpolar and long hydrocarbon like gasoline that is why it is suitable for use in gasoline vehicles without any modification. Additionally, the vaporization heat of butanol is little more than that of gasoline (Hönig et al. 2014). So, the gasoline blended with butanol does not cause cold start problems and could be utilized as 100% biobutanol fuel in place of gasoline (Pospíšil et al. 2014). In general, biobutanol has high miscibility, low volatility, high energy contents from 33.07 MJ Kg^{-1} (Klass 1998) to 36.1 MJ Kg^{-1} (Laza and Bereczky 2011), and density of 810 Kg m^{-3} (Pfromm et al. 2010).

Unlike biodiesel, the main feedstock used biobutanol production is carbohydrates. Carbohydrates can be monosaccharides, disaccharides, polysaccharides, or oligosaccharides on the basis of the length and composition of feedstock (Gloria et al. 2013). Algae contain more carbohydrates than lipids and carbohydrate content in algae differs substantially among the algal species. Some algae like chlorophytes have carbohydrates in the cell wall that are composed of mostly cellulose and soluble polysaccharides (Domozych et al. 2012). Starch or glycogen is found in most green algae and cyanobacteria (Singh and Olsen 2011; Chen et al. 2013). Some prominent species of green microalgae like *Chlorella* sp., *Dunaliella* sp., *Chlamydomonas* sp., and *Scenedesmus* sp. are being considered potential to produce biobutanol industrially (Singh and Olsen 2011).

7.6.3.1 Biobutanol Production

Biobutanol is being produced massively by the fermentative process. In general, biobutanol can be produced by ABE process that is acetone, butanol, and ethanol production process. The ABE fermentation process is accomplished in three main steps: (1) pretreatment of algae biomass, (2) fermentation, and (3) recovery.

Algae Pretreatment for Biobutanol Production

Algae pretreatment is a crucial phase because the process breaks polymer crystalline structure (like cellulose and starch) into simple sugars that are fermentable. So, this can result in faster hydrolysis and higher production (Mosier et al. 2005). A study showed that using intact algae without pretreatment generates lower biobutanol because of lower conversion rates (Wang et al. 2016). Therefore, a proper pretreatment method can increase subsequent hydrolysis and fermentation (Sun and Cheng 2002). In general, the microalgal starch can be transformed into biofuel directly by applying dark and anaerobic fermentation, though the biofuel production would be much lower (Ueno et al. 1998). Thus, algal feedstock needs treating with a pretreatment method to enhance the production. Thus, the selection of a suitable method for algae pretreatment needs to consider the cost of the production. The pretreatment process can be done using different three methods such as hydrolysis/saccharification, nourishment, or sterilization (Hemming 2011). Yet, saccharification is the most popular and effective process that is used for the conversion of carbohydrate polymers into simple fermentable monomers.

Hydrolysis/Saccharification Saccharification is the most important pretreatment phase in the fermentation of microalgal biomass especially lignocellulosic or cellulosic compounds. The process is done for the saccharification of raw feedstocks by enzyme digestion, alkaline, thermolysis, and acid hydrolysis. These processes can be divided into three main sections such as enzymatic saccharification, physical saccharification, and chemical saccharification.

These pretreatment saccharification methods have a certain economic cost that depends on several parameters including (1) alkaline or acid reagent, (2) electricity cost, (3) time of thermal pretreatment and working temperature, (4) surfactant loading during enzymatic hydrolysis, (5) type of hydrolytic enzymes used, and (6) type of feedstock used (Hernández et al. 2015). Regarding pretreatment costs, different methods may be sorted, from high to low costs as (1) enzymatic pretreatments (using amylases and cellulases), (2) chemical pretreatment (alkaline and acid), and (3) physical pretreatment (microwaving, sonication, high-pressure homogenization, and heat) (Talebnia et al. 2010; Tao et al. 2011).

Enzymatic saccharification is done by utilizing the hydrolytic enzymes like cellulases, amylases, and glucoamylases. Microalgae cell walls contain heavily cellulose and very few hemicelluloses but no lignin at all. So, lignin-degrading enzymes are not needed for this enzymatic saccharification process. Enzymatic saccharification shows some advantages like low cost of tools, higher glucose production without toxic by-products or sugar degradation products (Cara et al. 2007). Moreover, it requires low energy because of its low temperature and high selectivity of components present in microalgae (Mubarak et al. 2015). A comparative study showed that fermentation of enzymatic pretreated algae with xylanase and cellulase produced 9.74 g L ABE but, fermentation of acid-/alkali-pretreated algae produced 2.74 g L 623 -1 ABE only (Ellis et al. 2012). But, the enzymatic digestion process is a costly one that reduces the wide-ranging application of ABE production (Kumar and Murthy 2013).

Chemical saccharification is characterized by its short reaction time, though it needs higher temperature, pressure, and acid like H_2SO_4, HCl, and HNO_3 or base like NaOH, KOH, and Na_2CO_3. Moreover, it makes some inhibitor like furfural and 5-hydroxymethylfurfural that can downregulate the fermentative reaction (Mussatto et al. 2010). To stop producing these inhibitors and to increase saccharification efficacy, the appropriate reaction parameters like temperature, residence time, and moisture content are followed (Okuda et al. 2008). Optimizing these parameters, fermentable sugars production will be amplified (Castro 2014). Castro (2014) found 166.1 g kg^{-1} sugars from dry biomass of butanol-producing bacteria *Clostridium saccharoperbutylacetonicum* using acid hydrolysis. In case of treatment cost, the acid/alkali saccharification can be low costing yet than that of enzymatic saccharification (Choi et al. 2010). Nevertheless, a combined approach of acid hydrolysis and enzymatic digestion could obtain higher production (Park et al. 2012; Castro 2014).

Physical saccharification means the application of physical force to increase the hydrolysis and fermentation of carbohydrates (Talebnia et al. 2010; Tao et al. 2011). Still now, this pretreatment process is not much analyzed for microalgae biomass with the exception of macroalgae or seaweeds or lignocellulosic biomasses (Laghari et al. 2014). Nonetheless, most effective physical pretreatment like microwave and sonication was used in some cases. Microwave application is more popular for biomass transformation than conduction or convection heating. Because, it is a more direct, fast, and stable method that can directly interact with the heated substrates with an electromagnetic field to produce heat (Macquarrie et al. 2012). Moreover, ultrasonication can increase the rate of hydrolysis for simple fermentable sugar (Zhao et al. 2013).

ABE Fermentation

The ABE (acetone, butanol, and ethanol) fermentation is done by utilizing some microorganisms like bacterium (*Clostridium acetobutylicum*) that can produce saccharolytic butyric acid. Difference from yeast, clostridia can produce alcohol from many carbohydrates like hexoses, pentose, or same type carbon sources (Yoshida et al. 2012). Furthermore, some disaccharides like sucrose, mannose, and polysaccharides such as starch can also be fermented by clostridia (Campos et al. 2002). *Granulobacter saccharobutyricum*, *Amylobacter butylicus*, *Bacillus orthobutylicus,* and some other microorganisms can be used in biobutanol fermentation (Dürre 2007). Anyway, most of the *Clostridium* sp. like *C. acetobutylicum*, *C. beijerinckii*, *C. saccharoperbutylacetonicum*, and *C. saccharobutylicum* can be effective for the fermentation of biobutanols (Gao 2016). ABE fermentation is butyric acid fermentation that is done by anaerobic metabolism of bacteria. ABE fermentation has two steps, i.e. acidogenesis and solventogenesis.

