Microalgae-Based Biorefineries as a Promising Approach to Biofuel Production

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Abstract Microalgae are photosynthetic microorganisms that are capable of converting carbon dioxide, nutrients, and solar energy into biomass and oxygen. In addition, microalgae have high photosynthetic rates, do not require potable water and arable land for cultivation, and can use liquid and gaseous effluents as nutrients for growth. The biochemical composition of microalgae can be manipulated by changing the cultivation conditions and environmental stresses. Thus, these microorganisms can be induced to produce biomass that is rich in biocompounds of commercial importance. The microalgal biomass can be converted into biofuels and high value-added bioproducts. Thus, microalgae have potential uses as renewable raw materials and could provide promising materials for the development of biorefineries. In this context, this chapter examines microalgae within a biorefinery concept and describes the advantages of using microalgae, culture conditions, biocompounds from biomass and the potential for converting them into biofuel and bioproducts.

1 Introduction

The burning of fossil fuels is a major contributor to the increase in greenhouse gases (GHG) in the atmosphere and is directly linked to global warming. Fossil resources are not considered sustainable and are economically, socially, and environmentally questionable (Kamm et al. 2006). For these reasons, energy sources that are sustainable and environmentally friendly to society and the global economy are needed (Mabee et al. 2005).

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With their potential to generate sustainable clean energy, microalgal biomass has favorable characteristics for producing biofuels and high value-added bioproducts. In the multiproduct paradigm, microalgae are part of a select group of raw materials that can be used in biorefineries (Subhadra 2010).

The process of obtaining bioproducts becomes costly when it is based on only one conversion technology. Conversion technologies, such as thermochemically and biochemically derived items, can be combined by using biorefineries to reduce the overall cost of the process, yielding greater flexibility during the production of bioproducts (Naik et al. 2010). Some studies have focused on the use of microalgae products for different applications (Lu et al. 2004; Mandal and Mallick 2009; Chen et al. 2011); however, most studies are focused on obtaining only a specific product from microalgal biomass. Thus, the other available and valuable components of microalgae are lost (Vanthoor-Koopmans et al. 2013).

The microalgal biomass has high concentrations of lipids, proteins, and carbohydrates, which can be used for different applications. When the full potential of the microalgal biomass constituents is exploited, many bioproducts can be obtained simultaneously and the market value is greater than the production costs (Wijffels and Barbosa 2010).

The great advantage of using microalgae as a raw material for biorefineries is that they do not compete with food crops, because they do not require arable land, in addition to their use of effluents as nutrients for their development. Microalgae grow faster than land plants and thus have a higher CO_2 fixation rate (Chen et al. 2011). In addition, the biochemical composition of microalgae can be manipulated by changing the growing conditions and environmental stresses. Thus, these microorganisms can be induced to produce high concentrations of commercially important biocompounds (Hu et al. 2008; Goiris et al. 2015).

Based on these previous studies, this review examines the use of microalgae in designing a biorefinery. The advantages of using microalgal biomass compared to other substrates, the use of effluents as nutrients, and the conversion of biomass into biofuels and high value-added bioproducts are described.

2 Refinery Versus Microalgae Biorefinery

The demand for actions to mitigate GHG emissions and the increased costs of obtaining oil coupled with instability in oil prices due to geopolitical factors have motivated the creation of alternatives based on renewable resources (Bennett and Pearson 2009; Cherubini 2010; Kokossis and Yang 2010). In this context, biorefineries offer the opportunity to obtain products with the same applicability as products obtained from petroleum, but they are generated from renewable raw materials (Ghatak 2011).

Biorefineries use integrated industrial processes, in which biomass is converted into a series of biochemical compounds, energy, and chemical products with high added value. Biorefineries are analogous to oil refineries, in which multiple fuels

and chemicals are produced from fossil fuel (Romero-García et al. 2014). Biorefineries and refineries involve processes in which raw materials are separated into different fractions. In a petrochemical refinery, the crude oil is separated and "refined" into products such as fuel, the building blocks for chemicals and materials for road construction. However, the raw material used in a biorefinery (biomass) is separated into fractions that may consist of sugars, cellulosic components, proteins, and lignin, which will be "refined" later and then used for biofuel and chemical production, used as food ingredients, or burned to generate energy (Cherubini et al. 2009).

Bennett and Pearson (2009) argue that this analogy may be questionable. The fractions obtained from distillation and oil cracking are distinct, and they are manufactured separately during the production of gasoline, diesel, turbine oil or olefins. The initial steps of biomass processing will produce fractions, such as cellulose or synthesis gas, to serve as raw materials for fuels and biochemical compounds. Therefore, there is direct competition among biomass uses. According to Kamm et al. (2006), traditional refineries employ oil as the raw material that primarily supplies transport and energy fuels, and only a relatively small fraction is directed to chemistry. In a biorefinery, a relatively greater amount may be directed to biochemistry and the production of biocompounds; however, bio-based products can only compete with petrochemicals when the biomass resources are optimally processed by biorefinery systems.

By producing various bioproducts, biorefineries can be used to explore the full potential of biomass, adding value, increasing profitability, and reducing energy demand and GHG emissions. The ability to obtain different bioproducts also lowers production dependence on only one product, thereby improving the sustainability of the rational use of biomass, reducing the competition between uses for food or fuel (Ghatak 2011). In the context of microbial biorefineries, microalgae are intensively studied because they can consolidate the production of biofuels and high value-added bioproducts (Silva et al. 2014). Figure 1 shows a schematic diagram of a microalgae-based biorefinery.

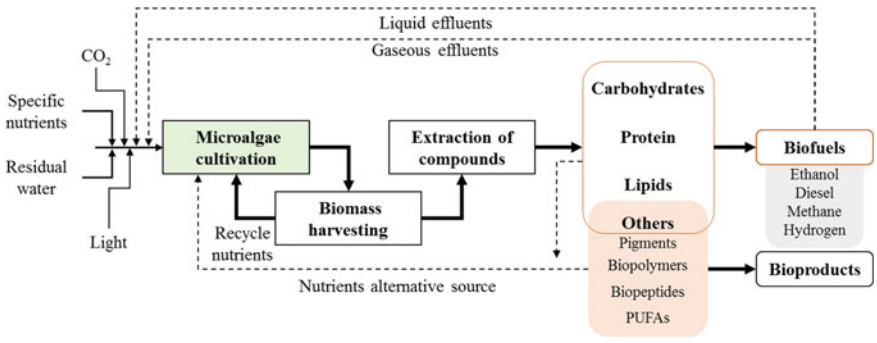

Fig. 1 Schematic diagram of a microalgae-based biorefinery

Table 1 Concentrations of the main macromolecules from microalgae on a dry basis (%, w w^{-1})

