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# Valorization of Microalgae and Energy Resources

*Cynthia V. González-López, Francisco García-Cuadra,  
Natalia Jawiarczyk, José M. Fernández-Sevilla  
and Francisco G. Acién-Fernández*

## Abstract

Microalgae biotechnology has grown very rapidly in the last few decades due to the multiple applications that these microorganisms have from pharmaceuticals and cosmetics to foods/feeds and biofuels. One of the main challenges in expanding this industry is to enlarge the single use of the biomass produced in addition to reducing the high biomass production cost of the current technologies. To overcome this bottleneck, the development of microalgae-based biorefineries has been proposed. The issue is to obtain as many bioproducts as possible from the cultivated biomass, including biofuels. Consequently, biodiesel production (from the lipid fraction), bioethanol (from carbohydrate fraction), and biogas or bio-oil (from the whole biomass) have been posited. In this book chapter, we review the current state of the art in the production of sustainable biofuels from microalgae and analyze the potential of microalgae to contribute to the biofuel sector.

**Keywords:** microalgae, biodiesel, bioethanol, biogas, biorefinery

## 1. Introduction

The policy trends regarding fuel consumption and greenhouse gas emissions are heading progressively towards an increase in renewable alternatives over the coming decades. There has been a significant rise in the production of solar, wind, marine, hydro, geothermal and biomass energy [1]. With regard to the transport sector, apart from electrification using renewable electricity, biofuels are the only sustainable alternative for reducing greenhouse gas (GHG) emissions. The current share of renewables in the transport sector is almost 3% as a result of using biofuels [2]. In 2014, global liquid biofuel production was 126 million m<sup>3</sup> of which 78 were bioethanol, 32 were biodiesel and 16 were advanced biofuels [2]. Focusing on the biomass, this can be converted into first, second or third-generation biofuels depending on the source of the organic material. First-generation biofuels are produced from food crops or vegetables. A serious debate still exists about their use as a source of biofuels given the land-use competition with food. Because of this, second-generation biofuels were developed to overcome the first-generation limitations. These are produced from non-food crops such as wood, organic waste, food crop waste and specific biomass crops such as jatropha or jojoba. However, the production capacity is low, so third generation biofuels were proposed to improve process sustainability.

Microalgae are the feedstock for third-generation biofuels. They possess several advantages over higher plants especially their rapid growth rate and photosynthetic yield [3]. Furthermore, they can be cultivated on non-arable lands and using water sources that are not intended for human consumption [4]. Their high metabolic plasticity is of great importance, as it allows the biomass composition to be modulated in response to culture conditions, thus the production of the metabolite of interest can be augmented [5]. However, the large-scale commercialization of biofuels from microalgae looks unlikely, mainly because of its negative economic balance resulting from the high production and processing cost of the biomass [6]. Nevertheless, an approach using the biorefinery concept would allow numerous compounds of interest to be obtained from the microalgae instead of just a single biofuel. The biomass would be fractionated into its main components, obtaining various bioproducts from each of them. The cultivation of microalgae must also be coupled with a reduction in greenhouse gas emissions by utilizing exhaust combustion gases as well as wastewater treatment services [7]. In this way, the generation of biofuels from microalgae would add to the contribution made by other types of renewable sources.

The 2011 biofuels roadmap used in the transportation sector [8] stated that up to 27% of worldwide transportation fuel could be supplied from biofuels by 2050. The European Union (EU) has established a 7% limit on the consumption of biofuels produced from agricultural crops in favor of advanced biofuels obtained from other feedstocks, which includes microalgae [9]. Within the international framework, several projects focusing on biofuels from microalgae production have been promoted over recent years [8]. In the United States of America (USA), the greatest producer of biomass-based biofuels, the National Renewable Energy Laboratory (NREL) resumed the R&D program for microalgae biofuels in 2006, and the National Alliance for Algal Biofuels and Bioproducts (NAABB) received 44 M\$ of funding in 2009 for three integrated biorefinery demonstration plants—Solazyme, Algenol and Sapphire—with a combined funding total of almost 97 M\$. In addition, several consortia were created, such as the Algal Biomass Organization (ABO), the Consortium for Algal Biofuels Commercialization (CAB-Comm), the Sustainable Algal Biofuels Consortium (SABC), the Cornell Marine Algal Biofuels Consortium, the Algae Testbed Public Private Partnership (ATP3) and the Regional Algal Feedstock Testbed (RAFT).

