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Review

Algae as potential feedstock for the production of biofuels and value-added products: Opportunities and challenges

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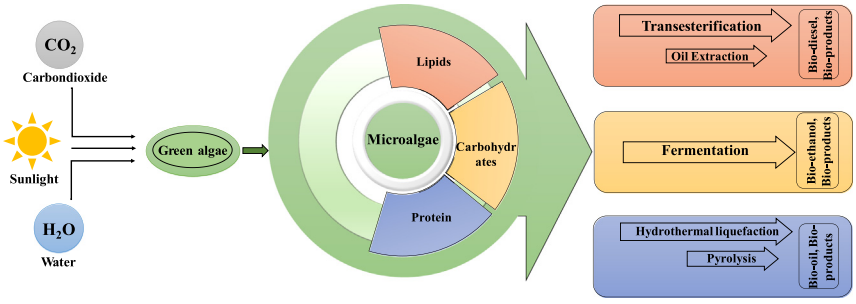
HIGHLIGHTS

- Critical analysis of pathways involves in bio-valorization of algal biomass.
- Mass of 1 kg oils extracted from algal biomass can produce 1 kg biodiesel.
- The yields of biochar per unit dry weight of algal biomass are in the range of 8.1–62.4%.
- The foremost challenges in production of 3rd generation biofuel are its non-cost effectiveness.

GRAPHICAL ABSTRACT



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ABSTRACT

The current review explores the potential application of algal biomass for the production of biofuels and bio-based products. The variety of processes and pathways through which bio-valorization of algal biomass can be performed are described in this review. Various lipid extraction techniques from algal biomass along with transesterification reactions for biodiesel production are briefly discussed. Processes such as the pretreatment and saccharification of algal biomass, fermentation, gasification, pyrolysis, hydrothermal liquefaction, and anaerobic digestion for the production of biohydrogen, bio-oils, biomethane, biochar (BC), and various bio-based products are reviewed in detail. The biorefinery model and its collaborative approach with various processes are highlighted for the production of eco-friendly, sustainable, and cost-effective biofuels and value-added products. The authors also discuss opportunities and challenges related to bio-valorization of algal biomass and use their own perspective regarding the processes involved in production and the feasibility to make algal research a reality for the production of biofuels and bio-based products in a sustainable manner.

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Contents

1. Introduction

Energy demands are increasing worldwide due to industrialization and modernization, leading to the over exploitation of limited available natural fuel reserves (Kumar et al., 2019; Kumar and Thakur, 2018). The production of bioenergy from biomass has recently gained attention due to the availability of biomass, the limited availability of fossil fuels, and the increasing concentration of carbon dioxide (CO_2) and other greenhouse gases (GHGs) in the environment (Kumar et al., 2018; Thakur et al., 2018). The search for alternate clean energy technologies to meet future energy demands is a major challenge considering the increasing GHG emissions and socioeconomic stability (Kumar and Thakur, 2018), imposing challenging questions about the development and adoption of new technologies for the production of biofuels and value-added products from biomass (Abdullah et al., 2019).

The production of biofuels from different biomasses concerns not only its production but also its cost-effectiveness, environmental sustainability, and minimization of waste generation during the operation (Srivastava, 2019; Kumar et al., 2016). Biofuels will play crucial roles in the near future by targeting the large fuel market and maintaining global energy security (Abdullah et al., 2019). Presently, the contribution of fossil fuels is nearly 70% of the total worldwide energy market, compared to the worldwide electricity demand, which contributes only 30% (www.iea.org, 2018). The importance of fuels is very well understood, but presently most technologies are under development for the generation of electricity from CO_2-free energy sources, such as photovoltaic, nuclear, geothermal, wind, wave, and hydroelectric sources (www.worldenergy.org, 2016; Medipally et al., 2015). Assuming the above circumstances, we can apply the potential use of biomass for the production of valuable fuels such as electricity, liquids or gaseous fuels. Various potential feedstocks have been used for the production of biofuels to reduce the dependency on conventional fossil fuels (Abdullah et al., 2019; Shuba and Kifle, 2018; Cao et al., 2018; Yu et al., 2019). The production of 1st generation biofuels is mainly dependent on the biomass of plants such as corn, soybean, sugarcane, and oil-palm, among others (Shuba and Kifle, 2018; Chen et al., 2017; Yu and Tsang, 2017), but simultaneously their application also creates ecosystem damage, water crises, and food vs fuel debates. Considering the problems related to 1st generation biofuels, the 2nd and 3rd generations have become alternative options, which are respectively produced from waste materials (plant and agricultural waste, municipal sludge) and microorganisms without disrupting the natural environment (Shuba and Kifle, 2018; Kumar et al., 2016, 2018).

Microorganisms such as cyanobacteria, bacteria, and microalgae can be applied as potential feedstocks for the production of biofuels and biomaterials in a cost-effective and sustainable manner, and they provide the opportunity to replace societal demands for fossil fuels (Abdullah et al., 2019; Shuba and Kifle, 2018; Kumar et al., 2017b). Most algae are aquatic photosynthetic organisms, but a few are terrestrial. They can produce biomass that is mainly composed of lipids, carbohydrates, and proteins using sunlight and CO_2 (Panahi et al., 2019). It has been estimated that 1.83 kg of CO_2 is required to produce 1 kg algal biomass (Khan et al., 2018). Numerous advantages makes algae and cyanobacteria potential candidates for the production of biomaterials and biofuels, such as (1) the use of water as an electron donor to perform oxygenic photosynthesis, (2) very high per-acre biomass productivity compared to oily seed crops, (3) ability to resolve food vs fuels debates as they are a nonfood feedstock, (4) no requirement for arable and productive agricultural land for cultivation, (5) adaption to growth in brackish water, seawater, and wastewater, and (6) production of a diverse range of products (De Bhowmick et al., 2019; Khan et al., 2018; Shin et al., 2018; Nguyen and Hoang, 2016). Several investigations have confirmed the ranges of fuels produced by algae and cyanobacteria, such as biohydrogen (H_2), fatty acids for the production of biodiesel and jet fuel, gasoline from hydrocarbons and isoprenoids, and bioethanol from algal extracted carbohydrates (De Bhowmick et al., 2019; Khan et al., 2018). Additionally, whole algal biomass can also be utilized in the production of syngas by the Fischer-Tropsch process, H_2 and methane (CH_4) production by hydrothermal gasification (HTL), CH_4 production by anaerobic digestion, and electricity production by co-combustion (De Bhowmick et al., 2019; Shuba and Kifle, 2018). Hence, for the future production of sustainable bioenergy and biomaterials, algae can be applied as a potential feedstock. In this context, several published research studies and reviews describe the technologies applied in the biovalorization of algal biomass, but its economic feasibility remains a challenge. Prior to scaling up this technology, several challenges, including biotechnological, economic, and environmental issues, must be overcome.

Considering the above discussion, the focus of the present review is to provide a framework for the use of microalgae as a potential source of

future biofuels and value-added products (biohydrogen, bioethanol, biodiesel, biomethane, BC, and pharmaceuticals). A detailed discussion is provided regarding the methods involved in the conversion of algal biomass to biofuels and co-products, along with opportunities and challenges.

2. Types of biofuels based on feedstock

Increasing energy demands, especially in industrial and transportation sectors; rising fuel prices; environmental pollution; and limited availability of fossil fuel reserves have led to the development of various social, economic, and environmental issues (Mathimani et al., 2019; Thakur et al., 2018; Nguyen and Hoang, 2016). To address these issues, communities worldwide must develop sustainable and ecofriendly biomaterial production technologies with a major emphasis on biofuel (Kumar and Thakur, 2018). Compared to conventional energy sources to meet and fulfil energy demands, such as solar, water, wind, and nuclear power, the production of bioenergy from biomass is gaining more attention due to the production of biofuels along with other high-end products and oleochemicals by applying a biorefinery approach (Michalak et al., 2019; www.worldenergy.org, 2016). Based on the feedstock, three generations of biofuels have been developed. The 1st generation biofuel was produced from oleaginous plants parts such as seeds grains, among others (Kuila and Sharma, 2017); the fuels produced from nonedible plants or their parts and from municipal, industrial, and household waste are called 2nd generation biofuels (Abdullah et al., 2019); and 3rd generation biofuels are based on bioenergy generated from microorganisms such as microalgae or macroalgae and cyanobacteria (Khan et al., 2018).

The microalgal biomass, which is mainly composed of carbohydrates and lipids, is produced by sunlight light, CO_2, and certain micronutrients such as nitrogen, phosphorus, and potassium. These carbohydrate and lipid components are raw materials for the production of a range of biofuels and biomaterials (Robak and Balcerek, 2018). Additionally, a small amount of hemicellulose and negligible lignin in the algal biomass escape the pretreatment process and enhance its hydrolysis and fermentation efficiency (Chandra et al., 2019). Moreover, along with biofuel production, algal biomass can also be used in the production of human nutrients, biofertilizers, animal feed, and waste water treatment (Mathimani et al., 2019; Behera et al., 2015). Due to the oleaginous nature of the algal biomass compared with oil seed plants, it is a forthcoming candidate for the production of biofuels and biomaterials by the adoption of various processes and technologies, as described in detail below.

