Mini Review

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Microalgae to biofuels production: a review on cultivation, application and renewable energy

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Abstract: Algae are increasingly emerging as one of the most promising sustainable and long-term sources of biomass and oils for fuel, feed food and other co-products. What makes them so attractive are the large number and wide variety of benefits associated with how and where they grow. This review presents added values and recent developments in resource recovery from microalgae. The main focus was in the cultivation and application of microalgae on biofuel recovery. Nearly all these benefits stem from the fact that these plants have evolved over billions of years to produce and store energy in the form of oil, and they do this more efficiently than any other known natural or engineered process. The results show that the investment in a microalgae biomass project can be associated with various processes, which include: growth of microalgae, harvesting, dehydration and extraction of oils. In addition, there are always project costs, which include engineering, infrastructure, installation and integration and contract fees.

Keywords: anaerobic digestion; biofuels; microalgae; pyrolysis; renewable energy.

Introduction

For three and a half billion years, microalgae have colonized almost all of the planet's ecosystems: from oceans to glaciers, through hyper-salt lakes, soils, rocks and trees.

These unicellular photosynthetic microorganisms, which use light as a source of energy to fix inorganic carbon (CO_2), play a key role in the functioning of marine ecosystems and shape the climate by modulating atmospheric CO_2 (1).

Nearly 50 gigatons of organic carbon are thus formed each year by these organisms, of which 8–15 gigatons are exported to the deep ocean (2–4).

Beyond their contribution to the carbon cycle and the production of oxygen, microalgae are promising for the future. At present, because of the climatic deregulation and the depletion of oil resources (5), the use of fossil fuels as a major source of energy is widely disputed. Thus, these micro-organisms are the focus of increasing attention in the field of bioenergy (6, 7). Their high productivity, high growth rates [doubling time can be only 3.5 h (8)] and far superior to those of terrestrial plants, as well as a capacity, for some species, to store large amounts of lipids have positioned them as a promising source of so-called third-generation biofuels that are based on a feedstock which does not compete with human food sources (9).

The interest of microalgae also lies in the range of molecules they can produce, such as antioxidants, pigment, long chain polyunsaturated fatty acids or vitamins. This diversity is expressed through a large number of applications and many markets in the future. Microalgae thus offer a great potential for innovation but remains to be explored in depth (10, 11). Nevertheless, despite a growing interest in the enhancement of microalgae since the mid-20th century, their industrial exploitation remains limited. Indeed, many technological locks remain, which must be lifted in order to increase yields, reduce costs, and thus ensure the economic viability of the sector. In particular, current culture processes imply a significant energy expenditure at all stages of the process: agitation of the medium to ensure homogeneity of the crops and keeping the algae in suspension, CO_2 injection, harvesting, drying and extraction. Therefore, the net energy balance remains in deficit (12). The challenge for the future is therefore to find solutions to improve the efficiency of each of these steps, so that the energy balance of the process is positive in its entirety. Reducing agitation energy, by decreasing

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the rate of movement of cells in raceways from 0.5 to 0.3 m.s⁻¹, for example, would allow an average decrease in energy costs by 26%. Thus, if this technology is properly established, net energy production from algae will be of valuable economic advantage (13).

This work has therefore mainly focused on the different types of microalgae crops, the factors influencing the growth of microalgae and ways of biofuels production. In this paper, we have given the methods of converting microalgae into energy or chemical products. We also discuss economic factors of microalgae culture and production of biofuels.

Nature and use of microalgae

Algae are plants considered to be the most primitive extant in nature. They do not have roots, stems or leaves, do not have sterile protection around their reproductive cells and contain chlorophyll as a pigment for photosynthesis (14). The term “microalgae” refers to microscopically sized algae and cyanobacteria. They are either uni- or multi-cell photosynthetic beings living in freshwater or marine waters. These organisms have a greater diversity than all terrestrial plants with no less than 200,000 species listed including 50,000 microalgae (9). However, of the thousands of species identified to date, only 100 have been studied and hardly a dozen are grown in industrial quantity. Such untapped diversity is a real potential for

research and industry (15, 16) beyond its nutritional value. Some microalgae nutrients are described in Figure 1.

