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MODELING, SIMULATION AND OPTMIZATION OF THE MICROALGAE OIL EXTRACTION PROCESS AND PRODUCTION OF PURE HYDROCARBONS (GREEN DIESEL)

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Abstract. *Microalgae appear as a good opportunity to produce biofuels, because in addition to the production of biodiesel, they also produce hydrocarbons that can be compared to hydrocarbons produced by mineral sources. These hydrocarbons can be used directly as fuels or as additives in petroleum-based fuels. The main objective of this work is to model, simulate and optimize the process of extracting oil from microalgae and producing pure hydrocarbons (diesel-green). For the mathematical modeling of the distillation column, the volume element model (VEM) was used. The governing equations are the principles of conservation of mass, energy and species applied to each volume element (VE). For the equation, some hypotheses were used: ideal gas; Joback method for calculating specific heats; Antoine's equation; and constant pressure. For adjustment and experimental validation of the mathematical model, several theoretical plates will be used to maximize the separation of compounds from the sample. The bottom and top temperatures were controlled to obtain a better fractionation of the sample, distilling only the compounds of interest (hydrocarbons ranging from* C_{12} *to* C_{19}*). The experimental data will be used for calibration and validation of the mathematical model. Parametric analysis will be conducted to assess the impact of the variation of selected process parameters on the obtained optimums. To carry out the thermodynamic optimization of the process, the model developed and experimentally validated will be used. An exergetic analysis will be added to the model, which will allow computing the entropy generation (2nd Law of Thermodynamics) to identify the thermodynamic losses that occur in the process, in order to minimize them. The objective function will be to maximize the distillation of the sample in order to maximize the production and purification of the compounds of interest. Optimal geometric parameters will be determined for maximum fractionation of the sample, such as the geometric configuration of the distillation dishes and the size of the column.*

Keywords: *microalgae, hydrocarbon, extraction, distillation, mathematical modeling*

1. INTRODUCTION

The increase in greenhouse gases (GHGs), mainly carbon dioxide (CO_2), due to anthropogenic activity can lead to global climate change (Mathimani et al., 2019). In addition to global warming, the increase in the concentration of CO_2 in the atmosphere can cause ocean acidification, negatively affecting biodiversity. The main reason is high dependence on fossil fuels used in transport, manufacturing, and energy production (Pires, 2017).

Biofuels are a promising and renewable source of alternative energy (Yadav et al., 2021), some regions of our world have used biofuels to partially replace the application of fossil fuels, for example, Brazil used sugarcane, Europe and some places in Asia applied palm oil as a biofuel source and in other cases the use of microalgae as biofuels (Alishah Aratboni et al., 2019).

The lipid fraction of microalgae biomass is used to produce biofuels. Triacylglycerides are converted into biodiesel, and this procedure has been extensively studied. However, other compounds produced by microalgae, such as hydrocarbons and terpenes, can also be used to produce biofuel and green diesel. For example, phytol stands out as a natural diterpene alcohol that can be used as a biofuel in diesel engines (Kumar and Saravanan, 2016) or converted into gasoline by catalytic cracking (Tracy et al., 2010). Another terpene, neophytadiene, is one of the dominant terpenes in green microalgae (Abdel-Aal et al., 2015) and can be converted into biofuel. Terpenes are hydrocarbons that are already important as bioactive compounds, with applications as functional compounds due to their broad spectrum of biological activity, such as antitumor and antiviral activity, among others (Abreu et al., 2012).

Hydrocarbons produced from microalgae can be used directly in mixtures with the diesel fraction (C_{12}-C_{22}) or can be subjected to a catalytic enhancement stage (hydroisomerization process or hydroisomerization plus hydrocracking), through which paraffin with better fuel properties can be obtained (Rossetti et al., 2009).

2. DISTILLATION AND MATHEMATICAL MODELING

Distillation is one of the most used separation processes in the chemical and petrochemical industries, taking advantage of the difference in volatility between components of the mixture. Batch distillation systems are useful for processes where different loads are processed on the same equipment, when small productions are expected or when high value products are obtained. The most common configuration is the conventional batch distillation column, which consists of a pot, a container where the contact between the phases takes place and a condenser. Most separation processes, including continuous and discontinuous distillation, are modeled through the so-called equilibrium model, which assumes that thermodynamic equilibrium is reached both at the column plates and along the packing height, where the phases contact liquid and vapor occur (May-Vázquez et al., 2020).

DiStefano (1968) proposed one of the first mathematical models based on equilibrium representing multicomponent batch distillation columns, assuming constant volume retention in the trays. In the case of columns with trays, the deviation between actual column performance and equilibrium is represented by efficiencies. However, the value of efficiency must be assumed for each tray, which can be underestimated or overestimated.

One proposal to overcome this problem involves using industrial operational data to estimate tray efficiency (Luo et al., 2012). An alternative way of modeling the interactions in the distillation columns is the rate-based model (Krishnamurthy and Taylor, 1985), which avoids the assumption of equilibrium along the column, instead of calculating the mass and heat transfer rates, assuming that equilibrium occurs only at the interface. The rate-based model has been proven to adequately represent the performance of experimental distillation devices such as packed batch distillation columns (Kreul et al., 1999) and continuous reactive distillation columns (Buchaly et al., 2007; He et al., 2007; He et al., 2010).