In the EU, the European Commission's (EC) 7th Framework Program (FP7) supported the development of biofuels from microalgae projects such as Sunbiopath, Algadisk and Aquafuels (2009) with the objective of selecting microalgae strains that are valuable for biofuel production, optimizing culture conditions and developing techno-economic reports for microalgae biorefineries. As a result, the European Algae Biomass Association (EABA) was created. In the United Kingdom, the Algae Biofuels Challenge was launched in the Advanced Bioenergy Accelerators strategy framework and promoted by The Carbon Trust. They are also developing the InteSusAl Project, having already built a 1 Ha pilot plant in Olhão (Portugal). In Germany, the BioEnergie 2021 program started in 2004 and led to the establishment of the European Algae Biomass Association (EABA) in 2009. Portugal obtained funding for the BioFAT Project, having built a 0.5 Ha pilot plant in Pataias (Portugal) and another in Camporosso (Italy) includes a projected construction of a 10 Ha facility. Spain has also shown great interest in biofuels and funded several projects using microalgae as the feedstock, such as CENIT CO<sub>2</sub>, MENOS CO<sub>2</sub>, Plan E, NOVARE and ALGAPLANE, which have also led to the construction of 2 pilot plants in Almería (Spain). Nowadays, All-Gas and SABANA Projects are currently underway. The objective of All-Gas is to develop a 10 Ha microalgae facility for biofuel production. SABANA is funded by the European Union's Horizon 2020

Research and Innovation program and is overseen by the University of Almería (Spain). SABANA aims to develop a large-scale integrated microalgae-based biorefinery based on a zero-waste process concept that is environmentally and economically sustainable. The EU is also presently funding several other projects in this field: AlgaeBioGas, which uses microalgae for the treatment of biogas digestate; DEMA, which produces ethanol; D-Factory, whose objective is to demonstrate the feasibility of *Dunaliella* cultivation at the large-scale (100 Ha); EnAlgae, which operates several pilot plants; and Fuel4ME, which produces biofuels at the pilot scale.

## 2. Large-scale production of microalgae biomass

Microalgae production can be accomplished in open systems such as open ponds or raceways, or in closed systems such as tubular photobioreactors or flat panels. Open systems are well established for commercial microalgae production, as they are the cheapest to operate and offer lower energy capture efficiency. For these reasons, facilities of up to 200 ha have recently been constructed in China although most conventional systems average up to 20 Ha. When using raceway reactors, the facilities comprise 5000 m<sup>3</sup> units operated in batch or semi-continuous mode, which achieve biomass productivities from 20 to 60 T·Ha<sup>-1</sup>·year<sup>-1</sup>. When high value products are the target, then closed systems (PBRs) are chosen. Furthermore, PBRs provide higher volumetric biomass productivities, which involve lower harvesting-associated costs. In this case, much smaller facilities are in operation worldwide, ranging from 1 to 10 Ha; these are typically composed of multiple reactors, each up to 20 m<sup>3</sup>. When using closed reactors, biomass productivities vary between 40 and 80 T·Ha<sup>-1</sup>·year<sup>-1</sup> although the most significant advantage is the high quality of the biomass produced. Whichever the type, the overall biomass productivity from any microalgae-related system depends on the production technology used, the geographic location and the culture conditions [10–12]. Light availability is the key factor for biomass generation, while for large-scale microalgae production, large amounts of nutrients are also required. Consequently, the only way to make the process feasible is to provide nutrients from waste.

To be sustainable, the energy balance in microalgae-related systems must be positive, so the Net Energy Ratio (NER) of the process must be considered. This represents the energy gained divided by the energy consumed. A value above 1.0 is required to make the process feasible. It has been shown that values of 1.01 are achievable with flat panels and 1.40 with raceways, whereas with tubular photobioreactors, a value of only 0.21 has been achieved [13, 14]. In microalgae-related systems, the energy consumption of the biomass processing step is very relevant. Therefore, depending on the technology used for this step, the energy consumption can be really high, making the use of biological processes more recommendable. In the next section, we discuss the various treatment possibilities.