Microalgae crop system and the benefits of their culture

The culture at the laboratory and semi-industrial level is already well studied, known and is mastered, which is not yet the case for large-scale culture (18). Two main means of microalgae cultivation have been developed (19), both at the laboratory and industrial scales. Open systems, where a significant part of the culture is exposed to the atmosphere, are commonly called basins. Closed systems are where cultures have little or no direct contact with the atmosphere and these systems are called photobioreactors (20). The choice of the production system depends on the degree of control necessary for the production of the desired product and its value (21). At the industrial level, microalgae are often grown in ponds but the production of molecules with high added value cannot be done in open systems (22).

Open systems

Open systems are the operating systems that have been predominantly used for the industrial culture of microalgae in recent decades. Open systems are easier and

Figure 1: Microalgae nutrients (17).

cheaper to build and operate than closed reactors. These systems are the least energy efficient and have easy maintenance and cleaning (14). For these reasons, they are still considered to be viable crop systems (23), despite their low productivity. Open systems usually use only natural light, so there is no cost associated with light input for these cropping systems. However, microalgae in these culture systems have only low light use (24) and are subject to daily and seasonal variations in temperature and light intensity (21). Contamination problems exist (by bacteria, fungi, protozoa and other microalgae) and large losses of water by evaporation (25) are observed in this type of culture system. Crop conditions are poorly controllable and there are only a few microalgae that are strong enough to grow under the extreme conditions that are common to open basins (high pH, high temperature or high salinity) (26).

Closed systems

Photobioreactors are reactors made from transparent materials. Their design is based on the illuminated surface, the efficiency of the mixture and the control of the culture parameters (temperature, carbon dioxide and oxygen content, pH), to achieve maximum productivity. Closed systems have been designed to alleviate the problems of the basin (14). They offer a closed culture environment, they protect the culture from direct contamination, allow better control of the conditions of cultures: the temperature is controlled effectively, the access to the light is increased in relation to the basin, the evaporation of the culture medium is minimized, the supply of CO_2 is facilitated and its losses are limited (27). The photobioreactor allows the effective disposition of light but also the removal of oxygen produced by photosynthesis (28). Through this control of the parameters, more fragile microalgae can be cultivated there. The photobioreactors allow the reproducibility of the culture conditions as well as a high cell concentration and a strong productivity. The basins have low productivity ($0.05\text{--}0.1 \text{ g} \cdot \text{L}^{-1} \cdot \text{day}^{-1}$) and low cell concentrations ($<1 \text{ g} \cdot \text{L}^{-1}$) compared to photobioreactors (concentration greater than $1 \text{ g} \cdot \text{L}^{-1}$ and productivity greater than $0.8\text{--}1.3 \text{ g} \cdot \text{L}^{-1} \cdot \text{day}^{-1}$) (29). However, according to Sierra et al., the design of photobioreactors should be optimized for each species of microalgae, relative to its physiological characteristics and growth characteristics. In addition, photobioreactors remain very expensive to produce and operate (26).

Photobioreactors exist in many forms but can be separated into several categories: photobioreactors planes,

cylindrical photobioreactors, plastic bag photobioreactors and a special type of reactor for microalgae culture in the absence of light: fermenters.

Advantages of microalgae culture

Microalgae have advantages for considering a significant potential for industrial exploitation (30, 31). Table 1 presents some advantages of microalgae culture. However, some of these characteristics remain theoretical values calculated on the basis of photosynthetic efficiency and the growth potential of microalgae.

Factors involved in the growth of microalgae

To grow, microalgae have many needs; the most important physical factors are a source of energy, usually light and an optimum temperature. There are also the chemical factors which are the available concentration of carbon dioxide and the contribution of macronutrient and trace elements. Algal growth is affected by several parameters such as mixture and oxygen concentration.