Microalga	Proteins	Carbohydrates	Lipids	Reference
Anabaena cylindrica	43–56	25–30	4–7	Demirbas (2010)
Chlamydomonas reinhardtii	64–66	20–25	13	Mahdy et al. (2014)
Chlorella vulgaris	61–66	19	18	Mahdy et al. (2014)
Dunaliella salina	28–30	16	7–8	Díaz-Palma et al. (2012)
Scenedesmus obliquus	42	19	32.5	Wu and Miao (2014)
Spirulina sp.	60–65	14–22	5–10	Rosa et al. (2015)
Tetraselmis maculate	52	15	3	Demirbas (2010)

The cultivation of microalgae is an efficient option for the bioremediation of wastewater through the recovery of high levels of nitrogen, inorganic phosphorus, and heavy metals from effluents. Furthermore, microalgae reduce CO_2 emissions from gaseous effluents and the atmosphere, converting carbon and solar energy into biomass through photosynthesis (Schneider et al. 2012). The composition of microalgal biomass may vary across species (Table 1) and cultivation conditions, and it primarily consists of lipids, carbohydrates, and proteins (Zhu 2015).

Microalgal biomass has the potential to provide renewable energy in forms such as biodiesel, bioethanol, biohydrogen, and biogas. Moreover, these photosynthetic microorganisms also have the capacity to synthesize bioactive molecules, such as carotenoids, polyunsaturated fatty acids, biopolymers, antioxidants, anti-inflammatory compounds and other organic compounds that can be used in human and animal nutrition, cosmetics, biomaterials, nanostructures, and drugs (Marques et al. 2011).

The development of the biorefinery concept may enable biofuel generation through the production of co-products to promote the better use of all the biomass components (Trivedi et al. 2015). Olguín (2012) reported a proposed biorefinery for two combined purposes, for cultivating oleaginous microalgae with wastewater and cultivating *Arthrospira* with effluent from the anaerobic digestion of animal waste and seawater, both of which are used for the production of biofuels and products with high added value. At this phase, oleaginous microalgae growth is proposed for the production of three biofuels, biodiesel, biogas and biohydrogen. *Arthrospira* cultivation is proposed for biogas production and high-value products, such as fish food, phycocyanin, and PUFAs.

2.1 Microalgae Cultivation Within the Biorefinery Concept

Microalgae are photosynthetic microorganisms that belong to a large and diverse group including both unicellular and multicellular organisms and both prokaryotes (cyanobacteria) and eukaryotes (Li et al. 2008). These microorganisms have high cell growth rates, with a division every one to two days under favorable growing

conditions (Williams and Laurens 2010). Compared to terrestrial plants, the cell growth of microalgae can be 100 times faster (Lam et al. 2012).

The microalgae habitat can be aquatic (Becker 2004) or terrestrial, with over 40,000 species already cataloged. Among the major groups of microalgae, Cyanophyceae (blue algae), Chlorophyceae (green algae), Bacillariophyceae (diatoms), and Chrysophyceae (golden algae) are often cited when describing desirable characteristics for the efficient and economical combination of CO_2 fixation, wastewater treatment and the synthesis of lipids for biofuel production (Kumar et al. 2010).

Due to the commercial potential of microalgal biomass, the research and development of technologies for the production and harvest of microalgae are being conducted by several private companies and academic institutions. Earthrise Nutritionals, which is located in California (USA), and Cyanotech Corporation, in Hawaii (USA), are two companies involved in the production of *Spirulina* using open raceway ponds. Sapphire Energy has an advanced facility for producing fuel from algae. This company has several patents on processes such as the heat treatment of crude seaweed, a process for the recovery of oily biomass compounds to produce biofuels from prokaryotes and eukaryotes and the induction of flocculating photosynthetic organisms (Christenson and Sims 2011). Seambiotic is an Israeli company that grows microalgae in outdoor reactors near power plants. Concentrated CO_2 from the flue gas is fed to the cultures (Weiss 2008). General Atomics Company has several patents related to algae cultivation (Christenson and Sims 2011).

Many companies market nutraceuticals that are developed using microalgal biomass. Natureza Beta Technologies in Israel provides a range of microalgae-based products such as cosmetics and food supplements. Tablets, chips, creams, liquid extract, and *Spirulina* powder are marketed in Yangon (Myanmar) (Spolaore et al. 2006).

In Brazil, the Laboratory of Biochemical Engineering (LEB) at the Federal University of Rio Grande (FURG) has been developing research on microalgae cultivation since 1996. Since then, the photobioreactor settings and cultivation modes (Reichert et al. 2006), medium renewal rate and blend concentrations (Reichert et al. 2006; Moreira et al. 2016), agitation (Henrard et al. 2014), light intensity, temperature, nutrient composition, and use of alternative substrates in the supplementation of the culture medium (Borges et al. 2013) have been studied. Native strains such as the cyanobacterium *Spirulina* (Morais et al. 2008) and microalgae with potential for CO_2 biofixation (Morais and Costa 2007a; Radmann et al. 2011) were also isolated (Morais and Costa 2007b).

Since 1998, LEB has been developing a study project on *Spirulina* cultivation on a pilot scale at the edge of Mangueira Lagoon (33° 30′13″ S, 53° 08′ 59″ W) (Morais et al. 2009). With this search, a pilot version of a *Spirulina* biomass production plant was designed and implemented in the city of Santa Vitória do Palmar (RS) (Fig. 2a), with a production capacity of 70 kg month^{-1}. The biomass

produced there is used to supplement local school lunches and for developing foods such as instant noodles, powdered cake mix, cookies, pudding, powdered chocolate, instant soup, powdered gelatin, cereal bars, and foods intended for practitioners of physical activity (Costa and Morais 2011).

The biomass produced by microalgae cultivation in several studies was evaluated for the production of fatty acids (Colla et al. 2004), biopolymer extraction (Martins et al. 2014), nanofibers (Morais et al. 2015a), the development of protein hydrolysates (Lisboa et al. 2014), and nanoemulsions. The potential for developing biofuels from compounds that could be extracted from the biomass, such as bioethanol (Margarites and Costa 2014), biodiesel, and biogas, was verified.

Among the LEB projects, the one focused on CO_2 biofixation by microalgae began in 2005 with an agreement with Eletrobrás and the Electric Power Thermal Generation Company (CGTEE). As the research advanced, a pilot plant for CO_2 biofixation by microalgae was designed and built in the Presidente Médici Thermal Power Plant in the city of Candiota (RS) (Fig. 2b). The plant has an area of 6,000 m^2, with 70 m^2 of laboratories, and three raceway-type bioreactors. Two of the bioreactors have a working volume of 18 m^3 each, and one has a volume of 1 m^3 for growth and inoculum maintenance (Costa et al. 2015).