Acidogenesis works at the time of exponential period of bacterial growth. In this process, carbohydrates are converted into granulose and accumulated inside the cells whose structures contain α-1,4-linked polyglucan sugar (Shaheen et al. 2000). In this phase, organic acids like acetate and butyrate are produced from re-assembled monosaccharides. These organic acids diminish the pH value in the medium that excites the solventogenesis phase (Li et al. 2011a). In the end, solventogenesis was found to be started only at pH less than 5.1 (Millat et al. 2013).

On the contrary, solventogenesis works at the end of exponential period to the early stationary period of bacterial growth in the cytoplasm. Then acid production inside the cytoplasm becomes slow and the excreted acetate and butyrate are converted into the acetone and butanol. Finally, as by-products acetone, butanol, and ethanol were found at 3:6:1 ratio (Qureshi et al. 2006). Anyway, about 1–2% butanol can inhibit bacterial growth by disrupting the cell membrane (Jin et al. 2011). Then, the cells synthesize endospores for survival. Because, the endospores can survive in different stress conditions, for instance, UV light, heat, drought, or frost, etc. After getting proper conditions, the spores grow again (Wang et al. 2014). In that way, ABE fermentation can be regulated.

Butanol production is different from ethanol production in the case of substrate fermentation. Therefore, biobutanol production from microalgae could be more effective compared to the production of methanol or ethanol.

7.6.4 Marine Biogas

Biogases are important trendy renewable biofuels produced from various sources of organic biomass. Biohydrogen, biomethane, bioethane are the most promising gaseous biofuel candidates. Biogas contains mainly CH_4 and CO_2, along with other compounds like H_2S, NH_3, water vapor, and certain trace elements. The effective composition of biogas depends on the nature of feedstock used in the production process and the reaction conditions used to digest the feedstock. The production of biogas by anaerobic digestion of algae is a new attention because of high polysaccharides (agar, alginate, carrageenan, laminaran, and mannitol), no lignin, and low cellulose content in the algae feedstock used. Macroalgae especially seaweeds are the best source of feedstock for biogas production. Some studies showed the application of some algae species to produce biogas that are *Scenedesmus*, *Spirulina*, *Euglena*, and *Ulva* (Ras et al. 2011; Zhong et al. 2012; Saqib et al. 2013). Besides these, a few more sources can be red algae, *G. vermiculophylla* (Tedesco et al. 2014); brown algae, *Macrocystis pyrifera* (Gurung et al. 2012), *S. latissimi* (Vivekanand et al. 2012), *Durvillaea antarctica* (Gurung et al. 2012). Moreover, microalgae can also be considered to produce biogas along with other carbonaceous feedstocks.

7.6.4.1 Anaerobic Digestion and Production Process

In general, anaerobic digestion (AD) means the fermentation of compound organic matter in the absence of oxygen, which causes decomposition of organic matter to produce CH_4, CO_2, H_2, and some volatile fatty acids (VFAs). The organic components in the macroalgae like carbohydrate, protein can easily be converted into biogas by anaerobic digestion. Anaerobic digestion is a multi-step process, and the four major steps are hydrolysis, acidogenesis, acetogenesis, and methanogenesis.

Hydrolysis treatment is the first step of anaerobic digestion in biogas production. In this rate-limiting step, the complex organic matter is dissoluted or disintegrated or broken down into simple monomers and this increases their bioavailability to the fermentative bacteria. Various pretreatment processes like milling, maceration, thermal pretreatment are reported for efficient breakdown of cell wall and biogas production (Bird et al. 1990). At first, using the enzymes released from some definite anaerobes the insoluble organic compounds and heavyweight molecular substances like lipids, proteins, and carbohydrates are hydrolyzed into soluble compounds. The prevalent bacteria in this step are facultative anaerobes of the genera *Clostridium*, *Bacteroides*, *Butyrivibrio*, *Bifidobacterium*, *Bacillus*, *Streptococcus*, and members of the *Enterobacteriaceae* family (Amani et al. 2010; Christy et al. 2014). An alarming issue is that more saline, sulfur, and halogens present in the production system prevent the production and growth of anaerobic microorganisms and also induce to grow fouling agents. Therefore, both water and weak acid pretreatment are necessary to eliminate a significant amount of mineral contents. This results in a high energy yield. This also helps in using biomass directly without drying and so any kind of microalgal biomass can be used as feedstock in the anaerobic digester system. A pretreatment can significantly increase the hydrolysis proficiency and enhance the methane synthesis capacity of the used feedstock. The pretreatment step is applied on the basis of the applied feedstock, energy needs, and the viability for use in large-scale production (Carrere et al. 2016). The common pretreatment methods like acid–base hydrolysis or mechanical pretreatments include using autoclave, homogenizers, microwaves, sonication, and also enzymatic methods. The important parameter to consider in biogas production is the ratio of C/N. The algae biomasses have a low ratio of C/N and it may inhibit the methane yield because it is undesirable for anaerobic digestion. To overcome this problem, the co-digestion of algae was used successfully to achieve a high C/N ratio and enhances the methane production by decreasing the levels of ammonia under its inhibitory levels (Mussgnug et al. 2010).

The second phase is acidogenesis that is the principal step. In this step, monomers are converted into higher organic acids, alcohols, aldehydes, and some gaseous products. The soluble compounds are converted with the help of enzymes released by the acidogenic bacteria. Obligate and facultative (fermentative) bacteria work on the monosaccharides found in sugars and convert them to organic acids (lactate, propionate, butyrate, propionate, and acetate) and alcohols (ethanol or methanol) by adding with CO_2 and H_2. Fatty acids and amino acids found in lipids and proteins can be used as carbon sources for anaerobic bacteria. Some important bacterial species working on this step can be *Bacillus*, *Clostridium*, *Micrococcus*, *Pseudomonas*, *Lactobacillus*, *Salmonella*, *Corynebacterium*, *Eubacterium*, *Escherichia coli,* etc. (Christy et al. 2014). There are some organic acids formed in this phase, but acetate and butyrate are selected to generate methane gas.

The next one is acetogenesis, where acetogenic bacteria convert higher organic acids to acetate and hydrogen by the process of acetogenesis. Acetogenic bacteria are obligate anaerobes that grow slowly at pH 6 optimally (Christy et al. 2014). Some important acetogenic bacteria found in this step are *Syntrophomonas wolfeii*, *Syntrophobacter wolinii*, *S. fumaroxidans*, *Pelotomaculum* sp., *Smithella* sp., and *Clostridium aceticum* (Amani et al. 2010). Hydrogen evolved in this phase is caused by the accumulation of electron sinks as higher acids and alcohols. Acetogenic bacteria catalyze to convert these electron sinks to acetate, CO_2, and H_2 (Christy et al. 2014). The evolved hydrogen is toxic for the acetogenic bacteria that is why a low partial pressure of hydrogen is recommended. A syntrophic relationship is seen between hydrogen-evolving acetogenic bacteria and hydrogen-consuming methanogenic one, and this relationship regulates the proficiency of biogas production (Weiland 2010). A higher concentration of hydrogen helps in methane formation, where lower concentrations of hydrogen help in the formation of acetate from CO_2 and H_2 through homoacetogenic bacteria. Some recognized homoacetogenic bacteria are *Acetobacterium*, *Butyribacterium*, *Clostridium*, *Eubacterium*, *Peptostreptococcus*, and *Sporomusa* (Saady 2013). Anyway, homoacetogens could develop methanogens in an anaerobic method at low temperatures and adverse environments (Ye et al. 2014).

