STOICHIOMETRIC MODEL OF THE CULTIVATION OF MICROALGAE IN INDUSTRIAL SYSTEMS

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Abstract. *Microalgae are photosynthetic microorganisms that grow in liquid media by consuming carbon dioxide and producing oxygen. These microorganisms produce many products of interest to the chemical industry and biotechnology. However the productivity of microalgae growth systems is still very low, making the technology economically unfeasible in some industrial applications. As an example the production of biodiesel from microalgae is technically feasible, but the biodiesel from microalgae production cost is six times higher than the production cost of fossil diesel. In this context, the mathematical modeling of systems becomes an indispensable tool for the optimization of this process. Nevertheless, the literature on microalgae cultivation modeling uses very simplified equations to describe the growth kinetics of microorganisms in industrial systems. Under these conditions, the cultivation of microalgae is done in photobioreactors, systems that are exposed to uncontrolled environmental factors such as light and temperature. The kinetics of microalgae growth in these conditions depends on many factors, such as carbon dioxide, oxygen, temperature and mineral salts. The equations used in the literature generally assess the effect of only one of these factors. As a result, this paper proposes a mathematical model for the microalgae cultivation system using an equation that describes the microalgae growth kinetics as a function of all factors that affect this kinetics. Moreover, this model makes the mass balance for all components of the system, using as criteria the reaction stoichiometry of the microalgae biomass production. Through simulations of stoichiometric model was possible to estimate the optimal concentration of all components of the system by optimizing the cultivation of microalgae.*

Keywords*: microalgae, mathematical model, optimization*

1. INTRODUCTION

Microalgae are prokaryotic or eukaryotic photosynthetic microorganisms that can grow rapidly and live in harsh conditions (Mata *et al.,* 2010), and reproduce themselves using photosynthesis to convert sun energy into chemical energy (Sheehan *et al.,* 1998). Algae mass production is a commercially attractive source of high value products, such as polyunsaturated fatty acids, natural colorants, biopolymers, therapeutic, biofuels and biomass (Belarbi, Molina and Chisti; 2000; Lorenz and Cysewski, 2000; Borowitzka, 1999). Nowadays, many advantages of using microalgae for biodiesel production in comparison with other crops had been reported (Li *et al.,* 2008; Chisti, 2007). However the productivity of microalgae growth systems is still very low, and for the most part has not been economically successful (Molina *et al.* 1997), once the use of natural conditions for commercial algae production may be limited by factors like sunlight and temperature variations and easily contamination; limiting the viability of commercial production. In closed systems – photobioreactors – this parameters can be controlled, but the costs of closed systems are substantially higher than open pond systems (Carvalho *et al.,* 2006), once the estimated cost of producing a kilogram of microalgal biomass is $2.95 for photobioreactors, while in the United States during 2006, the petrodiesel price ranged between $0.66 and $0.79/L (Chisti, 2007).

A challenge is to successfully operate biomass reactors under outdoor conditions, where the physical variables are used not controlled (Cohen *et al.,* 1991). In this context, the mathematical modeling of systems becomes an indispensable tool for the optimization of this process. Nevertheless, the literature on microalgae cultivation modeling uses very simplified equations to describe the growth kinetics of microorganisms in industrial systems, disregarding the interactions between growth kinetic parameters. The chemical composition of microalgae and their growth kinetic are influenced by environmental conditions, including temperature and light (Renaud *et al.,* 2002), nutrients source and pH (Araújo and Garcia, 2005). Several mathematical models consider only one of these factors, resulting in a optimization of an only parameter. The aim of this paper is to develop a mathematical model describing the behavior and the main characteristics of microalgal cultivation according the interaction of these factors: light intensity, CO_2 consumption, nutrients source andtemperature. Moreover, this model makes the mass balance for all components of the system, using as criteria the reaction stoichiometry of the microalgae biomass production, according methodology proposal by Roels.

(1983), where an overall stoichiometry characterizing the yields of conversion of substrates into products has been established based on the conservation of elements (Pruvost *et al.*, 2009).