Based on the signed agreement, several studies related to CO_2 biofixation by microalgae have been developed. These studies focus on the development and use of different photobioreactors, integrated chemical, and biological CO_2 fixation (Rosa et al. 2015), and the use of CO_2 and coal-combustion gas in the cultivation of microalgae species (Morais and Costa 2007a, 2007c; Radmann et al. 2011) as well as the evaluation of compounds in the biomass (Radmann and Costa 2008). In this sense, research on microalgae cultivation and the production and evaluation of the microalgal biomass potential were investigated to enable the sustainable development of a microalgae biorefinery.

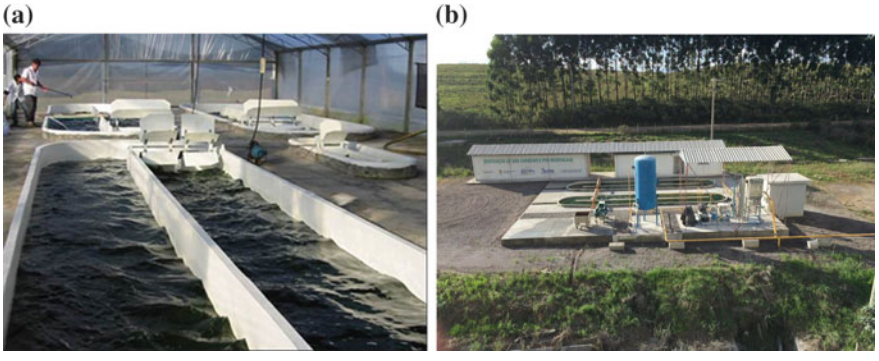

Fig. 2 **a** Pilot plant for producing *Spirulina* biomass in Santa Vitória do Palmar-RS, Brazil, and **b** a pilot plant for microalgal CO_2 biofixation in Presidente Médici Thermal Power Plant, Candiota-RS, Brazil

2.2 Microalgal Biomass Compared to Other Substrates

The term "biomass" refers to the raw materials that are used in biorefineries, which are renewable and carbon-based and come from four different sectors. Those sectors are agriculture (cultures and residues); forestry (growing trees); industrial (process residues) and urban (household and commercial residues); and aquaculture (microalgae and macroalgae) (Cherubini 2010). The term "biomass" may also be categorized into sections such as biomass originating from cultures or residues. The cultures include raw materials with sugarcane, grains of different cultivars, microalgae and macroalgae, and plant oils such as palm and lignocellulosic materials including wood and grass. Residues can be classified as being of agricultural, forestry, industrial, and municipal origin (Naik et al. 2010).

Agricultural residues include straw, bark, and mulch from crops such as rice, wheat, and corn, while forest residues may contain sawdust, shavings, and wood shavings. Wastewater and solid waste materials are classified as municipal sources and may come from households and commercial establishments (Naik et al. 2010).

As reported by Balat et al. (2008) and Naik et al. (2010), crops such as sugar cane, sugar beets, maize, sorghum, wheat, and barley can be used to produce bioethanol. The world's largest bioethanol producers are the United States and Brazil, and they use corn and sugarcane as raw materials, respectively (Sarkar et al. 2012). The disadvantages associated with the use of these raw materials are their influence on the food supply and their use of large amounts of land (Harun et al. 2010b).

Vegetable oils and animals fats are extracted or pressed to obtain crude oil or fat that can be used in biodiesel production (Ma and Hanna 1999). Conventional biodiesel primarily comes from soybean and vegetable oils, palm oil, sunflower oil, and rapeseed oil as well as restaurant waste oil. The production cost of biodiesel consists of two primary components, namely, the cost of raw materials (fats and oil) and the cost of processing (Huang et al. 2010). The sustainable and economic production of biodiesel from vegetable oils has been challenging due to their significant land use and sustainability issues. The use of residues such as cooking oil or animal fat is an effective method of recycling residues; however, refining and hydrogenation are needed to make biodiesel usable (Ma and Hanna 1999).

Agricultural and forest residues from the post-harvest industrial processing of food cultures can generate huge amounts of carbohydrates containing lignocellulosic residues (Huber and Corma 2007). Lignocellulosic biomass is made up of three primary building blocks, namely, cellulose, hemicellulose, and lignin. This raw material is considered the second-generation and can be used in the production of biofuels and chemicals through various conversion technologies (Naik et al. 2010). The biochemical and thermochemical routes (Cherubini 2010) may use lignocellulosic biomass for biofuel production. However, studies show that the major obstacle to the widespread utilization of this important resource is the absence of economically feasible technologies for overcoming the impediments of converting lignocellulosic materials to biofuel (Yousuf 2012). Therefore, it remains

debatable as to whether the use of second-generation biofuels could help to meet the global demand for fuels in the transportation sector by 2030 (Sims et al. 2008).

In this context, microalgae have attracted attention in recent years as a renewable source of biomass with advantages over traditional energy cultures (Demirbas 2011). The microalgal biomass is considered a rich source of phytochemicals that can be used in food and feed, aquaculture, pharmaceuticals, dietary supplements, cosmetics, and health products as well as for producing biofuels and other bioproducts (Pulz and Gross 2004; Spolaore et al. 2006; Brennan and Owende 2010).

In oleaginous energy cultures, the production cycle lasts for 3 months to 3 years; however, for microalgae, biomass harvesting may begin from 3 to 5 days and can be extracted daily. These photosynthetic microorganisms are produced throughout the year, unlike most vegetable crops, which are seasonal. With support for their high photosynthetic efficiency, algae have higher growth rates and biomass productivity compared to terrestrial plants as well as the ability to fix greater amounts of CO_2. Microalgae do not require potable water and fertilizer, given that they are able to absorb nutrients from wastewaters and gas effluents. Finally, due to the low cultivation demands of these microorganisms, these cultures can be implemented on degraded land, in the desert and even on offshore structures, thereby eliminating competition with the food sector (Demirbas 2011).

Microalgae have a favorable composition for use in biorefineries, with ash contents between 4 and 10% w w^{-1} and a low lignin concentrations in the cell wall. Therefore, at least 90% w w^{-1} of microalgal biomass can be converted into marketable bioproducts. The productivity of microalgae biomass (60–100 ton ha^{-1} a^{-1}) can be higher compared to other substrates used in biorefineries, such sugarcane (60 ton ha^{-1} a^{-1}), soybeans (3 ton ha^{-1} a^{-1}), and wood (pine) (3 ton ha^{-1} a^{-1}); however, applications are required at a larger scale (Gerardo et al. 2014). As a result of the features discussed here, microalgal biomass can be considered an excellent raw material for use in biorefineries to produce biofuels and high value-added bioproducts (Zhu 2015).

2.3 Liquid and Gaseous Effluents as a Source of Nutrients

2.3.1 Liquid Effluents

Several investigators have investigated the cultivation of microalgae with the aim of defining the ideal conditions for maximizing growth rates and composition of microalgal biomass; however, microalgal cultures are still dependent on (i) the cost, (ii) the CO_2 capture sources, (iii) the target product, and (iv) the nutrient sources (Cheah et al. 2015).