3. Cultivation of algal biomass for biofuels and co-products

Cultivation of algal biomass can be performed by three approaches: photoautotrophic, heterotrophic, and mixotrophic methods (Hammed et al., 2016). There are three essential requirements in the photoautotrophic mode of algal cultivation: the source of carbon (CO_2), energy (light), and nutrients, by which CO_2 is converted into chemical energy (Nie et al., 2019). The sources of carbon and light are the key factors influencing the maximum algal growth. Microalgae use atmospheric CO_2 as the sole carbon source, so it is highly recommended that the cultivation zone be closer to power plants or factories (Nie et al., 2019). In comparison to the photoautotrophic cultivation method, the heterotrophic mode of cultivation uses a diverse range of organic compounds as sources of carbon as well as energy (Wang et al., 2014). The heterotrophic approach of algal cultivation mainly requires water, a carbon source and an inorganic salt source (Venkata Mohan et al., 2015). The main advantage of the heterotrophic approach is that no external light source is required, which overcomes the light limitation of the photoautotrophic approach (Liang, 2013). Zheng et al. (2012) reported that, in comparison to photoautotrophic cultivation, heterotrophic cultivation produced better growth and a higher yield. Nevertheless, the heterotrophic mode of cultivation has also demonstrated some limitations such as the following: (i) the process is not cost-effective due to the cost associated with the carbon source; (ii) not all microalgae can be cultivated via heterotrophic processes; (iii) there is a higher chance of contamination (Zhan et al., 2017; Nie et al., 2019). Microalgae can also be cultivated via the mixotrophic method, which combines photoautotrophic and heterotrophic cultivation (Nie et al., 2019). Hence, both inorganic and organic components can be applied this process. In comparison to the other two approaches, the mixotrophic approach overcomes the light limitation as well as the carbon source issue of the phototrophic method; additionally, this method reduces the generation time and enhances the yield of biomass (Wan et al., 2011). The energy efficiency of the mixotrophic method is better than the phototrophic method but poorer than the heterotrophic method, and the mixotrophic method requires a light source, CO_2, and an organic carbon source and oxygen supply (Lowrey et al., 2015; Zhan et al., 2017).

4. Processes for the conversion of algal biomass to 3rd generation biofuels and co-products

There are several pathways reported in the literature for the conversion of algal biomass into ranges of biofuels and value-added biomaterials, depending on the feasibility and cost-effectiveness of the process (Fig. 1). The feasibility of high-end products and biofuel production from algal biomass is mainly governed by effective extraction methods (Marrone et al., 2018; Shin et al., 2018). An effective extraction process should be more specific towards the extraction of particular bioproducts and simultaneously minimize impurities.

4.1. Lipid or oil extraction from algal biomass

The microalgal cell wall is enriched with fatty acids and lipids compared with that of higher animals and plants. Several methods can be applied to extract oils or lipids from algal biomass, such as physical, chemical, mechanical, and enzymatic (biological) methods (Fig. 2) (Shin et al., 2018; Ramanathan Ranjith Kumar et al., 2015; Li et al., 2014). The extraction of lipids by frequently used solvent extraction methods at the commercial level is not eco-friendly or economical, has adverse effects on human health, and changes the inherent quality of the end products (Kapoore et al., 2018). Ryckebosch et al. (2012) applied various solvent ratios for the extraction of lipids from four different algal biomass and reported that a 1:1 chloroform:methanol ratio (v/v) provided comparatively better yield. Other well-known, efficient traditional lipids extraction techniques include simple and cryogenic grinding with the help of liquid nitrogen, but they are not economical at the commercial level (Kapoore et al., 2018). In overall known mechanical lipid extraction methods, bead milling is considered the most efficient method because it has been applied to extract lipids from algal biomass with an optimal bead size of 0.5 mm (Kapoore, 2014). Nevertheless, this technique was ineffective for the extraction of lipids from *Chlorella vulgaris* biomass (Kapoore et al., 2018). The bead beating method is frequently used at the laboratory scale, and similarly agitated beads are applied at the commercial level for lipid extraction (Gong and Bassi, 2016). Nevertheless, the application of beads on a large scale makes the process of lipid extraction more complex and requires further processing; additionally, overheating is a major drawback of this method (Gong and Bassi, 2016).

For the extraction of oils from soybeans, mechanical pressing is applied, but due to the smaller size of the microorganisms, this method is not very effective (Kapoore et al., 2018). Autoclaving as well as homogenization methods have been recommended at smaller scales, but at the large scale these methods are again considered noneconomical (Gong and Bassi, 2016). Soxhlet is possibly the most commonly employed method for oil and lipid extraction from food biomass, as well as nutrient and chemical extraction from plant biomass (Kapoore et al., 2018). The use of toxic solvents in large amounts, longer

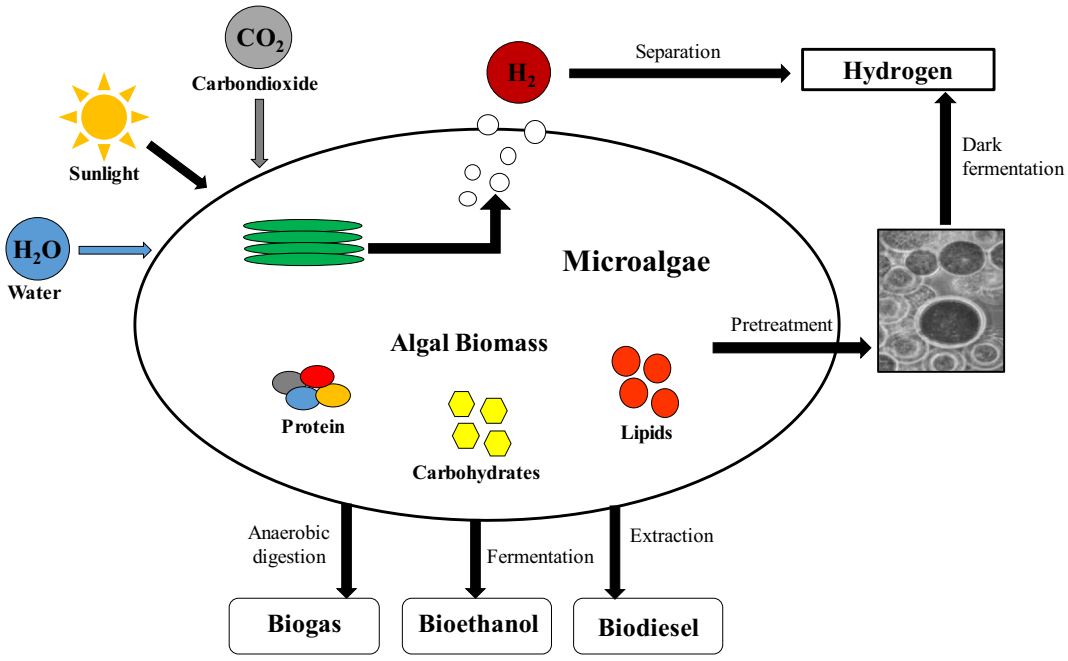

Fig. 1. Pathways for conversion of algal biomass in to biofuels and value-added products.

extraction times, and lower lipid yields make the process unfeasible (Mercer and Armenta, 2011). Several biological and chemical methods have been applied to avoid the application of toxic chemicals, but they also have several challenges such as the questionable purity of the end products, thus requiring further downstream processes (Kapoore et al., 2018). Several biological catalysts, such as pectinases, xylanases, and cellulase, are applied, but sometimes their lower catalytic activity and the economics of the processes are again challenging (Gong and Bassi, 2016).

To efficiently extract lipids from biomass, several innovative physical methods have been applied to date, such as supercritical fluid extraction (SFE) (Khaw et al., 2017), pressurized liquid extraction (PLE) (Gilbert-López et al., 2017), the nanosecond pulse electric field (nsPEF) (Hosseini et al., 2018), ultrasound-assisted extraction (Nogueira et al., 2018), and microwave-assisted extraction (de Moura et al., 2018). SFE has been recommended as an ecofriendly technology for the extraction of fatty acid components from biomass, in which CO_2 is applied as a solvent under supercritical conditions; similarly, PLE has also been applied for the extraction of polar and nonpolar lipids from oat and corn at high pressure using a diverse range of solvents (Esquivel-Hernández et al., 2017). Nevertheless, neither SFE or PLE are recommended for large scale application due to the increased energy requirements to maintain the higher operational temperature and pressure; additionally, this operation leads to degradation of the quality of end products at higher temperatures (Gil-Chávez et al., 2013). Hosseini et al. (2018) reported the extraction of the oil from *Botryococcus braunii* using nsPEF. Experimental findings suggested that 50 pulses with 16.7-J/mL energy consumption were sufficient for oil extraction, showing that the pulsed power approach could be used as an appropriate physical method for the extraction of oil; however, its large-scale application has not been evaluated. The operational frequency range of ultrasound is 20–100 MHz, which leads to the formation of cavitation bubbles, and the size of the bubbles further increases and causes cell wall rupture (Herrero et al., 2006). Bath sonication has been considered a more economically preferable option as it requires less power consumption in comparison to horn sonication (Al Hattab and Ghaly, 2015). Microwaves, compared with the traditional heating method, provide the advantage of rapid heating, and this process also dissipates less energy (Kapoore et al., 2018). The application of microwave-assisted extraction reduces extraction time and provides a better purity and yield of the products (de Moura et al., 2018). In comparison to other lipid extraction technologies, the microwave-assisted extraction method provides an eco-friendly technology by minimizing the use of solvents, and it seems to have practical feasibility for the extraction of fatty acid components and valuable chemicals from algal biomass (Kapoore et al., 2018).

