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MODELING OF MICROALGAE OIL EXTRACTION

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Abstract. *The microalgae fit into sustainable energy sources, besides contributing to the biofixation of CO2 in the process of photosynthesis and its biomass has high benefit. From this biomass, it is possible to extract lipids that can be used as source of raw material to produce biodiesel. Thus, this project will present the modeling and simulation of this crucial stage of the process, which is the extraction of the oil from the microalgae biomass. The model is based on the interactions between the solvent and the substrate, considering that each one has a different function in the process. Simulation results showed good agreement with the expected behavior in the extractions, since the states of equilibrium of the model approximate the values found in the literature.*

Keywords: *modeling, extraction and microalgae.*

1. INTRODUCTION

The search for new sources of energy is growing, due to the world's need for cleaner and renewable energy. In this scenario, biofuels stand out in parallel to the demand for different raw materials, such as microalgae, and these microorganisms present high lipid content in the constitution of their biomass (Kava et al, 2018).

The main processes involved in the production of biodiesel through microalgae biomass involve the following steps: cultivation, harvesting, biomass processing, lipid extraction and transesterification. Among these methods, a lipid extraction is an important and expensive step. In order to make the biodiesel production process an economical alternative, it is necessary to evaluate the energy required in the biomass processing and the type of lipid extraction (Kim et al., 2013). There are different techniques for microalgae oil extraction, such as mechanical mechanics, homogenization, solvent extraction, supercritical fluid extraction, enzymatic extractions, ultrasonic extraction and osmotic shock (CHISTI, 2008 cited by Souza, 2013). The exact mechanism of these techniques is different, but most involve disruption of the microbial cell to release the oil present in the cytoplasm.

For Molina et al. (1999), one of the criteria to be evaluated for the extractive method is time and temperature resistance, so that the degradation of lipids and triglycerides does not occur. In the case of solvent lipid extractions, the evaluation of the solvent to be used becomes essential. Lipids have a wide range of relative hydrophobicity, so it is virtually impossible to use a single universal solvent for lipid extraction (Shahidi, 1998). To achieve high extraction yield, different types of interactions are evaluated considering that extraction methods are based on solvent-solute affinity. Knowledge of the cellular structure of microalgae allows a better understanding of the action of solvents in the extraction process. Lipids, defined as any organic solvent-soluble biological molecule, can be in the cytoplasm as droplets (neutral lipids and free fatty acids used for energy storage), and in the cell membrane bilayer (polar lipids) (Halim et al., 2012). The interaction process proceeds as follows: nonpolar organic solvents disrupt van der Waals interactions between nonpolar and neutral lipids, whereas polar solvents act on hydrogen bonds between polar lipids (Johnson et al., 1983 cited by Escorsim et al., 2018)

Several solvents may be used for lipid extraction, Escorsim et al. (2018) studied the yield of different solvents and their mixtures and found that the ethanol-hexane mixture, with ratio of 1:2, had the best performance. The explanation for this can be attributed to the fact that ethanol interacts better with polar lipids located in the microalgae cell wall, due to its polarity, whereas hexane interacts better with fatty acids and neutral lipids that exist in the cell cytoplasm.

According to Ranjan et al. (2010) extraction may occur according to two basic mechanisms, the diffusion of lipids through the cell wall and disruption of the cell wall with release of cell content in the solvent.

2. METHODOLOGY

A study regarding extraction of the oil from the microalgae biomass is presented. The mathematical model was based on the behavior observed in other studies of microalgae oil extraction, as verified by Scorsim et al. (2018), in which they concluded that the hexane-ethanol mixture (70% -30%) has a higher yield compared to extraction using pure hexane. The explanation for this difference in behavior can be attributed to the fact that each component of the mixture acts differently in the extraction process. Ethanol is better adsorbed on the microalgae cell wall, facilitating access to hexane, which in turn, it better solubilizes lipid molecules.

The design of figure 1 represents the control volumes used in the mathematical model, considering the microalgae cell surrounded by the extraction solvent. VC1 represents the interior of the microalga, in which the oil molecules are inserted, VC2 represents the cell wall and VC3 represents the exterior of the cell.