In addition to carbon, microalgae can assimilate nitrogen and phosphorus from the culture medium to maintain efficient metabolic activity. Nitrogen is an important element and is a necessary nutrient of microalgae, as the primary constituent of nucleic acids and proteins (Green and Durnford 1996). Ammonium is the primary

nitrogen source for microalgae (Razzak et al. 2013). Furthermore, phosphorus is necessary for photosynthesis, metabolism, and the formation of DNA, ATP, and the cell membrane. Phosphorus is available in the medium as phosphate and is usually supplied in excess, because it is not readily bioavailable. Other inorganic salts and trace elements such as metals and vitamins are normally added to the medium to maintain photosynthetic activity (Cheah et al. 2015). Nutrients represent approximately 10% of the costs of cultivation (0.44 € $kg_{dry\ biomass}^{-1}$) (Norsker et al. 2011).

Microalgae are known for their high nutrient-removal efficiency because they require large amounts of nitrogen and phosphorous to synthesize proteins, nucleic acids, and phospholipids, which represent 40–60% w w^{-1} of the cell's dry weight (Silva-Benavides and Torzillo 2012). Nutrients for the cultivation of microalgae (primarily nitrogen and phosphorus) may be obtained from liquid effluents, such as wastewater. Depending on the source, effluents can be classified as municipal, domestic, or liquid waste from agriculture and industrial products (Chiu et al. 2015).

The use of wastewaters from primary or secondary wastewater treatment is an economically and environmentally promising solution because they contain significant amounts of these nutrients. In wastewater treatment plants, these nutrients must be removed because they contribute to eutrophication. This removal may increase the total energy consumption of treatment by 60–80% (Lam and Lee 2012).

The full process of nitrogen and phosphorus removal from tertiary wastewater treatment is almost four times more expensive than primary treatment (Noüe et al. 1992). Accordingly, the cultivation of microalgae offers a promising solution for tertiary treatment, because these microorganisms use inorganic nitrogen and phosphorus for their growth (Oswald 1988; Tam and Wong 1996). Microalgae can also remove heavy metals and toxic organic compounds, preventing secondary pollution (Chiu et al. 2015). In this context, microalgae can act as important agents in the bioremediation of wastewater (Zhou et al. 2014), with advantages over conventional systems including reduced costs through reduced energy consumption and low initial capital and operating costs (Wong and Tam 1998).

The concentrations of total nitrogen (TN) and total phosphorus (TP) following the secondary treatment of wastewater are relatively low (TN: approximately 15–90 mg L^{-1}, TP: approximately 5–20 mg L^{-1}). The TN and TP concentrations in wastewater from cattle breeding and agriculture are usually 185–3213 mg L^{-1} TN. For effluents such as manure from pig farms, chicken breeding facilities, and dairy farms, wastewater is digested anaerobically, and the resulting phosphorus concentration is approximately 30–987 mg L^{-1}. However, these types of wastewater contain extremely high nutrient concentrations and thus must be diluted before being used to cultivate microalgae (Chiu et al. 2015).

Gonçalves et al. (2014) evaluated the effects of light (36, 60, 120, and 180 μE m^{-2} s^{-1}), photoperiod (10:14, 14:10, and 24:0), CO_2 fixation and removal of nutrients (nitrogen and phosphorus) from the culture medium of four strains of microalgae (*Chlorella vulgaris*, *Pseudokirchneriella subcapitata*, *Synechocystis salina,* and *Microcystis aeruginosa*). The authors observed that all the microalgae showed high nitrogen-removal efficiencies, reaching 100% in the assay with the

highest brightness. Phosphorus removal increased with light irradiation and an increasing light-dark photoperiod ratio. The highest phosphorus removal efficiency (67.6% w w^{-1}) was attained by *C. vulgaris*.

2.3.2 Gaseous Effluents

The gas mixture generated by the combustion of fossil fuels is composed of CO_2, sulfur, and nitrogen oxides. These gases can be used as a source of nutrients for microalgae cultivation; however, they can also be toxic, reducing the pH of the culture medium and inhibiting growth if they are added directly and in an unstructured manner (Zhao et al. 2015).

Carbon is one of the major components of microalgae and is needed at high concentrations for cultivation. Microalgae are composed of approximately 50% w w^{-1} carbon. This nutrient may be provided by atmospheric CO_2 from industrial gases (flue gas) or various other sources (Becker 1994). According to Grima et al. (2003), the supply of CO_2 as a carbon source can represent up to 41.3% of the total cost of producing microalgal biomass. In this context, the use of waste gases from combustion containing from 5 to 15% v v^{-1} CO_2 can provide sufficient amounts of carbon to produce microalgae on a large scale (Kumar et al. 2010), adding value to the combustion processes.

Microalgae can efficiently fix CO_2 from the atmosphere and industrial combustion gases through photosynthesis. Their capture capacity is approximately ten times higher than that of land plants. These microorganisms may accumulate inorganic carbon in their cytoplasm at greater concentrations by several orders of magnitude compared to the outside of the cell, a phenomenon called CO_2 concentration (Kaplan and Reinhold 1999; Badger et al. 2006; Pires et al. 2012). As reported by Chisti (2007), 1.8 kg of CO_2 is required to generate 1.0 kg of biomass.

CO_2 fixation by microalgae is a promising method for the post-combustion capture and storage of carbon. Compared to other methods, the biological conversion of CO_2 by microalgae has several advantages, such as wide distribution, good adaptability to the environment and low operating costs. In addition, the microalgal biomass produced during this bioprocess can be used in the production of bioenergy as well as for extracting high value-added biomolecules, representing the additional benefits of the process (Zhao and Su 2014). These benefits expand on the integrated concept of a microalgae biorefinery (Zhu 2015).

The selection of appropriate strains for CO_2 fixation has a significant effect on cost competitiveness and process efficiency. The desirable characteristics of microalgae for high CO_2 fixation rates include high rates of growth and consumption of CO_2; a high tolerance of trace constituents in the flue gases, such as SO_x and NO_x; an ability to produce bioproducts; ease of harvest; characteristics associated with spontaneous sedimentation or flocculation; tolerance to high temperatures of the liquid medium to minimize cooling costs of flue gases; and the ability to be cultivated with wastewater treatment effluent (Brennan and Owende 2010).

The presence of SO_2 can inhibit microalgal growth. Some species of microalgae are capable of growing at high SO_2 concentrations; however, a longer acclimatization period is needed compared to cultures grown without SO_2. At increased SO_2 concentrations, the inhibitory effect is enhanced, resulting in a marked reduction in the carbon fixation and biomass productivity (Lee et al. 2000).