2. MODEL SCHEME

2.1. Stoichiometric equations

Pruvost *et al.* (2009) propose a stoichiometric reaction to produce microalgae biomass that shows the transformation of reagents in products, their quantities and proportions. This reaction considers that the entrance parameters are mainly the nutrients responsible to microalgal growth: CO_2, HNO_3, H_3PO_4, H_2SO_4 and H_2O. The consumption of these nutrients will result in increased biomass and oxygen production, as shown the Eq. (1).

$$\begin{aligned}&CO_2 + 0.148HNO_3 + 0.014H_2SO_4 + 0.012H_3PO_4 + 0.751H_2O\\ &\rightarrow CH_{1.715}O_{0.427}N_{0.148}S_{0.014}P_{0.012} + 1.437O_2\end{aligned} \tag{1}$$

Through this mechanism it is possible to establish the stoichiometric coefficients to obtain the necessary quantities of nutrients to produce 1g of biomass.

$$Y_{CO_2/x} = n.\frac{M_{CO_2}}{M_x} = 1.\frac{44gCO_2/mol}{23.439g.biomass/mol} = 1.877213gCO_2/gbiomas \tag{2}$$

Equation (2) represents the yield coefficient ($Y_{CO2/X}$) of carbon dioxide. This coefficient is the result of Eq. (1), where the molar ratio between CO_2 consumption and biomass production is 1:1. So, the molar ratio (n) is correlated with the molecular weight of carbon dioxide (M_{CO2}) and with the molecular weight of biomass (M_x).

Similarly the same procedures described above it is applied to other nutrients, to obtain the yield coefficients according their stoichiometric coefficients.

$$Y_{O_2/x} = n.\frac{M_{O_2}}{M_x} = 1.437.\frac{32gO_2/mol}{23.439g.biomass/mol} = 1.96gO_2/gbiomass \tag{3}$$

$$Y_{HNO_3/x} = n.\frac{M_{HNO_3}}{M_x} = 0.148.\frac{63gHNO_3/mol}{23.439g.biomass/mol} = 0.397gHNO_3/gbiomass \tag{4}$$

$$Y_{H_2SO_4/x} = n.\frac{M_{H_2SO_4}}{M_x} = 0.014.\frac{98.08gH_2SO_4/mol}{23.439g.biomass/mol} = 0.05835gH_2SO_4/gbiomas \tag{5}$$

$$Y_{H_3PO_4/x} = n.\frac{M_{H_3PO_4}}{M_x} = 0.012\frac{98gH_3PO_4/mol}{23.439g.biomass/mol} = 1.877213gCO_2/gbiomass \tag{6}$$

To water this relation is not necessary, once the culture medium is saturated with water, so, this is not a limiting factor.

From the calculated coefficients it is possible estimate the growth kinetics of microalgae and the effect of nutrients concentration in process. Thus, the specific growth rate μ (h^{-1}) can be written in this form:

$$\mu = \mu_{\max}.\mu(T).\mu(I_0).\mu(CO_2).\mu(O_2).\mu(NO_3).\mu(PO_4) \tag{7}$$

Where, μ_{max} (h^{-1}) represents the maximum specific growth rate. The effect of temperature under growth rate can be written such as presented by Eq. (8) (Pérez *et al*, 2009).

$$\mu(T) = A_1.e^{\frac{E_{A_1}R}{T}} - A_2.e^{\frac{E_{A_2}R}{T}} \tag{8}$$

Where A_1 and A_2 are the corresponding frequency factors (h^{-1}), E_{A1} is the activation energy of growth, E_{A2} is the activation energy of cellular degradation, R is the gas law constant (kJ/mol) and T is the incubation temperature (K).

The effect of luminous intensity incident (I_0) under the growth rate is dependent on the saturation constant (K_{Io}) and the photoinhibition (K_{iIo}) caused by excessive exposure to light. The equation is described below.

$$\mu(I_0) = \frac{I_0}{K_{I_0} + I_o + \dfrac{I_0^2}{K_{iI_0}}} \tag{9}$$

The effect of carbon dioxide under the growth rate has been given by Andrews (1968) as:

$$\mu(CO_2) = \frac{[CO_2]}{K_{CO_2} + [CO_2] + \dfrac{[CO_2]^2}{K_{iCO_2}}} \tag{10}$$

Where K_{CO2} is the saturation constant for carbon dioxide and K_{iCO2} is the inhibition constant.