Light

Light is the most important factor for the photosynthetic growth of algae. It has an effect on the cellular composition of microalgae (photoadaptation or photoacclimation) (34). The radiative energy does not accumulate; therefore, the light must be supplied at all times and should be considered as a substrate (35). Compensation intensity (I_c) is the value of the luminous intensity before which there is no photosynthesis activity. Only cellular respiration activity is present. The intensity of compensation is the intensity where the photosynthesis just compensates for the respiration. The luminous intensity of saturation (I_s) is the intensity where the efficacy of photosynthesis (or photosynthesis rate) is maximal (photolimitation). The luminous intensity of inhibition (I_{pi}) is the intensity or activity of photosynthesis is inhibited by light. According to Barbosa et al., the photoinhibition becomes pronounced for a luminous intensity greater than $1200 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ (36). The efficacy of photosynthesis is usually measured by the release of oxygen or by the consumption of carbon dioxide. Available light is expressed in photon flux density (μE or $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) or

Table 1: Advantages of microalgae culture.

Important biodiversity	The number of microalgae species present in ecosystems such as oceans, rivers and lakes is estimated to be between 200,000 and 7 million. Each species has a clean biochemical profile, and some of them contain unique molecules
Fast growth	The specific velocity is related to the environmental parameters and the species. Microalgae doubled their biomass between 0.3 and 3 times a day. Under optimum conditions, some species such as <i>Chlamydomonas reinhardtii</i> can reach a doubling time of 4.3 h (15)
High photonics conversion	The efficiency of photosynthesis is estimated at 9%, which is not far from the optimum yield of terrestrial plants between 6% and 13.4%. However, by comparing per hectare, the yield is higher (about 3–8% compared to 0.5% for terrestrial plants (32)
CO ₂ consumption	The production of 100 tons of algal biomass would allow the capture of 180 tons of CO ₂ (25). However, these figures are based on theoretical calculations, at the moment there is no evidence on a large scale. The efficiency of CO ₂ fixation by microalgae is strongly dependent on physicochemical and biological conditions
Nutrient availability and clean up	Significant nutrient availability especially for autotrophic species with large sources of carbon dioxide which is their main source of carbon. In addition, microalgae have the potential to capture NO _x and SO _x derivatives in industrial fumes, as well as nitrates and phosphates in liquid effluents
Non-competition with arable surfaces	Microalgae crops do not compete with agricultural land productivity
Waste water consumption	Microalgae can develop in wastewater using contaminants and waste water as nutrients (33). No competition with the use of water intended for human consumption. In addition, their culture under certain conditions allows to recycle the majority of the water used

in photon absorption rates (μE or $\mu\text{mol} \cdot \text{kg}^{-1} \cdot \text{cell}^{-1} \cdot \text{s}^{-1}$) (37, 38).

for photosynthesis, this must be solubilized (15). Carbon dioxide, dissolved in water, takes several forms, depending on the pH (Equation 1).

Temperature

Temperature is one of the most important physical factors influencing the growth of microalgae. For each temperature there is a specific luminous intensity to achieve the maximum photosynthesis rate. The optimum temperature increases therefore with the increase of the luminous intensity. There is also an optimum temperature for maximum biomass production, but the temperature variation also acts on the cell composition. The decrease in temperature increases the degree of lipid unsaturation and the increase in temperature results in increased concentrations of the pigments but also an increase in the concentration of oxygen radicals. If microalgae do not grow at optimum temperature, the need for carbon and nutrients to achieve the same growth rate is more important (34).

Carbon

Microalgae need inorganic carbon for photosynthesis, it can be brought in the form of salts (bicarbonate) or by enrichment of the air infused (because the ambient air does not contain enough CO₂ for the intensive cultivation of microalgae). For microalgae to be able to use CO₂

Microalgae usually live in a medium at a neutral pH. The dissolved carbon will therefore be in the form of carbon dioxide and carbonate ions.

Nutritional needs

Nitrogen is an essential element of structural and operating proteins, the most important element after carbon (39). The growth rate of microalgae is roughly identical depending on the nitrogen sources used (urea, nitrite, nitrate). Numerous studies show the improvement of lipid production and storage in the case of nitrogen deficiency. There is also an accumulation of secondary carotenoids in this case. Phosphorus is an important macronutrient in the processes of cellular metabolism. Phosphorus deficiency may cause pigment accumulation in some microalgae, but the impact is lower than a nitrogen deficiency (39). Microalgae require potassium, iron, silica (for diatoms), sulfur, metals in the form of trace minerals and vitamins. Iron is an essential trace element for the growth of microalgae by its involvement in the transport of electrons in the process of photosynthesis (34).