In flue gases, the NO_x levels may vary from hundreds to thousands of ppm, with more than 90–95% NO and 5–10% NO_2 (Yoshihara et al. 1996). When the SO_2 concentration is high (>400 ppm), the pH of the medium decreases, resulting in low biomass productivity; however, there is no evidence of a direct influence on microalgal growth by NO at concentrations of approximately 300 ppm because NO is absorbed by the culture medium and then converted into NO_2. It can thus be used as a nitrogen source (Kumar et al. 2010).

Several studies have been conducted over the years to examine the use of combustion gases in microalgae cultivation. Negoro and Shioji (1991) evaluated the effects of SO_x and NO_x on the growth of ten strains of halotolerant marine microalgae. With 15% v v^{-1} CO_2, the growth of *Nannochloris* sp. and *Nannochloropsis* sp. was not affected at 50 ppm SO_2; however, at 400 ppm, the pH was reduced and growth ceased after 20 h of cultivation. The same strains were tested at a high level of CO_2 and 300 ppm NO. In the absence of significant changes in the pH, both growth profiles were affected by the presence of these pollutants. *Nannochloropsis* sp. showed no cell growth, while *Nannochloris* sp. grew after a long latency period.

Morais and Costa (2008) evaluated the removal of GHG by *Spirulina* sp. and *Scenedesmus obliquus* in 2 L Erlenmeyer bioreactors, which were aerated with a synthetic gas mixture (6% v v^{-1} CO_2, 100 ppm NO, and compressed air). The authors report a maximum fixation of 22.3% for CO_2 and 27.1% for NO in cultivation with *S. obliquus*.

During the cultivation of *Chlorella* sp. MTF-7, (Chiu et al. 2011) found that the maximum biomass concentrations reached 1.67, 1.50 and 1.32 g L^{-1} in mixtures containing CO_2 at 2, 10 and 25% v v^{-1}, respectively, and 2.4 g L^{-1} using commercial combustion gas as a carbon source. Radmann et al. (2011) found that a synthetic flue gas injection containing 12% v v^{-1} CO_2, 60 ppm SO_2 and 100 ppm NO in *Spirulina* sp., *Chlorella vulgaris* and *Scenedesmus obliquus* cultures caused no growth inhibition, reaching maximum biomass yields of 80, 90, and 60 mg $L^{-1}d^{-1}$, respectively.

The liquid effluents of waste and gaseous waters from the combustion of fossil fuels can be used as nutrients for cultivating microalgae. The integration of liquid and gaseous effluent treatments by microalgae can not only contribute to sustainability in wastewater treatment (Rawat et al. 2011; Razzak et al. 2013), but also turn out to be a sustainable process for producing microalgal biomass within the biorefinery concept (Pires et al. 2012; Zhu 2015).

3 Production of Biofuels From Microalgae

3.1 Biodiesel

In recent decades, lipid production for biodiesel synthesis has been a recurring issue in microalgal biotechnology. In most applications, the lipids are triacylglycerides, which are found in various species of microalgae (Vanthoor-Koopmans et al. 2013). Biodiesel can be obtained from various raw materials using a process called transesterification (or esterification) with supercritical fluids or by catalysis with acid, alkali or enzymes (Fukuda et al. 2001).

Biodiesel is obtained through the conversion of lipids in the methyl or ethyl esters of fatty acids using methyl or ethyl alcohol, respectively (Xuan et al. 2009). After transesterification, the final reaction mass is composed of two phases that are separated by decanting or centrifugation. The heavier phase is crude glycerine, which contains excess alcohol, water, and impurities that are inherent in the raw material. Due to the low solubility of the glycerol esters, this type of separation typically occurs quickly. The phase containing water and alcohol is subjected to evaporation, which eliminates these volatile constituents from crude glycerin through the liquefaction of these vapors in a suitable condenser. The esters are centrifuged and dehumidified, which results in biodiesel that meets the established technical standards (Ma and Hanna 1999).

The results in Unpaprom et al. (2015) indicate that the *Scenedesmus acuminatus* strain can be a valuable candidate for biodiesel production, because it led to lipid productivity (84.4 mg L^{-1} d^{-1}). With pH adjustment (between 6.8 and 7.2) and artificial wastewater, *Chlorella zofingiensis* presented a biomass productivity of 66.9 mg L^{-1} d^{-1}, a lipid productivity of 37.5 mg L^{-1} d^{-1} and a biodiesel yield of approximately 20% (Zhu et al. 2014). The *Spirulina* genus is little studied for use in biodiesel production due its lipid concentration (with a maximum of approximately 12.0% w w^{-1}, as found by Rosa et al. 2016). However, *Spirulina* cultivations can be used in large facilities due to their hardiness to changes in pH, temperature and light, as verified by Morais et al. (2009). Biodiesel obtained from *Spirulina platensis* (8.6% w w^{-1} of lipids) showed approximately 50% saturated fatty acids, 41% unsaturated fatty acids and 74% yield. The lower percentage of unsaturated fatty acids in microalgae biodiesel makes it more stable. Thus, in comparing *Spirulina* biodiesel with palm and tallow biodiesels (both of which have 43% saturated fatty acids and 57% unsaturated fatty acids) *Spirulina* produces a better biodiesel (Nautiyal et al. 2014). Systems that were designed for commercial biodiesel production using microalgae have reported productivities of 12,000 L ha^{-1} $year^{-1}$ (Seambiotic Israel) and 98,500 L ha^{-1} $year^{-1}$ (HR BioPetroleum Inc. Hawaii). These values are more attractive when considering that the algal ponds or bioreactors for microalgae cultivation are situated on non-arable land (Schenk et al. 2008).

3.2 Bioethanol

Microalgal biomass is a promising raw material for bioethanol production, because it contains carbohydrates such as cellulose and starch. Both polysaccharides can be converted into fermentable sugars for the production of biofuel. The production of bioethanol from microalgae begins with cultivation, followed by cell harvesting. Later, carbohydrates are released into the liquid medium through cell rupture (Mussatto et al. 2010; Chen et al. 2013). This step can be performed by physical methods that include high-pressure homogenization, microwave, ultrasound, and heat (Halim et al. 2012; Hernández et al. 2014, 2015) or by the dissolution of cell walls using enzymes. This step is essential because most of these compounds are trapped inside the cell wall (such as cellulose and hemicellulose) or inside the cell in the form of starch (Domozych et al. 2012). Soon after, the carbohydrates are separated extracting with water or an organic solvent. Once extracted, these compounds can be used for bioethanol production using technology similar to that used for other raw materials involving the saccharification and fermentation processes (Matsumoto et al. 2003).