On basis of inhibitory oxygen, it is obtained the Eq. (11):

$$\mu(O_2) = \left(1 + \frac{K_{O_2}}{[O_2]}\right) \tag{11}$$

Where K_{O2} is the inhibition constant and O_2 is the level of oxygen according the culture growth.

The effect of nitrate concentration under the growth rate may be described considering the nitrate concentration (mg/L) and the saturation constant by nitrate K_{NO3} (mg.NO_3^-), like described by Araújo *et al.* (2009).

$$\mu(NO_3) = \frac{[NO_3]}{K_{NO_3} + [NO_3]} \tag{12}$$

The same is applied to phosphate, such as shown in Eq. (13) below:

$$\mu(PO_4) = \frac{[PO_4]}{K_{PO_4} + [PO_4]} \tag{13}$$

With the stoichiometric coefficients and the kinetics of microalgae growth it is possible deduce a mass balance in the system. An industrial photobioreactor is composed of two parts: a solar collector and a degasser. The degasser is responsible by remove the oxygen accumulated during the loop cycle, in order to avoid the inhibition of growth. This system also promotes the carbon dioxide injection to aid in photosynthesis. On the solar collector the microalgae will be in contact with sunlight, where will happens the photosynthesis and the nutrients consumption. (Figure 1).

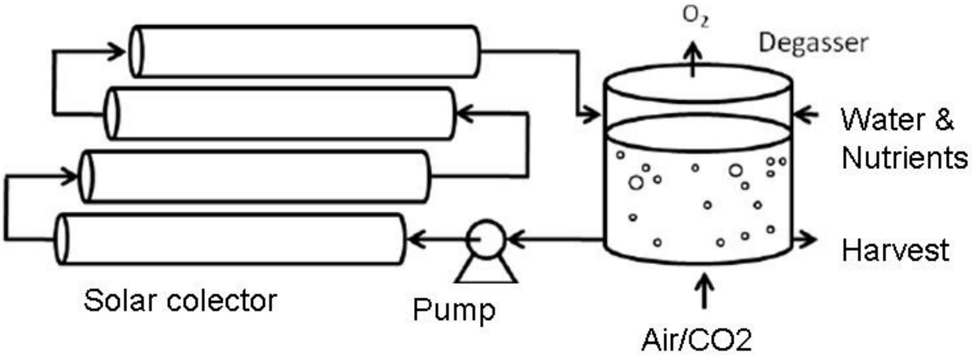

Figure 1. Industrial system to microalgae production.

2.2. Mass balance

The mass balance on solar collector was developed trough the Volume Element Model (VEM), using a MESH of 20 elements. In simulations the length of solar collector can be variable, but the mesh always is maintained in 20 elements. The differential equations that represent the growth and the nutrients consumption in the solar collector are presented below:

$$\frac{dX_i}{dt} = \frac{Q.X_{i-1}}{V} - \frac{Q.X_i}{V} + \mu.X_i \tag{14}$$

Where:
Q = Volumetric flow (m³.h^{-1})
V = volume (m³)
X_i = biomass concentration in control volume (g.L^{-1})
X_{i-1} = biomass concentration in previous control volume (g.L^{-1})
μ = specific growth rate (h^{-1})

$$\frac{dCO_2}{dt} = \frac{Q.CO_{2_{i-1}}}{V} - \frac{Q.CO_{2i}}{V} + Y_{CO_2/x}.\mu.X_i \tag{15}$$

Where:
CO_{2i}= carbon dioxide concentration in control volume (g.L^{-1})
$CO_{2(i-1)}$= carbon dioxide concentration in previous control volume (g.L^{-1})
$Y_{CO2/x}$ = yield coefficient of consumption to CO_2 (gCO_2/gbiomass)

The same is applied to oxygen, nitrate, phosphate and sulfate in Eqs. (16), (17), (18) and (19).