4.2. Transesterification of lipids or oil

The process of transesterification of lipids or oil is performed in the presence of a chemical catalyst such as acid and alkali or a biological catalyst such as lipase along with alcohol, and the end products are biodiesel and glycerol (Kumar and Thakur, 2018; Kumar et al., 2017b; Khosla et al., 2017). Various alcohols as used as a co-solvent in the transesterification process, including methanol, ethanol, butanol, propanol, and amyl alcohol, but at the commercial level, methanol and ethanol are more preferable due to physical and chemical advantages along with cost-effectiveness (Musa, 2016). The transesterification reaction requires 3 mol of alcohol for 1 mol of fatty acid, and the end product is 3 mol of fatty acid methyl ester (FAME) along with 1 mol of glycerol as byproduct (Surendhiran and Vijay, 2012). Due to the higher density of glycerol than biodiesel, the glycerol fraction can be separated out periodically from the reaction batch to process the reaction continuously. After the reaction, it is very important to remove the methanolic, catalytic, and soap components from biodiesel by distillation and water washing; otherwise, they will create problems with engine choking and failure (Munir et al., 2013). Compared to acid catalyzed transesterification, the base catalyzed reaction is faster, resulting in reduced processing time (Kumar et al., 2017b). Feedstock that have higher free fatty acid contents and water are not recommended for base catalyzed transesterification, as the end of the reaction produces soap, which increases the cost of the downstream separation (Kumar and Thakur, 2018). To overcome the problem of base catalyzed transesterification, acid catalysis was applied, which does not produce soap and increases the efficiency of the process. However, the major challenges involved in acid catalyzed transesterification are corrosiveness of the diesel fuel, the downstream separation, and susceptibility to a high water content (Saifuddin et al., 2015). At the industrial level, the acid catalyzed reaction is unfavorable as it requires a longer reaction

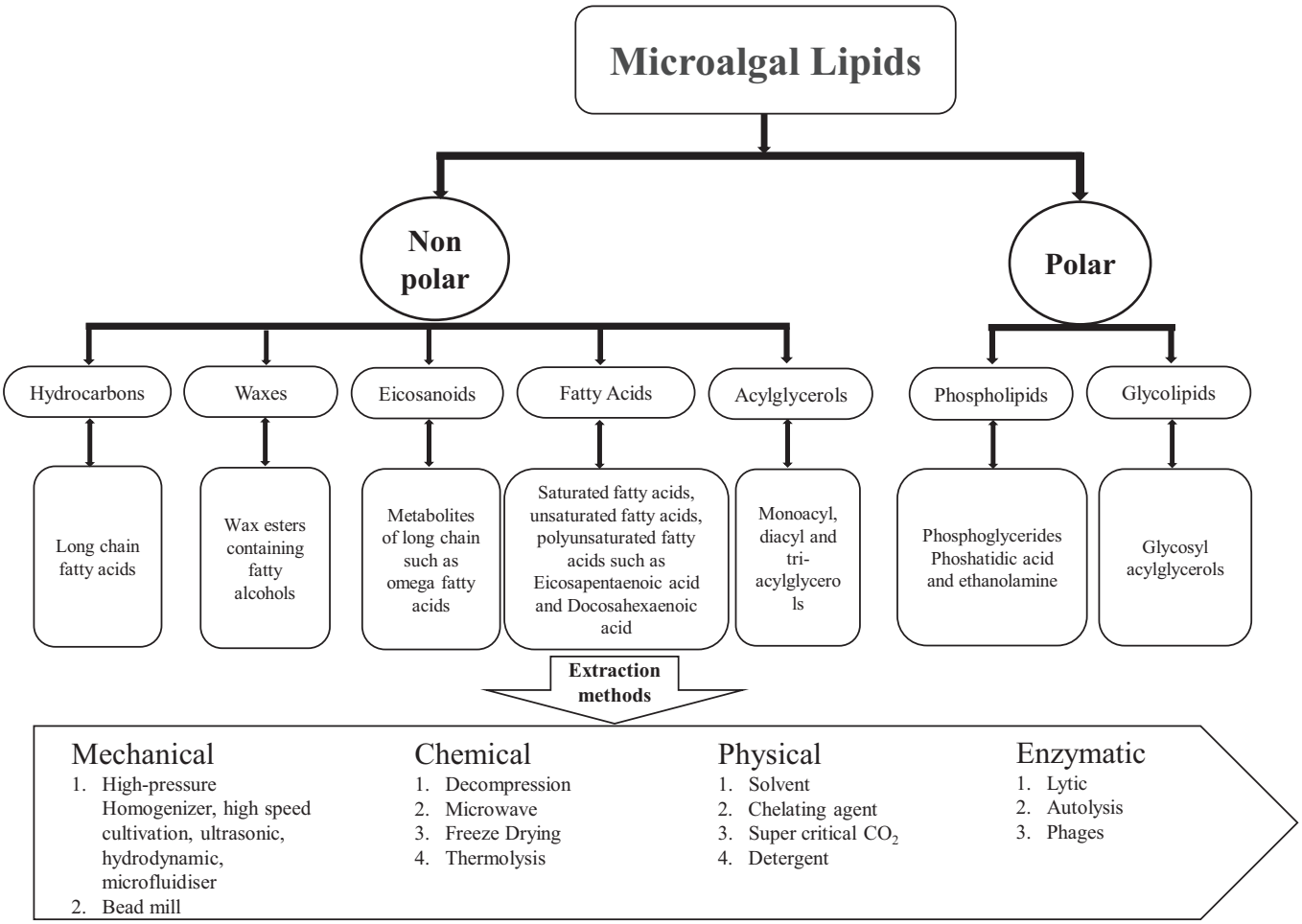

Fig. 2. Various types of lipids and their extraction methods from algal biomass.

time and recovery and corrosiveness of the catalyst are challenging, making it a noncommercial process (Saifuddin et al., 2015).

Based on the number of steps involved in the production of biodiesel, the transesterification reaction comprises two types, extractive and in situ transesterification. The process of extractive transesterification involves several steps, from cell drying to disruption of cells, lipid extraction, transesterification, and finally downstream processes and biodiesel purification (Saifuddin et al., 2015). The number of steps involved in this process makes it less attractive and useless. Additionally, the feedstocks contain a greater proportion of water, which is very obvious in the case of algal biomass, making the overall process noncommercial on a large scale. In the process of in situ transesterification, the extraction of lipids and transesterification were performed in a single step, resulting in a reduced processing time and lower utilization of solvent (Kumar et al., 2017a; Tang et al., 2016). The reduced generation of waste, processing time, and energy consumption along with higher yield of products make this process more feasible at the industrial scale (Patil et al., 2012). In this process, alcohol acts as a co-solvent as well as an extraction solvent because it can penetrate algal cell membranes and facilitate the release of dissolved lipids in the reaction mixture. During industrial production of biodiesel, the release of extraction solvent in the form of gaseous smoke makes this technology non-green. Thus, another option is needed to make industrial biodiesel production less energy intensive and more eco-friendly (Patil et al., 2012).

4.3. Pretreatment and saccharification of algal biomass

The cell wall of green algae such as *Spirogyra* and *Chlorococcum* contains large amounts of sugars in the form of polysaccharides. Microalgae such as *C. vulgaris* comprise approximately 37–55% cell dry weight (CDW) of carbohydrates that can be applied as feedstock for the production of bioethanol (Agwa et al., 2017). The production of biofuels from these saccharide-based feedstocks via the process of microbial fermentation requires prior pretreatment and saccharification. By applying potential microbial strains that can produce amylase enzyme and induce the process of saccharification, one can also produce bioethanol via the simultaneous fermentation process (Behera et al., 2015). The processes involved in the production of bioethanol from microalgae are similar to the corn-based 1st generation biofuel, although very limited information is available to explain fermentative bioethanol production using algal biomass as feedstock (Özçimen and İnan, 2015; Harun et al., 2014). The process of pretreatment plays a very crucial role in removing unwanted material such as lignin and facilitating the release of polysaccharides from biomass, while enzymes act on these polysaccharides and convert them in to their respective monomers (Table 1) (Behera et al., 2015). Acid and alkali pretreatments of biomass are widely acceptable because they are less energy intensive, efficient processes for the removal of unwanted materials together with the release of sugar (Jankowska et al., 2017). Along with chemical pretreatments, several other methods have also been applied to make this process eco-friendlier and sustainable (de Farias Silva et al., 2018). Some other groups of polymers (fucoidan, alginate, and mannitol) present in the algal biomass require additional processing before its application in the production of bioethanol. Yanagisawa et al. (2011) explored the lignin-free content of polysaccharides in seaweeds (*Ulva pertusa, Alaria crassifolia, Gelidium elegans*), and these biomasses did not require any pretreatment before its hydrolysis. The *Spirogyra* biomass has also

Table 1
Pretreatment methods of algal biomass for extraction of range of compounds.