Before fermentation, saccharification must be completed to hydrolyze the carbohydrates, making them fermentable. Saccharification may be chemical (acid or alkali) or enzymatic (Chen et al. 2013). The fermentation of microalgal biomass can occur with separate or simultaneous saccharification and fermentation (Balat et al. 2008). Fermentation occurs when yeasts metabolize carbohydrates under anaerobic conditions, turning them into bioethanol and CO_2. During the final step of the process, bioethanol is distilled and purified to remove water and other compounds that may be present in the final product (Mussatto et al. 2010).

The cultivation conditions (i.e., pH, temperature, illuminance, and primarily the concentration of the cultivation medium) influenced the microalgae composition directly. In this context, the removal of phosphorus and the reduction of the nitrogen concentration (0.125 g L^{-1}) in a *Chlorella minutissima* culture promoted the highest carbohydrate yields by microalga (Margarites and Costa 2014). The yield in ethanol was greater when using pretreated biomass from *Chlamydomonas reinhardtii* (51.2 $g_{ethanol}$ $g_{glucose}{}^{-1}$) compared to the reference medium (20.1 $g_{ethanol}$ $g_{glucose}{}^{-1}$) (Nguyen et al. 2009). Harun et al. (2010a) showed that *Chlorococcum* sp. has the potential to be used as a substrate for bioethanol production in the context of biorefineries. This research showed a significantly higher ethanol concentration (3.83 g L^{-1}) when the fermentation occurred with microalgae biomass that contained no lipids.

3.3 Biohydrogen

Biohydrogen is produced during anaerobic phases and under sulfur deprivation. Its advantage is its direct photoautotrophic production through the biophotolysis of

microalgae biomass (Kruse and Hankamer 2010), such that intensive energy is not expended in downstream processing. The remaining biomass from biophotolysis can be used for biogas production to improve yield, saving costs (Sialve et al. 2009). When there is a hydrogen production phase, half of the algal biomass is generated during the previous phase. Biohydrogen recovery is conducted in a separate reactor through membrane separation. Fluctuations in hydrogen production can be controlled in stable storage facilities for the discharge of hydrogen for its intended use (Meyer and Weiss 2014). The use of biomass, biodiesel, biomethane, and biohydrogen for energy production has aroused great interest (Wijffels and Barbosa 2010). Biohydrogen production by microalgae can be economically competitive with other technologies with this same purpose, such as wind-powered electrolysis (Ni et al. 2006).

The hydrolysis of biomass with lactic acid bacteria followed by the indirect photolysis of microalgal biomass led to photosynthetic H_2 production, resulting in H_2 yields of up to 8 mol H_2 mol^{-1} of starch–glucose from *Chlamydomonas reinhardtii* (66% starch conversion efficiency) (Ike et al. 1997). H_2 production occurs under the dark fermentation of *Chlorella vulgaris* and *Dunaliella tertiolecta* microalgae at 60°C (Carver et al. 2011). The integration of dark fermentation (with *Clostridium butyricum*) with the mixotrophic cultivation of *Chlorella vulgaris* presented maximum biohydrogen production (205 mL L^{-1} h^{-1}) and no discharge of chemical oxygen demand because the byproducts of dark fermentation and the cultivated biomass were reused (Liu et al. 2013). A *C. vulgaris* biomass concentration of 10 g L^{-1} with enzymatic pretreatment at thermophilic conditions increased the H_2 yields sevenfold (135 mL_{H2} $g_{volatile\ solids}{}^{-1}$) and the energy yield from the H_2 fermentation (1.46 kJ $g_{volatile\ solids}{}^{-1}$), which is higher than the reported values in the literature (Wieczorek et al. 2014).

3.4 Biomethane

Biomethane can be generated by the anaerobic digestion of microalgae biomass in combination with other materials. Raw biogas contains approximately 55–75% w w^{-1} biomethane, 20–35% w w^{-1} CO_2 and 3,000–5,000 ppm hydrogen sulfite (H_2S). Depending on the feedstock, biomethane can be present in the biogas, with trace gases such as nitrogen (N_2), ammonia (NH_3), sulfur dioxide (SO_2), and hydrogen (H_2) (Kao et al. 2012). For several species, its high proportion in proteins decreases the carbon/nitrogen ratio to an average of 10.2 for freshwater microalgae (Elser et al. 2000). More biomethane is obtained from microalgae after the using the same approach to produce hydrogen because the levels of starch and lipids in the residue are higher (Doebbe et al. 2010).

He et al. (2016) applied biopretreatment with *Bacillus licheniformis* bacterial culture in *Chlorella* sp. cultivations, which increased the chemical oxygen demands (27%), volatile fatty acids (27%), and biomethane production by 13.5%. Low concentrations of *Clostridium thermocellum* can increase the bacterial cell

disruption of *C. vulgaris* and increase biomethane production by approximately 5% (Lü et al. 2013). Another way to increase the biomethane production would be through the thermal pretreatment of algal biomass to increase its digestibility (Yen and Brune 2007). However, during this process, the energy consumed during pretreatment can be higher than the energy obtained through the combustion of the resulting biomethane.

4 Other Bioproducts of Microalgal Origin

4.1 Polysaccharides

In addition to the production of bioethanol, polysaccharides of microalgal origin are high-value compounds. These carbohydrates have applicability in food and textile products as stabilizers, emulsifiers, lubricants, and thickeners (Arad and Levy-Ontman 2010). The sulfated polysaccharides in the walls of microalgae cells exhibit pharmacological activity and may be used in the development of medicines and cosmetics. These polysaccharides have activity as antioxidants (Chen et al. 2010), anti-inflammatories (Matsui et al. 2003), antivirals (Kim et al. 2012), and anticancer compounds (Fedorov et al. 2013). Studies on animal feed have shown that rodents whose diets are supplemented with low concentrations of red-microalgae polysaccharide have significantly reduced serum levels of cholesterol, triglycerides and low-density lipoprotein (Dvir et al. 2009), with no evidence of toxic side effects (Arad and Levy-Ontman 2010).

The cell wall of *Porphyridium* sp. contains sulfated polysaccharides that have been shown to have antiviral and anti-tumor activities. This anti-tumor activity has been demonstrated against myeloid Graffi tumors, both in vitro and in vivo, in hamsters. Antiviral activity was observed against herpes simplex virus (type 1 and 2) and varicella zoster virus (Huleihel et al. 2001). *Porphyridium* sp. polysaccharides are not toxic compared to other sulfated sugars, making them promising candidates for use in the development of pharmaceuticals and cosmetics, especially for topical applications (Arad and Levy-Ontman 2010).