Methanogenesis is the final step which is mainly methane-producing phase. Methanogens metabolize acetic acids and hydrogen into methane and carbon dioxide (Cantrell et al. 2008; Brennan and Owende 2010; Romagnoli et al. 2010). Archaea regulate the phase because of their special metabolism capacity of using acetate, CO_2/H_2, formate, or other methylated carbons that can be a source of energy and carbon for methane production (Enzmann et al. 2018). Methanogenic organisms found in anaerobic digestion can be hydrogenotrophic methanogens or acetoclastic methanogens. Acetoclastic methanogens cause acetate decarboxylation and generate methane and CO_2. Few species like *Methanosarcina barkeri*, *Methanococcus mazei*, *Methanothrix soehngenii* are capable of acetoclastic methanogenesis (Weiland 2010). Methanogens determine the efficacy of the anaerobic digestion process. So, it is necessary to regulate the production parameters in anaerobic digestion that can favor methanogens. Finally, biogas (a mixture of CO_2 and CH_4) and the residual digestate are found as the resulting products. Then, the digestate can be solid and liquid fractions. The solid digestate can be applied as a biofertilizer because it is easy to handle and contains higher bioavailable nitrogen for plants. On the contrary, the liquid portion contains leftover organic acids and other macronutrients like NH_3 and phosphorus. This process is also associated with several challenges in the biogas production such as, inappropriate C:N ratio and high level of ammonia in pretreatment process and the presence of alkaline metals in macroalgae. These may inhibit the anaerobic process. Therefore, to get an increased yield of methane, an appropriate C:N ratio should be maintained and a lower ratio may result in the accumulation of ammonia in the bio-reactor that reduces the yield of biogas finally.

Overall, some issues can be considered regarding biogas production from marine sources. There are some factors like the requirement of suitable space, infrastructure, and heat required for the digesters may control the biogas yield (Collet et al. 2011; Jones and Mayfield 2012). Some proteins of algae cells can enhance ammonium synthesis that causes low carbon–nitrogen ratio. The C-N ratio can affect the production by inhibiting the growth of anaerobic microorganisms. Anaerobic microorganisms are also downregulated by the sodium ions. So, salt-tolerant microorganisms can be a better option for the anaerobic digestion of algae biomass (Brennan and Owende 2010; Jones and Mayfield 2012).

7.6.5 Biomethane Production from Marine Microalgae

Biomethane is considered as one of the most encouraging renewable fuels which has a great possibility to cause a transition of existing fossil fuel-dependent energy toward a sustainable energy for the future. Methane combustion emits a lower CO_2 compared to other traditional hydrocarbon fuels. But the ratio of molar weight (16.0 g/mole) to combustion heat (891 kJ/mole) reveals that methane produces more heat/unit weight than any other hydrocarbons (Shuba and Kifle 2018). Biomethane can be generated from various sources of biomass such as food wastes, agricultural residues, animal manure, forestry residues, energy crops, microalgae, organic-rich wastewaters, organic fraction of municipal solid waste, and industrial organic waste by the anaerobic digestion (Cucchiella and D’Adamo 2016; Jankowska et al. 2017). But, among them, microalgae are considered to be more suitable feedstock as they grow faster (5–10 times), have higher biomass production, and also are suitable to cultivate in the nonarable lands and nutrient-rich wastewaters. Moreover, microalgae are very potential to consume CO_2 so that accumulation of CO_2 in the atmosphere is reduced (Stephens et al. 2013; Ward et al. 2014). Microalgae contains enough biodegradable compounds, for instance, carbohydrates (4–57%), lipids (2–40%), and proteins (8–71%) of total solids (Prajapati et al. 2013) that can generate more biomethane around a theoretical yield of 0.42, 1.01, and 0.5 L STP CH_4/g, respectively (Guiot and Frigon 2012).

The anaerobic digestion is a widely accepted method for producing methane (CH4) from algal biomass (Ho et al. 2018). The anaerobic digestion to produce methane from microalgae can be two types: liquid AD (L-AD) and solid-state AD (SS-AD). The basic principles of these techniques are similar but can vary with the physical conditions of the system, especially moisture content of biomass (Li et al. 2011b). The methane production is almost the same in these two methods. But volumetric productivity can be higher in SS-AD than that of A-AD (Brown et al. 2012). The basic protocol to produce biomethane by anaerobic digestion of microalgae includes several steps such as cultivation, harvesting, pretreatment, and then anaerobic digestion of the microalgae. Besides, the biomethane production varies significantly on the basis of selecting suitable algal strain because microalgae show wide variation in their biomass composition.

7.6.6 Biohydrogen Production

Algal biohydrogen is a common commodity nowadays that is used as gaseous fuels or electricity generation. Biohydrogen production has various processes such as biophotolysis and photofermentation (Shaishav et al. 2013). Biohydrogen can be produced from various marine algal sources. Park et al. (2011) positively recommended *Gelidium amansii* (red alga) as the potential biomass source for biohydrogen production using anaerobic fermentation and the study produced 53.5 mL hydrogen per 1 g of dry algae with a production rate of 0.518 L H_2/g VSS/day. Moreover, Shi et al. (2011) found 71.4 mL hydrogen from per 1 g dry algae (*Laminaria japonica*) by anaerobic sequencing batch reactor for 6 days of hydraulic retention time maintaining mesophilic condition (35 ± 1 °C), pH 7.5. So, to maximize the biohydrogen production pretreatment method should be optimized importantly (Park et al. 2011; Shi et al. 2011). Saleem et al. (2012) decreased the lag period in hydrogen production from microalgae (*Chlamydomonas reinhardtii*) using an optical fiber for an internal light source and they found maximum hydrogen production rate using exogenic glucose.

Some of microalgae such as BGA (blue green algae) contain glycogen in their cell instead of starch. In this case, oxidation of ferredoxin is caused by the hydrogenase enzyme to produce hydrogen in the anaerobic situation. Nevertheless, this enzyme helps in the detachment of electrons too. Hence, some scientists have emphasized to identify the enzyme activities having interactions with ferredoxin and the other metabolic activities for microalgal photobiohydrogen synthesis (Yacoby et al. 2011; Rajkumar et al. 2014).