## 3. Production of biofuels from microalgae

### 3.1 Bioethanol production

Bioethanol is the biofuel produced in the greatest quantity worldwide and it is used mainly in the transport sector [15] as a gasoline additive. The biggest producer in the world is the USA at around 60.9 million m<sup>3</sup> (56%), followed by Brazil at around 30.1 (28%), then Europe at 5.4 (5%) [16]. Bioethanol can be used as a substitute for petrol, as a blend component, or as a feedstock to produce Ethyl Tertiary Butyl Ether (ETBE),



which is an additive that improves the combustion characteristics of petrol. ETBE is produced from ethanol and isobutylene in a catalytic reaction and it represents 60% of ethanol consumption; this is expected to remain constant until 2030 [17].

Nowadays, bioethanol is produced from feedstocks such as sugar crops (mainly sugarcane, sugar beet or sweet sorghum), starch crops (mainly corn; wheat is the main crop in Europe) or lignocellulosic biomass (agricultural and forestry residues and energy crops). Using microalgae as a source for third-generation bioethanol production has been proposed because of their various advantages over higher plants [18]. It has been suggested that microalgae could produce up to  $140 \text{ m}^3 \cdot \text{Ha}^{-1} \cdot \text{year}^{-1}$  of ethanol compared to values below  $8.0 \text{ m}^3 \cdot \text{Ha}^{-1} \cdot \text{year}^{-1}$  for sugarcane or sugar beet [19]. If a low biomass productivity of  $20 \text{ g} \cdot \text{m}^{-2}$  is assumed, an annual yield of  $73 \cdot 10^3 \text{ kg} \cdot \text{Ha}^{-1}$  would be achieved, which is comparable to that of sugarcane crops (reported at  $70\text{--}77 \cdot 10^3 \text{ kg Ha}^{-1}$ , equivalent to an ethanol production of  $5\text{--}7 \text{ m}^3 \cdot \text{Ha}^{-1} \cdot \text{year}^{-1}$ ) [20]. Microalgae biomass contains polysaccharides (cellulose or starch) and other complex carbohydrates composed of monosaccharides like glucose, galactose, mannose, xylose, ribose, arabinose and other sugars [20]. Some microalgae and cyanobacteria are even able to excrete exopolysaccharides into the culture broth [21]. Several species have been proposed for bioethanol production because of their high carbohydrate content [22] although culture conditions can greatly modify the biochemical composition of any selected strain. This makes culture optimization and process control a key issue to tackle.

The process of bioethanol generation from previously harvested microalgae begins with releasing the polysaccharides from the biomass and converting them into fermentable sugars [18]. Thus, the first step is to break the cell wall and perform physical, enzymatic or chemical hydrolysis. Of these, acid hydrolysis is the most widely used as it provides a good conversion yield at a lower cost [23, 24]. The use of sulfuric, hydrochloric, or nitric acid at temperatures of  $120\text{--}140^\circ\text{C}$  for 15–30 min allows saccharification and fermentation yields higher than 80% [25] to be obtained. If enzymatic hydrolysis is chosen, amylases, cellulases, and/or pectinases are available depending on the types of carbohydrates coming from the biomass, achieving similar ethanol yields.

Hydrolysis is followed by the alcoholic fermentation of the sugars to ethanol. The microorganism used to carry out the fermentation should be selected based on the specific sugars released from the microalgal biomass. Traditionally, the most widely used is *Saccharomyces cerevisiae* although other yeasts such as *Pichia stipitis* could be used, or bacteria such as *Zymomonas mobilis* and even recombinant bacteria (e.g. modified *Escherichia coli*) that are tolerant to high ethanol concentrations [26]. It is important to adjust the pH to make it optimal for the selected microorganism prior to fermentation. When performing acid hydrolysis at a high concentration, substances might appear after neutralization that inhibits subsequent fermentation [25] so this should be taken into account. Another possible approach would be to perform saccharification and fermentation simultaneously in a single step. This process must be combined with dilute acid or high temperature pretreatment; it also requires compatible conditions (pH, temperature, substrate concentration) for the enzymatic treatment and the fermentation process [27].