Pretreatment method	Conditions	Algal biomass	Extracted compounds	References
Acid hydrolysis	Acid hydrolysis H_2SO_4 1 M, 80–90 °C, 120 min	Mix of microalgae (*Scenedesmus, Chlorella, Ankistrosdemus, Micromonas, Chlamydomonas*)	Carbohydrates	Castro et al., 2015
Enzymatic	Endogalactouronase 800 U/g, Esterase 3600 U/g, Protease 90 U/g, pH 6, 50 °C, 24 h	*Scenedesmus obliquus*	Carbohydrates	Ometto et al., 2014
Alkaline-peroxide	H_2O_2 1–7.5% (w/w), 50 °C, 1 h	Scenedesmus *obliquus, Scenedesmus quadricauda, Nitzschia* sp. *Aphanothece sp. Desmodesmus spinosus Nitzschia palea*	Carbohydrates and byproducts	Juárez et al., 2016
Hydrothermal water	1:13 (w/v), 147 °C, 40 min	*Scenedesmus* sp.	Glucose	Yuan et al., 2016
Acid hydrolysis	H_2SO_4 2 N, 120 °C, 30 min	*Scenedesmus obliquus*	Carbohydrates	Miranda et al., 2012
Ultrasound	65–130 W, 40 kHz, 25 min	*Chlorococcum* sp.	Carbohydrates	Halim et al., 2012
High pressure homogenization	500–850 bar, 15 min	*Chlorococcum* sp.	Carbohydrates	Halim et al., 2012
Bead milling	200 μL glass beads, 10 min cycles, 30 s vortexing, 30 s cooling on ice,	*Synechocystis* sp.	Proteins	Zhou et al., 2014
Freezing/thawing	3 cycles, 10 min freezing - 80 °C, 5 min thawing 37 °C	*Synechocystis* sp.	Proteins	Zhou et al., 2014
Pulsed electric field	17.9–71.7 kWh/m3, 36–54 °C	*Synechocystis* sp.	Cell disruption	Sheng et al., 2011
High pressure homogenization	10 mL compression chamber, 50–270 MPa, 3 °C	*Nannochloropsis oculata Porphyridium cruentum*	Cell disruption	Montalescot et al., 2015
Microwave	Acetone, 50 W, 56 °C, 5 min	*Dunaliella tertiolecta*	Pigments	Pasquet et al., 2011
Pulsed electric field and solvents	1 cm electrode distance, 45 kV/cm, Ethyl acetate/methanol/water	*Ankistrodesmus falcatus*	Lipids	Zbinden et al., 2013
Ionic liquid and solvent	Ionic liquid 1 h, ambient temperature, Adding hexane mixture 30 s 15 min	*Chlorella vulgaris*	Cell disruption and lipids	Orr et al., 2015
Pulsed electric field	15–25 kV/cm, 60–150 μs, 10–40 °C	*Artrhospira platensis*	Pigments	Martinez et al., 2017
Enzymatic	Cellulase 140 mg/m^2, pH 4.6, 50 °C, 24 h	*Chlorella pyrenoidosa*	Carbohydrates and lipids	Fu et al., 2010

been investigated in the production of bioethanol by both direct saccharification (without pretreatment) and saccharification after pretreatment (Singh and Trivedi, 2013). The former method resulted in a 2% (w/w) higher yield than the latter one, highlighting the importance of *Spirogyra* in the production of cost-effective bioethanol.

4.4. Microbial fermentation of algal biomass

The production of biofuels such as bioethanol and biohydrogen occurs mainly by yeast fermentation and dark fermentation, respectively (Phwan et al., 2019; Wang and Yin, 2018). The production of bioethanol using yeast fermentation technology is well recognized at the commercial level. To enhance the production of bioethanol, various parameters have also been considered, such as the screening of robust strains, genetic manipulation, substrate selection and modification, along with minimum feedback inhibition at higher product concentrations (Westman et al., 2017; Gouveia, 2011). It has been estimated that 140,000 L/ha/year bioethanol can be produced from high starch-containing microalgae, which is comparatively several times higher than other liquid fuels (Cheryl, 2010). The average sugar content found in the microalgae is approximately 40–50% of their biomass, and even the species such as *Chlorella* and *Scenedesmus* show >50% carbohydrate content (Agwa et al., 2017; Gouveia, 2011).

After algal biomass pretreatment, the next step is microbial fermentation, in which the recovered sugar is converted into bioethanol. There are two well-known fermentation processes involved in the production of bioethanol: separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) (Table 2) (Özçimen and İnan, 2015; Xiros et al., 2013). The SHF is performed independently in two separate reactors, while hydrolysis is performed in one reactor under each optimal condition and the product of hydrolysis is used as the substrate of fermentation in another reactor under each optimal condition, which is the advantage of SHF (Xiros et al., 2013). The separation of wet biomass after hydrolysis is one of the major challenges in the SHF process as it limits the yield of bioethanol (Offei et al., 2018). Additionally, investigation of *C. infusionum* has revealed that after reaching a certain bioethanol concentration (product), this microorganism starts using the bioethanol in place of glucose due to a change in the metabolic pathway (Harun et al., 2011). To overcome this phenomenon, the recovery of bioethanol is performed in situ, making the process continuous to enhance the yield of bioethanol. In the process of SSF, both hydrolysis and fermentation are performed simultaneously in a single reactor, reducing the problem of substrate inhibition as the glucose (substrate) is obtained during hydrolysis and is simultaneously converted to bioethanol (product). Compared to SHF, SSF is more economical due to the lower enzyme dosage required along with the higher yield (Nguyen et al., 2017). It also eliminates the chances of contamination, installation cost of the fermenter, and reduces the reaction time. The main drawback of SSF includes the uncontrolled production process, as saccharification and fermentation take place simultaneously, and the questionable reusability of substrate and enzymes, which makes the process noneconomical at the commercial level.

Biohydrogen production from microalgae through dark fermentation using groups of microbes or pure microbial strains is currently gaining attention (Table 3) (Wang and Yin, 2018; Rajhi et al., 2016). However, the production potency of biohydrogen is quite low due to complex and various reactions involved in dark fermentation. Pretreatment is an important step of this process as it converts the polymers (carbohydrate) to monomers to facilitate easy accessibility of the monomers to microbes (Behera et al., 2015). Therefore, to depolymerize carbohydrate polymers into monomers and subsequently achieve higher yields of biohydrogen from algal biomass, various physical, chemical, and biological pretreatments are typically employed in the dark fermentation process (Table 3) (Wang and Yin, 2018).

Table 2
Production of bio-ethanol from algal biomass via different fermentation processes.

Algal species	Classification	Pretreatment method	Hydrolysis	Fermentation type	Yield %	Reference
Chlorococum sp.	Microalgae	Supercritical CO_2	_	SHF	38.30	Harun et al., 2010
Chlorella sp.	Microalgae	_	Acid HCl/$MgCl_2$	SHF	47	Zhou et al., 2011
Chlorococcum infusionum	Microalgae	0.75% (w/v) NaOH	_	SHF	26	Harun et al., 2011
Chlamydomonas reinhardtii UTEX 90	Microalgae	3% H_2SO_4	α-amylase + glucoamylase	SHF	29.10	Nguyen et al., 2009
Chlorococcum humicola	Microalgae	_	H_2SO_4	SHF	48	Harun and Danquah, 2011
Chlorella vulgaris	Microalgae	3% H_2SO_4	_	SHF	40	Lee et al., 2011
Dunaliella tertiolecta	Microalgae	_	HCl/H_2SO_4 + amyloglucosidase + endocellulase + β-glucosidase	SHF	14	Lee et al., 2013
Laminaria japonica	Macroalgae	_	endoglucanase + β-glucanase + amyloglucosidase	SSF	19.6	Lee et al., 2011
Schizochytrium sp	Microalgae	Hydrothermal treatment	Enzymatic hydrolysis	SSF	5.51	Kim et al., 2012
C. vulgaris	Microalgae	_	Cellulase + amylase	SHF	17.8	Ho et al., 2013
Chlamydomonas reinhardtii cw15	Microalgae	12 N H_2SO_4	_	SHF	44	Scholz et al., 2013
Gracilaria verrucosa	Macroalgae	_	Cellulase + β-glucosidase	SHF	43	Kumar et al., 2013
Gracilaria salicornia	Macroalgae	2% H_2SO_4	Cellulase	SHF	7.90	Wang et al., 2011
Saccharina japonica	Macroalgae	H_2SO_4	Cellulase + β-glucosidase	SSF	11.10	Lee et al., 2013
Gelidium elegans	Macroalgae	Meicelase	_	SHF	36.7	Yanagisawa et al., 2011
Saccharina latissima	Macroalgae	Shredding and saccharification	_	SSF	0.47	Adams et al., 2009
Laminaria japonica	Macroalgae	0.1 M H_2SO_4	Cellulase and cellobiase	SHF	11.3	Ge et al., 2011
Laminaria digitata	Macroalgae	Shredding and saccharification	_	SSF	13.2	Adams et al., 2011

4.5. Anaerobic digestion of microalgal biomass

The production of biogas from microalgal biomass using the anaerobic digestion process has become an attractive and sustainable approach. The production of biogas, control of GHG emissions, and production of organic manures are the various advantages of anaerobic digestion (Paolini et al., 2018). There are mainly four steps involved in anaerobic digestion: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Anukam et al., 2019), and the rate limiting step is methanogenesis. The feasibility of biogas production in its cost-effectiveness, which is directly related to the production of microalgal biomass along with an efficient digestion process (Wu et al., 2019). The yield of anaerobic digestion is important depending on the cell composition of the biomass. Microalgae cultivated under limited nitrogen show more fatty compound accumulation under the cell wall, which makes the cell wall rigid and less feasible for anerobic digestion (Klassen et al., 2017). The C:N ratio plays a key role in determining the feasibility of the anaerobic process. To obtain an improved methane

Table 3
Biohydrogen production from algal biomass after pretreatment at different fermentation conditions.