7.6.7 Bio-Oil and Syngas Production

Bio-oil is produced in the liquid phase of anaerobic digestion of algal biomass at high temperature. The proximate composition of bio-oil can be varied on the basis of different feedstocks and processing parameters used (Iliopoulou et al. 2007; Li et al. 2008). Some parameters like biomass composition, pyrolysis temperature, water, ash content, and vapor residence time can regulate the productivity of bio-oil (Fahmi et al. 2008). Anyway, crude bio-oil is not used as fuel because it contains water, oxygen content, unsaturated and phenolic moieties too. So, some treatments are needed to enhance its combustion quality (Bae et al. 2011). Bio-oils are treated to generate power with the help of an external combustion process using steam Rankine cycles and Stirling engines. Yet, power generation can also be done by internal combustion by applying diesel and gas-turbine engines (Chiaramonti et al. 2007). Existing evidence shows that few studies have been conducted on algae pyrolysis compared to lignocellulosic biomass. Some pyrolysis processes were applied to reduce their inherent disadvantages of carrier gas flow and excessive energy inputs, but high yields of bio-oil were found in fluidized-bed fast pyrolysis (Oyedun et al. 2012). Demirbas (2011b) examined the suitability of marine microalgae to produce bio-oil and got better quality than the wood one. Porphy and Farid (2012) conducted a study to produce bio-oil from the pyrolysis of extracted lipids from microalgae (*Nannochloropsis* sp.) by applying 300 °C. This contains 50% acetone (wt), 30% methyl ethyl ketone (wt), and 19% aromatics (wt), i.e. pyrazine and pyrrole. Choia et al. (2014) also conducted a study on pyrolysis of *Saccharina japonica* (brown algae) at 450 °C and found almost 47% bio-oil production.

Syngas is a mixture of some gases such as CO, CO_2, CH_4, H_2, and N_2 that can be generated by normal gasification. Gasification transforms biomass into the combustible gas mixture at high temperatures (800–1000 °C) with the help of partial oxidation. This combustible gas mixture is known as syngas or producer gas. The syngas has a calorific value of 4–6 MJ m^{-3} (McKendry 2002). It mainly contains a mixture of H_2 (30–40%), CO (20–30%), CH_4 (10–15%), ethylene (1%), nitrogen, carbon dioxide, and water vapor (Saidur et al. 2011). This gas is consumed to emit heat or convert into electricity and in gas-turbine systems (McKendry 2002). The syngas could be also used to generate methanol and hydrogen fuel for transport and other applications (Saidur et al. 2011), although the production cost from methane and marine biomass is theoretically estimated at 1.5–4 times more compared to the production cost of fossil fuel gas. In the gasification process, pyrolysis is done initially in a reaction producing char, then gasified with a gasifying agent such as O_2 or H_2O to produce syngas. Here, biomass reacts with oxygen and steam water to produce syngas. Different marine algal feedstocks like *Ulva lactuca* (Nikolaison et al. 2012), *S. latissimi* (Cherad et al. 2013), *S. japonica* (Kwon et al. 2012) can be used for syngas production through the gasification process.

7.7 New Opportunities for Biofuels and Advantages of Producing Biofuel from Marine Algae

There is a growing concern for increasing energy requirements on a global scale. To satisfy these excess energy needs, marine biotechnology was dedicated to providing an important contribution in very different ways. Moreover, the global production of oil was saturated and people are searching for an alternative option to fossil fuel. Therefore, biofuel is considered as a leading energy source for the future. The biofuel production from marine algae indicates a huge potentiality to be an alternative energy source replacing fossil fuel. Growing evidence suggest that marine microalgae and macroalgae, especially seaweeds are suitable sources for biofuel production. Microalgae can contain enough hydrophobic compounds that are converted into biodiesel. So, biodiesel production from microalgal tri-acylglycerides is much more focused on the biofuel industry. Some of the other advantages include:

1. The marine algal biomass are a huge and superior feedstock that act as an alternative to terrestrial biomass for bioenergy production (Chen et al. 2015).
2. These algae uptake enormous greenhouse gas and release extra oxygen while growing (Bharathiraja et al. 2015).
3. They are non-edible sources and so there exists no competition.
4. The algal species are a highly biodegradable resource with rapid bioremediation and are non-toxic (Chen et al. 2015).
5. They show rapid growth and result in high growth yield and increased productivity (Abbasi and Abbasi 2010).
6. They have high energy conversion efficiency by photosynthesis (Huber et al. 2006).
7. Prevent eutrophication and pollution in the aquatic ecosystem (Huber et al. 2006).
8. They can easily be adaptable to a wide range of climatic conditions (Bharathiraja et al. 2015).
9. These biofuels act as sustainable and environment-friendly fuel and are highly effective to meet the present energy demand (Ziolkowska and Simon 2014).
10. The biofuel from algae has great reactivity and decreases hazardous emission (Abbasi and Abbasi 2010).
11. Diversification of fuel supply.

7.8 Challenges and Disadvantages of Using Algae and Algal Biofuel

There are many arguments for and against the use of algae and algal biofuel. Marine algae cultivation for bioenergy production is a great challenge indeed. Even though this technique has the potential to deliver clean energy, before commercial use science should find solutions to address some of the serious drawbacks associated with this technique. The main challenges or/and disadvantages of marine algal biofuel are mentioned below:

1. Understanding of microalgal biodiversity is needed to decipher at the molecular level and on a global scale.
2. Achievement of a net energy gain along the whole production chain necessary to convert microalgal biomass into biofuels.
3. Achievement of full sustainability of the whole production chain in terms of regional and global impact.
4. Increased initial production cost for growing, harvesting, collection, transportation, storage, and pretreatment (Bharathiraja et al. 2015).

Lack of monitoring and algal growth control for fuel production (Sharma et al. 2013).

1. Use of extra water for algae processing.
2. Low ash fusion temperature (Ross et al. 2008).
3. Limited practical experience in biofuel production (Ziolkowska and Simon 2014).

7.9 Conclusions

Globally, there is a much potential for biofuel market. Biofuel from marine algae has the potential to replace fossil-based petroleum, seems technically feasible and conversion of extracted lipid to biodiesel is relatively easy. The commercial-scale production of algal biofuels requires careful consideration of several issues that can be broadly categorized as: selection of high oil and biomass yielding algal species, cultivation and harvesting technology, water sources, and nutrient and growth inputs. The promising and clear potential of algal biofuels for contributing to environmental, social, and economic sustainability needs to be transformed into a sustainable reality. As yet, there is no commercial production of such biofuels due to the high production costs and technical issues concerning post-cultivation processing. Therefore, for strengthening the global economy, mitigating climate change, increasing the feasibility, and reducing the production cost, the sector still requires technological development. Finally, it is expected that the prospects for liquid biofuel production from autotrophic marine microalgae will much improve in the near future, especially using genetically modified microalgae.

References

Abbasi T, Abbasi SA (2010) Biomass energy and the environmental impacts associated with its production and utilization. Renew Sust Energ Rev 14(3):919–937

Abomohra AEF, Elshobary M (2019) Biodiesel, bioethanol, and biobutanol production from microalgae. In: *Microalgae biotechnology for development of biofuel and wastewater treatment*. Springer, Singapore, pp 293–321

Adams JM, Gallagher JA, Donnison IS (2009) Fermentation study on Saccharina latissima for bioethanol production considering variable pre-treatments. Journal of Applied Phycology 21 (5):569

Adewuyi YG (2001) Sonochemistry: environmental science and engineering applications. Ind Eng Chem Res 40(22):4681–4715

Amani T, Nosrati M, Sreekrishnan TR (2010) Anaerobic digestion from the viewpoint of microbiological, chemical, and operational aspects—a review. Environmental Reviews 18:255–278

Bae YJ, Ryu C, Jeon JK, Park J, Suh DJ, Suh YW, Chang D, Park YK (2011) The characteristics of bio-oil produced from the pyrolysis of three marine macroalgae. Bioresour Technol 102 (3):3512–3520

