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MATHEMATICAL MODELING OF FRACTIONAL DISTILLATION OF MICROALGAE CRUDE OIL FOR PURE HYDROCARBON PRODUCTION

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Abstract. *With the burning of fossil fuels, new energy sources end up being required to prevent the increase of CO_2 and consequently global warming. To make microalgae hydrocarbons an usable fuel, a purification process is necessary since the hydrocarbons when extracted are contaminated with microalgae pigments and lipids. One type of purification is the fractional distillation, however this process consumes a lot of energy and therefore there is a need for optimization, which can be done by mathematical modeling. Therefore, the objective of this works mathematical modeling of fractional distillation of microalgae crude oil for pure hydrocarbon production. The methodology used was mass balance and energy by the volume elements method, which is based on the optimization of systems engineering of physical size of study. The advantage of this methodology is that consists of a simple sequence of validation of the model with necessary adjustments until the mathematical modeling reaches a value obtained experimentally. The simulations of the model describe the system well, correctly separating the proposed compounds at the beginning of the model. The model can be used for optimization of distillation after experimental validation.*

Keywords: *Mathematical Modeling, Hydrocarbons, Microalgae, MEV, Distillation Fractional.*

1. INTRODUCTION

Continued population growth has resulted in an increased demand for energy worldwide. Currently, fossil fuels supply about 90% of global energy demand (Yen *et al*., 2013). In addition to the fact that petroleum resources are limited, the extensive use of fossil fuels contributes to the increase of CO_2 in the atmosphere that results in global warming (Ortiz *et al*., 2016; Hoppe *et al*., 2016).

Therefore, the continued use of fossil fuels as the main source of energy is widely discussed as unsustainable. This has forced governments and research sectors to look into substitutes of fossil fuels for cleaner~~,~~ and more renewable sources. Biodiesel is considered to be the main alternative source for fossil fuels and has recently been receiving worldwide attention (Lins, 2014).

The microalgae can produce different types of renewable biofuels, among them biomethane, produced by anaerobic digestion of the algal biomass (Spoalore *et al*., 2006); the biodiesel, derived from microalgal oil (Gavrilescu and Chisti, 2005; Banerjee *et al*., 2002); the biohydrogen, photobiologically produced (Ghirardi *et al*., 2000) and long chain hydrocarbons, which can be used directly as fuel or as additives in petroleum-derived fuels (Vidyashankar *et al*., 2015).

2. MICROALGAE HYDROCARBONS

Hydrocarbons are organic compounds made entirely of hydrogen and carbon, the main source of fuels and basic chemicals in modern society. Hydrocarbons are formed largely by the abiotic process; they are also biosynthesized by microbes, plants and insects. Therefore, biosynthesis of hydrocarbons may lead to a new source of fuels and chemicals (Fu *et al*., 2015).

In contrast to higher organisms, microorganisms can be grown in photobioreactors which can lead to an industrial production of hydrocarbons (Xie *et al*., 2017). The proportion of hydrocarbons produced in an organism's body is generally less than 3% of its dry weight (Golebiowski *et al*., 2011; Ladygina *et al*., 2006). The hydrocarbon fractions are composed of short chain hydrocarbons, usually semi-volatile organic compounds; medium chain hydrocarbons, usually in liquid form; and long chain hydrocarbons, the waxy fractions (Jin *et al*., 2016).

Among microbes, microalgae are ideal for hydrocarbon production, as they are photosynthetic organisms that combine high biomass productivity and a strong ability to synthesize and accumulate fatty acids (Malcata, 2011; Hu *et al*., 2008; Liu and Benning, 2013). Microalgae are attractive producers of biofuels, such as lipids (long chain fatty acids), long chain hydrocarbons and alcohols that can be used directly as fuels or as additives in petroleum-based fuels (Sahu *et al*., 2013). Hydrocarbons produced by microalgae offer a biofuel that can be converted to gasoline by cracking or can be mixed directly with diesel and aviation fuel (Hillen *et al*., 1982).

2.1 Distillation and mathematical modeling

Distillation is today the most used unitary operation for the separation of liquid mixtures in the chemical and petrochemical industries. Distillation can be defined as a physical process in which, through heat, the volatile components are separated from a liquid mixture by evaporation. In this process, the concentration of the component more volatile is increasingly concentrated in the vapor phase, for example in the alcohol distillation, the component more volatile is the alcohol and the less volatile is the water. The process is carried out in industrial appliances called distillation columns or towers (Lima and Marcondes, 2002).

