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MICROALGAE GROWTH AND BIOMASS-TO-SYNTHETIC NATURAL GAS CONVERSION THROUGH HYDROTHERMAL GASIFICATION: DYNAMIC MODELING OF CULTIVATION PHASE IN OPEN POND AND CLOSED REACTOR

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Abstract

The present work analyses the microalgae cultivation process for energy production. The aim of this work is to create a dynamic mathematical model that is able to describe the operation of two different typologies of cultivation systems (open raceway pond and flat panel photobioreactor) through an accurate description of the microalgae growth process, together with the use of mass and energy balances. Moreover, a parametric analysis is conducted to evaluate the importance of some of the factors which influence microalgae growth.

In the first part of Chapter 2 microalgae metabolism is briefly presented, analyzing the growth processes of these microorganisms and their dependence on some physical parameters.

In the second part of Chapter 2, the most important technologies for microalgae cultivation are described, making the distinction between systems which allow direct mass exchange with the atmosphere and those which do not. Finally, harvesting methods are briefly taken into account.

Chapter 3 contains the description of the mathematical dynamic model for microalgae cultivation created with the use of Matlab software. After the presentation of system boundaries, geometric hypothesis and the definition of input and output of the model, the most important equations of the model are described: among them, main effort is spent to include an accurate modelling of the microalgae growth phase, in which the dependence on the most important physical parameters has to be as realistic as possible.

In Chapter 4, the results of the simulations are presented; results of other works taken from literature are used to validate the model and to test its reliability, observing its behavior also through a parametric analysis.

Sommario

Il presente lavoro prende in analisi il processo di coltivazione delle microalghe a fini energetici. L'obiettivo è la realizzazione di un modello dinamico che sia in grado di rappresentare il funzionamento di diverse tipologie di sistemi di coltivazione attraverso una descrizione dettagliata dei meccanismi di crescita delle microalghe, insieme con l'impiego di bilanci di massa e di energia. Inoltre, si è cercato di osservare attraverso un'analisi parametrica quali siano i fattori più importanti che condizionano il funzionamento del processo di coltivazione stesso.

Nella prima parte del Capitolo 2 viene brevemente presentato il metabolismo delle microalghe, ponendo l'accento sui meccanismi di crescita impiegati da questi microorganismi e sui fattori fisici che ne condizionano la proliferazione.

Nella seconda parte del Capitolo 2 si descrivono brevemente le tecnologie per la coltivazione delle microalghe, distinguendo tra sistemi aperti all'atmosfera, rispetto ai sistemi che invece non permettono lo scambio di massa diretto con l'atmosfera. Infine si è accennato anche alle tecnologie per la raccolta delle microalghe al termine della fase di coltivazione.

Nel Capitolo 3 viene descritto il modello dinamico che è stato realizzato attraverso l'impiego del software Matlab. A valle di una presentazione dei confini del sistema considerato, delle ipotesi sulla geometria e sulla definizione di input e output del sistema, sono descritte le equazioni che rientrano nel modello: tra queste, particolare attenzione è stata posta alla modellizzazione della crescita delle microalghe, cercando di includere in maniera più realistica possibile la dipendenza da fattori esterni quali la radiazione solare e la temperatura.

Infine, nel Capitolo 4 vengono presentati i risultati delle simulazioni compiute attraverso il modello realizzato, cercando di valutarne la validità e l'affidabilità attraverso il confronto con valori presi da lavori presenti nella letteratura specialistica, osservandone il funzionamento anche al variare di diverse grandezze di input.

Contents

List of figures

List of tables

Chapter 1

1.Introduction

In the recent years, as a consequence of climate changes and fossil fuel depletion, there is a rising interest of both industrial and academic worlds in renewable energy sources for the production of fuels, based on biomass transformation [1].
Microalgae represent an interesting alternative to the production of first and second generation biofuels ([2], [3]), which are based respectively on traditional crops and lignocellulosic biomass, thanks to high photosynthetic yield and a lower land competition with food production. In addition, the ability to use CO2 directly from industrial emissions as a carbon resource for microalgae growth is a promising feature for flue gases mitigation [1].

Microalgae are single cell organisms which can be found in colonies or individual cells. Their most interesting characteristic is their ability of realizing a photosynthetic reaction in a single cell. They are extremely resistant and may grow in many different environments, from fresh water, to marine and hyper-saline water ([4], [5]).
Studies on microalgae have been carried out since the 80's, but in the recent past few years, their importance has grown fast: the reason, as it is illustrated by Chisti [2], is that microalgae appear to be the only source of biodiesel that has the potential to completely displace fossil diesel. Moreover, compared to other biofuels sources, such as traditional crops and wood, microalgae have several advantages which can legitimize the researches led in these years: they grow extremely fast, thus reaching high areal and volumetric productivities, they do not require arable

land, they ask for less freshwater than normal crops, being able to use wastewater, they can directly capture CO2 released by industries and they overtake the food vs fuel debate; their ability of growing in a wide range of conditions, resisting to severe conditions of temperature, pH and salinity [6], make them even more attractive.

In 1978 the National Renewable Energy Laboratory of the United States started a 20-year program (Aquatic Species Program) to develop renewable transportation fuels from algae: the researches were focused both on genetic engineering for manipulating the metabolism of microalgae and on the engineering of microalgae production systems [6]. Many other academic studies have been carried all over the world since the 80's: some works focus their attention on microalgae metabolism, genetic engineering and strain selection, to evaluate the potential of microalgae ([7], [8]); then, other works analyse the cultivation phase, focusing on a single technology such as open systems ([9], [10]), which are still seen as one of the most promising technologies for extensive microalgae cultivation, or closed flat panels ([11], [12], [13], [14]) and tubular photobioreactors ([15], [16], [17], [18]); some recent studies analyse through LCA methodology the microalgae cultivation and transformation technologies ([19], [1], [20], [21], [22], [23], [24]).

1.1 Aims

This work have two main aims meaning to create a mathematical description of a realistic cultivation system unit, which can possibly represent an element for an extensive microalgae cultivation plant, and to evaluate the impact of the most important design and operating parameters which affect microalgae growth.

The first part of the thesis consists in a brief explanation of microalgae biology and metabolism, focusing on photosynthetic process for microalgae growth.

Since there are lots of technologies available for microalgae cultivation, this work present the most interesting and widespread systems, describing their main characteristics, virtues and vices.

The main core of this work is represented by the dynamic model for microalgae cultivation phase, which is described in the central part of the thesis: the two most promising technologies for extensive microalgae cultivation have been considered, being the open raceway pond configuration and the flat panel photobioreactor. In the same chapter, mass and energy balances have been performed.
The results of the model are presented in the last part of the thesis, together with a parametric analysis, consisting in applying a range of variation to a part on the input of the model, to analyse the consequent variations of the outputs.

Chapter 2

2.Microalgae for energy production

A growing interest in renewable sources of energy has affected the whole scientific community and the society in the past few decades. The reasons for this attention are both economic and environmental: the reduction of fossil fuel reserves and difficulties in their extraction, leading to an increase of its costs, energy security, climate changes and global warming, caused by greenhouse gases emissions, represent some of the fundamental driving forces for researchers and investors to focus their attention to the problem of finding a consistent substitute to the fossil sources of energy. Many solutions have been proposed and studied during the years to increase the percentage of energy coming from sustainable sources, but the largest part of them focus on substituting that part of fossil fuels that now is used for the production of electric energy.

Biofuels are currently the only relevant alternative to fossil fuel consumption in transportation sector and might represent a fundamental support in substitute the global energy demand for gaseous, liquid and solid fuels.
Biofuels can be divided into three main categories, depending on the of the biomass transformed into biofuel. The different “generations” of biofuels are more or less recent, the development is more or less advanced but production costs are still not competitive and for all of them research and development is still needed.
Biofuels are now obtained mainly from traditional crops, such as sugar cane, rapeseed, sunflower, corn. The first generation biofuel, that is already being commercialized and used in transportation sector in bled with gasoline and diesel,

has many disadvantages from the economic, environmental and ethic points of view: the main issues regarding the first generation biofuels are the requirement for arable land and the competitiveness with food production meaning that the same crop might be used as fuel and as food. Moving from the first to the second generation biofuels, the food vs fuel struggle is overtaken. The problem with the second generation biofuels is that the biomass sources to produce them are difficult to treat from an industrial point of view. Moreover, the requirement for arable land is still present.

Biofuels from microalgae represent the third generation. Microalgae might be considered an interesting alternative to traditional crops and lignocellulosic biomass for biofuel production, since their cultivation phase has less impact.

From a practical point of view, they are easy to cultivate, can grow with little or even no attention, using water unsuitable for human consumption and easy to obtain nutrients. They can grow almost anywhere, requiring sunlight and some simple nutrients, although the growth rates can be accelerated by the addition of specific nutrients and sufficient aeration [4].

Moreover, since microalgae are cultivated in a liquid medium, it is necessary to grow them inside a pool or a basin or a closed reactor; these cultivation plants do not require arable land and might be built where other traditional crops cannot grow. The need to grow microalgae inside water and the ability of microalgae to grow in really harsh conditions, gives some more advantages, such as the possibility to use wastewater instead of freshwater as a medium for microalgae growth obtaining two results, reducing freshwater consumption and cleaning wastewater via a biological treatment, which can remove a part of the compounds dissolved in water. The liquid medium also gives the possibility to supply the CO2 needed by microalgae through a bubbling system: the CO2 may come directly from the flue gases of an industrial plant, reducing its emissions to the atmosphere.

Moreover, when the supply of nutrients and CO2 in addition to light is done from a purposefully manufactured source, this not only adds to the operating costs but also reduces the life cycle environmental benefit of the otherwise promising algal system due to energy and raw material consumption and GHG (greenhouse gas) emissions in the process of producing these supplies. To circumvent these

problems, a popular idea has been growing algae in nutrient-rich wastewater and with unwanted CO2 that is present in flue gases generated in combustion processes. In this way, the purposefully manufactured supply of nutrients and CO2 may be completely avoided or reduced to a certain extent [9].
Finally, the most important advantage in using microalgae instead of traditional crops for biofuel production, is that they have a higher productivity reducing the need of land.

As it has been shown in several life-cycle assessments and energy analysis [25], fertilizer consumption, harvesting and oil extraction from algae represent a high energy debt which might reduce the interest in algal biofuel: according to Molina Grima et al. [26] the harvesting cost can represent from 20% to 30% of the production cost, and when combined with oil extraction, exceeds 50% [27].
For these reasons, it seems to be necessary to investigate the possibility to carry other kinds of transformation to obtain bioenergy from microalgae.
This work takes into account the possibility to convert microalgae directly into synthetic natural gas (SNG) via hydrothermal gasification: this technology allows to avoid the drying phase, which is extremely expensive for microalgae, and transform them keeping a wet state, with less than 15% of solids.
Hydrothermal gasification of biomass is the thermochemical conversion of biomass into gases by processing in a hot, pressurized water environment for a sufficient time to break down the solid biopolymeric structure to liquid components, which are subsequently gasified [28].

2.1 Microalgae metabolism and growth process using photosynthesis

Microalgae are microscopic photosynthetic single cells organisms. The most important characteristic of microalgae is that they are able to realize a photosynthetic process in a single cell: while the mechanism of photosynthesis in

microalgae is similar to that of higher plants, they are generally more efficient converters of solar energy because of their simple cellular structure. In addition, microalgae cells have more efficient access to water, CO2, and other nutrients because they grow in aqueous suspension [6]. The growth rates of microorganisms can be very high: some algae are able to divide, and thus to double their number, once every 3-4 hours, most divide every 1-2 days under favourable conditions.

Microalgae are extremely resistant organisms, which may be found in harsh environments, from freshwater, to marine and hyper-saline water.

The main classes of molecules which form microalgae cells are described in Williams et al., 2010 [5]:

1. *Carbohydrates*. They are used by microorganisms with both structural and metabolic functions and they serve as starting point for the synthesis of other biochemicals. Different classes of algae produce specific types of polysaccharides.
2. *Proteins*. They also have both structural and metabolic functions. As enzymes, they work as prime catalysts for cell metabolism to facilitate growth. Moreover, proteins serve a structural role for example as a scaffold for the chlorophyll molecules, where they are assembled in chloroplasts.
3. *Nucleic acids*. DNA and RNA provide the basis for algae division and growth.
4. *Lipids*. They serve both as energy and structural components (they form cell membranes) and are the most important classes of molecules from the biofuel production point of view. The simple fatty acid triglycerides are important energy reserves. Membrane are mainly constructed with phospholipids and glycolipids. Microalgae have the ability of rapid adaptation to new environments, thanks to the synthesis *ex novo* and recycling of fatty acids to maintain the membrane characteristics. The fatty acids of algal lipids are mainly unsaturated, especially in the membrane where their main function is to maintain membrane fluidity under different conditions. The preponderance of the shorter fatty acids has significance for their potential as diesel fuels.

In a context of nutrient limitation, microalgae adapt to this condition increasing the lipid content; as the lipid content increases, the percentage of the sum of the

other components must go down. The reduction of the protein content is critical for the cell, for two different reasons. First these molecules set the level of the cell's metabolism and, with the nucleic acids, determine the growth rate potential. Second, from an economic point of view proteins are valuable bulk components of the cell, generating valuable by-products [5]. As a consequence to the reduction of protein content in the cells, the growth rate decreases, causing a significant inverse relationship between growth rate and lipid content. It has been known that the cell lipid content increases during nutrient limitation. As nutrient limitation also affects growth rate, this provides an explanation for the apparent inverse relationship between growth rate and lipid content. It is possible to conclude that when the nitrogen ran out, the organisms were forced to terminate the production of nitrogen containing material (proteins and nucleic acids) but continued to synthesise lipid and carbohydrates[5].

After this brief description of microalgae as organisms, this work focuses on the photosynthetic process.

2.2 Description of the photosynthetic process

2.2.1 Photosynthesis

The uniqueness that separates the microalgae from other microorganisms and from terrestrial plants is due to the presence of chlorophyll inside each cell and the ability of having the photosynthetic process in a single microalgal cell [29].

Photosynthesis is a multistep process which allows terrestrial plants and algae to fix CO2 into sugar, using water and light as energy and electron source.

It can be represented by an overall reaction:

$$CO_2 + H_2O + light \rightarrow (CH_2O)_n + O_2$$

This expression is a simplified representation of a complex mechanism of reactions which can be divided into two groups:

i. *Light reactions*: these are extremely fast (milliseconds) photochemical and redox reactions, which may occur only with light support;

ii. *Dark reactions*: they are a sequence of enzymatic reactions, which may occur both in the light and in the dark: the time required by these light-independent reactions is longer, from seconds to hours.

If the energy levels of the input, which is mainly solar radiation, and of the output (chemical molecules) are taken into account, the global photosynthetic process has a low efficiency. The difference in the duration of light and dark reactions is a first reason of inefficiencies [5].

To evaluate the light availability for the photosynthetic process, starting from the incoming radiation on the Earth, there is a series of losses and mechanisms which have to be taken into account and analysed:

1. First of all, the spectrum of light arriving at the surface of the planet has been attenuated by 30% by the gases in the atmosphere and losses, due to light scattering and absorption by clouds.
2. Moreover, the primary pigment involved in photosynthesis in *chlorophyll*; it has strong absorption bands in the regions 400 – 450 and 600 – 700 nm. This delimits the useful range of incoming radiation to 400 – 700 nm, the so called photosynthetically active radiation (PAR). PAR amounts to 45 – 50 % of the total incoming radiation: if the clear sky radiation is considered, then 45 % of the total incoming radiation would be an appropriate value to adopt [5]. Because of its low absorption in the range 450 – 600 nm, chlorophyll itself only is able to capture some 30 – 40 % of PAR. Plants have overcome this by including pigments that fill in much of the chlorophyll window of the spectrum, increasing the portion of the spectrum that can be used for photosynthesis. Microalgae use the same strategy to compensate chlorophyll absorption limits and are able to change the quantities of these accessory pigments to optimize light capture; the adaptation process is slow compared with the time scale of the photochemical reactions. Anyway, the quantum efficiency may be considered more or less constant throughout the PAR spectrum.

3. The photosynthetically active parts of the chlorophyll spectrum lie at 680 and 700 nm. This means that when chlorophyll reaches higher excited states due to interaction with higher energetic photons, it very rapidly relaxes: photochemistry is driven in the photosynthetic reaction centre with the energy of a red photon, regardless of the wavelength that was originally absorbed. Consequently, photosynthesis is unable to store the additional energy of the blue photons[30]. The energy of the photons, captured at shorter wavelength , can be transferred to the 680 – 700 nm region very efficiently on a quantum basis, causing only a few losses in this transfer from high-energy region to lower energy.

The products of the light-dependent reactions, which are the first set of reactions of the photosynthetic process, is energy in the form of ATP (adenosine triphosphate, the biological energy currency) and "reducing power" which is used in the successive phase of carbon assimilation.

The products of light-dependent reaction are used in the enzymatic light-independent part of photosynthesis to enable the incorporation of CO2 into organic material: finally, the first stable products of the photosynthetic reaction are obtained, which are 3-carbon organic acids, the compounds from which all the major biochemicals (fats, fatty acids, proteins, sugars,…) are eventually formed.

Before the calculation of the maximum photosynthetic efficiency, it is necessary to introduce an alternative metabolic process used by microalgae and plants.

2.2.2 Respiration

Microalgae have a supplementary energy generating process, which occurs during the day, consuming chemical energy, and during night, consuming organic material [31]. It is fundamental for plants and microalgae to have an alternative to photosynthesis for creating metabolic energy; the two main reasons for plants are:

- The need to sustain their metabolism over periods of darkness, so plants need some energy generating process independent from light: dark respiration.
- The mismatch of time scales between the light dependent and independent reactions in photosynthesis, which may give rises to "traffic jams" into the

reaction locations in the cells, when the former reaction gets ahead of the latter.

However, the use of this alternative light-independent energy generating process causes wastage of the energy captured from the photons. This is the major limitation to achieve the maximum photosynthetic efficiency in other than ideal laboratory situations[5].

During the night, respiration represent a basic maintenance energy. During the day, respiration occurs not only to operate a decongestion process and solve the mismatch between light dependent and independent reactions, as explained above, but also to repair or replace the components of the light gathering system which suffer photo-damage.

2.2.3 Maximum photosynthetic efficiency

When the photosynthetic mechanisms and the losses described in the previous section are taken into account, it is possible to evaluate the efficiency of the global photosynthetic process under natural conditions.