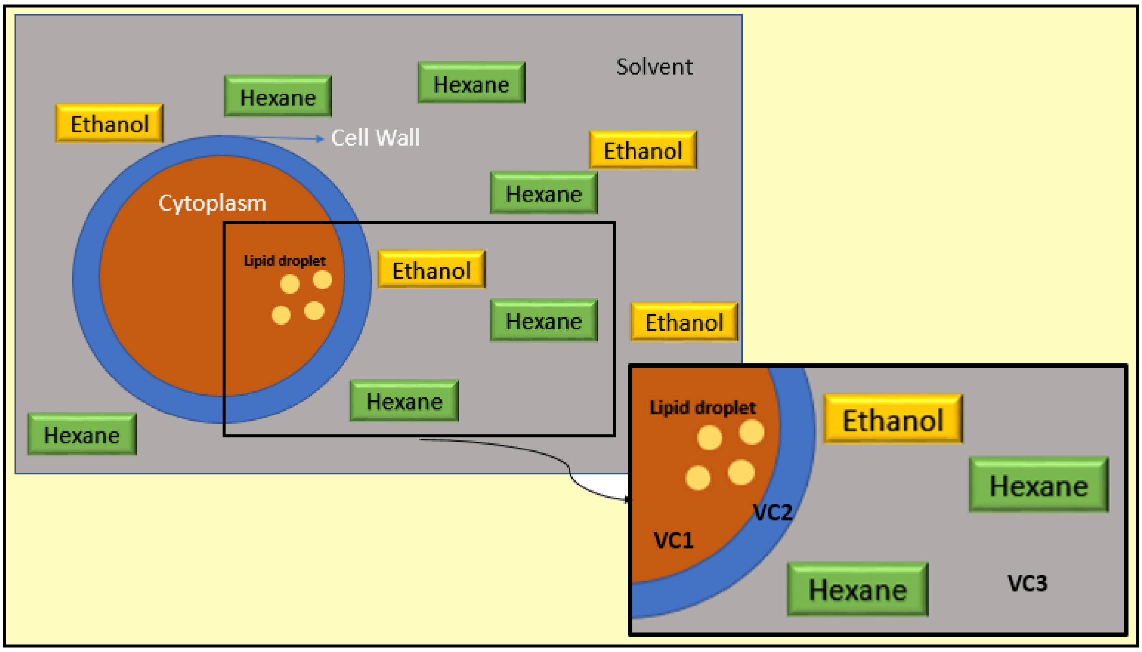

Figure 1. Schematic representation of control volumes for the development of the mathematical model

2.1 Mathematical model

Based on the Langmuir theory to explain the adsorption, which is based on a dynamic concept of the adsorption equilibrium, establishing equalities in adsorption and desorption rates. Thus, using equations 1 and 2, the equilibrium concentrations of hexane and ethanol (C^*_{hex} and C^*_{et}) were determined:

$$C^*_{hex}=\frac{C_{m-hex}.k_{hex}.[hex]_{solv}}{(1+k_{hex}.[hex]_{solv}+k_{et}.[et]_{solv})} \tag{1}$$

$$C^*_{et}=\frac{C_{m-et}.k_{et}.[et]_{solv}}{(1+k_{hex}.[hex]_{solv}+k_{et}.[et]_{solv})} \tag{2}$$

C_{m-hex} - Maximum equilibrium concentration of hexane (Kg/m^3);
$C_{m-et}.k_{et}$ - Maximum equilibrium concentration of ethanol (Kg/m^3);
k_{hex}- Adsorption equilibrium constant of hexane (m^3/Kg);
k_{et} - Adsorption equilibrium constant of ethanol (m^3/Kg);
$[hex]_{solv}$ - Concentration of hexane in the solvent (Kg/m^3);

$[et]_{solv}$ - Concentration of ethanol in the solvent (Kg/m^3).

The variations of solvent concentrations will be determined by equations 3 and 4 below:

$$\frac{d[hex]_{solv}}{dt} = kA_{hex}(C^*_{hex} - [hex]_{bar})\frac{V_{bar}}{V_{solv}} \tag{3}$$

$$\frac{d[et]_{solv}}{dt} = -kA_{et}.(C^*_{et} - [et]_{bar}).\frac{V_{bar}}{V_{solv}} \tag{4}$$

kA_{hex} - Mass transfer coefficient between the control volumes VC3 and VC2 for hexane (s^{-1});
kA_{et} - Mass transfer coefficient between the control volumes VC3 and VC2 for hexane (s^{-1});
$[hex]_{bar}$ - Concentration of ethanol in the cell barrier (Kg/m^3);
$[et]_{bar}$ - Concentration of hexane in the cell barrier (Kg/m^3);
V_{bar} - Volume of the barrier (m^3);
V_{solv} - Volume of solvent (m^3).

It is assumed that the adsorption constants will also vary from their initial values to their maximum values for ethanol (k_{et}) and for hexane (k_{hex}), from which there will be no further variations of these constants. Equations 5 and 6 represent this process.

$$\frac{d[k_{et}]}{dt} = k1.[et]_{bar}.\left(1 - \frac{[k_{et}]}{[k_{et\max}]}\right) \tag{5}$$

$$\frac{d[k_{hex}]}{dt} = k2.[et]_{bar}.\left(1 - \frac{[k_{hex}]}{[k_{hex\max}]}\right) \tag{6}$$

k_{etmax} - Maximum Adsorption equilibrium constant of ethanol (m^3/Kg)
k_{hexmax} - Maximum Adsorption equilibrium constant of hexane (m^3/Kg)

Ethanol and hexane diffuse through the cell wall, according to equations 7 and 8.

$$\frac{d[hex]_{bar}}{dt} = kA_{hex}(C^*_{hex} - [hex]_{bar}) - kA2_{hex}([hex]_{bar} - [hex]_{cel})\frac{1}{V_{bar}} \tag{7}$$

$$\frac{d[et]_{bar}}{dt} = kA_{et}.(C^*_{et} - [et]_{bar}) \tag{8}$$

$kA2_{hex}$ - Mass transfer coefficient between the control volumes VC2 and VC1 for hexane (m^3.s^{-1}).