$$\frac{dO_2}{dt} = \frac{Q.O_{2_{i-1}}}{V} - \frac{Q.O_{2i}}{V} + Y_{O_2/x}.\mu.X_i \tag{16}$$

$$\frac{dNO_3}{dt} = \frac{Q.NO_{3_{i-1}}}{V} - \frac{Q.NO_{3i}}{V} - Y_{NO_3/x}.\mu.X_i \tag{17}$$

$$\frac{dPO_4}{dt} = \frac{Q.PO_{4_{i-1}}}{V} - \frac{Q.PO_{4i}}{V} - Y_{PO_4/x}.\mu.X_i \tag{18}$$

$$\frac{dSO_4}{dt} = \frac{Q.SO_{4_{i-1}}}{V} - \frac{Q.SO_{4i}}{V} - Y_{SO_4/x}.\mu.X_i \tag{19}$$

The mass balance in degasser is different, because the growth does not occur because the system is closed and no light. The Figure 2 shows how the degasser was divided in two control volumes, one for a liquid part and other for a gaseous part.

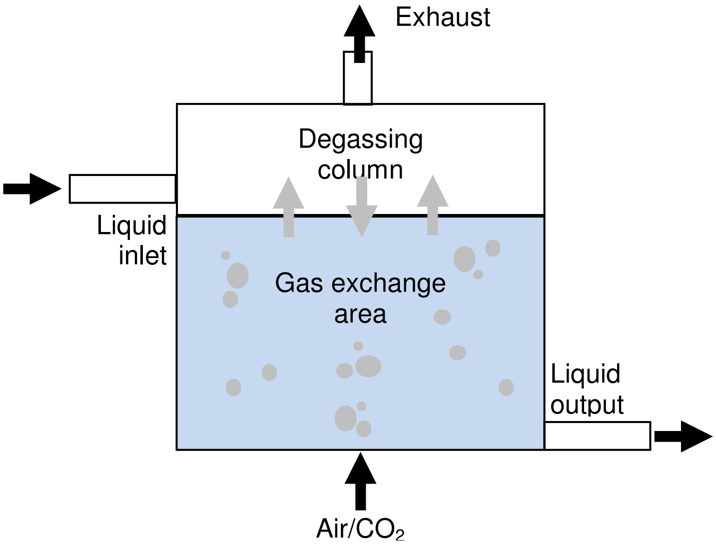

Figure 2. Volume elements to degasser

To liquid, the mass balance can be given as follows:

$$\frac{dX_i}{dt} = \frac{Q.X_{i-1}}{V} - \frac{Q.X_{\deg}}{V} \tag{20}$$

Where:
Q = volumetric flow on tabulation (m³.h^{-1})
X_{deg} = biomass concentration on degasser (g.L^{-1})
X_{i-1} = biomass concentration before entering the degasser (mg.L^{-1})

To gases, the mass balance considers the transfer coefficients between the gaseous and liquid phases when the gas entering the degasser Kla_{CO2ENT} (h^{-1}), and between the gaseous and liquid phases on the liquid surface Kla_{CO2OUT} (h^{-1}), as:

$$\frac{dCO_{2i}}{dt} = \frac{Q.[CO_{2i-1}]}{V} - \frac{Q.[CO_{2\deg}]}{V} + Kla_{CO_2ENT}.(P_{CO_2ENT}.H_{CO_2} - [CO_{2_i}]) - Kla_{CO_2OUT}.([CO_{2_i}] - P_{CO_2}.H_{CO_2}) \tag{21}$$

Where:
CO_{2deg} = carbon dioxide concentration on degasser (mg.L^{-1})
CO_{2i-1} = carbon dioxide concentration on liquid phase before entering the degasser (mg.L^{-1})
P_{CO2ENT} = partial pressure of carbon dioxide at the gas entrance of degasser (h^{-1})
P_{CO2OUT}= partial pressure of carbon dioxide at the degassing column (h^{-1})
H_{CO2}= Henry constant to carbon dioxide (h^{-1})
The same is applied to other gases:

$$\frac{dO_{2_i}}{dt} = \frac{Q.[O_{2i-1}]}{V} - \frac{Q.[O_{2i}]}{V} + Kla_{O_2ENT}.(P_{O_2ENT}.H_{O_2} - [O_{2_i}]) - Kla_{O_2OUT}.([O_{2_i}] - P_{O_2}.H_{O_2}) \tag{22}$$