If the incoming radiation is considered as the total energy which may be exploited, it is necessary to consider that only PAR radiation might be used by microalgae: this is 45% of the global incoming radiation, while the remaining 55% cannot be exploited. As it has been previously explained, chlorophyll transfers all the energy captured at different wavelength to the lower frequencies of the longer wavelength photons causing an energy loss equal to 20% and thus reducing the photosynthetic efficiency to 36%. The light-dependent and independent reactions may use 8 to 10 mole of photons to generate 1 mole of organic carbon with the elemental composition of CH_2O: their overall efficiency is 34%, with the major part of the losses occurring during the light dependent reactions; this leads the overall efficiency to 12%.

At this point, there are three further forms of loss which must be taken into account: first of all, there are losses associated to the metabolic conversion of CH_2O to proteins, lipids and carbohydrates; then it is necessary to consider concurrent respiration and photon wastage, which cause losses equal to 20%, reducing the overall efficiency of photosynthesis to approximately 10%.

As it is explained in Williams et al. [5], the overall photosynthetic efficiency for higher plants lies around 4.6 to 6%, the difference being due to greater respiration losses in higher plants.
The higher photosynthetic efficiency may be considered one of the advantages of using microalgae for biofuels production instead of other biomass sources.

2.3 Parameters which influence microalgae growth

There is a wide range of parameters which influence microalgae metabolism and the overall photosynthetic process; the most important of these parameters should be taken into account when modelling the microalgae cultivation phase.

2.3.1 Light

Light is the most important factor influencing microalgae growth. Each microalgae species require an optimal amount of light intensity for the photosynthetic process, which is called *saturation light intensity*.
Saturation light intensity roughly varies from 30 to 45 W/m^2 (140-210 $\mu E\ m^{-2}\ s^{-1}$) with a good estimation [29]. For example, according to Hanagata et al. [32] saturation light intensity of *Chlorella sp.* and *Scendesmus sp.* is around 200 $\mu E\ m^{-2}\ s^{-1}$.
Light may be supplied from natural sources (sunlight) or from artificial lighting systems, such as fluorescent lamps and optical fibre systems. Laboratory scale experiments often employ artificial light to obtain a constant production throughout day and night and to evaluate the influence of other parameters on microalgae growth, excluding the dependence from variable light intensity ([33], [34]): if this technique was applied to large scale mass algae cultivations, it would represent an excessive energy and economic demand. Moreover, the electricity supply for artificial lighting is often derived from fossil fuels thus negating the primary aim of developing a price-competitive fuel and increasing the system carbon footprint [3]. For these reasons, for outdoor algae production systems,

natural sunlight is used; the availability of sunlight is submitted to diurnal cycle and seasonal variations [3]: thus, light is a limiting factor to microalgae growth.

Natural light may influence microalgae growth in different ways, depending on its intensity: below the optimum light intensity, the growing phase would be in *light shortage* and light becomes the limiting factor for the microalgal productivity; in this case, the rate of photosynthesis is usually proportional to light intensity because photosynthesis is limited by the rate of capture of photons.

When light intensity is above the optimal value, microalgae become *light-saturated*: their photosynthetic rate is limited by the enzymatic light-independent reactions, which are slower than the light-dependent reactions. Under this condition, the rate of photosynthesis is usually maximal and independent from light intensity [31].

If light intensity increases beyond an inhibitory threshold, the rate of photosynthesis starts to decrease with light intensity, due to the deactivation of key proteins in the photosynthetic unit [35]: in case of *photo-inhibition* the reduction of the efficiency in capturing photons is a consequence to damage of repair mechanism of photosystem, leading to inactivation of other systems including the oxygen evolving systems and electron carriers [29].

If the high irradiances are sustained for an hour or so, then the algae will adapt to them, by either increasing their enzymatic capacity but more commonly by reducing the capturing efficiency of photons, through the reduction of the size of the light-collecting antenna [5]: this phenomenon is called *light-acclimation*. Thus, the algae can exist as two physiological types: low light adapted (high chlorophyll content) and high light adapted (low chlorophyll content); the low light adapted form is the default state.

When light is above the optimal value, the energy from the excess captured photons has to be disposed of in some manner, either by fluorescence or by one of the respiratory decongesting mechanisms explained in the previous sections. It is in the context of this effect that the time scale mismatch of the photochemical and enzymatic parts of photosynthesis becomes significant [5].

To avoid photo-inhibition, a good mixing inside the reactor is needed, as it would help the microalgae to change from a position in which they are affected by direct

irradiation, to other positions in the reactor, where light is attenuated by the water and the culture. A good mixing inside the reactor may also facilitate the *flashing light effect*: it has been suggested that when the frequency of the light/dark cycle increases to higher than 1 Hz, the photosynthetic efficiency of microalgae is improved [36]. The dark period between the flashes allows the slower enzymatic reactions to catch up with the extremely fast photochemical reactions. The optimum dark period is temperature dependent but generally it falls in the region of 50 ms[5]. Williams et al. [5] show that, to have a significant effect, the dark period needs to be 10 times greater than the light. The gains in efficiency are lost at flash periods shorter than 10 ms.

As it has been previously said, saturation light intensity assumes for most of the microalgae species a low value which can be easy reached and overtaken by direct sun light, causing photo-inhibition during summertime in certain locations. Since attenuation of light intensity depends on reactor geometry and microalgae culture density, reactor are design to solve this potential problem [37]. Fernandes et al. [38] studied the effect of circular and plan geometry in light penetration. For similar microalgae cell concentrations, circular geometry allows a better light penetration, than the plain geometry allowing a higher volume fraction of the reactor to receive sufficient amount of light however, plan geometry helps in uniform distribution of light [38]. Most of the geometries developed by different companies and academic laboratories aim to obtain a reduction and distribution of direct light in the whole culture, avoiding direct light peaks which can damage the microalgae and reduce the productivity of the cultivation plant.

Light utilization efficiency (E_S) and overall photosynthetic efficiency are greatly dependent on the ratio of incidence light intensity (I_0) and saturation light intensity (I_s). Mathematically it can be described by:

$$E_s = \frac{I_s}{I_0}\left(ln\frac{I_s}{I_0} + 1\right)$$

Eq. 1

For better utilization of light, photobioreactor should be designed in such a way to minimize (I_0/I_s) which can be done by either decreasing I_0 or increasing I_s. Therefore selection of algal species having high I_s is advisable.

2.3.2 Temperature

Temperature is the second most important factor affecting microalgae growth after irradiation and may limit the latitudinal extent to which the outdoor microalgae cultivation systems could be successfully used [5]. Many microalgae can easily tolerate temperatures up to 15 °C lower than their optimal, but exceeding the optimum temperature by only 2–4 °C may result in the total culture loss [4]: the exact value depends on microalgae species, but lethal temperature is usually between 30 °C and 40 °C.

The intolerance of microalgae to high temperatures is a great limitation for some typologies of reactor geometry: if there is the possibility of reaching the lethal temperature for the microalgae species cultivated, the reactor must be equipped with a system to remove part of the heat, maintaining the temperature of the medium under control.

Some different technologies have been proposed in literature to equip the cultivation systems with a temperature control technology: the most diffuse system is to spray a certain amount of water over the surface of the reactor, removing heat through water evaporation. Another solution recently presented uses a heat exchanger inside the flat panel reactor ([39], [13]) or a basin in which the closed reactor is submerged.([37], [40]).

The temperature problem typically affects closed photobioreactors, while the open systems do not require a temperature control technology, since open ponds are effectively cooled by evaporation, limiting the upper temperature to about 40°C [41]; on the other hand, water losses through evaporation must be taken into account and may represent a relevant quantity of additional water that must be supplied to the cultivation plant.

Low temperatures do not kill microalgae but may reduce their productivity: for this reason, microalgae cultivation systems cannot be built in cold weathers, unless the cultivation plant is stopped during winters.

2.3.3 Proper mixing

At high algae concentrations, almost all the available light is absorbed only by a thin top layer of cells [42], causing photo-inhibition in the top layer and a state of light shortage in the rest of the reactor: this may be avoided by proper mixing. Mixing must be sufficient enough to keep the algae cells in suspension and to provide uniform exposure of light to all the cells. Moreover, proper mixing contributes to uniform the distribution of nutrients inside the medium. If there is a good mixing inside the reactor, it may take advantage of flashing light effect. This effect increases the productivity in photo bioreactors up to 40 %, in the case of tubular geometry.

On the other hand, high liquid velocities and degrees of turbulence (due to mechanical mixing or air bubbles mixing) can damage microalgae due to shear stress [4].

2.3.4 pH

pH inside the culture is strictly related to dissolved CO2 and alkalinity: as it is explained by Sills [43], when two of these parameters are known, the third may be easily evaluated. This means that pH variations may lead to variations in the quantity of dissolved CO2, which should always remain at good levels, since dissolved CO2 is consumed by microalgae during the photosynthetic process. Microalgae have a certain pH range which allows their growth: above and below this interval, the growth is reduced or even ceased.

The pH and carbon availability are controlled simultaneously by injecting CO2. Injected CO2 is transferred to the culture as a function of mass transfer capacity into the reactor, then this variables also influencing the control strategy to be used and results obtained. The pH regulation in microalgae cultures is usually performed by classical on–off switching controllers, mainly because of the control scheme simplicity [44].

If the CO2 bubbled in the microalgae cultivation reactor is coming from flue gases, the pH of the culture medium can be influenced by dissolved CO2 and SOx. With elevated CO2 concentrations, pH drops down to 5, and with higher SOx

concentrations even down to 2.6 have been reported [45][46]. Whereas the pH change due to the CO2 had just minor influence on the algae growth, the strong pH change caused by SOx inhibited all growth [29].

2.3.5 CO2

CO2 is one of the reactants and also one of the limiting factors in the photosynthesis of microalgae and plants. The photosynthesis of microalgae requires a certain CO2 concentration, and the maximum photosynthetic efficiency is often achieved with CO2 concentrations from 1% to 5% (by volume) [36].

Microalgae can fix CO2 from three different sources which are CO2 from the atmosphere, CO2 in discharged gases from heavy industry, and CO2 from soluble carbonates. Under natural growth conditions, microalgae assimilate CO2 from the air (contains 360 ppmv CO2). Most microalgae can tolerate and utilize substantially higher levels of CO2, typically up to 150000 ppmv [3].

In aqueous environment dissolved CO2 always exists in equilibrium with H_2CO_3, HCO_3^-, and CO_3^{2-} which concentration depend on pH and temperature. Microalgae cell preferentially uptake HCO_3^- over CO2 despite of the fact the former is a poor source of carbon than the latter [29].

2.3.6 Nutrients

The major nutrients are carbon, oxygen, hydrogen, nitrogen, phosphorus, and potassium. The first three are obtained from water and air and the latter three have to be absorbed from the culture medium. During cultivation, N and P become limiting. They both play a role in controlling the growth ratio and lipid production of microalgae. Therefore, the ratio of N and P is often used as an important indicator, with too high a value meaning P restriction and too low a value showing that the supply of N is falling short. Nitrogen is one of the essential elements for the growth, development, reproduction, and other physiological activities of microalgae. The nitrogen source and concentration also affect the accumulation of lipid in microalgae. Usually, ammonium salts, nitrates, urea, etc. are used as nitrogen sources, but their absorption rates and utilization are different. Experiments showed the absorption and utilization of nitrogen have the following

order: ammonia → urea → nitrate → nitrite. This is because ammonia is directly used to synthesize amino acid while the other nitrogen sources have to be converted to ammonia to synthesize amino acid [36].

Phosphorus is of lesser importance and is required in very small amounts during algal growth cycle, but must be supplied in excess of basic requirement because phosphates ions bond with metals ions, therefore, not all the added P is bioavailable [3].

Nitrogen shortage may increase lipid concentration but it reduces biomass productivity.

2.3.7 Oxygen

Oxygen is by-product of photosynthesis and it has been long known that high concentrations of oxygen inhibit photosynthesis [5]. In the case of closed photo bioreactors, oxygen might accumulate at a rate of about 4 mol m^{-3} h^{-1}, thus reaching inhibitory concentrations in 20 – 30 minutes. Bioreactor systems use airlift pumps to circulate the water, which should strip off the accumulated oxygen. However these rapid rates of oxygen production imposes constraints on the maximum length of tubular photo bioreactors and on the minimum flow rates within the reactor.

2.4 Cultivation techniques

The growth characteristics and composition of microalgae are known to significantly depend on the cultivation conditions. There are mainly four types of microalgal cultivation techniques that are available; of these, the most dominant method commonly used for microalgal cultivation is phototrophic cultivation [47].

- *Phototrophic cultivation.* Phototrophic cultivation occurs when the microalgae use light, such as sunlight, as the energy source, and inorganic carbon (carbon dioxide) as the carbon source to form chemical energy

through photosynthesis. This is the most commonly used cultivation condition for microalgae growth.

Under phototrophic cultivation, microalgae composition is extremely variable, depending on the type of microalgae species. Normally a nitrogen-limiting or nutrient limiting condition is used to increase the lipid content in microalgae [4]. On the other side, growing microalgae in an environment with nutrient shortage reduces the biomass productivity, as it has been previously explained: thus, achieving higher lipid content is usually at the expense of lower biomass productivity. The major advantage of using autotrophic cultivation to produce microalgal oil is the consumption of CO2 as carbon source for the cell growth and oil production. However, when CO2 is the only carbon source, the microalgae cultivation site should be close to factories or power plants which can supply a large quantity of CO2 for microalgal growth. Compared to other types of cultivation, the contamination problem is less severe when using autotrophic growth. Therefore, outdoor scale-up microalgae cultivation systems (such as open ponds and raceway ponds) are usually operated under phototrophic cultivation conditions. [48]

- *Heterotrophic cultivation.* Some microalgae species can not only grow under phototrophic conditions, but also use organic carbon under dark conditions, just like bacteria. The situation when microalgae use organic carbon as both the energy and carbon source is called heterotrophic cultivation. This type of cultivation could avoid the problems associated with limited light that hinder high cell density in large scale photobioreactors during phototrophic cultivation.

  Using heterotrophic growth gives much higher lipid productivity, as the highest lipid productivity from heterotrophic cultivation is nearly 20 times higher than that obtained under phototrophic cultivation. However, the sugar-based heterotrophic system frequently suffers from problems with contamination.
- *Mixotrophic cultivation.* Mixotrophic cultivation is when microalgae undergo photosynthesis and use both organic compounds and inorganic

carbon (CO2) as a carbon source for growth. This means that the microalgae are able to live under either phototrophic or heterotrophic conditions, or both. Microalgae assimilate organic compounds and CO2 as a carbon source, and the CO2 released by microalgae via respiration will be trapped and reused under phototrophic cultivation. Compared with phototrophic and heterotrophic cultivation, mixotrophic cultivation is rarely used in microalgal oil production.

- *Photoheterotrophic cultivation.* Photoheterotrophic cultivation is when the microalgae require light when using organic compounds as the carbon source. The main difference between mixotrophic and photoheterotrophic cultivation is that the latter requires light as the energy source, while mixotrophic cultivation can use organic compounds to serve this purpose. Hence, photoheterotrophic cultivation needs both sugars and light at the same time. Although the production of some light-regulated useful metabolites can be enhanced by using photoheterotrophic cultivation, using this approach to produce biodiesel is very rare, as is the case with mixotrophic cultivation.

The cultivation phase can be operated with various strategies: batch mode, continuous mode and repeated batch mode.

In case of *batch cultivation* strategy, the mass cultivation system is often placed next to a photobioreactor system, which works as an inoculum, to start the new production phase. Industrial scale batch cultivation of photosynthetic microorganisms is generally unviable because of the time and the expense involved in loading, discharging and cleaning the reactor [49]. The most used strategy in pilot plant scale reactors is the *repeated batch* mode: in this case, the mass production system does not need a bioreactor as inoculum and it contains itself the biomass that is necessary to start again with the growth phase. The repeated batch cultivation is an alternative form of operation for microalgae production. In repeated batch cultivation the reactor is initially filled with the cultivation medium and incubated under ideal conditions. After a certain period a specific cultivation volume is removed and replaced with an equal amount of fresh medium [49]. Consequently a part of cultivation medium is kept into the reactor as

starting inoculum. Repeated batch cultivation presents several operational advantages, the most important of which are the maintenance of a constant inoculum and high growth rates. If *continuous* cultivation mode is applied, the cultivation system is fed continuously with water, nutrients and CO2, while the same amount of water and microalgae is removed from the reactor. Continuous photobioreactors provide a high degree of control, growth rates can be regulated and maintained for extended time periods and biomass concentration can be controlled by varying the dilution rate. With continuous cultivation mode, it may result difficult to control the parameters which are not directly related to the microalgae growth: for this reason, the continuous process often requires feed-batch culturing, and a continuous nutrient supply, making this operating technique similar to the repeated batch cultivation.

2.5 Cultivation technologies

Microalgae cultivation can be artificially grown in open-culture systems such as lakes or ponds and in highly controlled closed-culture systems called photobioreactors (PBRs), where nutrients and CO2 are supplied to the culture together with light, to enable the photosynthetic process. A bioreactor is defined as a system in which a biological conversion is achieved. Thus, a photo-bioreactor is a reactor in which phototrophs (microbial, algal or plant cells) are grown or used to carry out a photo-biological reaction [4].

The open systems generally need lower investment and maintenance costs, they are more durable, but they are not able to reach high values of productivity. Nevertheless, as said by Yang [9], these systems are still considered preferable for extensive mass algae cultivation for biofuel production. Closed systems require high capital costs, since the technology is more sophisticated, and have high operating costs; in recent years, they are getting more importance, since they can reach high productivity and generate more valuable by-products.

Apart from these two categories recent studies are developing new cultivation technologies and new reactor geometries, which are trying to combine high productivity and low auxiliary energy demand with low cost criteria for large-scale applications. Both the academic world and market companies are carrying research projects to reach these objectives: some of the most interesting designs are described in Morweiser at al. [40].

2.5.1 Open Reactors

The technology of open system groups together some different designs which have been all studied through the years.

The simplest design for an open reactor cultivation system is the *unmixed tank* filled with water and nutrients, in which no mixing is applied. Unmixed open ponds are generally used for the mass culture of *Dunaliella salina*, have low productivities (less than 1 gm^{-2} d^{-1}) and are comparatively unsuitable for the culture of most algal species [42].

A second typology of open pond cultivation systems is called *thin layer reactor*. This type of open pond is a modification of open raceway ponds in which the culture flows through a tilted surface by using a pump [50] from a tank. The slope of the surface range between 1 and 3 % and the depth of the culture is less than 2 cm. On these conditions, the surface-to-volume ratio is high and the energy demand can be reduced to 100 W m^{-3}: in this reactor, power is only required for elevating the culture from the tank to the upper part of the tilted surface and there is not any moving mechanical part helping the flow of the culture on the tilted surface. The CO2 is supplied inside the tank to reduce CO2 losses to the atmosphere. The major advantage of this reactor, apart from its low power consumption, is the high light availability at which the cells are exposed, thus biomass concentration can reach up to 30 g l^{-1} being reported by Doucha et al.[51]. The idea of this reactor is opposite to the concept of “diluting light” to maximize the photosynthetic efficiency, demonstrating that different approaches still remain valid to improve the performance of microalgae cultures [44].