4.2 Polyunsaturated Fatty Acids

Polyunsaturated fatty acids (PUFAs) are essential nutrients that cannot be synthesized by higher eukaryotes and are thus high-value compounds in the food market. Among all the PUFAs that are produced commercially by microalgae, eicosapentaenoic acid (EPA, 20: 5, ω-3) and docosahexaenoic acid (DHA, 22: 6, ω-3) are of particular interest due to their bioactivity. Studies have shown that microalgae may contain high concentrations of EPA and DHA, and these organisms are considered

potential sources of these fatty acids (Spolaore et al. 2006). When microalgae are subjected to stress conditions such as nutrient depletion, pH changes, and high salinity, the fatty acids can be found as triacylglycerols (Hu et al. 2008). In addition, microalgae contain two essential fatty acids, EPA (C20:5) and DHA (C22:6) as well as other ω-3 fatty acids that most other cultures do not have. These essential fatty acids must be ingested because they are not synthesized through animal metabolism. Therefore, it is very important to search for sources of EPA and DHA (Vanthoor-Koopmans et al. 2013).

4.3 Proteins, Protein Hydrolysates, and Peptides

The high protein content of microalgae has caused these organisms to be considered an unconventional protein source. The concentration of this macromolecule is based on crude protein, which is commonly used in the assessment of food and feed (Becker 2004). For example, the cyanobacterium *Spirulina* has a high protein content (greater than 65% w w^{-1}) as noted by Rosa et al. (2015).

Protein hydrolysates are monomers obtained during protein processing. They include peptides, which may be composed of two or more amino acids joined by peptide bonds. Hydrolysis may occur by chemical (acidic or basic), physical or enzymatic means. When it occurs enzymatically, hydrolysis is used to improve the physical, chemical, and functional food properties and the absorption of the matrix, without damaging the nutritional value (Lisboa et al. 2014). Lisboa et al. (2014) achieved a higher degree of protein hydrolysis in *Spirulina* sp. LEB 18 (55.3%) and *Chlorella pyrenoidosa* (52.9%) using the Protemax 580L enzyme.

Microalgae have been recommended as an alternative protein source due to their high protein contents and amino acid profile (Romero García et al. 2012). *Spirulina*, *Chlorella,* and *Dunaliella salina* are used in diets as sources of bioactive peptides due to their high protein content and good nutritional value (Castro-Puyana et al. 2013). Some studies have reported that peptides from various food sources have antihypertensive, antioxidant, anticancer, antimicrobial, immunomodulating, and cholesterol-reducing effects (Shahidi and Zhong 2008). Derivatives of marine bioactive peptides have attracted attention because of their numerous health benefits, such as their use in functional foods, nutraceuticals, and pharmaceuticals with therapeutic potential in the treatment or prevention of various diseases (Kim and Kang 2011).

4.4 Pigments

Pigments are specific molecules that are present in photosynthetic microorganisms to collect light energy. These compounds can be divided into chlorophylls, carotenoids, and phycobilins (Masojídek et al. 2013). Chlorophyll a is the primary

pigment in all photosynthetic organisms, followed by accessory pigments such as chlorophyll b, chlorophyll c, chlorophyll d, carotenoids, and phycobilins (Yen et al. 2013).

Chlorophyll (Chl) is made up of a tetrapyrrole ring containing a central magnesium atom and a long-chain terpenoid alcohol. All Chl have two major absorption bands, 450–475 nm (blue or blue-green) and 630–675 nm (red), which result in their characteristic green color (Masojídek et al. 2013). Chl is used primarily as a food additive to provide a green color to foods such as pasta, pesto and wormwood products. Pastes that contain *Spirulina* Chl are sold as a substitute for the strong roots used in Japanese cuisine (Hosikian et al. 2010), as an ingredient in deodorants and in pastilles to fight bad breath (Koller et al. 2015).

Carotenoids are yellow, orange, or red pigments. They are found in most photosynthetic organisms, are insoluble in water, and are usually linked to the membranes inside the cells within the chloroplast in most algae or in photosynthetic cyanobacterial lamellae (Xiao et al. 2011). Astaxanthin is used for the dietary supplementation of salmon and trout to give an orange pigment to their meat (Hussein et al. 2006). This compound can be found in microalgae biomass and orange crustaceans (Yen et al. 2013). Astaxanthin is a carotenoid with powerful antioxidant activity in comparison to β-carotene (with ten times the activity) and α-tocopherol (with five hundred times the activity) (Dufosse et al. 2005). In this context, astaxanthin has high potential for scavenging free radicals, consequently acting against cancer and several inflammatory processes (Hussein et al. 2006).

Blue phycobiliproteins are produced by the genus *Spirulina* and red-microalgae, such as the genera *Porphyridium*, *Rhodella,* and *Bangia*, at a kilograms-per-year scale. The global market was estimated at approximately $50 million in 1997, with prices ranging from US $3 to $25 mg^{-1} (Milledge 2011).

Spirulina is a unique mixture of carotenoids, zeaxanthin, and phycocyanin (Chopra and Bishnoi 2007), which create this organism's blue-green color. Green algae such as species in the *Chlorella* genus have the highest chlorophyll content of all the microalgae. *Chlorella* is marketed worldwide, with an annual output of 2,000 tons of dry powder, representing 50% of the *Chlorella* produced in Taiwan (Milledge 2011). *Spirulina* is rich in C-phycocyanin, which is generally present in cyanobacteria, rhodophytes, and cryptophytes (Glazer 1994). As a result, phycobiliproteins can improve the efficiency of photosynthetic microalgae. Among the various phycobiliproteins, C-phycocyanin is the predominant pigment present in microalgae, whereas allophycocyanins are a minority (Moraes et al. 2010). Therefore, C-phycocyanin has been investigated as a natural food coloring, replacing the synthetic pigments (Mary Leema et al. 2010) and acting as a colorant in cosmetic products such as lipstick and eyeliner (Sarada et al. 1999), among other uses. Furthermore, C-phycocyanin may be used in the pharmaceutical and cosmetic industries due to its antioxidant, anti-inflammatory, and neuroprotective properties (Romay et al. 2003).

4.5 Biopolymers and Polyhydroxyalkanoates

Biopolymers are considered plastics of biological origin, and they are analogous to polymers of petrochemical origin. The primary advantage of bioplastics is their rapid and total degradability when deposited in the environment (Somleva et al. 2013). The polyhydroxyalkanoates (PHAs) are a group of materials that are involved in carbon storage, energy, and stress metabolites; they accumulate in prokaryotic microorganisms, typically in response to unfavorable growth conditions. Poly-β-hydroxybutyrate (PHB) is the simplest constituent of these biopolymers; it is a natural thermoplastic polyester with properties similar to those of plastics derived from petroleum. The synthesis of PHA and PHB was demonstrated in cyanobacteria such as *Spirulina* sp. (Morais et al. 2015b), *Nostoc* sp. (Sharma and Mallick 2005), and *Synechocystis* sp. (Panda et al. 2006).