Mixture

Mixing is an important factor because it increases productivity and optimum concentration (40, 41). The increase in the turbulence of the environment also increases the exchange of nutrients and metabolites between the cells and the culture medium. However, algae are sensitive to shear (25, 42), all types of mixture are not usable (such as centrifugal pumps). The strong turbulence regimes are generally not used with microalgae because the increase in turbulence increases the risk of cellular damage. Cell damage is very likely in airlifts or bubble columns at high turbulence (43).

Current applications of microalgae

The different biochemical characteristics of microalgal biodiversity represent an important biotechnology potential for the production of metabolites. These organisms are genuine natural plants capable of producing a variety of bioactive compounds as shown in Figure 2.

Microalgae also represent a source of vitamins, and carotenoids (44) such as carotene, astaxanthin (45), lutein (46) and zeaxanthin, which has the ability to provide protection against oxidative stress (47). Some microalgae are capable of producing different types of sterols such as clionasterol, produced by *Spirulina* sp. It has been shown that clionasterol can increase the production of plasminogen activation factor in vascular endothelial cells and thus facilitate the prevention of cardiovascular disease

(48, 49). They are known for their production of polyunsaturated fatty acids, which act as potent antioxidants; especially the omega 3 and omega 6 series. These fatty acids are considered to be pharmacologically important for their dietary and therapeutic properties (50) and are also used in cosmetics (51). In this field of application, these metabolites present valuable activities, in particular anti-aging, moisturizing, sunscreen or even for hair care products, for example.

Microalgae or their derivatives are also used in the food industry as supplements and food additives (50). It is well known that hydrocolloids extracted from macroalgae such as alginate, agar and carrageenan are used as viscosity-modifying agents in the food processing industry and also in some pharmaceutical products (49). Similarly, astaxanthin, a pigment present in many species of microalgae, amplify the pink color of salmon and crustaceans (52). The species most commonly used as a food source in aquaculture belong to the genera *Chlorella*, *Tetraselmis*, *Isochrysis*, *Pavlova*, *Phaeodactylum*, *Chaetoceros*, *Nannochloropsis*, *Skeletonema* and *Thalassiosira*.

Their potential is due to non-toxicity and their ease of cultivation. These microalgae have a suitable size for ingestion. Their cell walls are highly digestible and have a high nutritional value due to their unsaturated fatty acid content and vitamins (51).

Methods of converting microalgae into chemicals products and energy

In Figure 3, there are several possible patterns of processes for transforming microalgae into primary energy or biofuel energy. It all starts with various physical pre-treatments that are intended to reduce the water content and change the physical form of the microalga in a phase that we can easily transport and homogenize (e.g. powder). From this stage, we can choose several means:

- *Anaerobic digestion*, which allows, in the absence of air, to transform the microalga into biogas by bacterial fermentation. This biogas is a conventional fuel that we can store and distribute (53).
- *Hydrothermal liquefaction* consists of transforming biomass in a complex process involving chemical and physical structural changes. Biomass is broken down into small molecules. These small molecules are unstable and reactive and can be repolymerized into oily compounds with a wide distribution of molecular weights. Hydrothermal liquefaction has the advantage of not requiring drying of the raw material (energy

Figure 2: Production of microalgae: bioproducts useful in different fields.

Figure 3: Different ways for converting microalgae biomass into biofuels and energy.

expenditure of water evaporation is avoided). This liquefaction is generally operated between 250 and 350°C, 5 and 20 MPa, and with or without catalyst. In some cases, hydrogen can be added and most often the water is maintained in the subcritical state which gives it special reactive properties. In some cases, the water is in the super-critical state. The product obtained is a mixture of oil and gas that can be valued (54–56). Generally, bio-oil is obtained after extraction and evaporation of an organic solvent (e.g. dichloromethane). An aqueous phase is also obtained, as well as a solid residue.