Raceway ponds are the most commonly used artificial systems for microalgae cultivation. They are generally cheaper to build and easier to operate than closed photobioreactors.

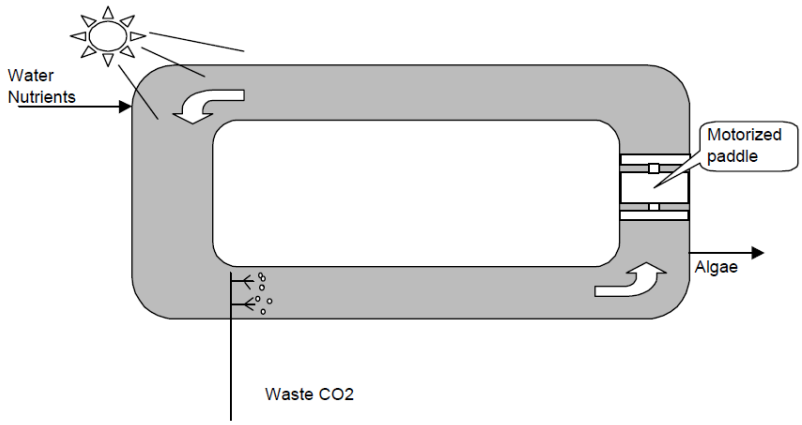


Figure 1: Basic design of an open raceway pond cultivation system [6]

The typical geometry of the raceway pond is a closed oval-shaped channel: they might be excavated (and so the walls and the bottom would be covered with impermeable materials [42]) or built in plastic material or concrete; the depth is generally between 0.2 and 0.5 m (being 0.3 m the most used value [2]). Circulation around the oval ring and mixing are required to stabilize algae growth and productivity and are guaranteed with the use of a mechanical rotating organ, usually a paddlewheel [3]: in a continuous production cycle, algae broth and nutrients are introduced in the front of the paddlewheel and circulated through the loop to the harvest extraction point, behind the paddlewheel. The paddlewheel is in continuous operation to prevent sedimentation, giving the water a speed between 0.15 and 0.25 cm/s, also during the night, when CO2 and nutrients are not supplied to the culture, which is not growing due to lack of irradiation for the photosynthetic process. If the microalgae CO2 requirement is satisfied only from the interaction between the water and the atmosphere, in certain operating conditions and for certain concentrations, CO2 may become a growth limiting factor: for this reason, open pond are often equipped with submerged aerators to enhance CO2 absorption.

The direct contact between the atmosphere and the medium in which the microalgae grow defines many of the characteristics of the open pond, since it

gives the possibility to have mass and energy exchanges between the cultivation system and the environment.

The mass exchange through the free surface involves that the water of the open pond is subjected to contamination and pollution. The possibility of contamination is often cited as a serious limitation of open systems: to avoid contamination, usually the algae species which are cultured in these systems grow in selective environments, under extreme and very harsh conditions: for example, as it is exposed in Bahadan et al. [52], some possible species are *Spirulina*, which requires high alkalinity, *Dunaliella salina*, which requires high salinity and *Chlorella*, which asks for high nutrients concentration. Another strategy that is often used to avoid contamination is to search for the best microalgae indigenous species: if this strategy is adopted, there is not any introduction of new species in the environment and the contamination has less chances to occur.

One of the problem related to the free interface between the water of the open pond and the atmosphere is that the pond use carbon dioxide much less efficiently than closed bioreactors [2]. About one third of the CO2 that is injected in the pond through bubbling columns is lost in the atmosphere and could not be captured by the microalgae for the photosynthesis reactions. On the other hand, the possibility to directly release the O2 produced through the photosynthetic mechanism to the atmosphere, solves the problem of oxygen inhibition that sometimes can occur in closed systems, in which the concentration of O2 can rise up to extremely high values. For this reason, the closed PBR always have a system to extract the O2 from the water and from the reactor.

Moreover, the presence of the free interface between atmosphere and the pond makes impossible to have any sort of artificial temperature control of the pond: any possible way to obtain it would be too energy and economically expensive. This means that the temperature of the water in the pond will vary with the atmospheric temperature, with daily and seasonal fluctuations: the mass of water which forms the pons has its thermal inertia and so the thermal fluctuations will be reduced and shifted in time.

Water evaporation through the free interface between the culture medium and the atmosphere is a loss which must be taken into account when analysing water

requirement of the cultivation technology, since for some locations might be a rather huge quantity. Evaporation losses can be seen as a natural cooling system, keeping a sort of control over the temperature in the pond.

2.5.2 Closed Reactors

Open cultivation technologies have several problems and limitations including low volumetric productivity, contamination, evaporation, limited species sustainability and the need for large land area [42]. Closed photobioreactors are designed to overcome the limitations of open systems. They have higher efficiency and biomass productivity, shorter harvesting times, high surface-to-volume ratios, reduced contamination risks, and can be used to cultivate greater range of algal species than open systems [52]. Unfortunately, closed systems are also more expensive to construct (need for transparent materials such as Plexiglas, glass, PVC, etc.) and difficult to operate and scale up [53].

The most important closed systems for microalgae production are flat panel reactors and tubular reactors. These systems do not suffer of many of the disadvantages to which open ponds are subjected, but have higher investment and operational costs which still make open pond technology more attractive for microalgae mass cultivation for an industrial scale production. The closed photo bioreactors do not have any risk regarding pollution and contamination, that means it is possible to successfully cultivate a single species of algae for a long period: for these reason, at present time, closed PBRs are mainly used to grow algae species which have high value products that are used in chemical industry, pharmaceutical and cosmetic industry.

The most important problem which affects closed systems is related with oxygen concentration: if the O2 concentration in the medium is too high, it can cause growth inhibition; this problem does not exist in case of open systems, since the oxygen produced through the photosynthetic process can be easily released to the atmosphere. For closed PBRs, it is necessary to think of a system for oxygen removal: usually this is done through aeration/bubbling systems which generate turbulence inside the reactor and strips the oxygen from the water taking it away

with the bubbles. This same method is used to inject CO2 in the medium and to generate mixing in the culture.

Tubular photobioreactors consist of a solar collector made of straight transparent plastic or glass tubes through which the culture flows, recirculated by aeration or mechanical pumps. The culture is passed through a bubble column or tank where air is supplied to avoid damaging dissolved oxygen levels. In this bubble column, air is supplied enriched with CO2, needed for the photosynthetic reactions [44]. The solar collector tubes are generally 0.1 m or less in diameter: the diameter is limited because light does not penetrate very deeply in the dense culture broth; high densities are necessary for ensuring a high biomass productivity of the photobioreactor [2]. The solar collector is always oriented to maximize sunlight capture: the solar tubes are generally placed parallel to each other, and flat above the ground.

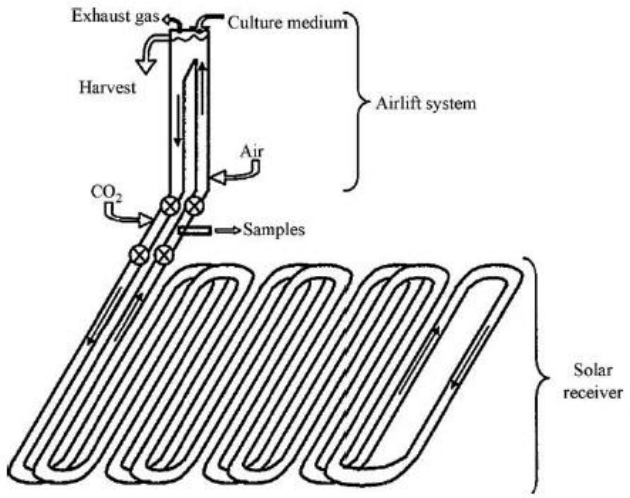


Figure 2: Basic design of a horizontal tubular photobioreactor [3]

Horizontal, parallel strait tubes are sometimes arranged like a fence, in attempts to increase the number of tubes that can be accommodated in a given area [2].

Tubular photobioreactors, as previously said, are affected by the problem of oxygen accumulation; moreover along the length of the tubes, there could be lack of CO2, fundamental component for photosynthesis reactions, and consequent pH changes [3]. To avoid these problems, tubular photobioreactors have design

limitations on the length of the tubes: therefore, they cannot be scaled up indefinitely.

Another major limitation for this kind of reactors is the energy requirement for bubbling, which is around 2000 W m^{-3}: this value should be compared with around 50 W m^{-3} as energy requirement for bubbling for flat panel reactors ([54], [13],[24]); the high energy consumption is necessary to reach turbulent velocities in the culture which permits to have sufficient short light/dark cycles.

Flat-plate photobioreactors are suitable for mass cultures of algae due to low accumulation of dissolved oxygen and high photosynthetic efficiency achieved [3]. The flat panel reactor is basically a flat, transparent vessel, generally made of glass or Plexiglas or plastic or other transparent material, in which mixing is carried out directly in the reactor with air bubbling: the air is introduced via a perforated tube at the bottom of the reactor . Flat panel PBRs are never thicker than 5 – 6 cm since the light entering the panel would not penetrate more in the culture. Height and width can be varied to some extent, but in practice only panels with both a height and width of <1 m have been studied [55]. The normal aeration level for flat panel photobioreactors is 1 liter of air per liter reactor volume per minute [22].

To reach a higher photosynthetic efficiency, the flat panel reactors are positioned vertically, closely spaced, to obtain a large specific surface and self-shading of the panels.

Due to the high photosynthetic efficiency and low accumulation of dissolved oxygen, flat plate reactors are more suitable for large scale culture than tubular reactors [47].

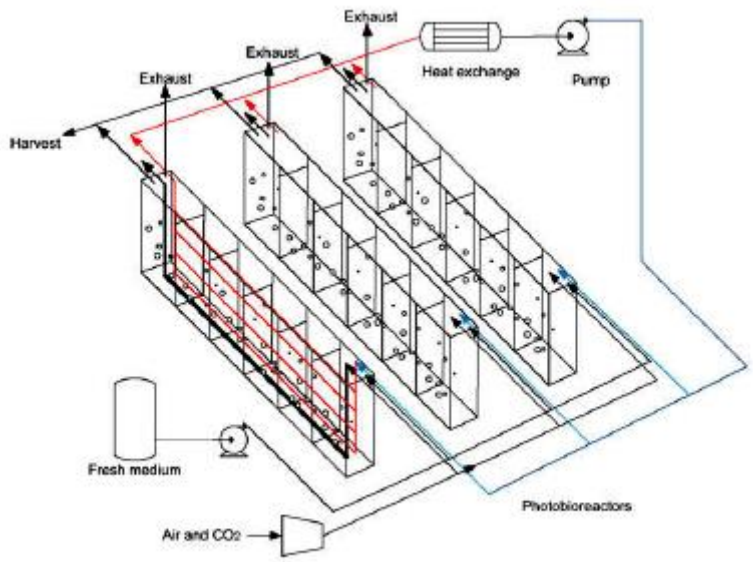


Figure 3: Basic design of a vertical flat panel photobioreactor [24]

Airlift photobioreactors are vessels with two interconnecting zones. One of the tubes is called riser, where gas mixture is bubbled, whereas the other region is called downcomer which does not receive the gas. Generally they exist in two forms: internal loop and external loop airlift photobioreactors. In the internal loop reactor, regions are separated either by a draft tube or a split-cylinder. In the external loop, riser and downcomer are separated physically by two different tubes. Mixing is done by bubbling the gas through a bubbler in the riser tube without any physical agitation. Riser is similar to bubble column where bubbled gas moves upward randomly and haphazardly. This decreases the density of the riser making the liquid to move upward. This upward movement is assisted by the gas hold up of riser. Airlift reactor has characteristics advantage of creating circular mixing pattern where liquid culture passes continuously through dark and light phase giving flashing light effect to algal cells [54].

Bubble column reactors are cylindrical vessel with height greater than twice the diameter. They have the advantage of low capital cost, high surface area-to-volume ratio, lack of moving parts, satisfactory heat and mass transfer, efficient release of O2 and residual gas mixture. Mixing and CO2 mass transfer is done through bubbling the gas mixture from a sparger. In scale-up, perforated plates are used in tall bubble column to break up and redistribute. Light is natural and so provided

externally. Photosynthetic efficiency greatly depends on light and dark cycles: since the liquid circulates regularly from central dark zone to external illuminated zone at higher gas flow rate, efficiency is related to gas flow rate. At gas flow rate less than 0.01 m s^{-1} circulation flow pattern does not exist because of the absence of a good mixing. The photosynthetic efficiency can be increased significantly by increasing the gas flow rate to 0.05 m s^{-1} or more, leading to shorter light and dark cycles [29].

2.6 Harvesting technologies

Algal harvesting phase from the cultivation system is expensive and may contribute up to 20 – 30 % of the total biomass production cost ([4], [3]): the main reason for this high cost is the fact that microalgae are extremely diluted during the cultivation phase, especially if open pond technologies are considered; in open raceway ponds, the concentration of algae usually does not go over 0.5 kg m^{-3}. For this reason, it is necessary to harvest and remove large quantities of water and process large algal biomass volumes.

A suitable harvesting method may involve one or more steps and be achieved in several physical, chemical or biological ways, in order to reach the desired algal concentration before processing: the selection of harvesting technique is dependent on the properties of microalgae, such as density, size, the value of the desired products [3].

Microalgae harvesting can generally be divided into a two-step process, including:

1. *Bulk harvesting.* The purpose of this phase is to separate the microalgae from the bulk suspension. The total solid matter can reach 2 – 7 % using flocculation, flotation or gravity sedimentation.
2. *Thickening.* The purpose of this harvesting technique is to concentrate the slurry, with filtration and centrifugation, usually applied in this process. This second step need more energy than the bulk harvesting.

Flocculation is used to aggregate the microalgal cells to increase the effective particle size and hence ease sedimentation, centrifugal recovery, and filtration [4]. Microalgae carry negative cell surface charges which, when neutralized, lead to the

agglomeration of the biomass into large clumps or “flocs”. These flocs can then be more readily separated from the culture medium. Flocculation can be induced in various ways like, chemical flocculation (inorganic chemicals), chemical flocculation (polyelectrolytes), bio-flocculation, electro-flocculation, and dissolved air floatation. It was concluded that chemical flocculation was too expensive for biofuels production. Polymeric organic flocculants (polyelectrolytes) on the other hand are highly charged organic aggregates, non-toxic, required in small amounts, produce more stable flocs and thus, are more attractive flocculation option. Some algal species are reported to naturally flocculate after transfer to settling ponds, when left quiescent for some time. This occurrence has been attributed to environmental stimuli, some of which have been identified, including nitrogen limitation, pH, and dissolved oxygen level. Electro-flocculation is a coagulation/flocculation process which is based on the movement of electrically charged particles in an electric field in which active coagulant species are produced by oxidation of a metal anode [42].

Centrifugation is a well-established industrial process that uses gravitational force to achieve separation. The morphology and sizes of the cells being harvested affect the recovery (and costs) as filamentous cells and large colonial cells will settle more readily than single smaller cells. Centrifugation is energy intensive and the estimates of the energy consumption required for various types of centrifuges are estimated to range from 0.3 to 8 kWh/m^3. The high capital and running costs associated with centrifuges limit their use to second-stage filtration in the processing of microalgae for biofuels.

Filtration involves introducing the particles onto a screen of given aperture size. The particles either pass through or are retained on the screen according to their size. Filtration can be performed under pressure or vacuum with energy requirement estimates ranging from 0.2 to 0.88 kWh/m^3 and 5 kWh/m^3. Although, the costs associated with filtration are low, screen clogging and membrane fouling limits its suitability to larger species of microalgae. In general, this technique is not considered feasible from an economic point of view for microalgae extensive scale cultivation.

Chapter 3

3.Cultivation phase model

The microalgae cultivation phase model is presented in this chapter. After the presentation of system boundaries, geometric hypothesis and the definition of input and output of the model, the most important equations of the model are described: among them, main effort is spent to include an accurate modelling of the microalgae growth phase, in which the dependence on the most important physical parameters has to be as realistic as possible.

3.1 Introduction

This chapter presents the dynamic model which describes the cultivation phase of microalgae. The model includes in its boundaries the reactor for microalgae cultivation, excluding the downstream and upstream processes. The reactor geometries considered in the model are the open raceway pond and the flat panel photobioreactor, being the most promising technologies for an extensive microalgae cultivation.

The growth model is dynamic because it uses as input data a weather file for the given location, which reports all the hourly weather data of a year: the model is able to face the hourly variation of these data and the consequent evolution of all the other parameters through time and to take them into account in the computation of the output. The software used for the model composition is Matlab: to follow the sequential logic of the solver, a system of differential equations has

been changed into a sequence of algebraic equations through the application of the finite differences approximation.

The central part of the model is represented by the growth equations which have to describe in the most accurate possible way the growth of the microalgae in the system. Moreover a pH control strategy is included, to maintain the optimal pH for microalgae growth in the medium. Time dependent mass and energy balances are presented for a complete description of the process.

3.2 System description

3.2.1 *System boundaries*

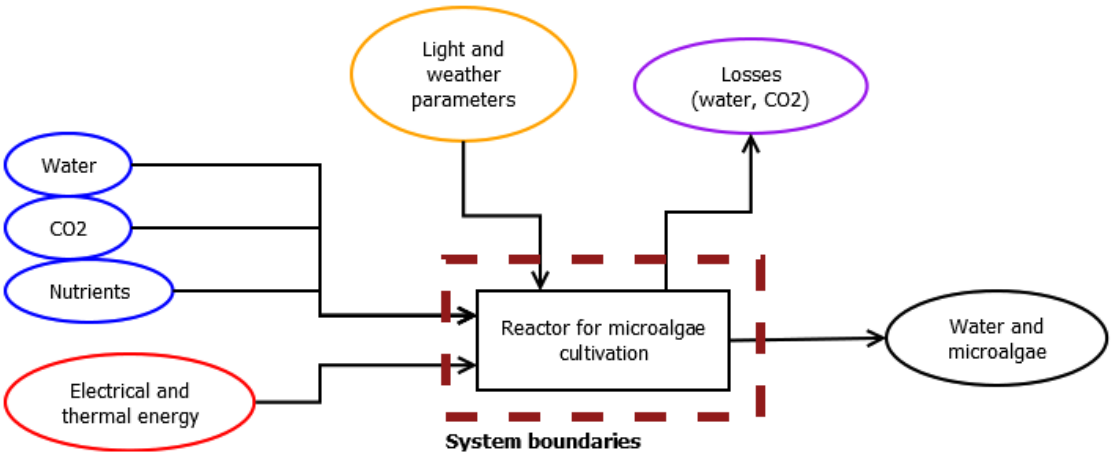


Figure 4: System boundaries

As shown in figure Figure 4, the system boundaries of the dynamic mathematical model take into account the cultivation system, the reactor in which the microalgae grow through an autotrophic photosynthetic process.