The ethanol yields obtained cover a very wide range, depending on the microalga strain, the culture conditions, and the hydrolysis and fermentation conditions (**Table 1**); hence all of the variables involved should be optimized for each specific case [20, 24].

The last step of the process is ethanol recovery and ethanol purification from the fermentation broth. This is usually performed using distillation or rectification, which is yet a well-established step for first and second-generation ethanol production processes.

Microalga	Hydrolysis	Fermentation	Ethanol production, g·g <sup>-1</sup> biomass	Reference
<i>Chlorococcum humicola</i>	Acid (3% v/v H2SO4, 160°C, 15 min)	<i>Saccharomyces cerevisiae</i>	0.52	[23]
<i>Chlorella vulgaris</i>	Acid (3% v/v H2SO4, 110°C, 105 min)	<i>Escherichia coli</i>	0.40	[28]
<i>Chlamydomonas reinhardtii</i>	Acid (3% v/v H2SO4, 110°C, 30 min)	<i>Saccharomyces cerevisiae</i>	0.29	[29]
<i>Scenedesmus obliquus</i>	Acid (2% v/v H2SO4, 121°C, 20 min)	<i>Zymomonas mobilis</i>	0.21	[30]
<i>Chlorococcum infusionum</i>	Basic (0.75% w/v NaOH, 120°C, 30 min)	<i>Saccharomyces cerevisiae</i>	0.26	[18]
<i>Chlorella vulgaris</i>	Enzymatic (pectinase)	<i>Saccharomyces cerevisiae</i>	0.89	[31]
<i>Chlamydomonas reinhardtii</i>	Enzymatic (amylase and glucoamylase)	<i>Saccharomyces cerevisiae</i>	0.23	[32]
<i>Chlamydomonas fasciata</i>	Enzymatic (glutase)	<i>Saccharomyces cerevisiae</i>	0.19	[33]
<i>Synechococcus sp.</i>	Enzymatic (lysozyme and α-glucanases)	<i>Saccharomyces cerevisiae</i>	0.27	[34]

**Table 1.**  
Bioethanol production under different conditions.

### 3.2 Biodiesel production

In the EU, diesel constitutes around 70% of total transport fuel; among biofuels, biodiesel is the most widely used, accounting for an annual production of 14.3 million m<sup>3</sup> [2]. In the USA, biodiesel production accounts for 72 million m<sup>3</sup> with a total capacity of 95 [35]; this includes fatty acid methyl esters (FAMES) and diesel blends (HVOs). Biodiesel can be used for transport as it is, or it can be blended with fossil diesel fuel at various dosages up to 7%, according to European legislation [17]. Biodiesel is produced from feedstocks such as soybean oil (the main feedstock in the USA), rape seed oil (the main feedstock in the EU), corn oil, canola oil, used cooking oils, sunflower seed oil, palm oil or animal fats. As with bioethanol, it can be a first, second or third-generation biofuel depending on the source.

Focusing on microalgae as the feedstock, biomass productivities above 30 g·m<sup>-2</sup>·d<sup>-1</sup> are easily attainable; however, this is not compatible with high lipid contents (%d wt.). The accumulation of fatty acids can be triggered by modulating the culture conditions, for instance, by inducing N starvation, but this leads to a drop in biomass productivity. As an example, [12] achieved biomass and fatty acid productivities of 33.1 and 3.5 g·m<sup>-2</sup>·d<sup>-1</sup>, respectively, under stress-free conditions. Even if a modest productivity of 8 g·m<sup>-2</sup>·d<sup>-1</sup> is supposed, 29·10<sup>3</sup> kg·Ha<sup>-1</sup>·y<sup>-1</sup> of biomass would be produced, which is much higher than the reported values for corn grains, at around 3.2–9.6·10<sup>3</sup> kg·Ha<sup>-1</sup>·y<sup>-1</sup> [8]. Therefore, the lipid fraction of the biomass can be destined for biodiesel production under the above-mentioned biorefinery concept.