A mathematical model is designed to simulate the response or behavior of a real system in a computer, which allows the calculation of the spatial and temporal distribution of any physical quantity within the study engineering system, e.g temperature, relative humidity, concentration of species, that is, according to the non-equilibrium thermodynamics (Prigogine and Kondepudi, 1999).

For the mathematical modeling of the distillation column, the volume element model (MEV) was used. The MEV methodology was initially proposed by Vargas *et al* (2001) for the thermal management of electronic packaging systems, being generalized to allow its use in diverse problems that include, in addition to thermal analysis, other phenomena such as mass and species transport among the volume elements (EV). The governing equations are the principles of conservation of mass, energy and species applied in each EV. Thus, the methodology can be summarized in three main steps: discretization, equation and numerical solution. For a fractionated distillation column, the system was divided into four volume elements according to the Figure 1.

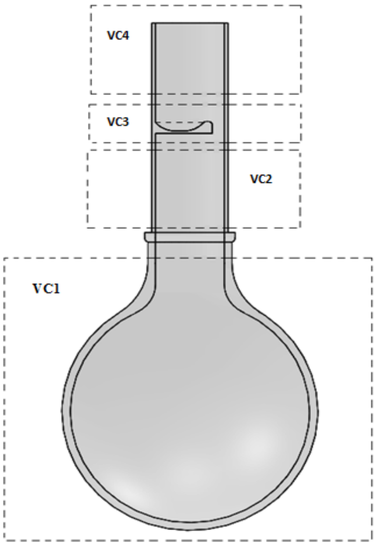

Figure 1. Division of Volume Elements.

For the equation some initial considerations were used:

- Ideal gas;
- Joback method to calculate the specific heats (Cp);
- Antoine equation;
- Only two compounds in the blend (dodecane and palmitic acid);
- Constant pressure;

• 1% mass dish (practically empty).

Volume element 1: liquid at the bottom of the flask. Mass balance in element 1:

$$\frac{dM_1}{dt}=\frac{\left(-\overset{\circ}{M}_{1dode}\times\rho\right)+\left(-M_l\times M_4\times\rho\right)-\left(M_1\times\frac{dM_3}{dt}\right)}{M_3} \tag{1}$$

$$\frac{dM_2}{dt}=\frac{\left(-\overset{\circ}{M}_{1ácido}\times\rho\right)+\left(-M_l\times M_5\times\rho\right)-\left(M_2\times\frac{dM_3}{dt}\right)}{M_3} \tag{2}$$

Equations (1) and (2) are, respectively, the mass balance of dodecane and palmitic acid. Where $\overset{\circ}{M}_{1dode}$ and $\overset{\circ}{M}_{1ácido}$ are flow rates, ρ density, M_l mass of liquid, M_3 total mass, M_4 and M_5 mass of dodecane and palmitic acid respectively, and $\frac{dM_3}{dt}$ total mass balance. Energy balance in volume element 1:

$$\frac{dT_1}{dt}=\frac{Q_{res}+C_1-\left(\frac{dM_1}{dt}\times T_1\times\rho\times C_{pdode}\right)-\left(\frac{dM_2}{dt}\times T_1\times\rho\times C_{pácido}\right)}{\left(\rho\times C_{pdode}\times M_1\right)+\left(\rho\times C_{pácido}\times M_2\right)} \tag{3}$$

Where Q_{res} is the heat dissipated by the resistance, C_1 the simplified constant, T_1 the temperature, ρ the density, C_{pdode} and $C_{pácido}$ specific heats, M_1 and M_2 mass of the components, $\frac{dM_1}{dt}$ and $\frac{dM_2}{dt}$ are the mass balances. Element of volume 2: gas just above the balloon. Mass balance in element 2:

$$\frac{dM_3}{dt}=\frac{\overset{\circ}{M}_{1dode}}{m_{dode}}-\frac{Xm_{total}\times P_1}{p_{total}}\times\frac{R_{gás}\times T_3}{V_{gás}}+\frac{P_1\times\frac{dT_3}{dt}}{T_3} \tag{4}$$

$$\frac{dM_4}{dt}=\frac{\overset{\circ}{M}_{1ácido}}{m_{ácido}}-\frac{Xm_{total}\times P_2}{p_{total}}\times\frac{R_{gás}\times T_3}{V_{gás}}+\frac{P_2\times\frac{dT_3}{dt}}{T_3} \tag{5}$$