Microalgae feedstock	Pretreatment	Fermentation conditions	H_2 production	References
C. vulgaris	Hydrolytic extracellular enzyme solution	Batch, 35 °C, heat-treated anaerobic sludge	43.1 mL H_2/gTS	Yun et al., 2014
C. vulgaris	Cellulase, pectinase, and hemicellulose degradation	Batch, 60 °C, heat-treated anaerobic sludge	135 mL H_2/gVS	Wieczorek et al., 2014
Scenedesmus sp. (lipid extracted)	Heat: 100 °C, 8 h	Batch, 37 °C, anaerobic sludge	35.38 mL H_2/gVS	Yang et al., 2010
Scenedesmus obliquus	Heat: 121 °C, 15 min	Batch, 30 °C, *Enterobacter aerogenes* ATCC 13048	10.8–56.5 mL H_2/gVS	Batista et al., 2014
Chlorella vulgaris	1.6% HCl, 35 min	Batch, 35 °C, heat-treated anaerobic sludge	36.5 mL H_2/gTS	Yun et al., 2014
Cyanobacterial blooms	pH 13 (6 mol/L NaOH) for 30 min	Batch, 35 °C, heat-treated anaerobic sludge	94 mL H_2/gVS	Cai et al., 2015
Scenedesmus obliquus	Heat: 121 °C, 15 min	Batch, 37 °C, *Clostridium butyricum* DSM 10,702	94.3–113.1 mL H_2/gVS	Batista et al., 2014
Scenedesmus obliquus	Milling	Batch, 58 °C, anaerobic sludge,	0.7–15.3 mL H_2/gVS	Ortigueira et al., 2015
Scenedesmus obliquus	Milling	Batch, 58 °C, *Clostridium butyricum* DSM 10702, anaerobic sludge	32.7–48.9 mL H_2/gVS	Ortigueira et al., 2015
Scenedesmus obliquus	Ultrasonication for 15 min at 45 °C	Batch, 55 °C, heat-treated anaerobic sludge	56 mL H_2/g biomass	Jeon et al., 2013
C. vulgaris	Ultrasonication (100,000 J/gTS)	Batch, 35 °C, heat-treated anaerobic sludge	37.9 mL H_2/gTS	Yun et al., 2014
Scenedesmus sp. (lipid extracted)	Heat: 121 °C, 4 h	Batch, 37 °C, anaerobic sludge	35.58 mL H_2/gVS	Yang et al., 2010
Scenedesmus sp. (lipid extracted)	Base: NaOH 8 g/L, 24 h	Batch, 37 °C, anaerobic sludge	16.89 mL H_2/gVS	Yang et al., 2010
Chlorella sorokiniana	Chemical: H_2O_2 2%, 12 h	Batch, 60 °C, anaerobic sludge	63 mL H_2/gVS	Roy et al., 2015
Chlorella sorokiniana	Sonication 130 W, 10 min	Batch, 60 °C, anaerobic sludge	52 mL H_2/gVS	Roy et al., 2015
Cyanobacterial blooms	170 °C for 20 min	Batch, 35 °C, heat-treated anaerobic sludge	113 mL H_2/gVS	Cai et al., 2015

yield, it has been reported the C:N ratio of the microbial growth culture be in the range from 20 to 30 for the anaerobic digestion process (Hidaka et al., 2014). For the production of biodiesel from algal biomass, lipids or oils are raw material, and after the extraction of lipids, the remining approximately 65% of algal residue is considered waste, which is the major challenge of biofuel industries. These microalgal residues enriched with carbohydrates and proteins can be further utilized as feedstock for the production of biogas by applying anaerobic digestion processes (Fig. 3) (Uggetti et al., 2014) The residues obtained after the anaerobic digestion process are in liquid and solid forms and enriched with nitrogen and phosphorous. These residues can be utilized for agricultural fields as fertilizer to complete the biorefinery cycle of anaerobic digestion (Macura et al., 2019).

4.6. Hydrothermal liquefaction (HTL) of algal biomass

HTL is a process that involves the conversion of organic material (biomass and biowaste) into oil (biofuel). In the HTL method, organic materials such as biomass and biowaste are subjected to direct liquefaction to bio-oil at temperatures below 400 °C in the presence of catalyst and water (Chen et al., 2014). The water molecules are in the supercritical state (neither liquid or gas) in this temperature range and high pressure, making the decomposition of biomass effective (Elliott et al., 2013). As there is no involvement of any toxic solvent in this process, it is environmentally friendly (Chen et al., 2014). The HTL process only consumes 10–15% of the energy produced from biomass, so its energy efficiency is very significant. The process involves the breakdown of major biomass components, such as proteins, fatty acids, and carbohydrates, into their respective monomers (Gollakota et al., 2018). Continuation of the process leads to the further removal of oxygen, sulfur, phosphorous, and nitrogen, ultimately providing lower-molecular-weight hydrocarbon (Elliott et al., 2013). To achieve better product yield though HTL, several crucial parameters must be considered, such as the oleaginous microalgal strains, biomass concentration, reaction type, type of catalyst, temperature, and heating rate, among others (Gollakota et al., 2018; Chen et al., 2014).

4.7. Gasification of algal biomass

The process of gasification involves the conversion of carbon-rich feedstocks into syngas through partial oxidation in the presence of a limited supply of oxygen or air of steam at temperatures ranging from approximately 100–1000 °C. Syngas is a mixture of various gases, mainly CO_2, CO, H_2, and CH_4 (Raheem et al., 2018). Additional syngas obtained through this process can be transformed into hydrogen via the water gas shift reaction or lower range liquid hydrocarbon via Fisher-Tropsch synthesis (Sanchez-Silva et al., 2013; Raheem et al., 2017). The syngas produced at 700 °C after complete gasification of the algal species. *Chlorella vulgaris* using Ru/TiO2 as catalyst was found to be rich in hydrogen (Chakinala et al., 2009). The composition of syngas obtained by Duman et al. (2014) after gasification of biomass of *N. occulata* was 40–53% H_2, 30–40% CO_2, 10% CH_4 and 6% CO. The catalyst plays a very important role in the conversion of biomass to syngas as it improves tar degradation and facilitates hydrogen production (Akubo et al., 2019). Syngas primarily composed of CO_2, CH_4, and H_2 has been reported by Rizwan et al. (2015) upon the complete gasification of the algal sp. *Spirulina platensis* in the presence of Ru as catalyst. Comparative studies performed by Stucki et al. (2009) among *Saccharina latissimi, C. vulgaris* and *S. platensis* for hydrogen production reported that *Saccharina latissimi* provided a better yield of hydrogen in the process of gasification.

4.8. Pyrolysis of algal biomass

Pyrolysis is a well-known process for production of the carbon-rich solid-phase and volatile organic phase when the feedstock is subjected to temperatures ranging from 400 to 800 °C. The vapor phase obtained in this process is finally converted to bio-oil and acid extract after condensation (Auersvald et al., 2019; Lee et al., 2017). The solid phase obtained after pyrolysis is porous in nature and generally called charcoal or BC (Xiong et al., 2017). The conversion of feedstock to bioproducts via pyrolysis is chemically defined as a redox reaction, in which one proportion is oxidized and the other reduced (Borole et al., 2018; Srinivasan et al., 2015). The oxidized part is then further used as starting material for the formation of organic compounds such as ketones, aldehydes, and acids via hydrolysis. Again, these compounds combine together and form more intricate organic compounds, such as polymeric substances and esters (Zhang et al., 2018). The residence time plays a crucial role in the process of pyrolysis because it influences the quantity and quality of end products. A higher temperature and longer residence time lead to the production of the incondensable gaseous phase, while a lower temperature and very high residence time result in a higher yield of the solid phase (Cao et al., 2019; Srinivasan and Sarmah, 2015; Dalmas Neto et al., 2014). During the pyrolysis of the algal biomass, char is use as an enhancer, which enhances the feedstock heating and act as an adsorbent (Gan et al., 2018). The biomass of *Chlorella* sp. is subjected to pyrolysis in a microwave oven and produces bio-oil making up approximately 28.6% wt/wt of the biomass (Du et al., 2011). The obtained bio-oil is composed of both aromatic and aliphatic hydrocarbons, phenols, nitrogenous compounds, and higher chain fatty acids. Wang et al. (2013) reported that the bio-oil produced from algal biomass shows a poor calorific value but better oxidation stability compared with the bio-oil produced after pyrolysis of lignocellulosic biomass (LCB). The algal bio-oil contains dissolved solid and nitrogenous substances, which can be further upgraded by the process of cracking and hydrogenation (Raheem et al., 2018). The genus *Chlorella* is well known for the production of bio-oil via pyrolysis; nevertheless, the production yield varies significantly and is dependent on the pyrolytic condition and algal species (Xu et al., 2018). Rapid pyrolysis of *C. vulgaris* and *C. protothecoides* biomass was found to produce 53% and 57.9% bio-oil by weight, respectively (Lam et al., 2019; Wang et al., 2013).

5. Biofuels and bioproducts obtained from the biovalorization of algal biomass

Compared to terrestrial plants, the algal biomass is composed of more lipids and proteins. The decreased generation time, higher photosynthesis efficiency, and reduced land requirement for cultivation makes algae a potential feedstock for the production of biofuels and bio-based materials (De Bhowmick et al., 2019; Khan et al., 2018; Shin et al., 2018; Nguyen and Hoang, 2016). Generally, algae can be grouped into macro and microalgae based on their morphological appearance. Green seaweed, brown algae, and red algae belong to the macroalgae, while green algae, *Chlorella*, and *spirulina* belongs to the group of microalgae (Demirbas, 2010). Compared to macroalgae, microalgae are preferable feedstocks for biofuels and bioenergy industries due to their oleaginous nature, higher biomass generation, and simple cellular structure, although only a few species of microalgae have been utilized to date (Richmond, 2004). The various biofuels and bioproducts obtained from algae are discussed below.