With regard to the process for biodiesel production from microalgae, it usually starts with cell rupture as a pretreatment to increase accessibility to intracellular

Microalga	Water content, %	Method	Solvents	Lipids extracted, %d wt. biomass	Reference
<i>Nannochloropsis gaditana</i>	—	Solvent extraction (30 ml·g <sup>-1</sup> biomass, 10 min)	Water:chloroform:methanol (1:1:2)	24.5	[39]
<i>Phaeodactylum tricornutum</i>	—	Solvent extraction (30 ml·g <sup>-1</sup> biomass, 10 min)	Water:chloroform:methanol (1:1:2)	13.1	[39]
<i>Chaetoceros calcitrans</i>	—	Solvent extraction (30 ml·g <sup>-1</sup> biomass, 10 min)	Water:chloroform:methanol (1:1:2)	8.7	[39]
<i>Chlorella vulgaris</i>	—	Solvent extraction (12 ml·g <sup>-1</sup> biomass, 2 h)	Chloroform:methanol (1:2)	28.5	[40]
<i>Nannochloropsis gaditana</i>	—	Solvent extraction (10 ml·g <sup>-1</sup> biomass, 60°C, 45 min)	Methanol	38.3	[41]
Microalga	—	Method	Solvents	FAME yield, %	Reference
<i>Schizochytrium limacinum</i>	80	Solvent extraction (8 ml·g <sup>-1</sup> biomass, 90 °C, 40 min)	Methanol (catalyst H2SO4)	8.45	[42]
<i>Chlorella pyrenoidosa</i>	90	Solvent extraction (10 ml·g <sup>-1</sup> biomass, 150°C, 2 h)	Hexane:methanol 6:4 (catalyst H2SO4)	89.8	[43]
<i>Nannochloropsis salina</i>	76	Solvent extraction (7.5 ml·g <sup>-1</sup> biomass, 100°C, 1 h)	Methanol (catalyst H2SO4)	99.8	[44]

**Table 2.**  
*Biodiesel production under different conditions.*

lipids. This is followed by lipid extraction using physical and/or chemical methods [36]. Normally, chemical extraction is performed with a single organic solvent, such as hexane, or preferably a mixture of polar and non-polar solvents to increase selectivity and extractability. Lipid extraction by supercritical CO2 is also an interesting alternative that offers multiple advantages [37]; however, at the moment it is not

economically feasible at the large-scale. Other novel methods are being studied at the lab-scale, such as ultrasound-assisted extraction, microwave-assisted extraction, and the use of ionic liquids or bio-based solvents [38]. The FAME extraction yield is highly dependent on the biomass composition, the extraction method used, the solvent/s chosen and their ratios, variables such as temperature and process time, and biomass to solvent/s ratios (**Table 2**). Therefore, all these issues need to be optimized in each case.

The extracted lipids can be used as a fuel in power-generating devices but not in vehicle engines because of their low thermo-physical properties and high viscosity. Consequently, once the lipids have been extracted, they can be hydrotreated to produce HVOs or transesterified to obtain FAMES.

Another alternative is to perform direct biomass transesterification to obtain biodiesel in a single step, thus enabling the use of wet biomass, which would avoid the high costs attached to biomass drying. The drawback is that this process requires very intensive treatment so it hinders the valorization of other biomass fractions under a biorefinery concept. The microalgal biomass is processed with a suitable solvent and catalyst (usually H<sub>2</sub>SO<sub>4</sub>) at a high temperature (the higher the temperature, the lower the reaction time required). If wet biomass is used, one must take into account that the presence of water will have a negative effect on the catalyst's activity and its interaction with the lipids. For example, [43] found that it was necessary to increase the temperature from 90 to 150°C in order to maintain a high FAME conversion yield when the biomass contained 90% moisture. Furthermore, the use of wet biomass requires the addition of a greater amount of extraction solvent.

### 3.3 Biogas production

Biogas is produced from the anaerobic digestion of organic matter. The technology for doing this is well established. Besides sewage, manure, agricultural residues and other wastes, microalgal biomass can be used as the feedstock, therefore obtaining a third-generation biofuel. Anaerobic digestion is a complex sequence of metabolic reactions (hydrolysis, acidification, acetogenesis and methanogenesis) that allows the biomass to be converted into biogas by means of an anaerobic bacteria consortium. Biogas is composed of methane (50–75%), carbon dioxide (around 25–500%) and small amounts of other gases such as nitrogen and oxygen [45]. After upgrading to biomethane, it can be used in transport as Liquid Natural Gas (LNG) or Compressed Natural Gas (CNG). Biogas can also be combusted to generate heat/electricity. Biogas production worldwide was 59·10<sup>3</sup> million m<sup>3</sup> in 2014. The EU leads this production with 29·10<sup>3</sup> million m<sup>3</sup>, followed by China with 15 and then the USA with 9 [2].