The downstream process is left outside these boundaries: the productivity of the cultivation system is not influenced by the downstream transformation process;

this implies that the model could be coupled with every kind of biofuel production chain, increasing its fields of application.
Furthermore, the upstream process is also not considered in the boundaries of the dynamic model: the incoming mass and energy streams which enter the cultivation system are taken without considering their origin; the realistic possibility of having recirculated mass and energy fluxes coming from the downstream process and entering the reactor is taken into account as a general consideration, without including it in the dynamic model.
The input of the cultivation phase are all required by microalgae growth, that gathers its energy through the photosynthetic process:

$$CO_2 + H_2O + light \rightarrow (CH_2O)_n + O_2$$

Moreover, microalgae need inorganic compounds, called nutrients in the figure above, to build the organelles and the intracellular structures: the most important nutrients are nitrogen and phosphorus, together with some other compounds (iron, silicon) that are needed in small quantities by the microalgae; these micronutrients are not monitored and directly injected in the cultivation systems, with the assumption that the algae may find the needed quantities in the water.

3.2.2 *Reactor geometry*

There is no commercial scale cultivation plant for biofuel production at present in the world. Microalgae are cultivated to obtain more valuable products than biofuels and the quantities needed by the market do not require the introduction of extensive biomass production.
For what concerns microalgae cultivation for biofuel production, there are a few pilot scale plants and R&D is still needed to reduce costs of the technologies and to optimize the productivity levels which can be reached in the reactors.
It comes from literature that the two most promising geometries for a commercial scale cultivation plant for biofuel production are the open raceway pond and the flat panel photobioreactor [24]. The most important characteristics of these microalgae production systems have already been described in the previous

chapters; in the following paragraphs, the hypothesis regarding the geometry of the reactors are listed.

Open raceway pond

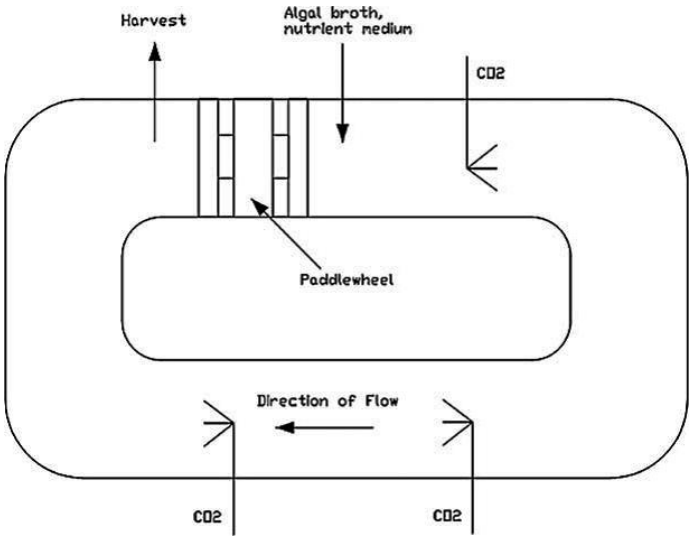


Figure 5: **Basic design of an open raceway pond cultivation system**

The main characteristics of the raceway pond used in the model have been taken from literature ([9], [14], [22], [56], [57]):

- The pond covers a surface of 1 hectare, having a length to width ratio equal to 10.
- The depth of the pond is 30 cm: this parameter will be varied within a range in a successive parametric analysis; the most common values which can be found in literature are all between 20 and 30 cm, as said in the previous chapter.
- The motion of water is provided by a paddle wheel, which works during day and night; the speed of the water in the pond is kept at a constant value of 0.20 m/s.
- The CO_2 needed by the photosynthetic process is supplied from the bottom of the open pond, through a sump system (with 90% efficiency for CO_2 dilution [58]): the CO_2 is injected during the day to compensate the consumption caused by the microalgae growth and the losses to the atmosphere; the bubbling systems works also during the night, when the photosynthetic process in not occurring, to replace the losses to the

atmosphere and so to guarantee a constant optimal pH in the reactor, as it is explained hereinafter. The air that is bubbled in the pond contains a CO_2 molar rate equal to 0.04.

Flat panel

As it has been done for the open raceway pond, also for the flat panel photobioreactor the main geometric characteristics have been taken from literature ([13], [55], [59], [39],[60], [61]):

- The system covers a surface equal to 1 hectare, the panels are positioned vertically, in parallel lines: the distance between two lines is 0,5 m.
- The height of the panels is 1,5 m, the thickness is 0,05 m.
- The panel is made of glass that is considered to be non-absorbing glass.
- The flat panel presents a bubbling system for CO_2 injection which has the double task to maintain a high level of CO_2 for the photosynthetic reactions and to generate enough mixing in the panel to avoid sedimentation and light saturation. For this reason, the CO_2 molar fraction of the injected gases is lower than in the case of the open pond: 0,02.
- In this typology of reactor, a constant temperature is wanted to be maintained: for this reason, a heat exchanger is supposed to be placed in the reactor, to remove or supply the heat that is necessary to reach this target.

  Other heating and cooling systems which have been tested in laboratory and pilot scale flat photobioreactors are: a temperature controlled basin in which the flat panels are dipped ([40], [62]), a sprinkler system to spray water on the surface of the reactor ([29], [44], [62], [20]) obtaining a cooling effect; the spraying system does not provide the possibility to obtain a heating effect.

The geometric characteristics (distance between the panels, height of the panel) and the direction faced by the parallel lines of the photobioreactor are parameters which have been varied during a later parametric analysis.

Although the model gives the possibility to vary the direction faced by the surfaces of the flat panel, many researches have been done to identify the optimal position for this typology of photobioreactors: the largest number of papers which have

been taken into account suggest that the optimal position is vertical, facing east and west ([12], [13]); some works suggest that, to obtain a higher productivity, the slope of the panel should be varied during the day and during the year ([63]).

3.2.3 *Sedimentation tank - settler*

In addition to the bioreactor for microalgae cultivation, the model considers a sedimentation tank, placed downstream to the reactor.

Thanks to this settler positioned after the bioreactor unit, the modelling of the cultivation phase could include a better and more general evaluation of the energy required by the bioreactor, taking onto account the electrical consumption of the pumps which are needed for the harvesting of the water and the biomass from the reactor.

Moreover, if each cultivation unit has its own settler, then the discharge of the reactor can be done in a relatively short time, without been conditioned by the time needed by the biomass concentration technology downstream: the time required by the microalgae to grow can be decoupled from the time of the downstream process.

As it has been explained in previous chapters , a sedimentation tank is also needed to obtain a first separation between water and biomass and to increment the microalgae concentration to higher levels from those reached in the reactor during the cultivation phase.

Finally, if a settler is considered for each unit of reactor (which covers 1 hectare) it is possible to create a sort of independent cultivation unit which can be seen as a repeatable unit for an extensive mass microalgae cultivation.

Therefore, the dimension of the tank should be sufficient to contain the whole volume of water which is in the reactor. The geometry of the tank is a cylindrical concrete tank with a 30 m diameter.

3.3 Operating strategy

The pilot scale plants and the mathematical models which can be found in literature consider three possible different ways to run a microalgae cultivation system: batch mode, continuous mode, repeated batch mode.
In this work, all the mathematical models which have been created consider the production to be led as a repeated batch cultivation ([49], [14], [64], [65]).
As it is explained in Radmann [49], the repeated batch cultivation is an alternative form of operation for microalgae production. After a certain period in the reactor, a specific culture volume is removed and replaced with an equal amount of fresh medium. Consequently a part of cultivation medium is kept in the reactor as a starting inoculum. Repeated batch mode of operation provides an excellent means of regulating the nutrients feed rate to optimize the productivity while at the same time preventing the over and underfeeding of nutrients. Repeated batch cultivation presents several operational advantages, the most important of which are the maintenance of a constant inoculum and high growth rates.

Another fundamental aspect of the operating strategy is that the mathematical model can work in two different ways: it is possible to fix the initial and final concentration which are required in the reactor or to fix the initial concentration and the hydraulic retention time (HRT) of the culture.
If the first strategy is adopted, the model will empty the reactor when two conditions are verified at the same time: the final concentration has to be reached and the light radiation incoming is zero; this second condition prevents the model to empty the reactor in the middle of the day that would cause the loss of a part of the incoming radiation which could have been helpful to produce more biomass. Throughout this first strategy, the minimum concentration acceptable for the harvesting is the input data, and it is possible to define a mean value for the HRT which can be used for the whole time period.
The second strategy is more similar to the one which is really applied in microalgae cultivation plants: the HRT value is set to a fixed value which is sufficient to reach an adequate microalgae concentration in the reactor. The initial

concentration for the batch cycle is also fixed, as in the first strategy previously described.

3.4 Model structure

Even if many laboratory scale cultivations use artificial light as irradiation input to the culture, many authors agree in saying that this solution cannot be adopted for extensive microalgae cultivation as it would be an excessive energetic and economic cost. Therefore, the irradiation input for mass microalgal cultivation has to be natural light: this implies that the cultivation is subjected to weather conditions, which change during time.

To obtain an accurate mathematical description of the cultivation phase through a Matlab model, it is thus necessary to include in the equations the dependence from weather conditions and so to consider their variations with time.

Therefore, the Matlab model developed has a dynamic logic, and uses a system of differential equations. To simplify the resolution of this system, the finite differences approximation has been adopted. All the differential equations have been threatened as finite differences, and the backward difference formula has been implemented:

$$\frac{dx}{dt} = f(t) \quad \rightarrow \quad \frac{x(t) - x(t-1)}{\Delta t} = f(t)$$

Eq. 2

This formula has been preferred to the forward difference strategy, since it is less vulnerable to instability. If this formula is applied to matrices and vectors, the following expression is obtained:

$$\bar{x}(t) = \boldsymbol{F}(t) * \Delta t + \bar{x}(t-1)$$

Eq. 3

The model includes more than one differential equation and some of them are strictly dependent on one another, making impossible to solve the various differential equation in a sequential logic: it is thus necessary to solve them

altogether as a system, with vector and matrices. Therefore, all the equations have been manipulated to separate the known terms from the unknown variables and to obtain an easily solvable system of algebraic equations. This strategy has been adopted in particular for the mass balances: the quantities of each substance dissolved in the water and the quantity of microalgae at a certain time *t* are all dependent on one another.

The mass and energy produced by the cultivation systems in the form of biomass is calculated by the Matlab model through the mass and energy balances. Before calculating the results of these equations, it is necessary to introduce some auxiliary equations, to calculate all the parameters included in the balances.

The auxiliary equations include the microalgae growth model, the pH control through CO2 injection, the equations to accurately take into account the light entering the reactor and affecting the microalgae cells, which is not merely the global horizontal irradiation measured.

Once that all the growth parameters and other parameters have been defined, it is possible to implement a cycle to calculate the dynamic mass and heat balance of the reactor at each time step.

The following figure represent the Matlab model created:

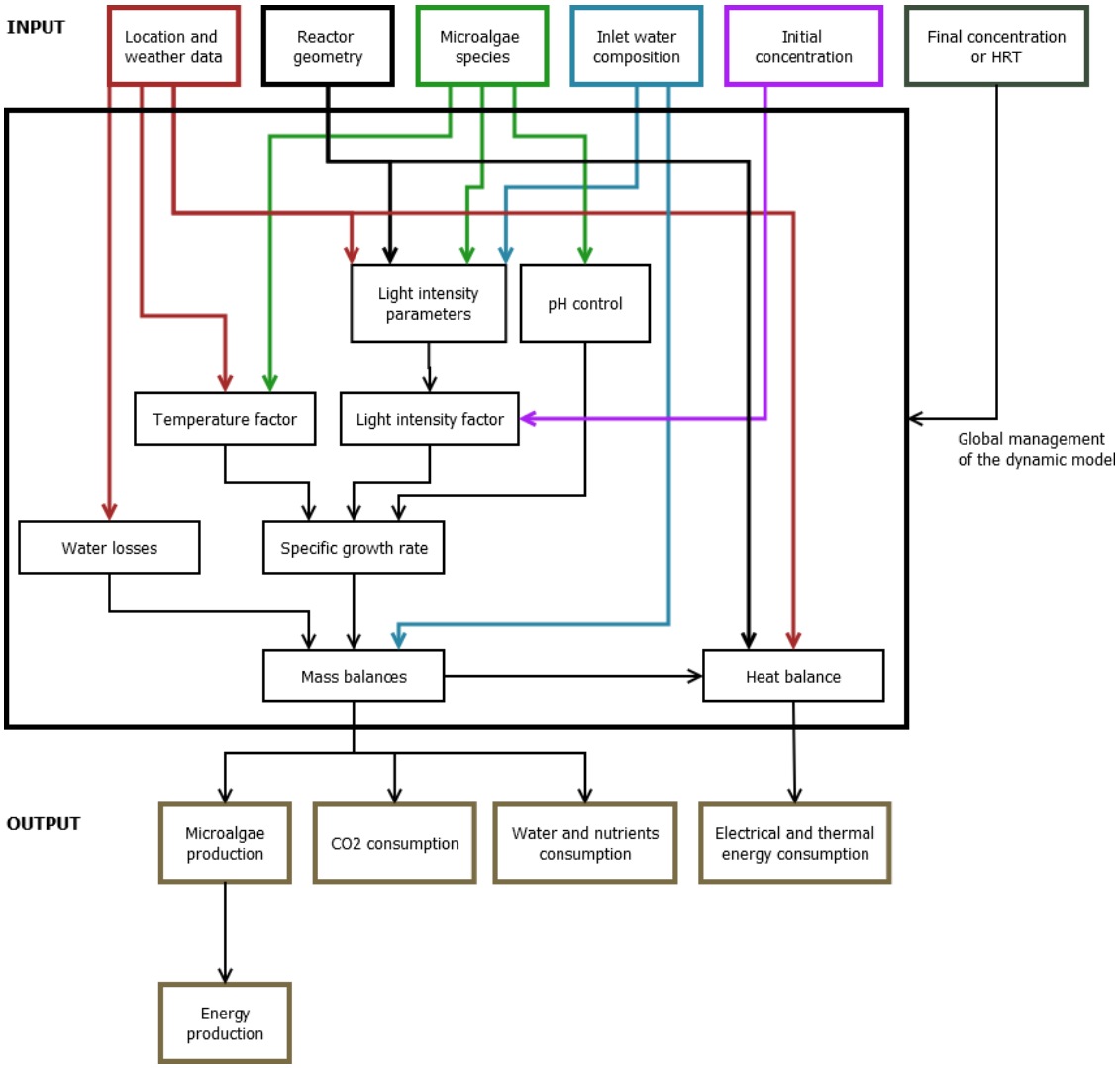


Figure 6: Model structure

3.5 Input of the model

Since the growth of the microalgae is strictly dependent on some weather parameters, most of all from light intensity and temperature, the mathematical model must take into account the values assumed by these parameters during the time period considered in the model.

To evaluate the productivity of the cultivation technology considered in the mathematical model, it was necessary to know a certain amount of input data, shown in Figure 6.

The input required by the model are:

- *Location data*: the open raceway pond model uses as input the longitude of the reactor and the hour difference between the location of the bioreactor and Greenwich; these data are needed to calculate the solar hour in the location. The flat panel model requires also the latitude of the reactor to evaluate, for each day of the year, the time at which the sun rises from the horizon of the flat panel and when the sun goes beyond the horizon of the flat panel.
- *Weather data* are needed by the models both to calculate the irradiation factor which influences the microalgae growth and to evaluate the thermal balance. The open raceway pond model requires the global irradiation over a horizontal surface, while for the flat panel model it is needed to have the direct and the diffuse radiation over an horizontal surface as two distinct data.

  Moreover, both the two models require other weather data, such as the atmospheric temperature, wind speed, relative humidity, etc.

  Hourly data are used in all the models: the computations of the mass production, CO2 consumption and of all the output, as well as the performance parameters are evaluate with a dynamic approach, as it has been explained.
- The *microalgae species* which is wanted to be grown in the given cultivation technology is another fundamental input: many parameters of the model depends on this input, such as the maximum growth rate, the optimal growth temperature, the saturation light irradiation,…all these characteristics assume different values depending on the microalgae species.

  As it is said in the previous chapter, the open raceway pond cultivation system has a huge limitation which consists in contamination and pollution: for this reason not all the microalgae species are able to grow in this typology of reactor. This limitation does not concern the flat panel which is a closed reactor where the growth conditions could be easily controlled.

In table Table 1 all the parameters included in the model which depend on algae species are listed: the two algae species in the table are those for which the model has been tested.

Typology	*P. tricornutum*	*T. pseudonana*
pH_opt	8,300	8,300
alk_opt [meq/l]	0,032	0,032
LHV [kJ/kg]	21527	21527
I_sat [W/m2]	37,118	21,834
μ_max [1/h]	0,058	0,137
T_let [°C]	30,310	31,400
T_opt [°C]	21,640	24,730
beta	1,570	1,830
decay rate [h^(-1)]	0,002	0,002

Table 1: Microalgae characteristics [66]

- The *composition of the inlet water* which is used to fill the reactor at the beginning of each cultivation phase is another input required: since each cultivation phase works as a batch reaction, it is necessary to have inside the medium the quantity of nutrients that is sufficient to feed the microalgae for the entire duration of the batch process.
  In case of shortage of nutrients, as it is explained in the previous chapter, the microalgae growth rate decreases and the production of new biomass with it, but the quantity of lipids in the biomass increases: this process can be extremely interesting if the downstream process aims to produce biodiesel. The models presented in this work do not consider the input condition of scarcity of nutrients, which are instead always supplied in excess. As a model output, it is possible to calculate the exact amount of nutrients consumed by the microalgae.
  The model gives as input a surplus of nutrients in the water, to guarantee they are not the limiting factor to microalgae growth; then, as output, it is possible to know the exact quantity of nutrients which have been consumed and thus to verify that the real water stream which would be used to feed the reactor contains that amount of nutrients: if it does not, then it is known that a certain amount of nutrients must be added to the quantity already existing in the water.