The concentrations of lipids and hexane within the cell are determined by equations 9 and 10.

$$\frac{d[lip]_{cel}}{dt} = -k_{remo}[lip]_{cel} * [hex]_{cel} \tag{9}$$

$$\frac{d[hex]_{cel}}{dt} = -k_{remo}[lip]_{cel} * [hex]_{cel} + kA2_{hex}([hex]_{bar} - [hex]_{cel})\frac{1}{V_{cel}} \tag{10}$$

$[lip]_{cel}$ - Concentration of lipids in the cell (Kg/m^3);
$[hex]_{cel}$ - Concentration of hexane in the cell (Kg/m^3);
k_{remo} - Mass transfer coefficient (s^{-1});
V_{cel} - Volume of cell (m^3)

The lipid found inside the cell combine with hexane, they form a lipid-hexane complex. It is only this complex that has mobility and can leave the interior of the cell. The rate of formation of this complex depends on the concentration of lipid and hexane inside the cell. The complex concentration inside the cell will be represented by equation 11.

$$\frac{d[liphex]_{cel}}{dt} = +k_{remo}[lip]_{cel} * [hex]_{cel} - kA3([liphex]_{cel} - [liphex]_{bar})\frac{1}{V_{cel}} \tag{11}$$

$[liphex]_{cel}$- Concentration of lipid-hexane complex in the cell (Kg/m^3);
$[liphex]_{bar}$- Concentration of lipid-hexane complex in the cell barrier (Kg/m^3);
$kA3$- Mass transfer coefficient between the control volumes VC1 and VC2 (m^3.s^{-1}).

The complex formed will diffuse from the interior of the cell passing through the barrier and reaching the outer environment, phenomena represented by equations 12 and 13.

$$\frac{d[liphex]_{bar}}{dt} = \left\{kA3.([liphex]_{cel} - [liphex]_{bar}) - kA4([liphex]_{bar} - [liphex]_{solv})\right\}\frac{1}{V_{bar}} \tag{12}$$

$$\frac{d[liphex]_{solv}}{dt} = kA4.([liphex]_{bar} - [liphex]_{solv})\frac{1}{V_{solv}} \tag{13}$$

$kA4$ - Mass transfer coefficient between the control volumes VC2 and VC3 (m^3.s^{-1});
$[liphex]_{solv}$- Concentration of lipid-hexane complex in the solvent (Kg/m^3).

3. RESULTS

The modeling parameters used are listed in table 1.

Table 1. Parameters that were used in modeling

Modeling parameters used	
V_{bar}	0.05 m³
V_{solv}	1 m³
V_{cel}	0.12 m³
kA_{hex}	0.01 (s^{-1})
kA_{et}	0.01 (s^{-1})
k_{etmax}	0.01(m³/Kg)
k_{hexmax}	1.00 (m³/Kg)
$kA2_{hex}$	1.00 (m^3/s)
k_{remo}	0.01 (s^{-1})
$kA3$	0.01(m^3/s)
$kA4$	0,01 (m^3/s)
Initial values	
Initial ethanol concentration	236.7 Kg/m^3
Initial concentration of hexane	458.5 Kg/m^3
Initial lipid concentration	12 Kg/m^3
k_{hex}	0.001 m^3/Kg
k_{et}	0.001 m^3/Kg

In order to obtain the results of the mathematical modeling, the simulations were performed using FORTRAN. The Figure 2 below presents the graph of results obtained.