When using microalgal biomass as the feedstock, a pretreatment is often required, mainly when the cell walls are composed of cellulose or hemicellulose, which are very hard and/or very thick. Once again, physical (ultrasound, high-pressure homogenization, heating...), chemical (oxidation, basic treatment...) or enzymatic treatments can be selected for this purpose [46]. Biodegradability mainly depends on the biochemical composition and the cell wall so anaerobic digestion is highly species-dependent. Moreover, it is preferable to use wet biomass as dry biomass diminishes biogas production by about 20% [47]. It is also important to pay attention to the biomass' C:N ratio since a low value reduces its digestibility—the optimal value is around 20–35. A high protein content makes the process difficult as it triggers the generation of ammonia, which has toxic effects on the bacteria. This is what happens when the biomass is previously subjected to lipid extraction to obtain biodiesel and the residual biomass is used for anaerobic digestion. To increase the C:N ratio, co-digestion with another raw material can be performed.



However, other inhibitory factors usually influence the process such as the presence of sulfate/sulfide, volatile fatty acids or high salinity.

Anaerobic digestion of the biomass is usually carried out at temperatures of 25–38 or 50–55°C [48], no higher as this would also inhibit biogas production. Ehimen et al. [49] found a 61% greater CH<sub>4</sub> yield at 35°C when compared to 25°C. Ward et al. [50] found faster biogas production when working at 55°C, achieving a 95% methane yield in only 11 days. However, this process requires higher energy inputs. With regard to the hydraulic retention time in the system, this should be maintained at around 30 days as it has been shown that methane production tends to rise asymptotically to a maximum value reached at around 30 days [51].

Taking all the above into account, we can see that the biomass conversion yield into biogas varies considerably (**Table 3**). A maximum biogas yield of 611 L·kg<sup>-1</sup> volatile solids (ash-free biomass) was reported for a biomass composed of several microalgae species [55].

After anaerobic digestion, a separation step is carried out. A solid residue is obtained that can be used as a biofertilizer and a liquid stream that can be recirculated into the cultivation system. This provides the nitrogen, phosphorous and other nutrients required to cultivate the biomass, which helps to make the process sustainable. Accordingly, [56] recycled 40.7 g of nitrogen (74%) and 3.8 g of phosphorous (35%) from 1 kg d wt. of biomass.

3.4 Biocrude production

A different approach is to perform a thermochemical conversion of the whole microalgal biomass into hydrocarbon fuels by thermochemical conversion. If the biomass is dry, the processes for this would be torrefaction, pyrolysis and gasification for solid, liquid and gas feedstocks, respectively. These processes could technically be an option but, as mentioned before, it is mandatory to work with wet biomass to make the process economically viable. Thermochemical processes for wet biomass are hydrothermal carbonization, hydrothermal liquefaction and hydrothermal gasification for solid, liquid and gas feedstocks, respectively. Of these, hydrothermal liquefaction (HTL) seems to be the most promising [57]. The chemistry of the process is still not known in full but it involves three main steps: depolymerization, decomposition and recombination. The process consists

Microalga	Reaction time, d	T, °C	Biogas production, m <sup>3</sup> ·kg <sup>-1</sup> volatile solids	Methane content, %	Reference
<i>Arthrospira maxima</i>	30	35	0.200	72	[52]
<i>Chlamydomonas reinhardtii</i>	32	38	0.587	66	[47]
<i>Dunaliella salina</i>	32	38	0.505	64	[47]
<i>Chroococcus</i> sp.	30	36	0.487	55	[53]
<i>Euglena gracilis</i>	32	38	0.485	67	[47]
<i>Arthrospira platensis</i>	32	38	0.481	61	[47]
<i>Chlorella vulgaris</i>	32	30	0.467	75	[54]
<i>Chlorella kessleri</i>	32	38	0.335	65	[47]
<i>Scenedesmus obliquus</i>	32	38	0.287	62	[47]