- **Pyrolysis** is the chemical decomposition of a substance under the action of heat. In the case of biomass, it is converted into bio-oil, syngas and a carbon residue, at temperatures ranging from 350°C to 700°C, in the absence of air and under low pressure. Short residence times, rapid heating rates and moderate temperatures tend to promote liquid product yield. The relative proportions of each product depend on the residence time (slow pyrolysis promotes the formation of carbonaceous residues, while fast pyrolysis promotes the formation of bio-oil) (55, 57).
- **Gasification** is a process that converts carbonaceous materials, such as coal, oil or biomass, into carbon monoxide and hydrogen by reaction of the raw material with a controlled amount of oxygen at very high temperatures high (800–1000°C). In the case of biomass, gasification uses air or oxygen and water vapor as a reaction medium to convert the organic fraction and generate a syngas that is a mixture of CO, H₂, CO₂, N₂, and CH₄ with low molecular weight hydrocarbons.

The CO/H₂ ratio of this syngas is about 1 and therefore requires the addition of hydrogen to convert this gas into fuels by the reaction of Fischer-Tropsch (53, 58).

Economic factors of microalgae culture and production of biofuels

The investment in a microalgae biomass project can be described by various associated costs: growth of microalgae, harvesting, dehydration and extraction of oils. In addition, there are always project costs, which includes engineering, infrastructure, installation and integration and contract fees. When the process starts, there are always operating and maintenance costs, which includes nutrients, CO₂ distribution, water refills, etc. In addition, we cannot overlook the rental costs of the land (17). The production of bio-fuels from microalgae must be highly competitive with oil-derived fuels, which are currently the cheapest. This competitiveness depends largely on the costs of producing microalgae. One way to estimate competitiveness is to calculate the maximum price that could reasonably be paid for bio-oil, if oil can be bought at a given price as a source of energy. This estimated price should be compared to the current cost of biomass production. The amount of biomass (M, tons) that is the energy equivalent of a barrel of oil can be estimated according to the following equation:

$$M = \frac{E_{\text{oil}}}{a(1-x)E_{\text{biogas}} + bx E_{\text{biodiesel}}} \quad (2)$$

With E_{oil} (~6100 MJ) the energy of a barrel of oil; a ($\text{m}^3 \cdot \text{ton}^{-1}$) the volume of biogas produced by anaerobic digestion of residual biomass of microalgae; b Biodiesel yield; x the oil content of the biomass, in percent mass; E_{biogas} ($\text{MJ} \cdot \text{m}^{-3}$) biogas energy; $E_{\text{biodiesel}}$ the average energy content in biodiesel. Typically, b in Equation 2 is 80% pds and $E_{\text{biodiesel}}$ ~37800 MJ/ton. Staying on typical values for organic, E_{biogas} should be around $23 \text{ MJ} \cdot \text{m}^{-3}$ and $400 \text{ m}^3 \cdot \text{ton}^{-1}$, respectively. Using these values, M is calculated for the value of x selected.

Assuming that the conversion of one barrel of oil into several fuels for transport has about the same costs as converting M tonnes of biomass into energy, the maximum acceptable price that could be paid for biomass would be the same as the price of a barrel of oil:

$$\text{Acceptable biomass price (\$ tonne)} = \frac{\text{Oil barrel price (\$)}}{M} \quad (3)$$

Imagine that the price of the barrel of oil is \$100, which is an average value. At this price, a biomass with a 55% oil content must be produced at less than \$340 per tonne to be competitive with petroleum-derived diesel. The literature suggests that, at present, microalgae biomass can be produced at about \$3000 per tonne (22). Therefore, the production price of biomass must be reduced by a factor of ~9 so that the production of biofuels from microalgae is feasible. It should be noted, however, that this analysis does not take into account the potential for biomass residuals and, on the other hand, the cost of converting biomass may be lower than that of oil (6).

Conclusion

This article presents the exploration of different thermochemical conversion pathways of catalytic preference, allowing the transformation of microalgae into valuable products and possibly similar to petroleum products, usable as liquid fuels for automobiles or as a basic chemical. The interest of microalgae in this context appears for several reasons:

- Microalgae cultures are characterized by very high growth rates;
- The development and cultivation of microalgae does not compete with agricultural production for food;
- Microalgae constitute a biomass rich in lipid, carbohydrates and also renewable proteins, thus non-fossil, and transformable by chemical means into fuels;
- The consumption of CO_2 for their culture.

At present, it can be said that after the development of agrofuels (first generation) produced from maize or sugarcane and second-generation biofuels obtained by converting lignocellulose, the conversion of microalgae into biofuels is a third generation whose interest must be confirmed.

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