5.1. Biomethane

The production of biomethane (CH_4) via anaerobic digestion of algal residual biomass is well known as it produces a mixture of gases in which the CO_2 proportion ranges from 30 to 50% and CH_4 contributes 50–70%. Typically, the production yield of CH_4 from algal biomass is in the range from 0.2–0.4 m^3 CH_4/kg or 0.024–0.6 L CH_4/g VS (volatile solid), depending on the algal species and experimental conditions (Rabii et al., 2019; Milledge et al., 2019). The yield of CH_4 even varies among the same species, as reported by Milledge et al. (2019) for the production of biomethane from *Dunaliella* sp., where the yield was

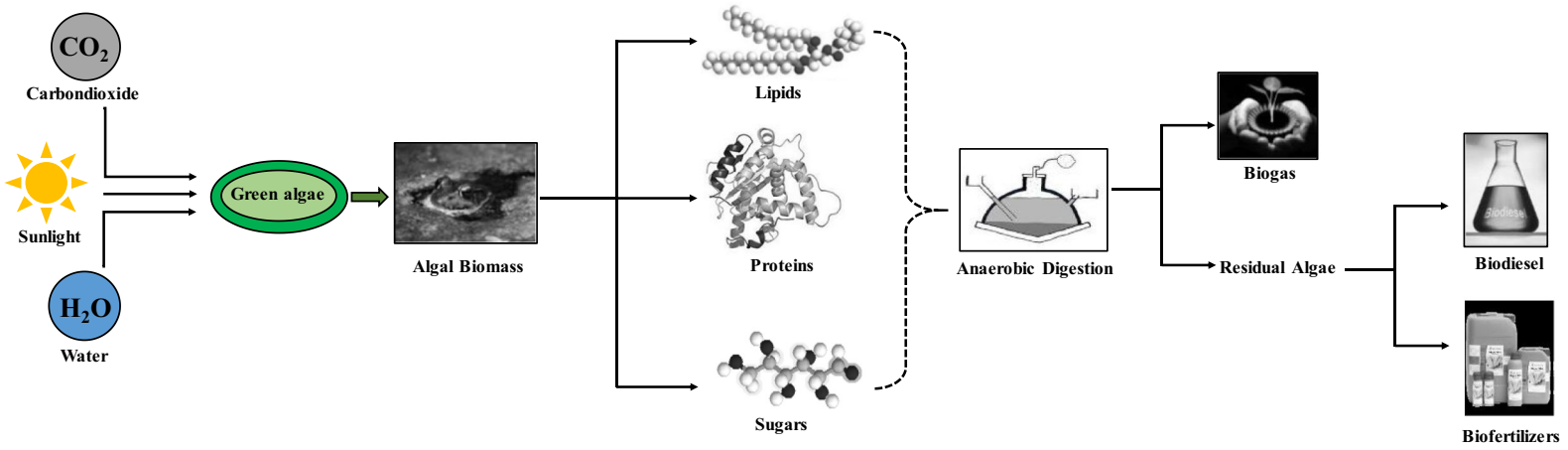

Fig. 3. Schematic representation of anaerobic digestion process for bio-valorization of algal biomass.

0.063 L CH_4/g VS and 0.323 L CH_4/g VS. The production of biomethane is expressed in the form of biomethane potentials (BMPs) and is defined as the maximum volume of CH_4/g of VS produced in batch experimental tests in the laboratory (Jingura and Kamusoko, 2017). Allen et al. (2015) reported BMPs of the cast brown seaweed *Saccharina latissimi* and *A. nodosum*, and the yield was 342 L CH_4/kg and 166 L CH_4/kg of VS, respectively.

The production yield of biomethane from algal is governed by various parameters, such as temperature, biomass loading rate and volume, duration, bacterial strains, and algal cell wall composition, among others (Barbot et al., 2016; Sialve et al., 2009). Another imperative factor that highly influences the yield of biomethane is the C:N ratio (McKennedy and Sherlock, 2015). It has been estimated that the C:N ratio of the algal residual biomass is low (6–9), while mixing of the algal biomass with higher carbonaceous feedstocks have been recommended for better yields of biomethane (Mussgnug et al., 2010). Due to the low biomethane yield and higher production cost, this process must be coupled with some other biofuel and biomaterial production processes using a biorefinery approach to make the process cost-effective (Cesaro and Belgiorno, 2015). A range of biofuels is produced from algal biomass, such as biodiesel, bioethanol, biomethane, and biohydrogen, among others, in which former two are considered primary products and the latter two co-products in biorefinery production model (Wang et al., 2013). By adopting bioenergy production along with the Carbon Capture and Storage (BECCS) strategy, sustainability is projected to improve with the consideration of microalgae as potential candidates for the sequestration of CO_2 along with the production of a range of biofuels including CH_4 (Milledge et al., 2019; Xia et al., 2016).

5.2. Biodiesel

Oleaginous microalgal cells are typically composed of lipids, of which 95% are contributed by triglycerides (TAGs) and the rest are mono and diglycerides along with small amounts of free fatty acids. The fatty acid composition of algal lipids is dominated by stearic acid, palmitic acid, and oleic acid, which is similar to the biodiesel standard (Tripathi et al., 2015). To produce biodiesel, the key raw materials are oils or lipids (Fig. 4). There are several studies available that describe the production of lipids from algal biomass. Enamala et al. (2018) reported a yield of lipids from various microalgal sp. in the range from 2.40–62.0% of dry biomass. Mitra et al. (2012) reported the production of lipids from *Chlorella vulgaris* is in the range from 11.0–43.0% of its biomass. *Scenedesmus* sp. ISTGA grown in the presence of sodium bicarbonate (Na_2HCO_3) produced 20% lipids of dry biomass (Tripathi et al., 2015). In other studies, *Chlorella, Haematococcus*, and *Scenedesmus* produced lipids ranging from 14.0–18.0% in the presence of Na_2HCO_3 (Tripathi et al., 2015).

Biodiesel is produced by the process of transesterification, which has been previously described in Section 4.2. The oils and lipids extracted from the algal biomass are used in transesterification reaction, in which the ratio of alcohol to oil is either 3:1 or 6:1 in the presence of acid, alkali, or lipase (biological) as catalyst (Kumar et al., 2017a, 2017b). The end product of the transesterification reaction is methyl ester (biodiesel), and the side product is glycerol (Kumar et al., 2020), which is further separated from biodiesel. Biodiesel produced from microalgae shows a higher percentage of unsaturated fatty acid compared with saturated fatty acid, which is prerequisite for fuel engineering (Tripathi et al., 2015; Demirbaş, 2008). A higher degree of unsaturation leads to better cold flow properties, but it simultaneously enhances the possibility of hydroperoxide generation, which increases polymerization, acidification, and the production of insoluble particle and jelling materials, choking the filter (Kumar and Thakur, 2018). The biodiesel produced from algal biomass should uphold American Society of Testing Material (ASTM-D-6751) and European Standard (EN-14214) norms (Mostafa and El-Gendy, 2017) (Table 4). The viscosity of algal biodiesel is 10–20 times higher than conventional diesel, and therefore blending or engine modification is an alternative option (Kumar and Thakur, 2018; Demirbaş, 2008). A mass of 1 kg oil extracted from algal biomass can produce 1 kg biodiesel, which is a carbon neutral biological product (Mata et al., 2010). Applied biorefinery and biovalorization technology make biodiesel production from algal biomass cost-effective, as these processes produce multiple products from single feedstocks. As in the case of algae, the biomass left over after oil or lipid extraction can be further used directly for combustion, electricity production, and biomethane production via anaerobic digestion, as well as animal feed (Srivastava, 2019; Saad et al., 2019).

5.3. Bioethanol

Bioethanol is considered a carbon neutral fuel, which is mostly produced from plant waste material (Hanaki and Portugal-Pereira, 2018; Davis et al., 2014). Algal biomass can also be applied for the production of bioethanol using several groups of microbes, such as yeast, bacteria, and fungi, under anaerobic fermentation conditions (Robak and Balcerek, 2018; Nguyen and Vu, 2012). Currently, *S. cerevisiae* and *Z. mobilis* are considered potential microbes for the production of bioethanol via microbial fermentative processes. A specific polymer such as mannitol is present in several algal species. That requires an oxygen supply during the process of sugar to bioethanol conversion, in which case *Zymobacter palmae* is applied as a fermentative organism (Khan et al., 2018; Kostas et al., 2016). Agar is a polymer of galactose and galactopyranose that is present in a few groups of marine algae, and it can also be used as feedstock for bioethanol production (Offei et al., 2018). Yanagisawa et al. (2011) used *S. cerevisiae* IAM 4178 as a fermentative organism for the fermentation of glucan and galactan extracted from agar weed and produced 5.5% (wt/wt) ethanol. The red algal biomass was composed of polymers of glucose and galactose, which could be further depolymerized and applied in the microbial fermentation process (Behera et al., 2015). In brown seaweeds, along with glucose and mannitol sugar, approximately 14% additional polymeric carbohydrates are present as alginate (Wargacki et al., 2012). The presence of laninaran, mannitol, alginate, and fucoidan along with cellulose in a few brown seaweeds make them potential feedstock for the production of bioethanol (Ale and Meyer, 2013). The production of bioethanol after extraction of mannitol from brown seaweed has been reported by Horn et al. (2000), and the yield was 0.38 g ethanol per gram of mannitol. Simultaneous production of bioethanol and butanediol has been reported by Hon-Nami (2006) using an algal culture of *Chlamydomonas perigranulata*. The leftover biomass after extraction of lipids from *Chlorococcum* sp. was used by Harun et al. (2010) to produce bioethanol, resulting in 60% more ethanol production than the intact algal biomass. This finding supports the biorefinery approach

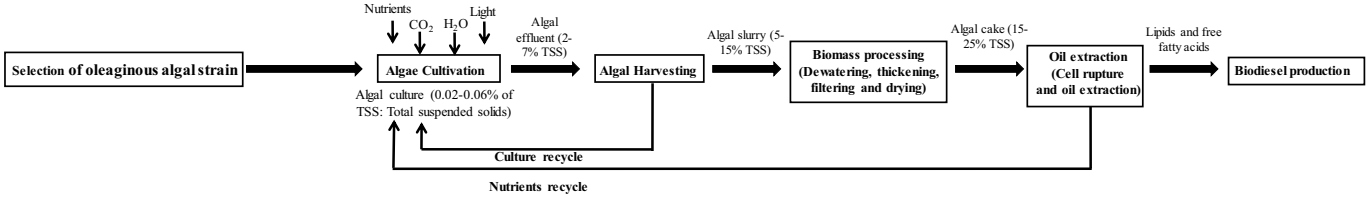

Fig. 4. Steps involve in production of biodiesel from algal biomass.