Balat M (2011) Challenges and opportunities for large-scale production of biodiesel. Energ Educ Sci Technol Part A 27:427–434

Barnwal BK, Sharma MP (2005) Prospects of biodiesel production from vegetable oils in India. Renew Sust Energ Rev 9(4):363–378

Baskar G, Abarna Ebenezer Selvakumari I, Aiswarya R (2018) Marine Algae – Future Source of Biofuels. Int J Mod Sci Technol 3(4):72–82

Becker W (2004) 21 microalgae for aquaculture. In: Handbook of microalgal culture: biotechnology and applied phycology. Wiley, Hoboken, NJ, p 380

Behera S, Singh R, Arora R, Sharma NK, Shukla M, Kumar S (2015) Scope of algae as third generation biofuels. Front Bioeng Biotechnol 2:90

Bharathiraja B, Chakravarthy M, Kumar RR, Yuvaraj D, Jayamuthunagai J, Kumar RP, Palani S (2014) Biodiesel production using chemical and biological methods–A review of process, catalyst, acyl acceptor, source and process variables. Renew Sust Energ Rev 38:368–382

Bharathiraja B, Chakravarthy M, Kumar RR, Yogendran D, Yuvaraj D, Jayamuthunagai J, Kumar RP, Palani S (2015) Aquatic biomass (algae) as a future feed stock for bio-refineries: a review on cultivation, processing and products. Renew Sust Energ Rev 47:634–653

Bird KT, Chynoweth DP, Jerger DE (1990) Effects of marine algal proximate composition on methane yields. J Appl Phycol 2(3):207–213

Bosma R, van Spronsen WA, Tramper J, Wijffels RH (2003) Ultrasound, a new separation technique to harvest microalgae. J Appl Phycol 15(2–3):143–153

Bozbas K (2008) Biodiesel as an alternative motor fuel: Production and policies in the European Union. Renew Sust Energ Rev 12(2):542–552

Brennan L, Owende P (2010) Biofuels from microalgae—a review of technologies for production, processing, and extractions of biofuels and co-products. Renew Sust Energ Rev 14(2):557–577

Briggs M (2004) Widescale biodiesel production from algae. University of New Hampshire. Physics Department, 5

Brown D, Shi J, Li Y (2012) Comparison of solid-state to liquid anaerobic digestion of lignocellulosic feedstocks for biogas production. Bioresour Technol 124:379–386

Campos EJ, Qureshi N, Blaschek HP (2002) Production of acetone butanol ethanol from degermed corn using Clostridium beijerinckii BA101. In: Biotechnology for fuels and chemicals. Humana Press, Totowa, NJ, pp 553–561

Cantrell KB, Ducey T, Ro KS, Hunt PG (2008) Livestock waste-to-bioenergy generation opportunities. Bioresour Technol 99(17):7941–7953

Cara C, Moya M, Ballesteros I, Negro MJ, González A, Ruiz E (2007) Influence of solid loading on enzymatic hydrolysis of steam exploded or liquid hot water pretreated olive tree biomass. Process Biochem 42(6):1003–1009

Carrere H, Antonopoulou G, Affes R, Passos F, Battimelli A, Lyberatos G, Ferrer I (2016) Review of feedstock pretreatment strategies for improved anaerobic digestion: from lab-scale research to full-scale application. Bioresour Technol 199:386–397

Castro YA (2014) Optimization of wastewater microalgae pretreatment for acetone, butanol, and ethanol fermentation. Theses and Dissertations, Utah State University

Chen CY, Zhao XQ, Yen HW, Ho SH, Cheng CL, Lee DJ, Bai FW, Chang JS (2013) Microalgae-based carbohydrates for biofuel production. Biochem Eng J 78:1–10

Chen H, Zhou D, Luo G, Zhang S, Chen J (2015) Macroalgae for biofuels production: Progress and perspectives. Renew Sust Energ Rev 47:427–437

Cherad R, Onwudili JA, Ekpo U, Williams PT, Lea-Langton AR, Carmargo-Valero M, Ross AB (2013) Macroalgae supercritical water gasification combined with nutrient recycling for microalgae cultivation. Environ Prog Sustain Energy 32(4):902–909

Chia SR, Ong HC, Chew KW, Show PL, Phang SM, Ling TC, Nagarajan D, Lee DJ, Chang JS (2018) Sustainable approaches for algae utilisation in bioenergy production. Renew Energy 129:838–852

Chiaramonti D, Oasmaa A, Solantausta Y (2007) Power generation using fast pyrolysis liquids from biomass. Renew Sust Energ Rev 11(6):1056–1086

Choi SP, Nguyen MT, Sim SJ (2010) Enzymatic pretreatment of Chlamydomonas reinhardtii biomass for ethanol production. Bioresour Technol 101(14):5330–5336

Choia JH, Woob HC, Suha DJ (2014) Pyrolysis of seaweeds for bio-oil and bio-char production. Chem Eng 37:121–126

Christy PM, Gopinath LR, Divya D (2014) A review on anaerobic decomposition and enhancement of biogas production through enzymes and microorganisms. Renew Sust Energ Rev 34:167–173

Collet P, Hélias A, Lardon L, Ras M, Goy RA, Steyer JP (2011) Life-cycle assessment of microalgae culture coupled to biogas production. Bioresour Technol 102(1):207–214

Cravotto G, Boffa L, Mantegna S, Perego P, Avogadro M, Cintas P (2008) Improved extraction of vegetable oils under high-intensity ultrasound and/or microwaves. Ultrason Sonochem 15 (5):898–902

Cucchiella F, D’Adamo I (2016) Technical and economic analysis of biomethane: a focus on the role of subsidies. Energy Convers Manag 119:338–351

Davis SC, Anderson-Teixeira KJ, DeLucia EH (2009) Life-cycle analysis and the ecology of biofuels. Trends Plant Sci 14(3):140–146

Demirbas A (2005) Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. Prog Energy Combust Sci 31(5-6):466–487

Demirbas A (2009) Biofuels securing the planet’s future energy needs. Energy Convers Manag 50 (9):2239–2249

Demirbas A (2011a) High quality water supply for the production of algae. Energ Educ Sci Technol Part A 27(2):467–476

Demirbas MF (2011b) Biofuels from algae for sustainable development. Appl Energy 88 (10):3473–3480

Domozych D, Ciancia M, Fangel JU, Mikkelsen MD, Ulvskov P, Willats WG (2012) The cell walls of green algae: a journey through evolution and diversity. Front Plant Sci 3:82

Dürre P (2007) Biobutanol: an attractive biofuel. Biotechnol J 2:1525–1534. https://doi.org/10.1002/biot.200700168

Ellis JT, Hengge NN, Sims RC, Miller CD (2012) Acetone, butanol, and ethanol production from wastewater algae. Bioresour Technol 111:491–495

Enzmann F, Mayer F, Rother M, Holtmann D (2018) Methanogens: biochemical background and biotechnological applications. AMB Express 8(1):1–22

Fahmi R, Bridgwater AV, Donnison I, Yates N, Jones JM (2008) The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. Fuel 87(7):1230–1240

Farrell AE, Plevin RJ, Turner BT, Jones AD, O'hare M, Kammen DM (2006) Ethanol can contribute to energy and environmental goals. Science 311(5760):506–508