$$\frac{dN_{2_i}}{dt} = \frac{Q.[N_{2i-1}]}{V} - \frac{Q.[N_{2i}]}{V} + Kla_{N_2ENT}.(P_{N_2ENT}.H_{N_2} - [N_{2_i}]) - Kla_{CO_2OUT}.([N_{2_i}] - P_{N_2}.H_{N_2}) \tag{23}$$

$$\frac{dNO_{3_i}}{dt} = \frac{Q.[NO_{3_{i-1}}]}{V} - \frac{Q.[NO_{3_i}]}{V} \tag{24}$$

$$\frac{dPO_{4_i}}{dt} = \frac{Q.[PO_{4_{i-1}}]}{V} - \frac{Q.[PO_{4_i}]}{V} \tag{25}$$

$$\frac{dSO_{4_i}}{dt} = \frac{Q.[SO_{4_{i-1}}]}{V} - \frac{Q.[SO_{4_i}]}{V} \tag{26}$$

In the gaseous phase on degasser will be present only nitrogen, oxygen and carbon dioxide. Thus, the mass balance will be made only for the partial pressure of these three species.

$$F_{gas} = \frac{K_{laCO_2OUT}}{44}.([CO_2] - P_{CO_2}.H_{CO_2}.44) + \frac{K_{laN_2OUT}}{32}.([O_2] - P_{O_2}.H_{O_2}.32) + \frac{K_{laN_2OUT}}{28}.([N_2] - P_{N_2}.H_{N_2}.28) \tag{27}$$

Where F$_{gas}$ is the molar total flux of gases from liquid part of degasser. The model assumes that the flux of gases is unidirectional, always go up to the top of degasser. The model assumes too that the gaseous part of degasser have a constant pressure, so the number of moles of gas is constant in the gaseous part however the partial pressure of gaseous phase can change along the time. Thus a balance for partial pressure can be done below for three species.

$$\frac{dP_{CO2}}{dt} = \frac{R.T}{V_g}.\left[Kla_{CO_2OUT}.([CO_{2_i}] - P_{CO_2}.H_{CO_2})V / M_{CO2} - F_{gas}.V.\frac{P_{CO2}}{PT} \right] \tag{28}$$

$$\frac{dP_{O2}}{dt} = \frac{R.T}{V_g}.\left[Kla_{O_2OUT}.([CO_{2_i}] - P_{O_2}.H_{O_2})V / M_{O2} - F_{gas}.V.\frac{P_{O2}}{PT} \right] \tag{29}$$

$$\frac{dP_{N2}}{dt} = \frac{R.T}{V_g}.\left[Kla_{N_2OUT}.([CO_{2_i}] - P_{N2}.H_{NO_2})V / M_{N2} - F_{gas}.V.\frac{P_{N2}}{PT} \right] \tag{30}$$

Where V$_g$ is the volume of gaseous degasser, PT is total pressure of degasser (bar).

3. RESULTS AND DISCUSSION

The main objective of the mathematical model is to assist in the design of photobioreactors, assessing how the variables involved in the process affect the efficiency of the system. In this case the efficiency can be measured by the volumetric productivity of biomass on the photo bioreactor. As the system is very complex, some variables were kept constant during the optimization of the system, such as incident light intensity and temperature, i.e., the system is isothermal. Yet in a real photo bioreactor incident light intensity and temperature cannot be kept constant, which shows the need for further optimization by evaluating these parameters. The first parameter to be evaluated was the length of the pipe solar collector. As can be seen in figure 3 peak biomass production was achieved with 200 meters of tubing. In the literature (Chisti, 2007) recommended the typical values are around 80 to 160 meters, which shows that the model simulations have reached similar results to those obtained empirically.