Where $\overset{\circ}{M}_{1dode}$ and $\overset{\circ}{M}_{1ácido}$ are the flows, m_{dode} and $m_{ácido}$ masses, Xm_{total} total gas flow, p_{total} total pressure, $R_{gás}$ universal gas constant, $V_{gás}$ gas volume, $\frac{dT_3}{dt}$ energy balance, T_3 temperature and finally pressures P_1 and P_2. Energy balance in gas:

$$\frac{dT_3}{dt}=\frac{\left(\overset{\circ}{M}_{1dode}\times C_{pdode}\times T_1\right)+\left(\overset{\circ}{M}_{1ácido}\times C_{pácido}\times T_1\right)-\left(Xm_{total}\times m_{dode}\times P_1\right)+}{C_2} \tag{6.a}$$

$$\frac{+\frac{\left(P_{gás}\times C_{p2dode}\times T_3\right)}{P_{total}}-\left(Xm_{total}\times m_{ácido}\times P_2\right)\times\frac{\left(C_{p2ácido}\times T_3\right)}{P_{total}}}{C_2} \tag{6.b}$$

Where, $\overset{\circ}{M}_{1dode}$ and $\overset{\circ}{M}_{1ácido}$ are the flows, C_{pdode} and $C_{pácido}$ are the specific heats with respect to temperature T_1, m_{dode} and $m_{ácido}$ are the masses of the components, C_{p2dode} and $C_{p2ácido}$ are the specific heats in relation to temperature T_3, P_{total} is the total pressure, Xm_{total} the total gas flow, $P_{gás}$ is the pressure of the inert gases, P_1 and P_2 are partial pressures. Volume element 3: liquid in the dish. Mass balance in element 3:

$$\frac{dM_5}{dt}=\frac{\left(-\overset{\circ}{M}_{2dode}+M_l\right)\times M_5}{V_{prato}} \tag{7}$$

$$\frac{dM_6}{dt}=\frac{\left(-\overset{\circ}{M}_{2ácido}+M_l\right)\times M_6}{V_{prato}} \tag{8}$$

Where $\overset{\circ}{M}_{2dode}$ and $\overset{\circ}{M}_{2ácido}$ how are the flows, M_l the mass of the liquid, V_{prato} the volume of the dish, M_5 and M_6 the masses. Energy balance:

$$\frac{dT_2}{dt}=\left(\frac{C_3}{V_{prato}\times C_{p3dode}\times C_{p3ácido}}\right)-\frac{(T_2\times M_5)-(T_2\times M_6)}{(M_5+M_6)} \tag{9}$$

Where C_3 is the simplified equation term, V_{prato} the dish volume, C_{p3dode} and $C_{p3ácido}$ the specific heats, M_5 and M_6 are the masses and T_2 the temperature. Volume Element 4: Gas above the plate. Mass balance in element 4:

$$\frac{dM_7}{dt}=\frac{\overset{\circ}{M}_{2dode}}{m_{dode}}+\frac{Xm_{total}\times P_1}{P_{total}}-\left(\left(\frac{Xm_{2total}\times P_3}{P_{total}}\right)\times\left(\frac{R_{gás}\times T_4}{V_{gás}}\right)\right)+\frac{P_3\times\frac{dT_4}{dt}}{T_4} \tag{10}$$

$$\frac{dM_8}{dt}=\frac{\overset{\circ}{M}_{2ácido}}{m_{ácido}}+\frac{Xm_{total}\times P_2}{P_{total}}-\left(\left(\frac{Xm_{2total}\times P_4}{P_{total}}\right)\times\left(\frac{R_{gás}\times T_4}{V_{gás}}\right)\right)+\frac{P_4\times\frac{dT_4}{dt}}{T_4} \tag{11}$$