- The last input required by the model is strictly dependent on the operating strategy: as it has been previously explained, the mathematical models to predict microalgae production can be run in two different ways: if it is wanted to define the HRT required to reach a certain microalgae concentration in the reactor, then it is necessary to give as input information to the model, *the initial and the final concentration* ([g/m^3]). If the HRT is fixed along the whole time period taken into account, then the input data will be the *initial concentration and the HRT*, leaving the final concentration in the reactor free to change.

3.6 Output of the model

Among the outputs of the Matlab model, the mass production of microalgae is the most important. Starting from this result, it is possible to define two global performance parameters which are the *volumetric productivity* (expressed in [g/(l*d)] or in [kg/(m^3*d)]) and the *areal productivity* (expressed in[t/(ha*y)] or in [kg/m^2*d)]). These two indicators are fundamental as they give the possibility to compare the reactor to the performance of other models with different geometries and operating conditions, given by literature, and also to prove the accuracy of the model and its reliability.

Moreover, as shown in Figure 6**Errore. L'origine riferimento non è stata trovata.** the model is able to give as output the exact quantities of all the compounds consumed or produced in the time period considered by the simulation (usually 1 year). For example, the model gives the CO_2 that is needed to be bubbled in the reactor to maintain a constant pH level and to feed the microalgae which need the injected CO_2 for the photosynthetic process. In this way, the model gives the possibility to analyse the carbon footprint of the technology or at least to understand the quantity of CO_2 which can be fixed by the biomass produced; it is important to understand that a part of the injected CO_2 is lost to the atmosphere:

this quantity can be relevant in the case of open raceway pond while is quite limited in the case of flat panel photobioreactor.
Another fundamental output of the model is the total electrical and thermal energy required by the reactor: to evaluate these quantities, the energy balance is not sufficient, as it is necessary to include the electrical energy spent at the boundary of the system, to re-fill the reactor and to harvest the biomass from the reactor itself; the electrical energy also includes the quantities which are needed for the mixing and for the air bubbling in the bioreactor.
Finally, another output of the model is the quantity of water needed from the reactor, without considering the possible water recirculation coming from the downstream process.

3.7 Auxiliary equations

3.7.1 *Growth model*

In the previous chapter, the most important parameters which influence algae growth have been described. Here follows how these parameters have been taken into account in the growth phase mathematical model.
The growth rate of algae is expressed by the following equation, taken from Yang [9]:

$$r_{gA} = \mu_A X_A$$

Eq. 4

Where X_A is the mass concentration of microalgae [g/m^3] and μ_A is the specific growth rate ([d^{-1}]or [s^{-1}]).
In the equation of the specific growth rate μ_A , it is possible to identify the influence of the most important parameters which affect the growth:

$$\mu_A = \hat{\mu}_A \left(\frac{CO_{2D}}{K_C + CO_{2D}}\right)\left(\frac{N_T}{K_{NA} + N_T}\right) f_I f_T$$

Eq. 5

$\hat{\mu}_A$ is the *maximum specific growth rate*: it depends on the microalgae species [1/day]; CO_{2D} , N_T are quantities of dissolved nutrients and CO_2 [mol/m^3] at time *t*.

As it can be seen in equation Eq. 5, nitrogen is the only nutrient that has been taken into account in the specific growth rate expression; other nutrients, such as phosphorus, are not explicitly taken into account, as it is suggested by Yang [9], with the assumption that the metabolism of the microalgae is not limited or inhibited by these compounds. The specific growth rate can reach higher values thanks to the use of some micronutrients, such as iron and silicon ([2], [5], [52], [67], [68]).

The expression used in equation Eq. 5 to represent how the quantities of nitrogen and CO2 affect the specific growth rate is a Monod model. K_C and K_{NA} are the *half-saturation constants*: the compound concentration when $\mu_A = \hat{\mu}_A/2$. When nitrogen and carbon dioxide concentrations are high, these terms assume a value next to 1 and they do not affect the microalgae growth: if this situation occurs, it means that the quantities are in excess.

The Monod model is represented in Figure 7.

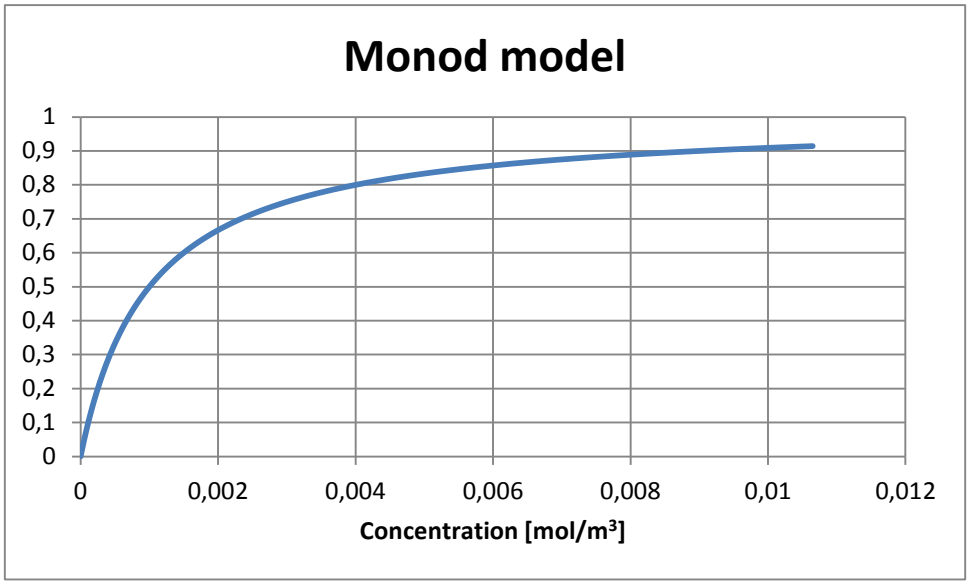


Figure 7: Evolution of the Monod model equation

f_I is the *light intensity factor*: the expression of this term has been taken from literature ([9], [44]):

$$f_I = \frac{I_a}{I_s} exp\left(1 - \frac{I_a}{I_s}\right)$$

Eq. 6

Where I_a is the *average light intensity* in the bioreactor in a given moment *t*, while I_s is the *saturation light intensity*, which depends on the microalgae species considered; as it has been said in the previous chapter, the saturation intensity factor is usually in the range between 30 and 100 W/m^2 [29].

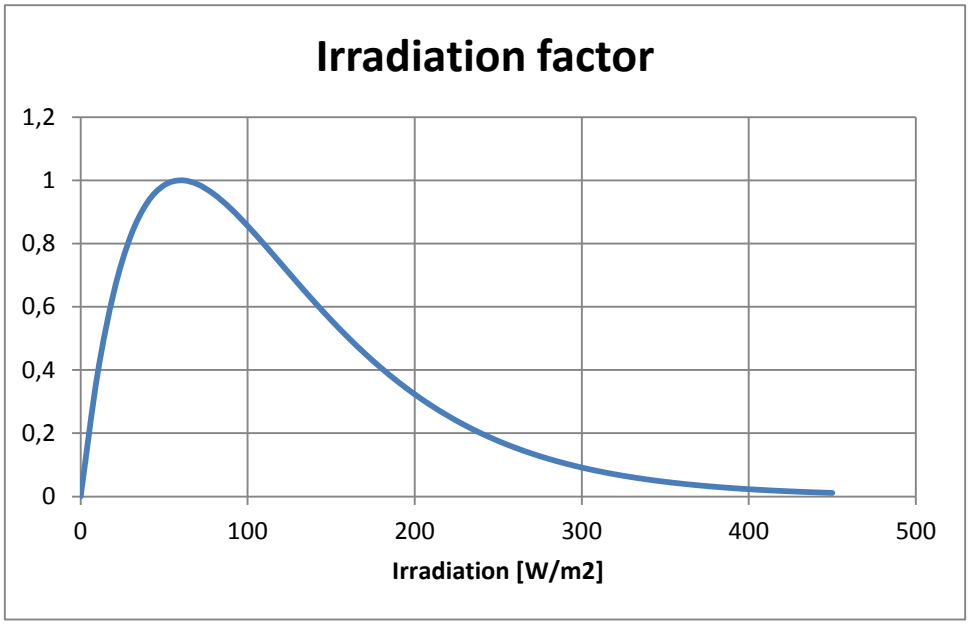


Figure 8: Irradiation factor

The average light intensity I_a is calculated in a different way depending on the geometry of the reactor, as it is explained hereinafter. It depends on the weather data given as input, on the turbidity caused by the microalgae and other substances in the water and on the reactor depth.

The model includes the hypothesis of perfect mixing: with this assumption, it is possible to consider that the whole quantity of microalgae in the water is affected by the same quantity if light intensity. If the perfect mixing hypothesis is not acceptable, the reactor should be divided in different zones, especially for the open

raceway pond reactor: in this case, there is an upper layer where photosynthesis yield is high, but there is low energy efficiency and in some cases inhibition may occur as well, because light intensity is higher than the saturation light intensity. Then there is an intermediate layer, where both photosynthesis yield and efficiency are high. Finally the internal layer, where photosynthesis yield is high but algae use less energy than what would be possible, since the incoming light is not sufficient.

f_T is the *temperature factor*: the microalgae growth is affected by this parameter, and each microalgae species has an optimal growth temperature; when the medium temperature corresponds to this value, then the growth is not affected by temperature and the value of f_T is 1: this is what happens in the closed reactor, where a heat exchanger is used to keep a constant optimal temperature. Below and above the optimal growth temperature, the growth is negatively influenced by the water temperature. Above the optimal temperature, the value of f_T decreases fast and reaches 0 for a certain temperature that again depends on the algae species: this value is called *lethal temperature* (T_{let}) and the growth is not possible at all. The expression of the temperature factor is shown in the following equation and was taken from Slegers et al. [66]:

$$f_T = \left(\frac{T_{let} - T_w}{T_{let} - T_{opt}}\right)^{\beta} exp\left(-\beta\left(\frac{T_{let} - T_w}{T_{let} - T_{opt}} - 1\right)\right)$$

Eq. 7

As it is possible to see in the equation, there is a parameter β, that depends on the algae species and that it is a curve modulating constant.

The following figure (Figure 9) shows the shape of the temperature factor f_T: the parameter overestimates the growth for low temperature values.

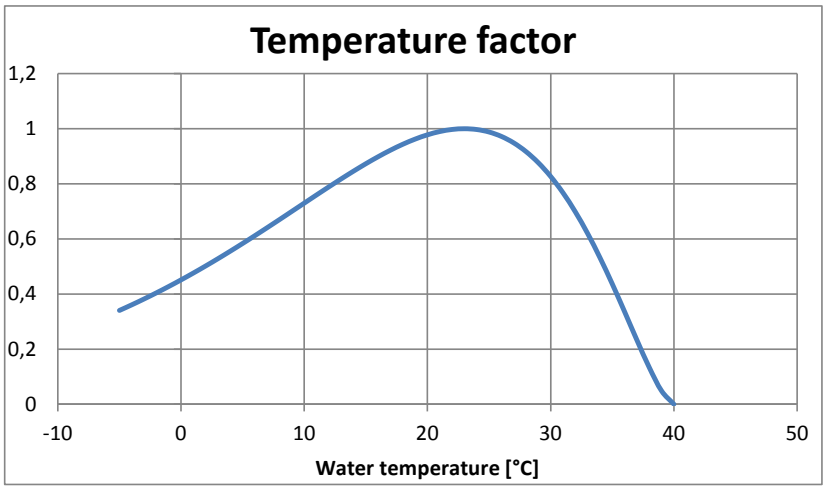


Figure 9: Temperature factor

3.7.2 *pH control strategy*

Each microalgae species has an optimal pH value: the model includes a control system to keep the optimal value of pH in the reactor.

As shown in the following equations from Sills [43], pH level depends on dissolved CO_2 concentration and alkalinity; if these two parameters are kept constant, it is possible to control the pH value.

C_T is defined as the total concentration of carbonate species in solution.

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

Eq. 8

Note that $[H_2CO_3^*] \cong [CO_{2(aq)}]$.

The molar concentration of each carbonate species (as a fraction of C_T) is dependent on pH, as it is shown by the following equations:

$$[H_2CO_3^*] = \frac{C_T}{1 + \frac{k_1}{[H^+]} + \frac{k_1 k_2}{[H^+]^2}} = \alpha_0 C_T$$

Eq. 9

$$[HCO_3^-] = \frac{C_T}{1 + \frac{[H^+]}{k_1} + \frac{k_2}{[H^+]}} = \alpha_1 C_T$$

Eq. 10

$$[CO_3^{2-}] = \frac{C_T}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 k_2}} = \alpha_2 C_T$$

Eq. 11

Finally:

$$C_T = \frac{alk - OH^- + H^+}{\alpha_1 + 2\alpha_2}$$

Eq. 12

From equations Eq. 10 and Eq. 11, α_1 and α_2 are calculated; , since pH is the concentration of dissolved $[H^+]$ in the water and pH = 14 – pOH, all the terms in equation Eq. 12 are known and the total concentration of carbonate species may be obtained, remembering that dissolved CO_2 concentration is $\left[CO_{2(aq)}\right] \cong [H_2CO_3^*]$, it is possible to define the dissolved CO_2 quantity which must be kept constant to preserve the optimal pH value.

This term will be a part of the time dependent CO_2 mass balance, that is used to calculate the CO_2 injection at each time *t*.

3.7.3 *Mean light intensity for open pond*

The light intensity factor in the specific growth rate (Eq. 6) expression contains I_a, the *average light intensity* in the bioreactor in a given moment. Starting from global horizontal radiation, the model evaluates I_a using the Beer-Lambert's law; it assumes an exponential decay of the light intensity from the external surface of the cultivation system:

$$I_a(s) = I_0 exp(-\sigma X_a s)$$

Eq. 13

As it is explained by Béchet et al. [31], $I_a(s)$ is the local light intensity, s is the distance from the external surface of the system to the position under consideration, I_0 is the incident light intensity, σ is the extinction coefficient, and X_a the cell concentration.

To apply the Beer–Lambert's law, the culture medium must be isotropic (i.e. the optical properties of the broth are independent from light direction) and algae cells must not scatter light. Unfortunately, if the first condition is often met in well-mixed outdoor cultivation systems, algae cells do scatter light. The model considers that both these two conditions are always verified.

The equations to calculate I_a are strictly dependent on the geometry of the bioreactor: for the open pond, as it is suggested by Yang [9], it has been used an integration through the pond depth of the Beer-Lambert's law:

$$I_a = \frac{1}{Z}\int_0^Z I_0 exp(-K_e z)dz$$

Eq. 14

Where I_0 is obtained directly from the global horizontal radiation I_{GHR}: $I_0 = PAR * I_{GHR}$. *PAR* is the photosynthetic active radiation, the quantity of solar radiation which is used by the microalgae for the photosynthesis and which corresponds to 45% of the total.

K_e is correlated to algal concentration in the pond, and it is called *extinction coefficient*:

$$K_e = K_{e1} + K_{e2}X_A$$

Eq. 15

If K_e is constant through the pond depth, then it is possible to integrate the expression of I_a:

$$I_a = \frac{I_0}{K_e Z} exp(-K_e Z - 1)$$

Eq. 16

3.7.4 *Light intensity for flat panel*

In case of flat panel, the complexity of the geometry requires the use of different equations from those applied for the open pond. First of all, the input data are direct and diffuse radiation on the horizontal surface; moreover, the equations

must take into account also the reflection of the radiation on the surface of the panel. It is fundamental to remember that the two faces of the flat panel are both made of transparent material, and so the radiation may enter from both the sides of the panel.

As it is explained in Slegers et al. [69], if the direct horizontal radiation is given, since the panel is vertical, it is necessary to introduce a geometrical parameter for direct radiation:

$$G_{direct}(t) = \frac{\cos\theta}{\cos\theta_z}$$

Eq. 17

In which θ is the solar incidence angle, and θ_z is the solar zenith angle. The values assumed by these angles during each day of the year depend on the location and have been calculated with the equations taken from Duffie [70]. For large scale cultivations, parallel positioned flat panels are used. Parallel placement causes shading and consequently part of the panels no longer receive direct sky light. The shadow height on vertical reactor panels is given by:

$$h_{shadow} = h - \frac{d\ \tan(90 - \theta_z)}{\cos(\gamma - \gamma)}$$

Eq. 18

Which is a function of the reactor height h [m], the distance between the reactor panels d [m], the solar elevation, which is equal to 90-θ_z and the angle between the solar rays and the azimuth of the surface.

If h_{shadow} is greater than 0, then the flat panel is divided into two parts. The upper part receives direct and diffuse radiation, the lower part only diffuse light. The separation between the upper and the lower part varies with the solar position and is calculated every simulation step.

Parallel placement of the reactors also influences the penetration of diffuse sky light into the space between the panels; the light intensity decreases from the top to the bottom. Similarities can be seen with the penetration of light in urban street canyons [71].

For these reasons, the geometrical factor for diffuse light is different for the heights inside the panel which are above h_{shadow} [m] and those which are below.

At height $y < h_{shadow}$

$$G_{diffuse} = \frac{1 + \cos(\beta + u)}{2}$$

Eq. 19

Where u = atan(y/d), β [°] is the slope of the reactor, the angle that the surface makes with the surface of the earth.

At height $y > h_{shadow}$

$$G_{diffuse} = \frac{1 + \cos(\beta)}{2}$$

Eq. 20

The reactor panels at the border of the algae plant experience a different light pattern. In the model it is assumed that this effected is negligible on large scale. Therefore, all the panels are treated similarly in the calculations. Moreover, ground reflection is low for parallel placed panels and is therefore not taken into account.

The total amount of light falling on each reactor surface at a given height y, for a given moment t is:

$$I_0(y,t) = G_{direct}(t)I_{direct}(t) + G_{diffuse}(y)I_{diffuse}(t)$$

Eq. 21

At this point, it is fundamental to consider the reflected fraction of the irradiation which does not enter into the reactor and so does not contributes to the growth of the microalgae.

The amount of reflected light on each interface is related to the differences in refractive indices and the angle of incidence [72]. The angle of refracted light follows from Snell's law.