Table 4
Physico–chemical characteristics of biodiesel prescribe by American Society of Testing Material (ASTM- D-6751) and European Standard (EN-14214).

Parameters	Unit	Biodiesel D-6751	Biodiesel (EN14214)
Kinematic Viscosity @ 40 °C	cSt	1.9–6	3.5–5
Total acid number	mg KOH/g oil	<0.8	<0.5
Cloud point	°C	—	− 4
Flash point	°C	>130	>101
Density @ 15.56 °C	g/cm^3	—	0.86–0.9
Copper strip corrosion @ 100 °C	—	No. 3 Max.	Class 1
Iodine number mg I_2/100 g oil	—	—	<120
Cetane number	—	>47	>51
Calorific value	MJ/kg	—	32.9
Sediment content	wt%	<0.05	—
Water content	ppm	<300	<500
Carbon residue	wt%	<0.05	<0.03
Ash content	wt%	<0.02	<0.02
Total sulfur content	wt%	<0.05	<0.01

of algal biomass for the production of bioethanol as well as biodiesel. The production of bioethanol is a less energy intensive process. Further, the CO_2 emitted during this procedure can be used again in the cultivation of algal biomass, similarly to the carbon cycle of biofuel production (Gupta and Demirbas, 2010). The algal biomass can be considered a promising feedstock for the production of bioethanol, although its commercialization is still challenging; however, technological advancements in the near future may make this process cost-effective (Khan et al., 2018).

5.4. Biochar (BC)

BC is a carbonaceous material produced by the thermal treatment of biomass at a moderate temperature under a limited supply of O_2 (Sun et al., 2019; Rajapaksha et al., 2018). The production of algal BC from wet algal biomass takes place at a moderate temperature for a short duration via the process of HTL (Gollakota et al., 2018). Compared to lignocellulosic BC, BC produced from algal biomass shows a low carbon content and reduced surface area but a higher cation exchange capacity (Michalak et al., 2019). Due to higher pH of algal BC, it could be applied as a better material to reclaim acidic soil. The higher nitrogen content and diverse inorganic elemental composition are also beneficial for maintaining good soil health (Sun et al., 2019). Furthermore, due to the presence of various specific functional groups, BC can also be applied in the removal of organic and inorganic contaminates from wastewater (Filote et al., 2019; Awad et al., 2017). The presence of specific functional groups on BC leads to better treatment capacity of soil and wastewater toxic chemicals (Shen et al., 2018; Zheng et al., 2017). Nevertheless, the availability of cost-effective raw materials along with the preparation methodology are still under development for the preparation of BC and its application in wastewater treatment (Inyang et al., 2016).

Several studies have indicated that the relative yield of algal BC is superior to other feedstocks per unit algal biomass. The yield of BC per unit dry weight of the macroalgal biomass is in the range from 8.1–62.4% (Michalak et al., 2019; Yu et al., 2017). Compared to LCB such as pine wood, plant waste, and wheat straw, the yield of algal BC is lower under a similar set of experimental conditions (Ronsse et al., 2013). The decrease in yield was observed when the pyrolysis temperature was increased from 300 to 750 °C and the pyrolysis duration from 10 to 60 min. Tag et al. (2016) observed a similar trend and postulated that such results might be due to variation in the chemical structure and composition of the algal and plant biomasses, especially in cell wall composition. Additionally, the higher ash content in algal compared with plant biomass may alter the product distribution during the pyrolysis process. Recently, Salimi et al. (2019) reported the synthesis of olive-shaped magnetic BC by a slow pyrolysis process catalyzed by iron. The synthesized magnetic BC has a high surface area (296.4 m^2 g^{-1}) with an enriched carbonaceous structure that makes it appropriate for application as an electrode in Li-ion batteries. The electrochemical analysis confirmed a higher initial specific discharge capacity (740 mAh g^{-1}) and improved cyclic stability of the synthesized magnetic electrode in comparison to the BC electrode. The simultaneous production of biofuels and BC using biorefinery approaches makes this process interesting for the future expansion and exploration of algal biomass as feedstock (De Bhowmick et al., 2019). However, there are very limited investigations and reports describing the preparation of BC from algal biomass and its application, opening new avenues for researchers in this particular area (Shukla et al., 2017).

5.5. Pigments, nutraceuticals, and functional foods

The production of a single product at a time cannot control the economy of production process; in such a case, the biorefinery approach has emerged as a cost-effective technique for the production of range of products from single feedstock (Milledge et al., 2019). The algal biomass emerges as a potential feedstock for the production of multiple products, such as biofuels, pigments, and nutraceuticals, having several applications in the fields of healthcare, pharmaceuticals, and cosmetics (Table 5) (Enamala et al., 2018). Algae such as *Chlorella* have been used as direct food sources of protein for several decades. More than 20 commercial and distinguished products have been extracted from microalgae (Fig. 5).

Among the overall bioproducts obtained from algal biomass, polyunsaturated fatty acids (PUFAs) are the key products with several applications (López et al., 2019). PUFAs are widely applied in promoting the growth and development of the brain, heart, and vascular system, especially in children (Lee, 2013). The production of pigments from algal biomass is very common and produces a range of pigments such as chlorophyll *a*, b, c, phycocyanin and carotenoids (Barkia et al., 2019). Carotenoids have been used as scavengers of free radicals generated inside the body to protect the cells of the body from their harmful effects (Matos, 2017). There are several types of carotenoids, such as lutein, zeaxanthin, β-carotene, and α-carotene, which are applied as anticancer drugs in medical fields (Dickinson et al., 2017). *Spirulina* and *Arthrospir*a are well known for the production of phycobilin pigments such as phycocyanin, which is used as an anti-inflammatory agent (Stanic-Vucinic et al., 2018). C-phycocyanin is directly used as a functional food obtained from *Spirulina*. Several microalgae produce phenolic compounds during environmental stress for survival. *Spirulina* can produce volatile chemicals (hydrocarbons) such as heptadecane and tetradecane, which can be used as antibacterial agents (Seddek et al., 2019). Similarly, *D. salina* can also produce β-cyclocitral and phytol, which are also volatile compounds with antimicrobial characteristics. Several products, such as sterols, proteins, vitamins, and polysaccharides, extracted from algal biomass have diverse applications in the cosmetic and pharmaceutical fields (Dickinson et al., 2017; Varela et al., 2015). Recently, microalgae have also been applied for the production of feed additives and several recombinant proteins. *Dunaliella tertiolecta* has been applied for the production of industrial enzymes, as well as a diverse range of value-added recombinant proteins including functional antibodies, erythropoietin hormone, and human growth-promoting hormones (Dickinson et al., 2017). *Scenedesmus quadricauda* produces an ultraviolet protective compound called sporopollenin when grown in raceway ponds (Priyadarshani and Rath, 2012).

6. Opportunities and challenges in the production of biofuels and value-added products from algal biomass

In the prior 25 years, an exponential increase in energy consumption (1.8%/year) has been observed by the International Energy Agency (IEA). The increasing energy demands and limited availability of fossil fuels will soon lead to a worldwide energy crisis. To fulfil global energy

Table 5
Potential application of pigments and vitamin extracted from algal biomass.

Products	Potential algal sp.	Application	References
Chlorophylls	All phototrophic oxygenic algae	Pharmaceutical and cosmetics (deodorant)	Koller et al., 2014
Astaxanthin	*Haematococcus pluvialis, Botryococcus braunii*	Food additive, antioxidant	Panis and Carreon, 2016
Canthaxanthin	*Haematococcus pluvialis, Chlorella zofingiensis*	Food additive, tanning pills	Matos, 2017
Fucoxanthin	*Phaeodactylum tricornutum*	Anti-adipositas	Loredo et al., 2016
Lutein	*Chlorella salina, C. zofingiensis, D. salina*	Food additive, pharmaceutical (anti-macular degeneration), cosmetics	Nwachukwu et al., 2016; Gayathri et al., 2016
Violaxanthin	*Botryococcus braunii, Dunaliella tetriolecta*	Food additive	Koller et al., 2014
Zeaxanthin	*Phaeodactylum tricornutum*	Food additive E161 h, animal feed, pharmaceutical (anti-colon cancer, eye health)	Nwachukwu et al., 2016; Eilers et al., 2016
β-Carotene	*Dunaliella salina, D. bardawil*	Pro-vitamin A, antioxidant food	Koller et al., 2014
Bixin	*Dunaliella salina*	Food additive, cosmetics	Koller et al., 2014
Phycoerythrin	*Porphyridium*, cyanobacteria	Immunofluorescence techniques, labels for antibodies	Pangestuti and Kim, 2011; Tang et al., 2016; Han et al., 2013
Phycocyanin	*Arthrospira, Spirulina*	Food colorant (beverages, ice cream, sweets), cosmetics, fluorescent marker in histochemistry, antibody labels, receptors	Henrikson, 2009; Business Communications Company, 2015
α-Tocopherol	*Chlorella* sp., *Nannochlropsis oculata, Euglena gracilis*	Food additive, antioxidant in cosmetics and foods	Millao and Uquiche, 2016; Pangestuti and Kim, 2011

demands with minimal environmental damage, various alternative technologies have been adopted in recent few years, such as 1st generation, 2nd generation, and 3rd generation biofuel production technology. There are mainly three types of 1st generation biofuels (i.e., biodiesel, bioethanol, and biogas), with established production technologies and large-scale production (Stafford et al., 2019; Naik