Ferreira AF, Ortigueira J, Alves L, Gouveia L, Moura P, Silva C (2013) Biohydrogen production from microalgal biomass: energy requirement, CO_2 emissions and scale-up scenarios. Bioresour Technol 144:156–164

Gao K (2016) ABE fermentation from low cost substrates. Electronic Thesis and Dissertation Repository. 4087. https://ir.lib.uwo.ca/etd/4087

Girardet H, Mendonça M (2009) A renewable world: energy, ecology and equality. A report for the world future council. Green Books & Resurgence Books, Cambridge, UK

Gloria M, Colmenares M, Catholic P (2013) Biofuels potential of Peru. The University of Queensland, Australia, p 211

Gouveia L, Oliveira AC (2009) Microalgae as a raw material for biofuels production. J Ind Microbiol Biotechnol 36(2):269–274

Guiot SR, Frigon JC (2012) Anaerobic digestion as an effective biofuel production technology. In: Microbial technologies in advanced biofuels production. Springer, Boston, MA, pp 143–161

Gurung A, Van Ginkel SW, Kang WC, Qambrani NA, Oh SE (2012) Evaluation of marine biomass as a source of methane in batch tests: a lab-scale study. Energy 43(1):396–401

Hamelinck CN, Van Hooijdonk G, Faaij AP (2005) Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle-and long-term. Biomass Bioenergy 28(4):384–410

Harun R, Danquah MK (2011) Influence of acid pre-treatment on microalgal biomass for bioethanol production. Process Biochem 46(1):304–309

Haye S, Hardtke CS (2009) The roundtable on sustainable biofuels: plant scientist input needed. Trends Plant Sci 14(8):409–412

Heger M (2009) A new processing scheme for algae biofuels. Technology review. http://www.technologyreview.com/energy/22572

Hemming D (ed) (2011) *Plant sciences reviews 2010*. Cabi, Wallingford

Hernando J, Leton P, Matia MP, Novella JL, Alvarez-Builla J (2007) Biodiesel and FAME synthesis assisted by microwaves: homogeneous batch and flow processes. Fuel 86 (10-11):1641–1644

Ho SH, Nagarajan D, Ren NQ, Chang JS (2018) Waste biorefineries—integrating anaerobic digestion and microalgae cultivation for bioenergy production. Curr Opin Biotechnol 50:101–110

Hönig V, Kotek M, Mařík J (2014) Use of butanol as a fuel for internal combustion engines. Agron Res 12(2):333–340

Horn SJ, Aasen IM, Østgaard K (2000) Ethanol production from seaweed extract. J Ind Microbiol Biotechnol 25(5):249–254

Huang H, Yuan X, Zeng G, Wang J, Li H, Zhou C, Pei X, You Q, Chen L (2011) Thermochemical liquefaction characteristics of microalgae in sub-and supercritical ethanol. Fuel Process Technol 92(1):147–153

Huber GW, Iborra S, Corma A (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem Rev 106(9):4044–4098

Huesemann M, Roesjadi G, Benemann J, Metting FB (2010) Biofuels from microalgae and seaweeds. Biomass to Biofuels 1:165–184

Iliopoulou EF, Antonakou EV, Karakoulia SA, Vasalos IA, Lappas AA, Triantafyllidis KS (2007) Catalytic conversion of biomass pyrolysis products by mesoporous materials: effect of steam stability and acidity of Al-MCM-41 catalysts. Chem Eng J 134(1–3):51–57

Jankowska E, Sahu AK, Oleskowicz-Popiel P (2017) Biogas from microalgae: review on microalgae's cultivation, harvesting and pretreatment for anaerobic digestion. Renew Sust Energ Rev 75:692–709

Ji J, Wang J, Li Y, Yu Y, Xu Z (2006) Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics 44:e411–e414

Jin C, Yao M, Liu H, Chia-fon FL, Ji J (2011) Progress in the production and application of n-butanol as a biofuel. Renew Sust Energ Rev 15(8):4080–4106

Jones CS, Mayfield SP (2012) Algae biofuels: versatility for the future of bioenergy. Curr Opin Biotechnol 23(3):346–351

Khambhaty Y, Mody K, Gandhi MR, Thampy S, Maiti P, Brahmbhatt H, Eswaran K, Ghosh PK (2012) Kappaphycus alvarezii as a source of bioethanol. Bioresour Technol 103(1):180–185

Kim NJ, Li H, Jung K, Chang HN, Lee PC (2011) Ethanol production from marine algal hydrolysates using Escherichia coli KO11. Bioresour Technol 102(16):7466–7469

Klass DL (1998) *Biomass for renewable energy, fuels, and chemicals*. Elsevier, Amsterdam

Kumar D, Murthy GS (2013) Stochastic molecular model of enzymatic hydrolysis of cellulose for ethanol production. Biotechnol Biofuels 6(1):63

Kumar S, Gupta R, Kumar G, Sahoo D, Kuhad RC (2013) Bioethanol production from Gracilaria verrucosa, a red alga, in a biorefinery approach. Bioresour Technol 135:150–156

Kumar P, Mehariya S, Ray S, Mishra A, Kalia VC (2015) Biodiesel industry waste: a potential source of bioenergy and biopolymers. Indian J Microbiol 55(1):1–7

Kwon EE, Jeon YJ, Yi H (2012) New candidate for biofuel feedstock beyond terrestrial biomass for thermo-chemical process (pyrolysis/gasification) enhanced by carbon dioxide (CO2). Bioresour Technol 123:673–677

Laghari SM, Isa MH, Saleem H (2014) Microwave individual and combined pre-treatments on lignocellulosic biomasses. IOSR J Eng 4(2):14–28

Laza T, Bereczky Á (2011) Basic fuel properties of rapeseed oil-higher alcohols blends. Fuel 90 (2):803–810

Lee SM, Lee JH (2012) Ethanol fermentation for main sugar components of brown-algae using various yeasts. J Ind Eng Chem 18(1):16–18

Lee HY, Lee SE, Jung KH, Yeon JH, Choi WY (2011) Repeated-batch operation of surface-aerated fermentor for bioethanol production from the hydrolysate of seaweed Sargassum sagamianum. J Microbiol Biotechnol 21(3):323–331

Li Y, Horsman M, Wu N, Lan CQ, Dubois-Calero N (2008) Biofuels from microalgae. Biotechnol Prog 24(4):815–820

Li SY, Srivastava R, Suib SL, Li Y, Parnas RS (2011a) Performance of batch, fed-batch, and continuous A–B–E fermentation with pH-control. Bioresour Technol 102(5):4241–4250

Li Y, Park SY, Zhu J (2011b) Solid-state anaerobic digestion for methane production from organic waste. Renew Sust Energ Rev 15(1):821–826

Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, Mingdong D (2011) Opportunities and challenges for biodiesel fuel. Appl Energy 88(4):1020–1031

Lora EES, Palacio JCE, Rocha MH, Renó MLG, Venturini OJ, Del Olmo OA (2011) Issues to consider, existing tools and constraints in biofuels sustainability assessments. Energy 36 (4):2097–2110

Macquarrie DJ, Clark JH, Fitzpatrick E (2012) The microwave pyrolysis of biomass. Biofuels Bioprod Biorefin 6(5):549–560

Marchetti JM, Miguel VU, Errazu AF (2007) Possible methods for biodiesel production. Renew Sust Energ Rev 11(6):1300–1311