The angle of incidence for diffuse radiation which is considered to evaluate the light reflection is assumed to be 60°, as it is suggested by Duffie et al. [70].
Light reflection by the flat panel walls follow Fresnel equations:

$$R_s = \left[\frac{\eta_i \cos(\theta_i) - \eta_t \sqrt{1 - \left(\frac{\eta_i}{\eta_t}\sin(\theta_i)\right)^2}}{\eta_i \cos(\theta_i) + \eta_t \sqrt{1 - \left(\frac{\eta_i}{\eta_t}\sin(\theta_i)\right)^2}}\right]^2$$

Eq. 22

$$R_p = \left[\frac{\eta_i \sqrt{1 - \left(\frac{\eta_i}{\eta_t}\sin(\theta_i)\right)^2} - \eta_t \cos(\theta_i)}{\eta_i \sqrt{1 - \left(\frac{\eta_i}{\eta_t}\sin(\theta_i)\right)^2} + \eta_t \cos(\theta_i)}\right]^2$$

Eq. 23

Where θ_i [rad] is the incidence angle, η_i [-] is the refractive index of the material before the interface, η_t [-] is the refractive index for the material after the interface. Normal sunlight is non-polarized, therefore the overall reflection coefficient equals the average of the reflection coefficients for *s*-polarized and *p*-polarized light:

$$R' = \frac{R_s + R_p}{2}$$

Eq. 24

The light reflected within the reactor wall is completely transmitted to the air, introducing the hypothesis of a non-absorbing material for the walls of the reactor. The light transmitted to the culture, which has to be calculated separately for direct and diffuse radiation, is:

$$I_i(t) = I_0(t)(1 - R'_1 R'_2) T_m$$

Eq. 25

Additional light may be lost due to a low transparency of the wall material, indicated by T_m [-].

The calculation is done for both the two sides of the reactor and, for parallel positioned panels, for each height. R'_1 and R'_2 are the reflection coefficients for the air-reactor wall interface and the reactor wall-culture volume interface respectively.

Two light intensity gradients exist in the culture volume. First, as a function of height due to shading and the penetration of diffuse light between parallel positioned panels. Second, in the liquid between the two reactor walls. The second gradient runs from the reactor wall to the centre of the reactor and is caused by the absorption of light by the medium and the algae [69].

Only the photosynthetic active radiation (*PAR*) of the spectrum is absorbed by the algae. This accounts for about 45% of the total light.

The Lambert-Beer's law, as it was for the open pond, is used for the overall light gradient in the culture volume:

$$I(y,z,t) = I_{front}\, e^{-(K_{e1}+K_{e2}X_A)z} + I_{back}\, e^{-(K_{e1}+K_{e2}X_A)(s-z)}$$

Eq. 26

This equation gives the light intensity at location z [m] inside the reactor thickness [m], at a given height y [m] in the reactor at a time t.

At this point, to simplify the model, the values of light intensity $I(y,z,t)$ from equation Eq. 26 are integrated to find a mean value of irradiation for the whole culture inside the whole reactor in a given time t: with these integrations, it is possible to obtain a single value of radiation to use in the growth model, for the whole panel, at a given time t.

The hypothesis of a perfect mixing inside the culture at each time t is necessary to integrate above the whole reactor geometry.

3.8 Mass and energy balances

3.8.1 *Mass balances*

The balance of nitrogen and oxygen can be modelled in a similar way, suggested by Yang [9]:

$$\frac{dM}{dt} = \mu_A X_A Y_{AM} - k_{Lg}\alpha(M - M^*)$$

Eq. 27

Where M is the concentration of the respective component in the water in the bioreactor, Y_{AM} is the mass of the respective component consumed or generated by the microalgae per unit mass of microalgae produced. The last term of the right-end side of the equation represents the mass transfer between the atmosphere and the pond, where $k_{Lg}\alpha$ is the mass transfer coefficient for a given element, M^* is the saturation concentration of the respected dissolved element.

For total inorganic carbon, the mass balance assumes a different formulation, since during the growth phase, the CO_2 is injected continuously in the pond, to keep a constant concentration of dissolved CO_2 in the reactor, balancing the losses of CO_2 to the atmosphere and the consumption of CO_2 by the microalgae.

$$\frac{dCO_2}{dt} = \mu_A X_A Y_{ACO_2} + f_{CO_2} - k_{Lg}\alpha(CO_2 - {CO_2}^*)$$

Eq. 28

Where f_{CO2} represents the flux of CO_2 introduced by the supply of gas flow into the system. Since the quantity of dissolved CO_2 is wanted to remain constant ($dCO_2/dt = 0$), the mass balance can be written again as

$$f_{CO_2} = -\mu_A X_A Y_{ACO_2} + k_{Lg}\alpha(CO_2 - {CO_2}^*)$$

Eq. 29

Finally the mass balance for microalgae species can be written as

$$\frac{dX_A}{dt} = \mu_A X_A - k_{dA} X_A$$

Eq. 30

Where all the terms in the equation have been already explained.

As it can be seen, all these equations are time dependent, and are all strictly dependent from one another: this means that they form altogether a system of differential equations.

To solve this system in Matlab, it has been adopted the strategy to solve each differential equation with the finite different methodology, and thus to solve the system of differential equations as a system of algebraic equations.

3.8.2 *Thermal balance for open pond*

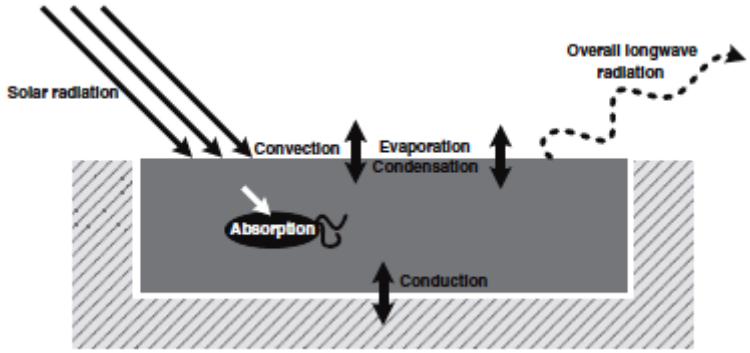


Figure 10: Thermal balance for open pond [66]

The expression of the thermal balance is different for the bioreactor considered, as it is strictly dependent on the reactor geometry. For the open raceway pond, the model uses the thermal balance as it is suggested by Slegers et al. [66].

$$V_R cp_W \rho_W \frac{dT_W}{dt} = Q_{irr} - Q_{algae} - Q_{rad} - Q_{evap} - Q_{conv} - Q_{cond}$$

Eq. 31

With V_R [m³] volume of the pond, cp_w [J/(kg °C)] the heat capacity of the growth medium, ρ_w [kg/m³] the density of the growth medium, T_w [°C] the temperature in the pond, Q_{irr} [W] the heat flow to the pond by the sunlight, Q_{algae} [W] the light

energy flow to algae during growth, Q_{rad} [W] the heat flow by emission of long-wave radiation in the infrared region, Q_{evap} [W] the heat flow caused by either evaporation or condensation, Q_{conv} [W] the heat flow by convection and Q_{cond} [W] the heat flow between the pond and the ground via conduction.

The water in the pond is heated by sunlight that enters the culture volume. Solar energy that is not used by algae for growth is considered as thermal energy. The total heat flow by the sunlight is given by:

$$Q_{irr} = A_w I_{surface}(t)$$

Eq. 32

with A_w [m^2] the water surface area of the pond and $I_{surface}$ [J/(kg °C)] the total light falling on the pond. Part of this light is absorbed by microalgae for growth:

$$Q_{algae} = h_{comb}\mu_{growth}X_A V_R$$

Eq. 33

which is a function of the combustion energy of algae biomass h_{comb} [J/kg], the specific growth rate μ_{growth} [s^{-1}] and the biomass concentration X_a [kg/m^3].

The water in the pond emits thermal energy by long-wave radiation. The overall long-wave radiation flow between the water in the pond and the sky is calculated using Duffie [70]:

$$Q_{rad} = A_w \varepsilon_W \sigma\left((T_w + 273.15)^4 - T_{sky}^4\right)$$

Eq. 34

Where ε_w [-] is the emissivity of the water in the infrared region, σ [W/(m^2 K^4)] the Stefan-Boltzmann constant and T_{sky} [K] the equivalent sky temperature for clear sky days, which is expressed by Duffie [70] as:

$$T_{sky} = (T_{atm} + 273.15)(0.711 + 0.0056T_{dew} + 0.000073T_{dew}^2 + 0.013\cos(15t_{solar}))^{0.25}$$

Eq. 35

Where T_a [°C] is the air temperature, T_{dew} [°C] the dew point temperature and t_{solar} [-] the number of hours after solar midnight. The effect of cloud covers is not included in the calculation. Evaporation has a large effect on the water temperature, especially in locations with low humidity and high wind velocities. The evaporation rate depends on the shape of the water area, wind velocity, thus also movement of the water. The evaporation flow is driven by the difference of water vapour pressures between the ambient air and the saturated water body. The evaporation energy flow is given by:

$$Q_{evap} = A_w h_{evap}(p'_s - p'_a)$$

Eq. 36

The evaporation flow depends on the heat exchange coefficient for evaporation h_{evap} [W/(m^2 Pa)], the saturated water pressure p'_s [Pa] at water temperature T_w and the water pressure of air p'_a [Pa] at air temperature T_a. The evaporation rates have been calculated using the heat exchange coefficient h_{evap} found in Duffie [70]:

$$h_{evap} = 0.036 + 0.025v$$

Eq. 37

Where v [m/s] is the wind speed.

The Antoine equation is applied to calculate the saturated water pressure p'_s [Pa] at water temperature T_w, and the water pressure of the air p'_a [Pa] at air temperature T_a:

$$p' = RH\ 10^{\left(8.07131 + log_{10}\left(\frac{101325}{760}\right)\right) - \frac{1730.63}{233.46+T}}$$

Eq. 38

Where RH [-] is the relative humidity and T [°C] the temperature.

Convection and evaporation are related processes. The flow for passive and forced convection at the water surface mainly depends on the difference between water and air temperature. The convection flow is given by:

$$Q_{conv} = C_{Bowen} \frac{p_a(T_w - T_a)}{p_{ref}(p'_s - p'_a)} Q_{evap}$$

Eq. 39

Where C_{Bowen} is the Bowen constant [Pa/°C], p_a is the ambient pressure [Pa] and p_{ref} the reference pressure [Pa], p'_s and p'_a are derived using equation Eq. 38.
Conductive heat transfer takes place between the open pond and the soil. The soil is assumed to be an infinite source for heat transfer. This heat transfer calculation is derived from Fourier's law:

$$Q_{cond} = h_{soil} A_{soil} (T_w - T_{soil})$$

Eq. 40

Where h_{soil} [W/(m² °C)] is the heat transfer coefficient of the surrounding soil layer, A_{soil} [m²] is the area of the pond that is embedded in the soil and T_{soil} [°C] is the temperature of the soil surrounding the pond.

2.8.3 *Thermal balance for flat panel*

Due to the significant difference in the geometry of the reactor and the temperature strategy adopted, the thermal balance for the flat panel assumes another form from the one that has been implemented for the open raceway pond.
For the flat panel, the temperature of the water is wanted to be maintained at a constant value, using a heat exchanger placed at the bottom of the reactor to remove or supply the heat necessary to reach this aim.

$$V_R cp_W \rho_W \frac{dT_W}{dt} = Q_{irr} - Q_{algae} - Q_{exch} - Q_{conv+cond}$$

Eq. 41

Equation Eq. 41 represents the thermal balance for the flat panel. As it has been said, the water temperature T_W [°C] in the reactor should remain constant. For this reason, the thermal balance can be written as follows:

$$\frac{dT_W}{dt} = 0 \rightarrow Q_{irr} - Q_{algae} - Q_{exch} - Q_{conv+cond} = 0$$

Eq. 42

Q_{irr} [W] is given by the following expression:

$$Q_{irr} = 2\, A_{panel}\, I_{mean}$$

Eq. 43

Where A_{panel} is the surface of the reactor, that is multiplied by 2, as it is necessary to consider both the front and the back surfaces; I_{mean} [W/m^2] is the radiation previously calculated taking into account both the direct and the diffuse radiation and the reactor geometry: it is the radiation which interacts with the water in the reactor and with the microalgae.

As calculated for the open pond, a part of the incoming heat is used by the microalgae for the growth:

$$Q_{algae} = h_{comb} \mu_{growth} X_A V_R$$

Eq. 44

which is a function of the combustion energy of algae biomass h_{comb} [J/kg], the specific growth rate μ_{growth} [s^{-1}] and the biomass concentration X_a [kg/m^3]; V_R [m^3] is the reactor volume.

The model takes into account the natural convection over the panel surface caused by the wind and the conductivity of the glass:

$$Q_{conv+cond} = 2\, A_{panel}\, U_{tot}\, (T_w - T_{atm})$$

Eq. 45

Where

$$U_{tot} = U_{cond} + U_{conv}$$

Eq. 46

Where U_{cond} is the conductivity of the glass [W/(m²K)] and U_{conv} is the conductivity of the natural convection: it is obtained from Duffie [70].

Using the equations above, it is possible to evaluate the quantity of heat which has to be removed or supplied by the heat exchanger at each time *t*.

Since the flat panel temperature is always kept between 20 and 30 °C, depending on the optimal temperature for microalgae growth, it is supposed that the heat exchange through radiation can be omitted.

3.8.4 Electrical energy for harvesting, refilling, mixing and bubbling

For both the open pond and the flat panel, the harvesting of the water from the reactor and its re-filling are carried out in 8 hours, during 1 night: 3,5 h for the harvesting and 3,5 hours for the refilling. These operations are run with a pump, which electrical consumption has been calculated has follows:

$$E_{harv/refil} = P_{pump} t_{harv/refil}$$

Eq. 47

Where the power of the pump comes from:

$$P_{pump} = \frac{\rho g Q h}{\eta_{pump}}$$

Eq. 48

Where ρ is water density [kg/m³], g is the acceleration of gravity [m/s²], η_{pump} [-] is the efficiency of the pump, set at 0.85, Q [m³/s] is the volumetric flow rate which has to be pumped if the time for each harvesting and refilling is wanted to be followed and h [m] is the height difference between the two basins before and after the pump: thanks to the fact that the model includes also the design of a settler

positioned after the bioreactor, it is possible to know the exact *h* for the harvesting, which has been increased to consider the losses in the pipes, while for the refilling, data have been taken from literature, considering *h* equal to 1 m for the open pond and 3 m for the flat panel: the difference between these two values is again related to energy losses in pipes.

For what concerns the mixing in the open pond, the following formula has been implemented:

$$P_{mix} = \frac{\rho g Q h}{\eta_{paddlewheel}}$$

Eq. 49

Where Q [m^3/s] is obtained from the speed of the water that should be kept in the reactor (0.20 m/s) and from the cross-section of the open pond (which depends on the geometry), h is the given height difference before and after the paddle wheel, taken from literature (0.05 m). $\eta_{paddlewheel}$ is lower that the efficiency of a normal pump and is equal to 0.25.

Both for the open pond and from the flat panel, a bubbling system has to be taken into account: for the flat panel, this system should be able both to supply the CO2 necessary for the photosynthesis of the microalgae and to guarantee an adequate mixing inside the reactor: for this reason, the air bubbled in the flat panel is a higher quantity than the air supplied in the open pond. These quantities are controlled by the CO2 molar fraction inside the injected air which are 0.04 in the case of open pond, 0.02 for the flat panel. The design and the energy consumption for the bubbling system have been calculated through Belsim Vali, using a compressor. The results is that it is necessary to supply 4 kJ for each kg of air injected in the reactor.

Chapter 4

4.Model Results and Parametric Analysis

This chapter presents the results obtained from the dynamic model for microalgae cultivation developed. The most significant results obtained from both the geometrical configurations (meaning the open raceway pond and the flat panel photobioreactor) have been compared to values coming from literature, to evaluate the reliability of the model. From this comparison, it came out that the model created is able to evaluate the performance of open raceway pond with good accuracy, since results are consistent to those coming from literature. Model results for flat panel photobioreactor find less correspondence in literature and it seems that they are quite optimistic . Moreover, different sets of input data have been used to study the behaviour of the model to input variation.

As explained in the previous chapter, the dynamic models for microalgae growth have been created considering two different possible operating strategy:

1. Both the initial concentration of microalgae in the reactor and the final concentration are known. The initial concentration is necessary to start again the cultivation after the harvesting. The final concentration, that is the concentration at which the microalgae are harvested, depends on the technology which is used to separate microalgae from water: this phase

may be more or less extreme depending on which is the downstream process used to convert microalgae into biofuels or other bioenergy forms.

The final concentration also depends on the cultivation system. Open pond is not able to reach high concentrations, since the light distribution and the consequent light regime would cause a reduction in microalgae productivity. For flat panels, it is possible to obtain higher concentrations.

This system configuration is used to evaluate, depending on the location and the variable weather data, which is the mean time needed by microalgae to reach the target concentration, the mean hydraulic retention time (HRT). When HRT in known, it is possible to run the model with the second operating strategy.

2. In this case, the known input data are the initial concentration and the mean HRT, which is used during the whole year, or at least for the whole season.

   This second strategy is usually applied in real cultivation systems in which the harvesting is always done after the same amount of days, without considering if the target concentration has been reached or overtaken.

4.1 Open raceway pond

The following table groups the input data used for the open pond modelling, for both the first and second operating strategies:

HRT not fixed, X target fixed		HRT fixed, X target not fixed	
Location	Sevilla (SPA)	Location	Sevilla (SPA)
	Petrolina (BRA)		Petrolina (BRA)
Tipology	P. Tricurnutum	Tipology	P. Tricurnutum
	T. pseudonana		T. pseudonana
Xa_init [g/m^3]	100	Xa_init [g/m^3]	100
Xa_target [g/m^3]	490	HRT [day]	7
Tw_in [°C]	15	Tw_in [°C]	15
CO_2 rate [%]	0.04	CO_2 rate [%]	0.04
Z_pond [m]	0.3	Z_pond [m]	0.3
LW [-]	10	LW [-]	10

Table 2: Input data for open raceway pond cultivation model

Sevilla (Spain) and Petrolina (Brazil), have been chosen between other locations because they have good weather conditions for the whole year, which might ensure high productivity values for the supposed microalgae cultivation plant. Moreover in Petrolina there is a sugar industry which might supply to the cultivation plant both a wastewater stream containing nutrients and flue gases to supply CO2 to the culture. The weather data file available for the two locations represents a standard year, since it contains measured data coming from different years: this increases the reliability of the results of the simulations, as they do not refer to the weather conditions of a single year, but to a standard year for the location. It is important to notice that the model is able to operate with real measured data and to deal with dynamic physical quantities.