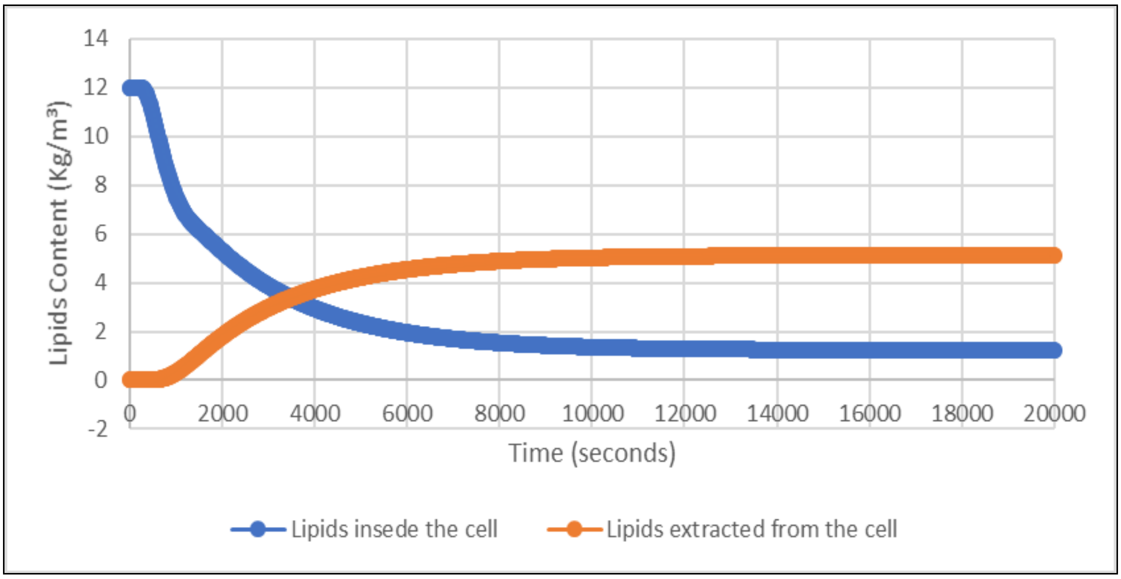

Figure 2. The simulation results for a mixture of solvents (70% hexane and 30% ethanol).

The result can be verified over time that the system reaches the steady state at around 8000 seconds (2 hours, 13 minutes and 20 seconds). The steady state for the hot extractions conducted in the Nucleus of Research and Development of Self-sustaining Energy (NPDEAS) of UFPR took approximately 2 hours. Thus, a reasonable agreement with the presented cause is observed.

Another simulation was generated to evaluate the influence of the presence of ethanol according to the developed mathematical model. Therefore, an initial concentration value of ethanol equal to zero was stipulated. The obtained response is demonstrated by the graph of Figure 3. The time to reach the steady state took more than 40.000 seconds. This result validates the proposed theory that ethanol facilitates the access of hexane to the extraction, since it occurs, however it uses a considerably longer time interval.

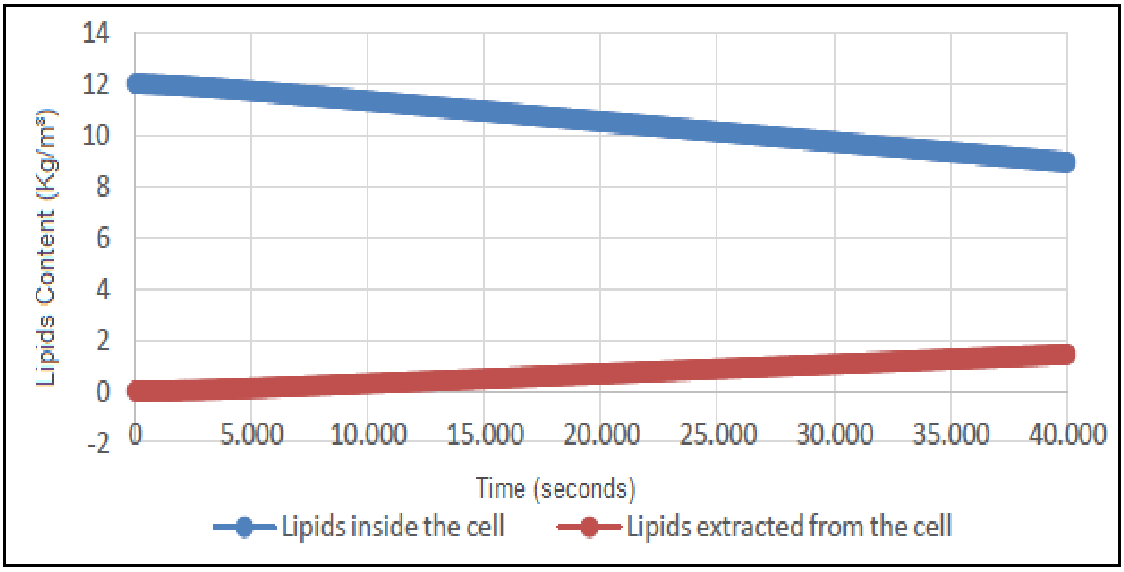

Figure 3. The results of simulations using Hexane as a solvent.

4. CONCLUSION

Through the modeling it was possible to prove the experimental behavior verified in the extraction of microalgae oil using a mixture of hexane and ethanol. It was also described by the model, the influence of the mixture in the mass transfer process, which was demonstrated by the longer extraction time when using pure hexane, that is experimentally verified.

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6. RESPONSIBILITY NOTICE

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