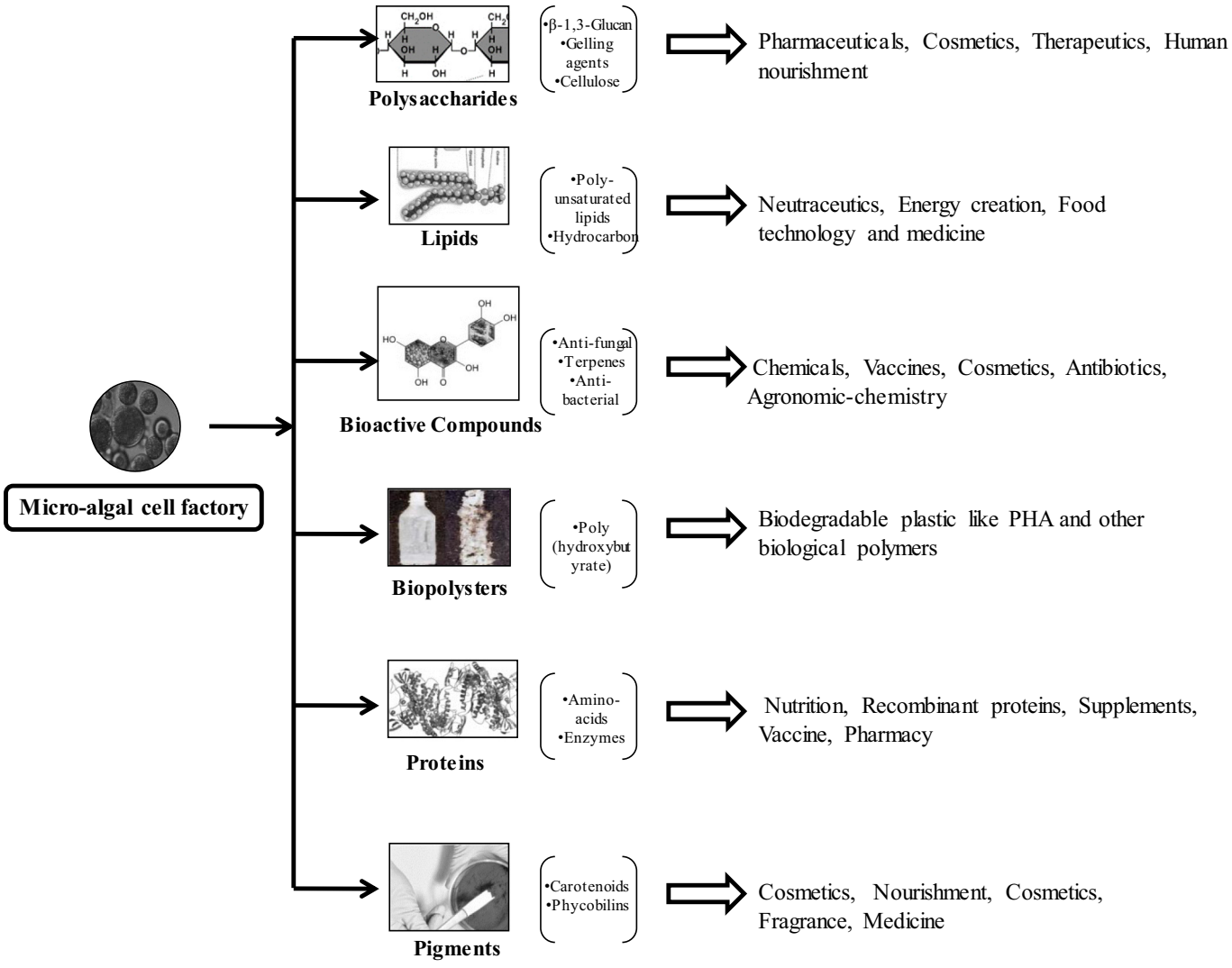

Fig. 5. Schematic representation of various type of biomaterials produces from algal biomass.

et al., 2010). Feedstocks used for the production of 1st generation biofuels belong to edible oils and other useful commodities, so their production creates a food vs fuel debate, which is the major stumbling block in the development of 1st generation biofuel technology (Satari et al., 2019). The production of 2nd generation biofuels is much more sustainable compared to 1st generation biofuels. Generally, 2nd generation biofuels are produced from LCB and waste materials (sludge, waste oils, etc.), and they provide a viable option in the sense of a true carbon neutral nature or even sometimes a carbon negative status due to reduced CO_2 emission (Gomiero, 2015). To date, 2nd generation biofuel production is not highly economical and commercialized due to several technical barriers, including the removal of lignin (pretreatment), which must be overcome before its commercialization (Satari et al., 2019).

Festel et al. (2014) modeled and predicted the production costs of 1st and 2nd generation biofuels in comparison to existing fossil fuels up to 2020, taking various influencing parameters into consideration such as feedstocks, crude oil prices, and conversion costs, among others. At the crude oil market price of €100/barrel, according to the model, the most economical biofuel is biodiesel produced from waste oil (€Cent 55/L), which is even more cost-effective than fossil fuel (€Cent 68/L), followed by biodiesel produced from palm oil (€Cent 81/L) and bioethanol from LCB (€Cent 86/L). In 2020, presuming a crude oil market price of €150/barrel, ethanol produced from LCB (€Cent 91/L) and biodiesel produced from both waste oil and palm oil have a predicted cost of €Cent 64/L and €Cent 98/L, respectively, which is less than fossil fuel (€Cent 99/L). Furthermore, considering the market price of crude oil of €200/barrel, three types of biofuels can be considered economical in comparison to fossil fuel (€Cent 131/L): biodiesel produced from waste oil (€Cent 74/L), ethanol produced from LCB (€Cent 95/L) and biodiesel produced from palm oil (€Cent 116/L). However, this study suggested the cost-effective production of different types of 1st and 2nd generation biofuels in comparison to fossil fuels but again also raised thoughtful uncertainty regarding whether an adequate quantity of feedstock could be available to fulfil the increasing demand for energy and trigger the shift from fossil fuel to biofuels.

The 3rd generation biofuel technology is gaining attention, in which algae is used as a feedstock. Unlike 1st generation biofuel feedstock, microalgae do not impede the human food supply. The continual exploitation of conventional available energy resources is also imposing several global environmental pollution issues such as global warming, GHG emissions, oil spills, and forest fires, among others. To resolve these issues, microalgae have become a potential feedstock for the production of eco-friendly biofuels and bioproducts, as indicated in several studies. There are several befits of using algal biomass as a bioenergy precursor, such as a reduced generation time, the ability to accumulate lipids and sugars (carbohydrates), no or minimal fresh water requirements for growth, and no competition with the human food supply, among others. There are several pathways by which algal biomass is converted into different biofuels and valuable bioproducts. Apart from several advantages of microalgae as a precursor for 3rd generation biofuels and chemicals, very few successful cost-effective technologies have emerged, especially in 3rd world countries. The main hindrance to the cost-effective production of 3rd generation biofuels is the higher production costs of lipids, along with several other costs such as processing and capital investments, leading to a negative energy balance.

The integrated system or biorefinery approach, in which total algal biomass can be utilized for the production of a range of biofuels and bioproducts, has shown successful results from a techno-economical viewpoint. Following the extraction of oils and sugars from algal biomass, the left-over biomass can be subjected to the production of biohydrogen and biogas via fermentation and anaerobic digestion technology, respectively, by applying different sets of conditions and microbes. The left-over waste material from the anaerobic process can be further utilized as manure and animal feed. To make 3rd generation biofuels competitive with conventional fuels, the cost must be reduced ten times more than the existing cost. As reported by United State Renewable Fuel Standards, to fulfil the bioenergy demands of 2022, 36 billion gallons of biofuel is required from algal biomass. To produce this huge quantity of bioenergy from algal biomass, several factors must be taken into consideration, such as power consumption, water requirements in terms of both algal growth as well as downstream processes, carbon, energy, and nutrient sources for algal cultivation. Millions of tons of nutrients such as nitrogen and phosphorous required for the growth of microalgae makes 3rd generation biofuel technology noneconomical. Additionally, harvesting the algal biomass and downstream processes add extra costs, which makes the process challenging from a sustainability perspective. Hoffman (2016) reported the costs associated with the production of algal biomass and 3rd generation biofuels by applying HTL downstream processing. According to his findings, the costs involved in the production of biomass and biofuel using an algal turf scrubber system were $510/ton and $8.34/gal and using the open raceway pond system were $673/ton and $6.27/gal, respectively. The fabrication of new technologies or integration with some existing technologies in such a manner with minimum waste generation and maximum outcomes is desirable, which is the main objective of many biofuel industries. It is important to identify how algal biomass can be valued (biofuels, bioactive materials, pharmaceuticals, and nutraceuticals, etc.) and how its economical production can be achieved by applying biorefinery approaches.

7. Conclusions

Algal biomass has shown tremendous potential for the production of biofuels and bioproducts in more eco-friendly, sustainable, and cost-effective manners. The application of biorefinery models and integration of processes such as biodiesel, biohydrogen, and biofertilizer production makes the process more economical. The production of a range of biofuels, such as biodiesel, biohydrogen, bio-oils, and biomethane, along with solid BC and its application, has demonstrated the importance of microalgal research. Various processes, such as lipid extraction, transesterification, gasification, pyrolysis, HTL, and anaerobic digestion, along with the coupling of two or more processes, make production economical. Microwave-assisted lipid extraction technology has been shown to be a more environmentally sustainable technique by minimizing the use of solvents. The anaerobic digestion process produces biomethane and does not require any additional external energy supply, and the secondary product of the process is used as a biofertilizer to resolve water body eutrophication. The production of bioethanol via fermentation of algal biomass is less energy intensive than biodiesel production, which represents another interesting approach. Algal biomass can be considered a promising feedstock for the production of a diverse range of products, although its commercialization is still challenging. However, technological advancements in the near future may make this process commercially viable in developing countries.

Declaration of competing interest

The authors declare no Conflict of interests.

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