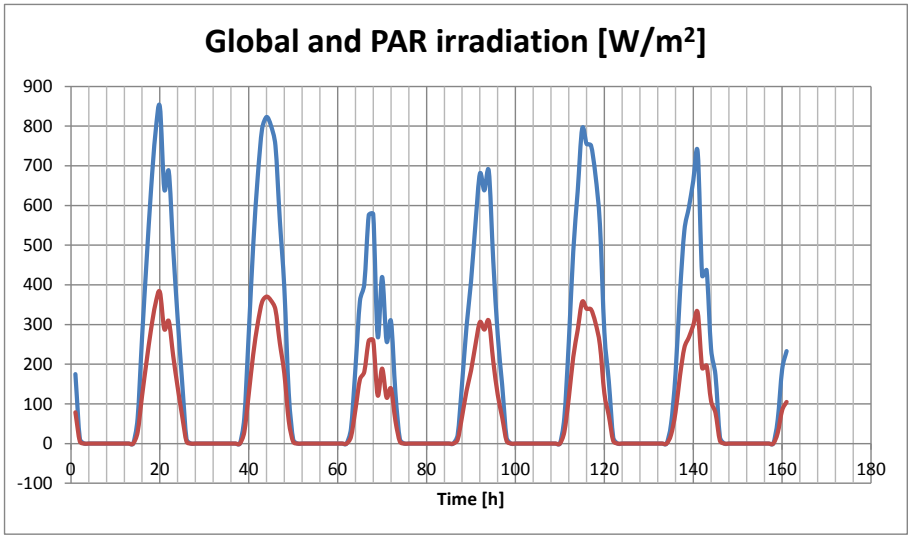
Microalgae species chosen for the simulations have been taken from literature: Slegers et al. [66] uses these typologies of microalgae to evaluate the productivity of an open pond. This work uses the same microalgae species for the open raceway pond and for the closed flat panel photobioreactor to have the possibility to compare the technologies.

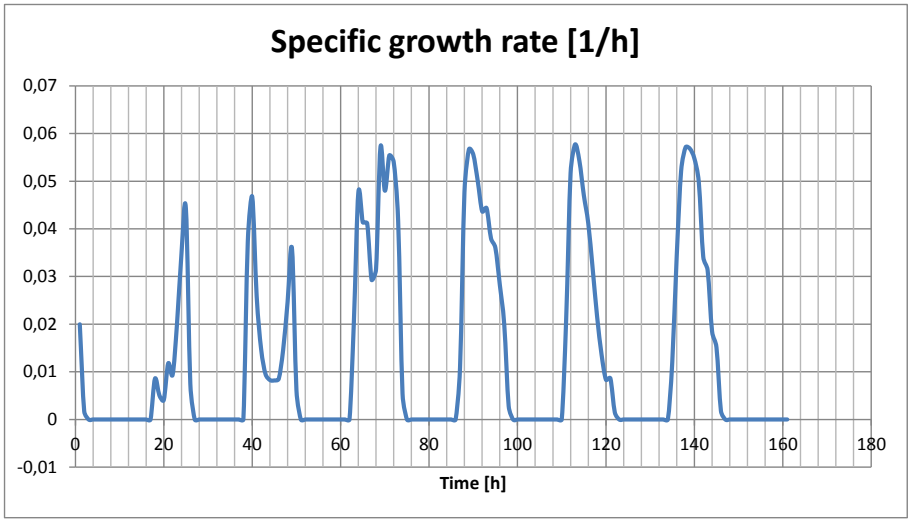
All the other input data have been chosen from literature, taking the most common values applied in other simulations and models, as presented in the previous chapter.

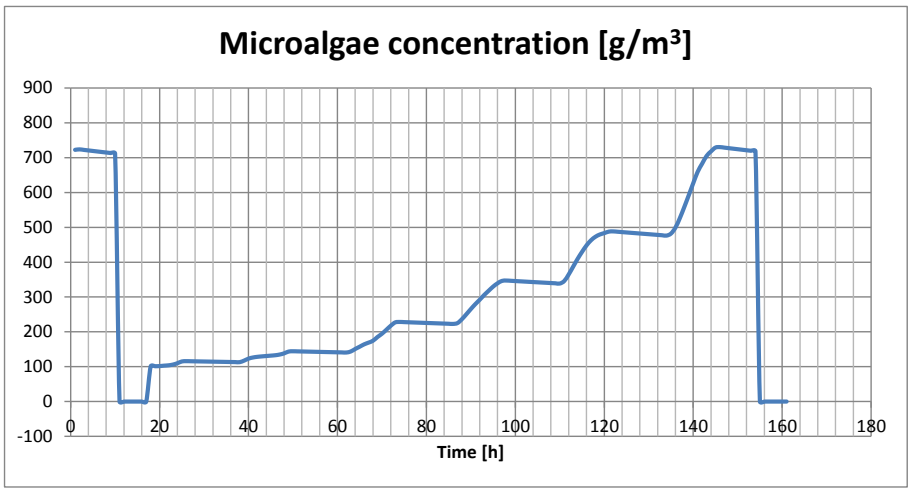
The value of the final target concentration has been set to 490 g/m^3 since in open raceway ponds higher concentrations would be difficult to reach, as suggested in

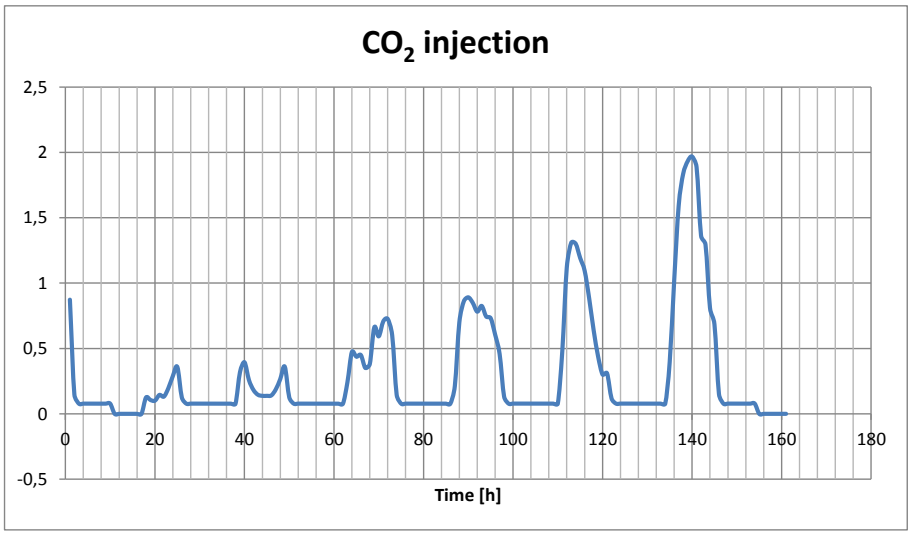
literature: Jiménez [73] uses 470 g/m^3 as output concentration while Lee [74] sets the output concentration at 500 g/m^3.

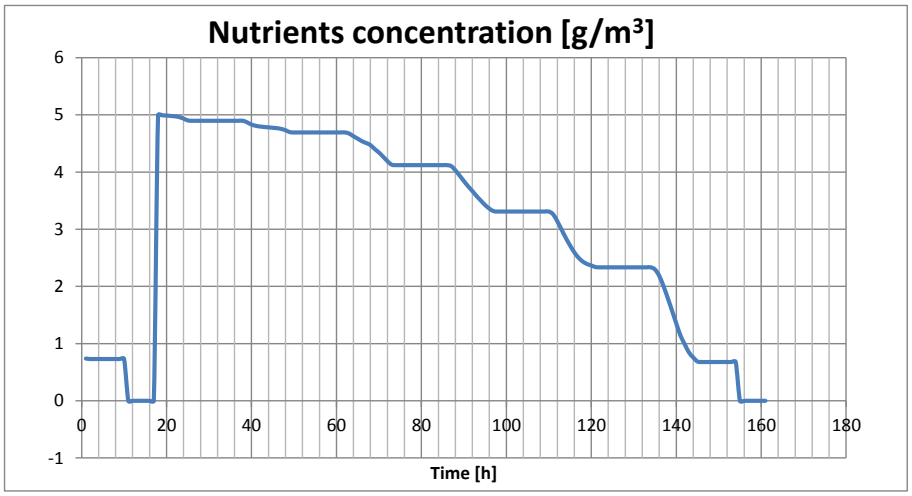
The following figures show the dynamic variations of some of the most important input and output parameters of the model for a time interval higher than HRT.

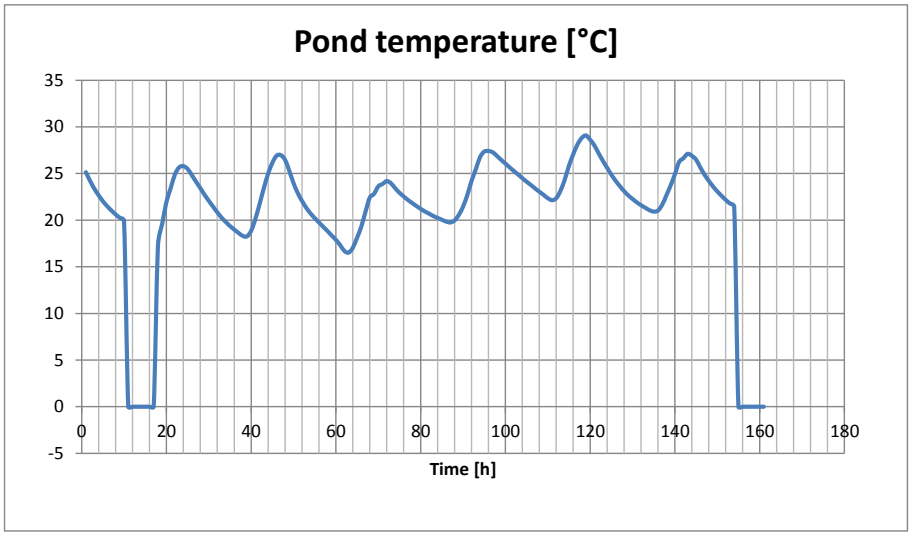

Global and PAR irradiation [W/m²]
900
800
700
600
500
400
300
200
100
0
-100
0
20
40
60
80
100
120
140
160
180
Time [h]


Specific growth rate [1/h]
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
-0,01
0
20
40
60
80
100
120
140
160
180
Time [h]


Microalgae concentration [g/m³]
900
800
700
600
500
400
300
200
100
0
-100
0
20
40
60
80
100
120
140
160
180
Time [h]


CO_2 injection
2,5
2
1,5
1
0,5
0
-0,5
0
20
40
60
80
100
120
140
160
180
Time [h]


Nutrients concentration [g/m³]
6
5
4
3
2
1
0
-1
0
20
40
60
80
100
120
140
160
180
Time [h]


Pond temperature [°C]
35
30
25
20
15
10
5
0
-5
0
20
40
60
80
100
120
140
160
180
Time [h]

After the dynamic modelling which evaluates the data for each hour of the year, some global analysis has been done, obtaining the results showed in the following table:

	HRT not fixed		HRT fixed	
	X target fixed		X target not fixed	
	Petrolina	Sevilla	Petrolina	Sevilla
N harvesting / HRT	45	50	7	7
Mass microalgae [t]	57.29	64.68	54.04	67.88
CO_2 captured [t]	140	156	133	163
CO_2 injected [t]	243	260	235	268
CO_2 lost to atmosphere [t]	78.62	77.35	78.14	77.27
CO_2 ratio losses	0.324	0.298	0.33	0.29
CO_2 ratio algae	0.57	0.6	0.56	0.61
N absorbed [t]	5.8	6.55	5.57	6.8
Water injected [t]	109210	121640	120220	119600
Water evaporation [t]	5.8	5.01	5.83	5.24
Energy microalgae [kWh]	342610	386790	323180	405930
Electrical energy [kWh]	18497	19024	18522	19111
Thermal energy [kWh]	-	-	-	-
Volumetric productivity [kg/(m^3*d)]	0.0523	0.0591	0.0494	0.062
Areal productivity [kg/(m^2*d)]	0.0157	0.0177	0.0148	0.0186
NER	0.108	0.0603	0.1146	0.0942

Table 3: Output from open raceway pond cultivation model

Open pond productivity obtained are consistent with values found in literature: Slegers et al. [66] estimated an annual biomass production for Netherlands and Algeria respectively equal to 41.5 t/(ha y) and 63.7 t/(ha y). Acién Fernàndez et al. [44] gave a maximum microalgae areal productivity equal to 30 g/(m^2 d), higher than what results from the model calculations, but still of the same order of magnitude. Jiménez et al. [73] obtained for a location in Southern Spain (Malaga) a volumetric productivity equal to 0.05 kg/(m^3 d), cultivating the microalgae until a maximum concentration of 470 g/m^3: the cultivation conditions and the results from the dynamic model are consistent with the results of this work.

One of the most important results from the model is the Net Energy Ratio (NER), which is defined by Jorquera et al. [24] as the ratio of the total energy produced over the energy content of photobioreactor construction and materials, plus the

energy required for all plant operation; in this work, the Net Energy Ratio is defined in a slightly different way:

$$NER = Net\ Energy\ Ratio = \frac{total\ energy\ requirement\ for\ operation}{total\ energy\ production\ (biomass)}$$

If NER is defined as above, it expresses the fraction of the energy produced in the cultivation system used by the system itself to generate the biomass. If this value is next to 1, the production of microalgae is too energy intensive, requiring a big share of the energy produced.

From the table above, it appears that for both the locations analysed by the model, the NER is quite far from 1, showing that the energy demand for the operation of the cultivation system in Petrolina is 10.8% of the energy contained in the biomass produced, while for Sevilla is 6%. This values are quite promising for a potential production of microalgae in these locations, since NER is far enough from 1: even if the energy content of open pond construction and materials are added to the total energy requirement, it seems reasonable to say that the plant would still be convenient from an energetic point of view.

The mass of biomass produced in 1 year and the number of harvesting is higher in Sevilla than in Petrolina: this result may appear not so obvious, since light irradiation in Petrolina is higher and more uniform along the year than in Sevilla. The reason of a lower productivity in Petrolina might be seen in the temperatures reached by the pond, which are higher during the whole year, due to higher irradiation: if the temperature of the water is higher than the optimal value for microalgae growth, the productivity decreases fast, as showed in the previous chapter, where the temperature factor affecting the growth rate is presented (Figure 9). Since there is no temperature control and the temperature of the water in the pond varies depending on weather conditions, the thermal energy requirement for the open system is 0.

Another important output of the model is the quantity of CO2 fixed by the microalgae during the growth process; this result is interesting from an environmental point of view: the downstream process to transform microalgae biomass into biofuel releases CO2 to the atmosphere, with a negative

environmental impact. Since the cultivation phase captures more CO2 than the quantity released, using the data of CO2 fixed in the algae it is possible to generate a global balance for the CO2, for the entire biofuel production chain: this environmental analysis may lead to a comparison to other biofuel chain production and with traditional fossil fuel, to evaluate which product has a positive or negative environmental impact.

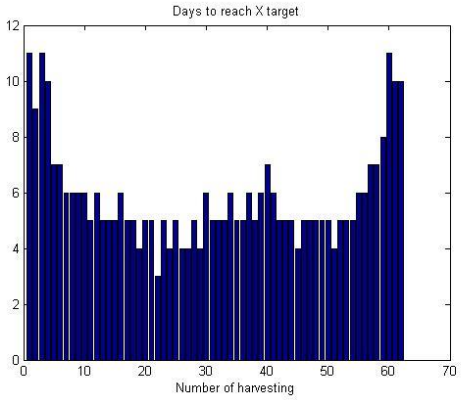
About one third of the CO2 injected in the pond is lost to the atmosphere due to gas exchange through the surface of the pond; the saturation concentrations of the substances in the water vary with the temperature of the water: the higher the temperature is, the lower the CO2 saturation limit is. For this reason, the quantity of CO2 lost to the atmosphere is higher in Petrolina than in Sevilla.

The higher biomass production in Sevilla implies a higher value of injection of CO2, to ensure the growth of the microalgae: CO2 is not wanted to be a limiting factor to the growth.

At each re-filling of the pond, for the restart of the cultivation phase, nutrients are supplied in excess, to ensure that the nutrients would not be a limiting factor: the model gives as output the exact quantity of nutrients consumed by the microalgae. If the hydrothermal gasification is the downstream process to the cultivation, this process includes also a phase of salt separator: this means that all the nutrients added in excess might be collected and reused in the pond.

The electrical energy supplied to the pond is higher for Sevilla than for Petrolina: even if there is more energy requirement in Petrolina for CO2 injection, the energy required for the harvesting and the refilling, which are more in Sevilla than in Petrolina, determines this situation.

In the model is run with the first operating strategy (meaning that the inputs are the initial and final concentration), one of the output would be the days needed to reach the target final concentration. As showed in the following figures (Figure 11 and Figure 12), the number of days is not the same along the year, since it varies with weather conditions.



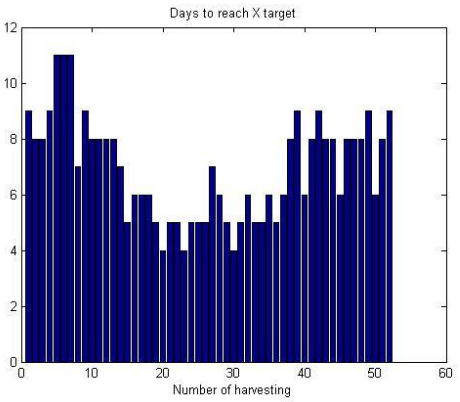


Figure 11 and Figure 12: Hydraulic Retention Time evaluation for Sevilla and Petrolina

For Sevilla (Figure 11), in wintertime, the harvesting time is extremely long, due to low irradiation and low temperatures, which make the microalgae growth in the pond slow and difficult. A possible strategy to overcome this limitation might be to interrupt the production during the winter and being operative only in summertime: in this case, the productivity during the whole year would decrease, since a part of the biomass would not be produced, but the NER would positively decrease, because there would not be any energy consumption during the winter: the production lost is less than the energy saving obtained, and so the overall effect would be positive.

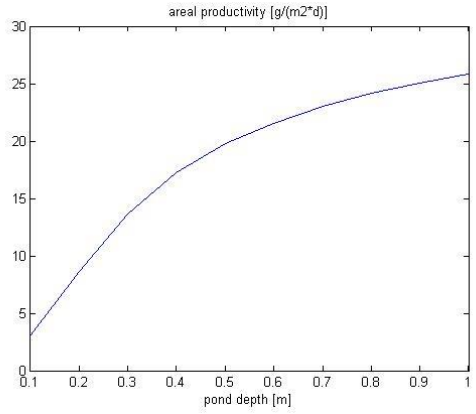
For Petrolina (Figure 12) the hydraulic retention time is more homogeneous along the year, but longer: the reason might be that weather conditions in Petrolina cause a strong increase of pond temperature, that may cause a consequent reduction in microalgae productivity, when pond temperature is higher than the optimal temperature for microalgae growth (see Figure 9, temperature factor). This is a reasonable explanation to the lower productivity of Petrolina, if compared to Sevilla, since the longer hydraulic retention time occurs in summer, when atmospheric temperature is higher.