Mata TM, Martins AA, Caetano NS (2010) Microalgae for biodiesel production and other applications: a review. Renew Sust Energ Rev 14(1):217–232

McKendry P (2002) Energy production from biomass (part 2): conversion technologies. Bioresour Technol 83(1):47–54

Meher LC, Sagar DV, Naik SN (2006) Technical aspects of biodiesel production by transesterification—a review. Renew Sust Energ Rev 10(3):248–268

Mercer P, Armenta RE (2011) Developments in oil extraction from microalgae. Eur J Lipid Sci Technol 113(5):539–547

Millat T, Janssen H, Thorn GJ, King JR, Bahl H, Fischer RJ, Wolkenhauer O (2013) A shift in the dominant phenotype governs the pH-induced metabolic switch of Clostridium acetobutylicumin phosphate-limited continuous cultures. Appl Microbiol Biotechnol 97(14):6451–6466

Miranda I, Gominho J, Pereira H (2012) Incorporation of bark and tops in Eucalyptus globulus wood pulping. Bioresources 7(3):4350–4361

Mohn FH (1980) Experiences and strategies in the recovery of biomass from mass cultures of microalgae. In: Shelef G, Soeder CJ (eds) Algae biomass: production and use. Elsevier/North-Holland Biomedical Press, Amsterdam

Molina Grima E, Acién Fernández FG, García Camacho F, Chisti Y (1999) Photobioreactors: light regime, mass transfer, and scaleup. J Biotechnol 70(1-3):231–247

Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch M (2005) Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol 96 (6):673–686

Mubarak M, Shaija A, Suchithra TV (2015) A review on the extraction of lipid from microalgae for biodiesel production. Algal Res 7:117–123

Mussatto SI, Dragone G, Guimarães PM, Silva JPA, Carneiro LM, Roberto IC, Vicente A, Domingues L, Teixeira JA (2010) Technological trends, global market, and challenges of bio-ethanol production. Biotechnol Adv 28(6):817–830

Mussgnug JH, Klassen V, Schlüter A, Kruse O (2010) Microalgae as substrates for fermentative biogas production in a combined biorefinery concept. J Biotechnol 150(1):51–56

Nagarajan D, Lee DJ, Chang JS (2019) Biogas upgrading by microalgae: strategies and future perspectives. In: Microalgae biotechnology for development of biofuel and wastewater treatment. Springer, Singapore, pp 347–395

Nigam PS, Singh A (2011) Production of liquid biofuels from renewable resources. Prog Energ Combust Sci 37(1):52–68

Nikolaison L, Dahl J, Bech KS, Bruhn A, Rasmussen MB, Bjerre AB, Nielsen HB, Ambus P, Rost KA, Kadar Z (2012) Energy production from macroalgae. In Proceedings of the 20th European Biomass Conference, Milan, Italy. pp 18–22

Nüchter M, Ondruschka B, Jungnickel A, Müller U (2000) Organic processes initiated by non-classical energy sources. J Phys Org Chem 13(10):579–586

Okuda K, Oka K, Onda A, Kajiyoshi K, Hiraoka M, Yanagisawa K (2008) Hydrothermal fractional pretreatment of sea algae and its enhanced enzymatic hydrolysis. J Chem Technol Biotechnol: Int Res Process, Environ Clean Technol 83(6):836–841

Oyedun AO, Lam KL, Gebreegziabher T, Lee HKM, Hui CW (2012) Optimisation of operating parameters in multi-stage pyrolysis. Chem Eng Trans 29:655–660

Park JH, Yoon JJ, Park HD, Kim YJ, Lim DJ, Kim SH (2011) Feasibility of biohydrogen production from Gelidium amansii. Int J Hydrogen Energy 36(21):13997–14003

Park JH, Hong JY, Jang HC, Oh SG, Kim SH, Yoon JJ, Kim YJ (2012) Use of Gelidium amansii as a promising resource for bioethanol: a practical approach for continuous dilute-acid hydrolysis and fermentation. Bioresour Technol 108:83–88

Petrusevski B, Bolier G, Van Breemen AN, Alaerts GJ (1995) Tangential flow filtration: a method to concentrate freshwater algae. Water Res 29(5):1419–1424

Pfromm PH, Amanor-Boadu V, Nelson R, Vadlani P, Madl R (2010) Bio-butanol vs. bio-ethanol: a technical and economic assessment for corn and switchgrass fermented by yeast or Clostridium acetobutylicum. Biomass Bioenergy 34(4):515–524

Pogson M, Hastings A, Smith P (2013) How does bioenergy compare with other land-based renewable energy sources globally? GCB Bioenergy 5(5):513–524

Porphy SJ, Farid MM (2012) Feasibility study for production of biofuel and chemicals from marine microalgae Nannochloropsis sp. based on basic mass and energy analysis. ISRN Renewable Energy 2012:156824

Pospíšil M, Šiška J, Šebor G (2014) Biobutanol as fuel in transport, Biom. www.biom.cz. Accessed 17 Jan 2014

Potts T, Du J, Paul M, May P, Beitle R, Hestekin J (2012) The production of butanol from Jamaica bay macro algae. Environ Prog Sustain Energy 31(1):29–36

Prajapati SK, Kaushik P, Malik A, Vijay VK (2013) Phycoremediation coupled production of algal biomass, harvesting and anaerobic digestion: possibilities and challenges. Biotechnol Adv 31 (8):1408–1425

Qureshi N, Li XL, Hughes S, Saha BC, Cotta MA (2006) Butanol production from corn fiber xylan using Clostridium acetobutylicum. Biotechnol Prog 22(3):673–680

Rajkumar R, Yaakob Z, Takriff MS (2014) Potential of micro and macro algae for biofuel production: a brief review. Bioresources 9(1):1606–1633

Ras M, Lardon L, Bruno S, Bernet N, Steyer JP (2011) Experimental study on a coupled process of production and anaerobic digestion of Chlorella vulgaris. Bioresour Technol 102(1):200–206

Romagnoli F, Blumberga D, Gigli E (2010) Biogas from marine macroalgae: a new environmental technology—life cycle inventory for a further LCA. Environ Climate Technol 4(1):97–108

Ross AB, Jones JM, Kubacki ML, Bridgeman T (2008) Classification of macroalgae as fuel and its thermochemical behaviour. Bioresour Technol 99(14):6494–6504

Saady NMC (2013) Homoacetogenesis during hydrogen production by mixed cultures dark fermentation: unresolved challenge. Int J Hydrogen Energy 38(30):13172–13191

Saidur R, Abdelaziz EA, Demirbas A, Hossain MS, Mekhilef S (2011) A review on biomass as a fuel for boilers. Renew Sust Energ Rev 15(5):2262–2289

Saleem M, Chakrabarti MH, Raman AAA, Daud WMAW, Mustafa A (2012) Hydrogen production by Chlamydomonas reinhardtii in a two-stage process with and without illumination at alkaline pH. Int J Hydrogen Energy 37(6):4930–4934

Saqib A, Tabbssum MR, Rashid U, Ibrahim M, Gill SS, Mehmood MA (2013) Marine macroalgae Ulva: a potential feed-stock for bioethanol and biogas production. Asian J Agri Biol 1 (3):155–163

Saxena RC, Adhikari DK, Goyal HB (2009) Biomass-based energy fuel through biochemical routes: A review. Renew Sust Energ Rev 13(1):167–178