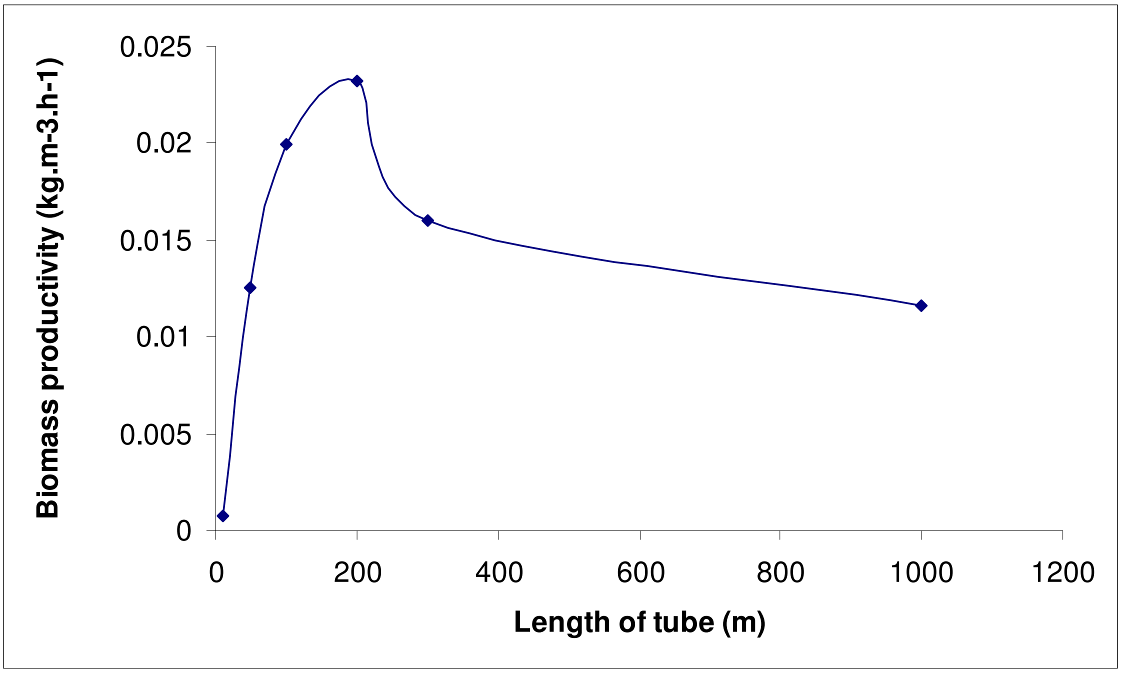

Figure 3. Effect of length of pipe solar collector on biomass production

The next parameter evaluated was the recirculation flow in the system. As seen in Figure 4, according to the recirculation flow is increased, the biomass production also increases, reaching maximum biomass production when the flow is 60 cubic meters per hour. Flows greater than 60 cubic meters will not result in any increase in the productivity increase of biomass. Importantly, very high flow rates can damage the microalgae and detrimental to the growth effect not computed in the model. Moreover, the greater the flow, the greater the energy used for pumping. Thus the best value according to simulations of the mathematical model is 45 cubic meters per hour, when have a great production with a low consume of energy in pumping.