Where, $\overset{\circ}{M}_{2dode}$ and $\overset{\circ}{M}_{2ácido}$ are the flows, m_{dode} and $m_{ácido}$ the masses of the compounds, Xm_{total} and Xm_{2total} are the total gas flows, P_1, P_2, P_3, P_4 are partial pressures, P_{total} total pressure, $R_{gás}$ universal gas constant, $V_{gás}$ gas volume, T_4 temperature, $\frac{dT_4}{dt}$ energy balance . Energy balance in element 4:

$$\frac{dT_4}{dt}=\frac{\left(\overset{\circ}{M}_{2dode}\times C_{p4dode}\times T_4\right)+\left(\overset{\circ}{M}_{2ácido}\times C_{p4ácido}\times T_4\right)+\left(Xm_{total}\times m_{dode}\times P_1\right)+\frac{P_{gás}\times C_{p2dode}\times T_3}{P_{total}}}{C_4}+ \tag{12.a}$$

$$\frac{+\frac{Xm_{total}\times m_{ácido}\times P_2\times C_{p2ácido}\times T_3}{P_{total}}-\left(Xm_{2total}\times m_{dode}\times P_3\right)+}{C_4} \tag{12.b}$$

$$\frac{\frac{P_{gás2}\times C_{p4dode}\times T_4}{P_{total}}-\frac{Xm_{2total}\times m_{ácido}\times P_4\times C_{p2ácido}\times T_4}{P_{total}}}{C_4} \tag{12.c}$$

Where, $\overset{\circ}{M}_{2dode}$ and $\overset{\circ}{M}_{2ácido}$ are the flow rates, C_{p4dode} and $C_{p4ácido}$ the specific heats in the volume element 4, T_3 and T_4 are the temperatures, Xm_{total} and Xm_{2total} gas flows, m_{dode} and $m_{ácido}$are dodecane mass and palmitic acid, $P_{gás}$ and $P_{gás2}$ gas pressure, P_{total} total pressure and C_4 the simplification constant, P_1, P_2, P_3, P_4 the partial pressures. The Runge-Kutta method was programmed in FORTRAN® language for solutions of differential equations (Vargas and Araki, 2017).

3. RESULTS AND DISCUTION

According to Figure 2 it is observed that the mass of the sample tends to reduce as the time increases, that is, while the temperature in the volumetric flask containing the sample gradually increases the more volatile components inclines to evaporate first, the basic principle of a distillation and that the mathematical model was able to describe.

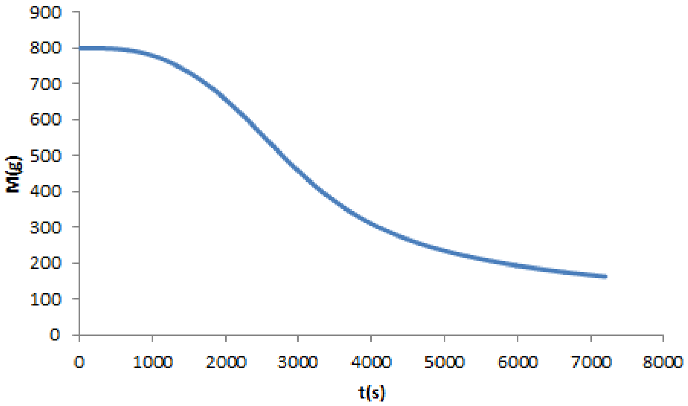

Figure 2. Mass Decrease in the Time.

Figure 3 shows the increase in the concentration of palmitic acid at the bottom of the volumetric flask with respect to time. As the most volatile compounds in the sample evaporate first (dodecane) in the event of an increase in temperature, those with a higher boiling point are being disposed at the bottom of the volumetric flask while not receiving enough energy to evaporate. The model was designed to have total control over temperature and that only the compounds of interest would be distilled, in this case dodecane, i.e palmitic acid tends to remain at the bottom of the volumetric flask.