A study by Martins et al. (2014) showed that *Spirulina* sp. LEB 18 produced a maximum of 44% w w^{-1} of biopolymer when grown autotrophically in Zarrouk medium modified through the reduction of 90% w w^{-1} $NaNO_3$ and 50% w w^{-1} $NaHCO_3$. For the same microalgal strain grown with Zarrouk medium diluted to 20% v v^{-1} with water from the Mangueira lagoon, Morais et al. (2015a) found a maximum PHB concentration of approximately 30% w w^{-1}. The PHA concentration produced by *Spirulina subsalsa* increased by approximately 12% w w^{-1} when the NaCl concentration was doubled (Shrivastav et al. 2010). In mixotrophic cultures of *Synechocystis* sp. PCC 6803, the synergistic effect of phosphorus deficiency and limitations in the gas exchange increased the PHB concentration up to 38% w w^{-1} (Panda and Mallick 2007).

The cyanobacterium *Nostoc muscorum* showed 8% w w^{-1} PHB when grown photoautotrophically, but when cultivated mixotrophically with the addition of 0.4% w v^{-1} glucose and acetate, the polymer concentration increased to 35% w w^{-1} (Sharma and Mallick 2005). Bhati and Mallick (2012) also reported the accumulation of other copolymers such as poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and P(3HB-co-3HV) in *Nostoc muscorum* up to 58 to 60% w w^{-1} under phosphorus and nitrogen deficiency and supplementation with 0.4% w w^{-1} acetate and valerate. P(3HB-co-3HV) is a copolymer that gives plastics a lower hardness compared to poly-3-hydroxybutyrate (Borowitzka 2013).

5 Residual Biomass of Microalgae

Biofuels produced from a wide range of raw materials have the potential to reduce GHG emissions (Bucy et al. 2012). In particular, the use of microalgae as a feedstock has been highlighted in recent years (Zhu and Ketola 2012). Studies have been conducted on the commercialization of microalgae-based biodiesel production (Singh et al. 2011), but this production is still expensive (Yusuf et al. 2011). For the relevant processes to be economically feasible, an alternative is the use of most of

the cellular components (proteins, carbohydrates, and lipids) in biorefineries (Demirbas 2009).

The residual biomass that forms after lipid extraction for biodiesel production is high in protein and carbohydrates. These proteins may be used for animal feed (Mata et al. 2010), and carbohydrates can be exploited as a raw material for bioethanol production (Harun et al. 2010a). Rashid et al. (2013) presented a brief overview of residual biomass applications using microalgae. According to these authors, this biomass can be converted into biofuel and other products, including a food supplement for cattle, biosorbents of heavy metals from industrial effluents and dyes.

To utilize the cellular components fully, the residual material that remains after the production of biodiesel and ethanol can be subjected to pyrolysis to convert it into bio-oil (Mirsiaghi and Reardon 2015). Thangalazhy-Gopakumar et al. (2012) performed a catalytic pyrolysis of green algae to produce hydrocarbons using the HZSM-5 catalyst in a fixed-bed reactor. These authors identified negative attributes of the bio-oil from algae, such as high levels of nitrogen and oxygen, which were reduced by using HZSM-5 as a catalyst.

Kim et al. (2015) investigated the pyrolysis characteristics and kinetics of *Dunaliella tertiolecta* by examining the residual biomass obtained after the extraction of lipids and saccharification. The initial biomass of *D. tertiolecta* was composed of 22.0% w w^{-1} lipids, 40.5% w w^{-1} carbohydrates, 27.2% w w^{-1} proteins and 10.3% w w^{-1} ash. After lipid extraction, the residual biomass was analyzed. The carbohydrate, protein, and ash contents then increased by 51.9, 35.0, and 13.1%, respectively. Saccharification was performed on the residual biomass, yielding a second residual biomass composed primarily of protein (67.7%, w w^{-1}). Finally, the authors concluded that the residual biomass remaining after the pyrolysis of *D. tertiolecta* could contribute to a microalgal biorefinery.

Both the biomass of microalgae in nature and the residual biomass from lipid extraction may be used for ethanol production (Harun et al. 2010a). To facilitate fermentation, several methods have been used to convert biomass to fermentable substrates, including thermal and alkaline conditions (Yang et al. 2011), acid treatment (Talukder et al. 2012) and sonication (Jeon et al. 2013). Mirsiaghi and Reardon (2015) evaluated the effects of different cell wall carbohydrate hydrolysis methods on the residual biomass of *Nannochloropsis salina*. The authors found that hydrolysis with sulfuric acid increased the yield of the released carbohydrates, while the highest rate of carbohydrate release was obtained through hydrochloric acid treatment. Thus, the authors concluded that the hydrolysates that were generated from the residual biomass could be used as a substrate for producing biofuel and bioproducts by fermentation.

The carbohydrate content and composition of the residual biomass obtained from lipid extraction depends on the microalgal species (Schwede et al. 2013), cultivation phase (Fernández-Reiriz et al. 1989), growth conditions (Sukenik et al. 1993; Schwede et al. 2013) and lipid extraction process (Yang et al. 2011). According to Park et al. (2012), residual biomass defatted with organic solvent (hexane) is recommended for biogas but not for bioethanol production. After the

lipids and pigments are extracted from the microalgal biomass, they can be used as substrates for fermentation to produce biohydrogen. Yang et al. (2011) observed a decrease in biohydrogen production when the initial concentration of residual microalgal biomass was increased from 4.5 to 45 $g_{volatile\ suspended\ solids}\ L^{-1}$.

Nobre et al. (2013) used the biomass of the Nannochloropsis sp. microalga as raw material to produce fatty acids for biodiesel, biohydrogen and high value-added compounds. The microalgal biomass, which contained high levels of fat and pigments (primarily carotenoids), was subjected to supercritical extraction with CO_2. It was possible to extract 45% w w^{-1} of the lipids and recover 70% w w^{-1} of the pigments. Furthermore, the authors found that the remaining biomass was effectively usable as a raw material for the production of biohydrogen through fermentation by *Enterobacter aerogenes*, resulting in a biohydrogen yield of 60.6 g mL^{-1} of dry biomass.

Extraction residues of microalgal biomass have potential for use as feedstock in biorefineries. The use of residual biomass contributes to the production of renewable energy and the sustainable development of a microalgae biodiesel industry. The focus has been lipid extraction; nevertheless, for the more efficient use of the biorefinery concept, the residual biomass from the extraction of other macromolecules, such as proteins, carbohydrates, and several others biocompounds, can be further explored.

6 Final Considerations

Microalgae have the potential to produce biofuels and high value-added bioproducts with various applications. Using microalgal biomass within a biorefinery concept contributes to the production of clean energy and products for nutrition and health, bringing benefits to society such as food safety, employment and income. In addition, the cultivation of microalgae can positively influence the environment, for example, through sustainable land use and reductions of GHG emissions and wastewater. Therefore, as shown in this review, the development of a microalgae-based biorefinery is a promising, environmentally friendly, and self-sustaining alternative.

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