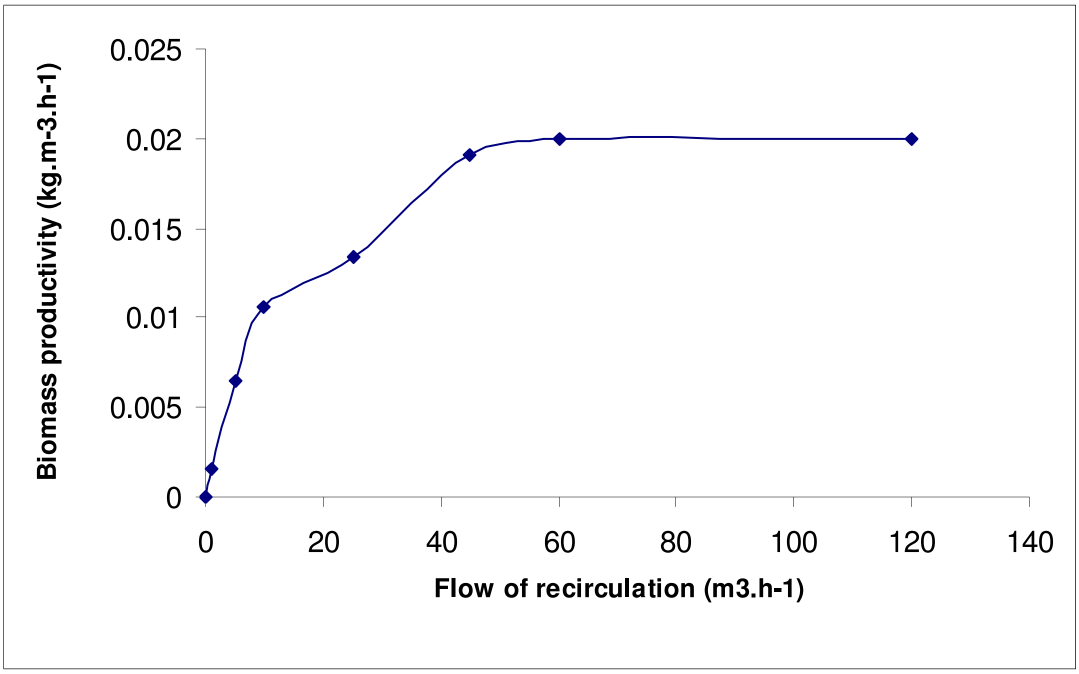

Figure 4 Effect of recirculation flow on the volumetric productivity of the system

The last parameter to be evaluated was the effect of pressure of carbon dioxide in the gas entering the degasser. It is very common that some photobioreactors operate with addition of pure carbon dioxide gas in the degasser entry. The percentage of carbon dioxide is very low in the air, about 0.004% which limits the amount of carbon for photosynthesis. Usually it is customary to use a mixture of air with 2% carbon dioxide (Chisti, 2007). As can be seen in figure 5 below the pressure that had the highest biomass productivity was 0.015 bar. As the pressure in the inlet gas was kept at one bar, this is equivalent to a mixture of air with 1.5% carbon dioxide, a value very close to what the literature determined empirically. Importantly, these simulations were done in a photo bioreactor with a solar collector of 1000 meters, and can be observed that the addition of carbon dioxide has tripled the productivity of the photo bioreactor. However it is not always possible or economically feasible to obtain carbon dioxide to enrich the air entering in the degasser. In addition, carbon dioxide in excess can inhibit growth as shown in Figure 5.

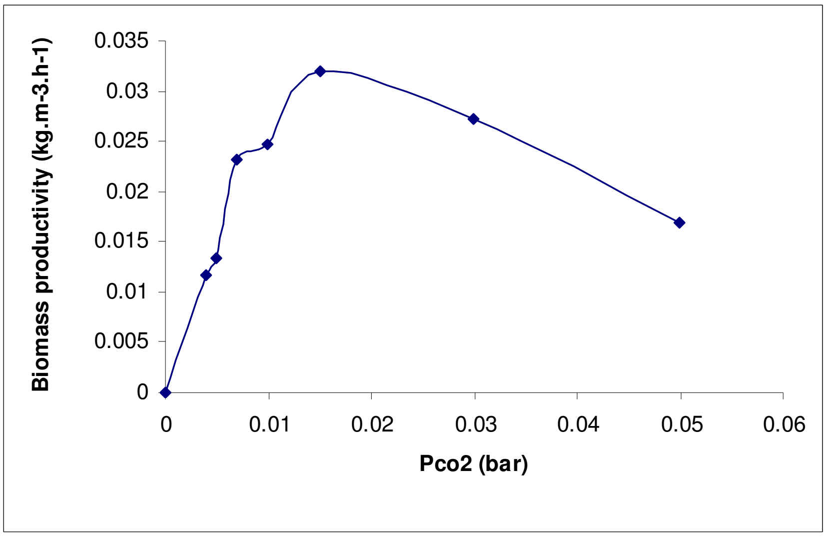

Figure 5 Effect of pressure of carbon dioxide on the volumetric productivity of the system

4. CONCLUSION

It was concluded that the optimized industrial photobioreactor should have 200 meters of solar collector, a recirculation flow of 45 cubic meters per hour and operate with air enriched with 1.5% carbon dioxide. However these optimizations are not conclusive. It is necessary that the model is experimentally validated and that the improvements are made over a cross-optimization. For the simulations above, all parameters were kept constant and evaluated the effect of a single variable. It requires a simultaneous optimization. Another limitation is made with respect to light intensity and temperature made on growth. In these simulations these parameters were kept constant, but in an industrial system that is constantly changing. But the model is able to incorporate these effects, however you need an energy balance and a balance of light distribution in the system. Thus the next step is to do the energy and light distribution in the system and experimentally validate the mathematical model and perform a cross-optimization of the main parameters of operation and construction of a photobioreactor.

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