After a first analysis has been conducted using the input data from literature, a parametric analysis took place, and some of the inputs have been changed within a range, trying to evaluate how to increase the productivity of the open reactor.

Many of the input data might not be modified without implying a strong change in the reactor: these are, for example, the location or the microalgae species; also the microalgae output concentration cannot be higher than the value already used in the simulation, being 0.5 kg/m^3 the most used concentration in literature.

For these reasons, the depth of the open raceway pond and the initial concentration of the microalgae are the most significant parameters that might change within a range. A parametric analysis has been carried out, varying the values of these input characteristics, for both the locations. Here are reported the results for Petrolina, being those for Sevilla quite similar.

Before creating a simulation tree, pond depth has been varied between 0.1 m and 1 m, to understand which are the most interesting values to analyse in a further simulation. All the other input of the model have been kept constant, assuming the values reported in Table 2. Here the most interesting results are reported:



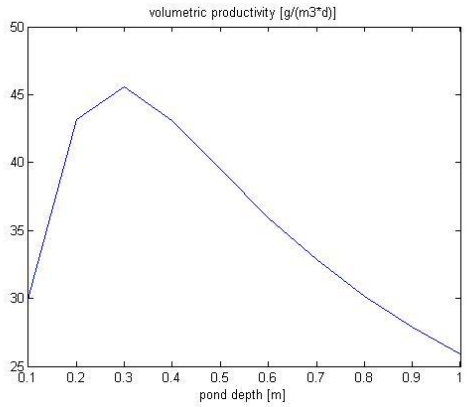


Figure 13 and Figure 14: areal [g/(m^2*d)] and volumetric [g/(m^3*d)] productivity for open raceway pond when pond depth varies between 0.1 and 1 m

From the figures above, areal productivity increases with depth: this is quite obvious, since the more volume per unit area there is, the more biomass is produced per unit area; the slope of the curve, after an initial linear trend until approximately 0.4 m depth, gradually decreases and it seems that for deeper ponds, areal productivity might reach an asymptote. Volumetric productivity reaches a maximum value for 0.3 m depth, showing that the most interesting values to consider for a further analysis are between 0.2 m and 0.4 m. The volumetric and areal productivities of the open raceway pond change with depth

for a combination of different factors; all of them are related with light penetration in the pond, and pond temperature: light in particular is the most relevant factor which determines the evolution of these parameters.

If depth is analysed together with the initial microalgae concentration in the pond, the following simulation tree is created:

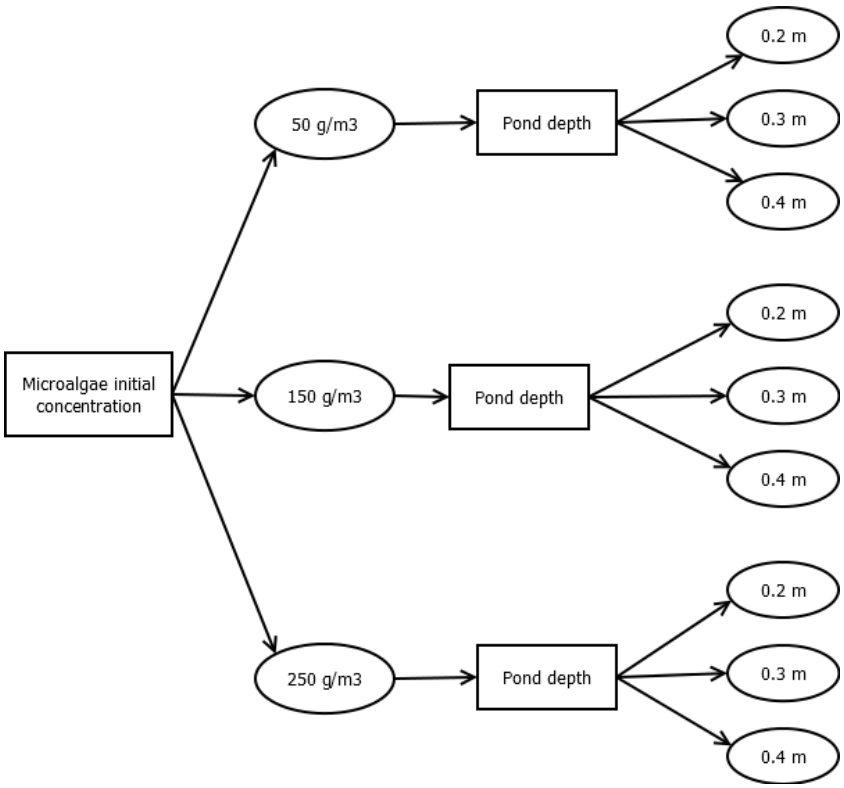


Figure 15: Simulation tree for open pond parametric analysis

Table 4 , in the following page, shows the results of this parametric analysis, giving for each couple of values of depth and initial concentration the values assumed by some of the most important parameters.

The production of microalgae mass increases when the initial concentration changes from 50 g/m^3 to 250 g/m^3: keeping in the pond a higher initial concentration implies to have the possibility to start the consecutive growing phase after the harvesting with a higher growth rate of the reactor, which means that in the same amount of time, the reactor produces more biomass. For this same reason, HRT decreases when biomass initial concentration assumes higher values.

Volumetric productivity maintains the same trend with pond depth seen in figure 14 only when initial concentration assumes low values. For higher initial concentrations, volumetric productivity reaches its peak for low depths: when the pond is deep and microalgae concentration is high, solar radiation cannot easily enter the reactor. Areal productivity increases with initial concentration biomass and with pond depth, since it does not take into account in its expression pond depth itself: the higher the biomass produced is, the higher areal productivity would be.

Finally, NER is higher in case of high initial concentration, because more energy is required for the more frequent phase of harvesting and refilling of the pond.

X_init [g/m3]	50	Z_pond [m]	0.2	mass [t]	31.54
				HRT [d]	10
				Vol prod	0.0432
				Ar prod	0.008
				NER	0.12
			0.3	mass [t]	49
				HRT [d]	11
				Vol prod	0.0452
				Ar prod	0.0136
				NER	0.12
			0.4	mass [t]	61
				HRT [d]	11
				Vol prod	0.042
				Ar prod	0.0168
				NER	0.13
	150	Z_pond [m]	0.2	mass [t]	42
				HRT [d]	7
				Vol prod	0.0589
				Ar prod	0.0118
				NER	0.1
			0.3	mass [t]	60
				HRT [d]	7
				Vol prod	0.0557
				Ar prod	0.0167
				NER	0.1
			0.4	mass [t]	73
				HRT [d]	7
				Vol prod	0.0503
				Ar prod	0.0201
				NER	0.11
	250	Z_pond [m]	0.2	mass [t]	49
				HRT [d]	5
				Vol prod	0.0663
				Ar prod	0.0133
				NER	0.09
			0.3	Vol prod	68
				HRT [d]	5
				Vol prod	0.0622
				Ar prod	0.018
				NER	0.095
			0.4	mass [t]	80
				HRT [d]	5
				Vol prod	0.0554
				Ar prod	0.0221
				NER	0.1

Table 4: Parametric analysis results for open raceway pond

4.2 Flat Panel Photobioreactor

The following table shows the input data for the flat panel model, for both the two operating strategies:

HRT not fixed, X target fixed		HRT fixed, X target not fixed	
Location	Sevilla	Location	Sevilla
	Petrolina		Petrolina
Tipology	P. Tricurnutum	Tipology	P. Tricurnutum
	T. pseudonana		T. pseudonana
azimuth [°]	0	azimuth [°]	0
	-90		-90
slope [°]	90	slope [°]	90
Xa_init [g/m^3]	3000	Xa_init [g/m^3]	3000
Xa_target [g/m^3]	6000	HRT [d]	4 or 5
CO_2 rate [%]	0.02	CO_2 rate [%]	0.02
h [m]	1.5	h [m]	1.5
s [m]	0.05	s [m]	0.05
d [m]	0.5	d [m]	0.5

Table 5: Input data for flat panel photobioreactor cultivation model

The same locations and microalgae species have been used for both the open raceway pond and the flat panel simulations, to have the possibility of a comparison between the two cultivation systems taken into analysis.

The azimuth of the panel is an input which may vary from 0°, when the panel faces south, to -90°, when the panel faces east. The model is not able to consider different slopes of the reactor, which may only be positioned vertically: this position is the most favorable for light distribution and dilution, leading to the highest values of productivity ([13]).

CO2 molar concentration in the injected gases is lower than for the open raceway pond, since injected gases in flat panel photobioreactor do not only have the task to supply the CO2 needed by the microalgae for the photosynthesis, but also to generate the necessary mixing in the reactor: as explained in the previous chapter,

adequate mixing is essential to obtain good levels of productivity in every microalgae cultivation system.

Since the flat panel photobioreactor has a complex geometry, more geometrical data are needed as input, if compared to the open raceway pond system. As explained by Acién Fernàndez et al. [44], heights lower than 1.5 m and widths less than 0.10 m are preferred; following this indication and data from Slegers et al. [69], the distance between the vertical panels has been set equal to 0.5 m, the height of each panel to 1.5 m and the thickness to 5 cm. Both the height and the distance between panels have been varied within a range of possible values in a further parametrical analysis.

The initial and final concentrations have been suggested by Münkel et al. [11]; the values are higher than in the case of open raceway pond: the more sophisticate closed photobioreactor allows to reach higher concentrations without compromising the productivity of the cultivation system. This is possible thanks to an optimal light distribution over the whole reactor, for the entire operational time, guaranteed also by an adequate mixing of the medium.

The flat panel model, as the open raceway pond model, is able to produce the dynamic trend of all the time dependent physical quantities which are included in the analysis: the results are graphically similar to those produced by the flat panel and for this reasons they are not reported here.

The global results for the flat panel reactor are shown in the following tables: the first table reports the results for the first operating strategy, meaning the case in which both the input and output concentrations of microalgae are known, while the second table corresponds to the second operating strategy, when the input parameters are the input concentration and the hydraulic retention time.

	HRT not fixed		HRT not fixed	
	south		east	
	Petrolina	Sevilla	Petrolina	Sevilla
N harvesting	65	77	88	81
Mass microalgae [t]	289	345	393	366
CO_2 captured [t]	860	976	1083	1025
CO_2 injected [t]	956	1085	1204	1139
CO_2 ratio algae	0.9	0.9	0.9	0.9
N absorbed [t]	35.92	40.77	45.2	42.77
Water injected [t]	46023	54592	62353	57742
Energy microalgae [kWh]	1733700	2063700	2350700	2191100
Electrical energy [kWh]	35634	40476	44906	42473
Thermal energy [kWh]	1310300	2124000	1267400	2093900
Volumetric productivity [kg/(m^3*d)]	0.5851	0.6965	0.7934	0.7395
Areal productivity [kg/(m^2*d)]	0.0794	0.0946	0.1077	0.1004
NER	1.55	2.09	1.1165	1.95

Table 6: Output from flat panel photobioreactor cultivation model (1)

	HRT fixed		HRT fixed	
	south		east	
	Petrolina	Sevilla	Petrolina	Sevilla
HRT	5	5	4	4
Mass microalgae [t]	284	367	390	380
CO_2 captured [t]	844	1041	1081	1052
CO_2 injected [t]	938	1157	1201	1168
CO_2 ratio algae	0.9	0.9	0.9	0.9
N absorbed [t]	35023	43044	45.11	43.88
Water injected [t]	46691	52620	62422	57201
Energy microalgae [kWh]	1701300	2197000	2336600	2273000
Electrical energy [kWh]	34973	43043	44819	43542
Thermal energy [kWh]	1292400	2264900	1262700	2113900
Volumetric productivity [kg/(m^3*d)]	0.5742	0.7415	0.7886	0.7672
Areal productivity [kg/(m^2*d)]	0.078	0.1007	0.1071	0.1041
NER	1.56	2.101	1.1192	1.8983
Xa final mean [kg/m^3]	5.87	6.707	6016	6.077

Table 7: Output from flat panel photobioreactor cultivation model (2)

For the two operating strategies, the results are reported for both the locations (Sevilla and Petrolina) and for the two most significant orientations, meaning when the flat panel is facing south (and north) and when it is facing east (and west).

For both the locations, the east-west orientation appears to be preferable, since it leads to a higher microalgae production: as explained by Sierra et al. [13], if the orientation of the two faces of the reactor is east-west, the intercepted radiation is maximum during the first and last solar hours, because of the orientations towards sunrise and sunset. Therefore, light availability during the daylight solar cycle is also more homogenous for this configuration.

Areal and volumetric productivities are consistent with values found in literature: Chisti [2] reports a volumetric productivity equal to 1.535 kg m^{-3} d^{-1}, higher than the values obtained from the model; if compared to some other works, the results coming from the dynamic model, especially the areal productivity, seem to be optimistic: for example, the microalgae production coming from the model (~ 400 t/(ha*year)) is two times higher than the production obtained by Slegers et al. [69] from a flat panel reactor located in Algeria which produces up to 200 t/(ha*year). Moreover, the volumetric productivity for a flat panel reported by Jorquera et al. [24] is equal to 0.27 kg m^{-3} d^{-1} , where the model reports values equal to 0.8 kg m^{-3} d^{-1}. Form a recent work by Münkel et al. [11], volumetric productivities equal to 1.25 kg m^{-3} d^{-1} have been reached in experimental analysis.

The difference to some values found in literature could be a consequence of a series of related factors: the microalgae species chosen may strongly influence the productivity of the reactor; moreover, the model created in this work contains a temperature control which fixes the temperature inside the reactor at the optimal level for microalgae growth: this means that the specific growth rate is not infected by the temperature factor (which is always equal to 1), and consequently it is nearer to the maximum growth rate than in the real operating conditions, where the temperature is kept inside a range of acceptable values for the growth of microalgae; moreover, the locations chosen for the analysis present optimal values of irradiation, next to the saturation irradiation, where the light intensity factor affecting the growth rate is next to 1.

From Table 6 and Table 7 it is possible to see that there is a high difference in productivity in Petrolina depending on the orientation of the panel: if the two faces of the reactor are oriented towards east and west, the productivity is higher than in the case in which the reactor is oriented towards south and north. A possible explanation might be related to radiation reflection by the panel: when the sun is high in the sky, the radiation hits the flat panel with an incident angle next to 90°; if the incidence angle is too high, radiation could not enter the reactor, due to glass reflection. For this reason, if the panel is oriented towards south, the largest part of the radiation during summer is lost and do not contribute to microalgae growth: if the orientation if east-west, the radiation is collected during the morning and the afternoon with a incidence angle next to 0°.

The same situation does not take place in Sevilla, because the sun does not reach high elevations during the whole year; the east-west orientation is preferable also in Sevilla, as suggested by Sierra et al. [13].

In general, higher volumetric and areal productivity values have been reached both in Sevilla and in Petrolina, and the difference between the two locations is less remarkable than it was for the open pond; flat panel photobioreactor growth model includes a temperature control which maintains the temperature of the water at a constant level.

In spite of the high productivities reached in Sevilla, this location appear to be less suitable for a flat panel photobioreactor, than Petrolina, as shown by the NER parameter. The thermal energy requirement is extremely high in Sevilla, where winter time brings low atmospheric temperatures: the photobioreactor should operate only during summertime.

Microalgae mass production in flat panel reactor is much higher than in open raceway pond, CO2 absorption is more efficient, but the thermal energy requirement implies a NER value higher than 1; there are different possible strategies to solve this problem: it might be chosen to keep the water in the reactor within a range of suboptimal temperatures, where the productivity of microalgae is still high, and the thermal energy requirement is lower; moreover, there is the possibility to leave the temperature in the reactor without any control during the night: this might be an interesting solution also to limit the microalgae losses due

to dark respiration which are higher for optimal temperature: if water temperature is lower than the optimal value for growth, the metabolic energy required by the microalgae for their maintenance during the night is lower.

Chapter 5

5.Conclusions

The aim of this work is to create a dynamic mathematical model that is able to describe the operation of two different typologies of cultivation systems (open raceway pond and flat panel photobioreactor) through an accurate description of the microalgae growth process, together with the use of mass and energy balances. Moreover, a parametric analysis is conducted to evaluate the importance of some of the factors which influence microalgae growth.

In the first part of Chapter 2, microalgae biology is presented, together with the reasons which make this biomass an interesting alternative to traditional crops and lignocellulosic biomass for energy production. Moreover, microalgae metabolism and the photosynthetic process are described dedicating some attention to the parameters which influence microalgae growth, which will be later used in the cultivation phase modelling. In the second part of Chapter 2 an overview of the technologies for the cultivation of the microalgae is performed.

Chapter 3 contains the description of the model of the microalgae cultivation phase which has been developed. After the description of the system boundaries the reactor geometry is analysed: two different configurations have been taken into account, being the open raceway pond and the flat panel photobioreactor. The central and most important part of the model is the microalgae growth model which includes the mathematical description of the dependence on physical parameters.

In Chapter 4, the results of the simulations are presented; results of other works taken from literature are used to validate the model and to test its reliability, observing its behavior also through a parametric analysis.

From the analysis that has been conducted, open raceway pond appeared to be a promising technology for extensive microalgae cultivation: low investment and maintenance costs and a favourable value of NER demonstrate the possibility of cultivating microalgae with a positive economic and energy balance. On the other hand, low productivity dictates the necessity of covering wide surfaces of ground.

Although the mass produced by the flat panel photobioreactor in 1 year is more than five times higher than the production reached by the open pond, the energy demand of this technology is extremely high: in particular, thermal energy requirement makes the production of microalgae with this technology inconvenient from an energetic point of view. Research and development are needed to make this technology more competitive.

Both the two cultivation technologies are strictly dependent on the microalgae species that is cultured: light and temperature factors, together with maximum specific growth rate assume different values changing from one microalgae species to another. A possible strategy to increase the productivity of these technologies might be to operate a genetic engineering research to create an sort of "optimal" microalgae species for energy production: at present, there are many researchers which are exploring this possibility.

The dynamic model for microalgae growth phase that has been created is a flexible instrument for the evaluation of the productivity of cultivation systems. The possibility of varying all the input data of the model, such as the location, the microalgae species considered or the geometry of the reactor make the model an interesting tool for different kind of applications. Moreover, the use of a wastewater stream as a source for nutrients and the use of flue gases for CO_2 injection allow the model to be coupled with tradition power plants; coupling a microalgae cultivation and transformation plant with some typologies of industries such as, sugar cane industry, it is possible to create a system with no CO_2 emissions and with a positive exploitation of the industrial wastes.

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