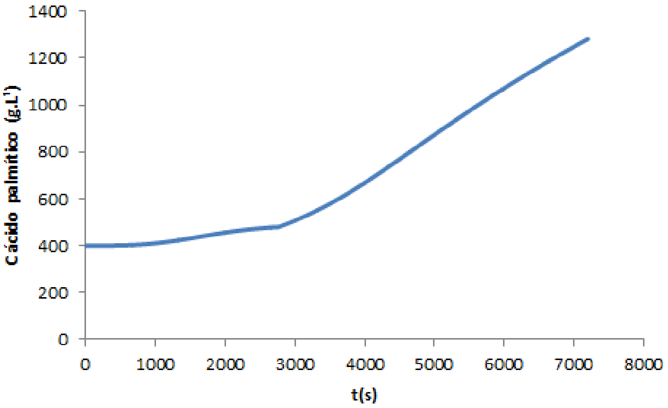

Figure 3. Concentration of Palmitic Acid.

The mathematical model was designed only for two compounds, palmitic acid and dodecane. Figure 4 shows the behavior of sample distillation based on these compounds. Because dodecane has a lower boiling point than palmitic acid, it evaporates firstly. The sample was predominantly composed of dodecane, about 65% being the compound of most interest because it is a hydrocarbon. The palmitic acid was not a desired compound in the distillation because it is a saturated fatty acid, in that case, the temperature at the bottom of the flask was controlled, so that only dodecane was distilled.

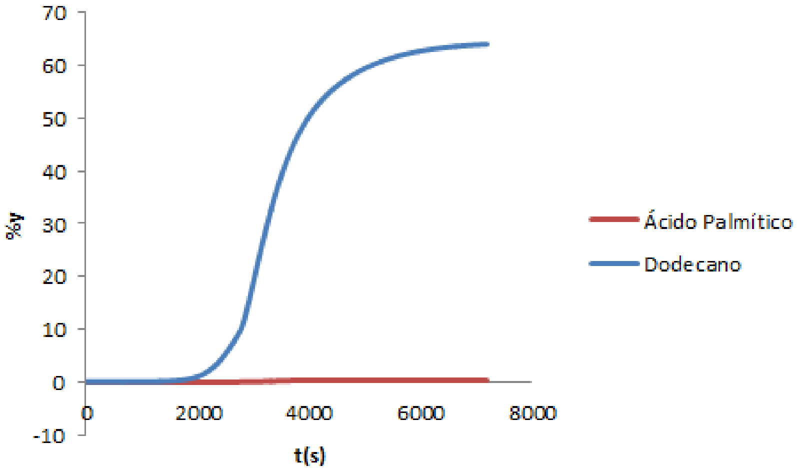

Figure 4. Distillation Behavior.

Figure 5 shows an analysis of the behavior of palmitic acid during distillation. The volume variation in relation to time does not present a significant change; this is due to the fact that temperature is controlled in the model, resulting in insignificant evaporation of the compound. It is important to ensure a temperature range where distillation control is the best possible, if a little fatty acid is distilled or charged together with other components, that amount is small.

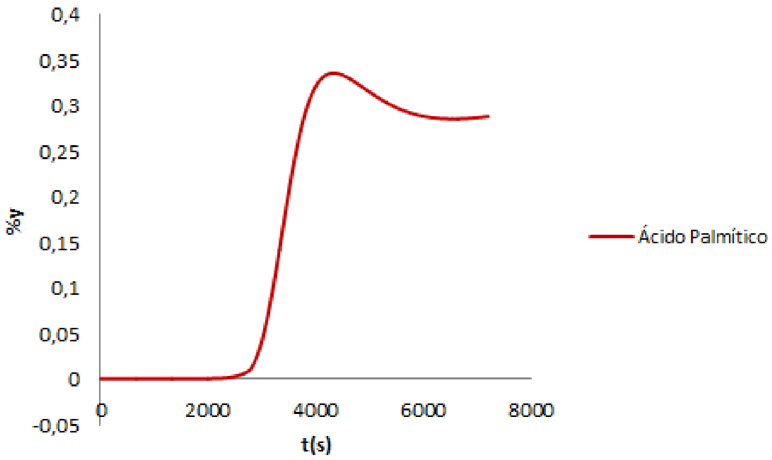

Figure 5. Behavior of palmitic acid in distillation.

4. CONCLUSION

The mathematical model met the objectives of this work, which was to show the fractional distillation of a sample with different compounds (dodecane and palmitic acid) and to analyze the behavior of each of them inside the column, even having only one theoretical plate. More compounds can be added to the model so you can analyze the behavior more accurately. The model can be improved as needed for future research. The model must be validated experimentally.

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