Schultz-Jensen N, Thygesen A, Leipold F, Thomsen ST, Roslander C, Lilholt H, Bjerre AB (2013) Pretreatment of the macroalgae Chaetomorpha linum for the production of bioethanol–comparison of five pretreatment technologies. Bioresour Technol 140:36–42

Shaheen R, Shirley M, Jones DT (2000) Comparative fermentation studies of industrial strains belonging to four species of solvent-producing clostridia. J Mol Microbiol Biotechnol 2 (1):115–124

Shaishav S, Singh RN, Satyendra T (2013) Biohydrogen from algae: fuel of the future. Int Res J Environ Sci 2(4):44–47

Sharma B, Ingalls RG, Jones CL, Khanchi A (2013) Biomass supply chain design and analysis: Basis, overview, modeling, challenges, and future. Renew Sust Energ Rev 24:608–627

Sheehan J, Dunahay T, Benemann J, Roessler P (1998) A look back at the US Department of Energy's aquatic species program: biodiesel from algae. Natl Renew Energy Lab 328:1–294

Shi X, Jung KW, Kim DH, Ahn YT, Shin HS (2011) Direct fermentation of Laminaria japonica for biohydrogen production by anaerobic mixed cultures. Int J Hydrogen Energy 36 (10):5857–5864

Shuba ES, Kifle D (2018) Microalgae to biofuels: 'Promising' alternative and renewable energy, review. Renew Sust Energ Rev 81:743–755

Sims RE, Mabee W, Saddler JN, Taylor M (2010) An overview of second generation biofuel technologies. Bioresour Technol 101(6):1570–1580

Singh A, Olsen SI (2011) A critical review of biochemical conversion, sustainability and life cycle assessment of algal biofuels. Appl Energy 88(10):3548–3555

Singh A, Nigam PS, Murphy JD (2011) Mechanism and challenges in commercialisation of algal biofuels. Bioresour Technol 102(1):26–34

Stavarache C, Vinatoru M, Maeda Y (2006) Ultrasonic versus silent methylation of vegetable oils. Ultrason Sonochem 13(5):401–407

Stephens E, Ross IL, Hankamer B (2013) Expanding the microalgal industry–continuing controversy or compelling case? Curr Opin Chem Biol 17(3):444–452

Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 83(1):1–11

Takeda H, Yoneyama F, Kawai S, Hashimoto W, Murata K (2011) Bioethanol production from marine biomass alginate by metabolically engineered bacteria. Energy Environ Sci 4 (7):2575–2581

Talebnia F, Karakashev D, Angelidaki I (2010) Production of bioethanol from wheat straw: an overview on pretreatment, hydrolysis and fermentation. Bioresour Technol 101(13):4744–4753

Tao L, Aden A, Elander RT, Pallapolu VR, Lee YY, Garlock RJ, Balan V, Dale BE, Kim Y, Mosier NS, Ladisch MR (2011) Process and technoeconomic analysis of leading pretreatment technologies for lignocellulosic ethanol production using switchgrass. Bioresour Technol 102 (24):11105–11114

Tedesco S, Barroso TM, Olabi AG (2014) Optimization of mechanical pre-treatment of Laminariaceae spp. biomass-derived biogas. Renew Energy 62:527–534

Tsukahara K, Sawayama S (2005) Liquid fuel production using microalgae. J Jpn Pet Inst 48(5):251

Ueno Y, Kurano N, Miyachi S (1998) Ethanol production by dark fermentation in the marine green alga, Chlorococcum littorale. J Ferment Bioeng 86(1):38–43

Vaishnavi J, Arulprakash A, Selvi A, Rajasekar A (2020) Marine biomass toward biofuel production. In: Refining biomass residues for sustainable energy and bioproducts. Academic Press, Cambridge, MA, pp 451–462

van der Wal H, Sperber BL, Houweling-Tan B, Bakker RR, Brandenburg W, López-Contreras AM (2013) Production of acetone, butanol, and ethanol from biomass of the green seaweed Ulva lactuca. Bioresour Technol 128:431–437

Vivekanand V, Eijsink VG, Horn SJ (2012) Biogas production from the brown seaweed Saccharina latissima: thermal pretreatment and codigestion with wheat straw. J Appl Phycol 24 (5):1295–1301

Wang B, Li Y, Wu N, Lan CQ (2008) CO_2 bio-mitigation using microalgae. Appl Microbiol Biotechnol 79(5):707–718

Wang X, Liu X, Wang G (2011) Two-stage Hydrolysis of Invasive Algal Feedstock for Ethanol Fermentation F. J Integr Plant Biol 53(3):246–252

Wang Y, Janssen H, Blaschek HP (2014) Fermentative biobutanol production: an old topic with remarkable recent advances. In: Bioprocessing of renewable resources to commodity bioproducts. Wiley, Hoboken NJ, pp 227–260

Wang Y, Guo W, Cheng CL, Ho SH, Chang JS, Ren N (2016) Enhancing bio-butanol production from biomass of Chlorella vulgaris JSC-6 with sequential alkali pretreatment and acid hydrolysis. Bioresour Technol 200:557–564

Ward AJ, Lewis DM, Green FB (2014) Anaerobic digestion of algae biomass: a review. Algal Res 5:204–214

Weiland P (2010) Biogas production: current state and perspectives. Appl Microbiol Biotechnol 85 (4):849–860

Widjaja A, Chien CC, Ju YH (2009) Study of increasing lipid production from fresh water microalgae Chlorella vulgaris. J Taiwan Inst Chem Eng 40(1):13–20

Yacoby I, Pochekailov S, Toporik H, Ghirardi ML, King PW, Zhang S (2011) Photosynthetic electron partitioning between [FeFe]-hydrogenase and ferredoxin: NADP+-oxidoreductase (FNR) enzymes in vitro. Proc Natl Acad Sci 108(23):9396–9401

Yanagisawa M, Nakamura K, Ariga O, Nakasaki K (2011) Production of high concentrations of bioethanol from seaweeds that contain easily hydrolyzable polysaccharides. Process Biochem 46(11):2111–2116

Ye R, Jin Q, Bohannan B, Keller JK, Bridgham SD (2014) Homoacetogenesis: A potentially underappreciated carbon pathway in peatlands. Soil Biol Biochem 68:385–391

Yoshida T, Tashiro Y, Sonomoto K (2012) Novel high butanol production from lactic acid and pentose by Clostridium saccharoperbutylacetonicum. J Biosci Bioeng 114(5):526–530

Zabed HM, Qi X, Yun J, Zhang H (2019) Anaerobic digestion of microalgae biomass for methane production. In: Microalgae biotechnology for development of biofuel and wastewater treatment. Springer, Singapore, pp 397–421

Zhao G, Chen X, Wang L, Zhou S, Feng H, Chen WN, Lau R (2013) Ultrasound assisted extraction of carbohydrates from microalgae as feedstock for yeast fermentation. Bioresour Technol 128:337–344

Zhong W, Zhang Z, Luo Y, Qiao W, Xiao M, Zhang M (2012) Biogas productivity by co-digesting Taihu blue algae with corn straw as an external carbon source. Bioresour Technol 114:281–286

Ziolkowska JR, Simon L (2014) Recent developments and prospects for algae-based fuels in the US. Renew Sust Energ Rev 29:847–853