**Table 3.**  
Biogas production for several microalgae with no pre-treatment.

Microalga	Reaction time, min	T, °C	Biocrude yield, %	Reference
<i>Tetraselmis</i> sp.	5	350	65	[61]
<i>Nannochloropsis</i> sp.	60	350	43	[62]
<i>Chlorella pyrenoidosa</i>	30	280	64	[63]
<i>Chlamydomonas reinhardtii</i>	60	230	71	[64]
<i>Desmodesmus</i> sp.	5	375	49	[65]

**Table 4.**  
*Biocrude production for several microalgae.*

of heating wet biomass up to 370°C and 25 MPa for less than 30 min [58]. The bio-oil obtained is later separated from the aqueous phase. Subsequently, it has to be upgraded to liquid fuel and then refined to jet fuel, diesel or gasoline in order to make it suitable for use in transportation. The aqueous phase could be partially recycled to the algae photobioreactor [59] or to the hydrothermal reactor [60]. Alternatively, it could be upgraded to fuel gas (CO<sub>2</sub> and CH<sub>4</sub>) by catalytic hydrothermal gasification.

The conversion yield of microalgal biomass into biocrude by HTL depends on the biomass loading, temperature, pressure, reaction time and catalysts used; values close to 70% have been reported (**Table 4**). This product provides a heating value of up to 39 MJ·kg<sup>-1</sup> [66], similar to that from petroleum crude but containing large amounts of nitrogen and sulfur that lead to higher NO<sub>x</sub> and SO<sub>x</sub> emissions and greater viscosity and oxidation processes. Selecting adequate homogeneous/heterogeneous catalysts to increase the conversion yield and improve the quality of the obtained biocrude is being researched in depth.

#### 4. Biorefinery concept

Microalgae production facilities must operate under a biorefinery concept in order to obtain as many bioproducts as possible in addition to the biofuels. As explained before, the production of biofuels from microalgae is technically but not economically feasible. It is essential to lower the biomass production cost by improving the photobioreactors design and the biomass harvesting. It is also important to optimize extraction processes based on wet biomass, as drying imposes one of the greatest production costs. Furthermore, the process should be coupled with wastewater treatment and the use of CO<sub>2</sub> from exhaust gases to reduce costs; however, this would limit the end use of the obtained products because of contamination.

With regard to the process chain, one should bear in mind that this depends, to a large extent, on the species and culture conditions employed. Therefore, it is not possible to propose a general process flow diagram as this depends on the strain, its biochemical composition, and if it produces a specific compound of interest as a bioproduct, etc. In whichever case, the first step is to break down the cells (mechanical, chemical or enzymatic processes). Then, the main objective is to separate each fraction of interest without damaging the others. For example, some authors propose using the protein fraction of the biomass first, followed by the carbohydrates and finally the lipids [67]. This would preserve the quality of the amino acids, which would otherwise be diminished by the steps involved in carbohydrate and lipid valorization. It was then proposed to use the carbohydrates first, followed by the proteins and finally the lipids as the process was more efficient [68]. Further

approaches are available in the literature [69], some recommending the valorization of the carbohydrates first [70] while others start with lipid valorization [71]. In any case, the residual biomass will finally undergo an anaerobic digestion process to obtain biogas and recycle nutrients to the system.

## 5. Conclusions

Nowadays, microalgae production is considered as part of a biorefinery concept. The challenge is to obtain as many bioproducts from the biomass as possible—the production of biodiesel (from the lipid fraction), bioethanol (from the carbohydrate fraction) and biogas (from the residual biomass) or biocrude (from the whole biomass)—all part of a biomass valorization chain. These products will not replace current fuels but, together, they will help to improve transport sustainability when used in conjunction with other renewable energies.

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## Conflict of interest


The authors declare no conflict of interest.

## Author details

Cynthia V. González-López\*, Francisco García-Cuadra, Natalia Jawiarczyk,  
José M. Fernández-Sevilla and Francisco G. Ación-Fernández  
Department of Chemical Engineering, University of Almería, Almería, Spain

\*Address all correspondence to: [cynthiagonzalez@ual.es](mailto:cynthiagonzalez@ual.es)

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