In the case of distillation columns in discontinuous trays, Mehlhorn et al. (1996) reported rate-based modeling of a batch column using reported mass transfer models. An important reference in the area is the work of Kooijman and Taylor (1995), who stated that the use of an equilibrium model is not recommended for dynamic systems, such as batch distillation columns, because the efficiency of the dishes varies. with time.

For the mathematical modeling of the distillation column, the volume element model (VEM) was used. The VEM 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 (VE). The governing equations are the principles of conservation of mass, energy and species applied in each VE. 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 some volume elements. Figure 1 shows the distillation column that was used in the process

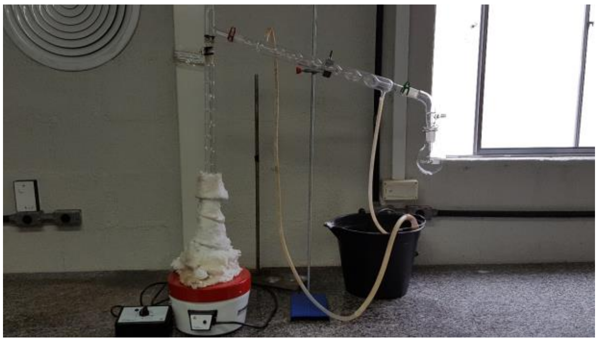

Figure 1. Fractional distillation column.

2.1 Mathematical equations

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 nonadecane);
- Constant pressure;

Using Antoine's equation to calculate the saturation pressure of dodecane (C_{12}) and nonadecane (C_{19}):

$$\log_{10} P_{sat} = A - \frac{B}{y_1 + C - 273{,}15} \tag{1}$$

Using saturation pressure with Raoult's Law, we have:

$$X_{12}^{*} = \frac{\dfrac{y_6}{m_{tot,gás}}}{P_{sat12}} \tag{2}$$

$$X_{19}^{*} = \frac{\dfrac{y_7}{m_{tot,gás}}}{P_{sat19}} \tag{3}$$

Balloon flow calculations for C_{12} and C_{19}:

$$m_{v12} = ka_{12} \cdot \left[\frac{y_2}{y_4} - X_{12}^{*} \right] \tag{4}$$

$$m_{v19} = ka_{19} \cdot \left[\frac{y_3}{y_4} - X_{19}^{*} \right] \tag{5}$$

Using Antoine's equation to calculate the saturation pressure of dodecane (C_{12}) and nonadecane (C_{19}), above the balloon:

$$\log_{10} P_{sat} = A - \frac{B}{y_8 + C - 273{,}15} \tag{6}$$

Using saturation pressure with Raoult's Law above the balloon, we have:

$$X_{12,gás}^{*} = \frac{\dfrac{y_6}{m_{tot,gás}}}{P_{sat12}} \tag{7}$$

$$X_{19,gás}^{*} = \frac{\dfrac{y_7}{m_{tot,gás}}}{P_{sat12}} \tag{8}$$

Flow calculation above the balloon for C_{12} and C_{19}:

$$m_{v12,gás} = -ka_{12,gás} \cdot \left[\frac{y_9}{m_{tot,liq}} - X^*_{12,gás} \right] \tag{9}$$

$$m_{v19,gás} = -ka_{19,gás} \cdot \left[\frac{y_{10}}{m_{tot,liq}} - X^*_{19,gás} \right] \tag{10}$$

Mass calculation:

$$m_{gás,out} = m_{v12} + m_{v19} - m_{v12,gás} - m_{v19,gás} \tag{11}$$

$$m_{gás,out,liq} = m_{v12,gás} + m_{v19,gás} \tag{12}$$

Energy balance:

$$\frac{dy_1}{dt} = \frac{\left[Q - m_{v12} \cdot h_{v12} - m_{v19} \cdot h_{v19} + \left(\frac{c_{p12,liq} \cdot m_{gás,out,liq} \cdot y_9}{m_{tot,liq}} \right) + \left(\frac{c_{p19,liq} \cdot m_{gás,out,liq} \cdot y_{10}}{m_{tot,liq}} \right) \right]}{y_2 \cdot c_{p12,liq} + y_3 \cdot c_{p19,liq}} \tag{13}$$

Mass balance in C_{12}:

$$\frac{dy_2}{dt} = \frac{-m_{v12} + m_{gás,out,liq} \cdot y_9}{m_{tot,liq}} \tag{14}$$

Mass balance in C_{19}:

$$\frac{dy_3}{dt} = \frac{-m_{v19} + m_{gás,out,liq} \cdot y_{10}}{m_{tot,liq}} \tag{15}$$

Total mass balance:

$$\frac{dy_4}{dt} = -m_{v12} - m_{v19} + m_{gás,out,liq} \tag{16}$$

Gas temperature:

$$\frac{dy_5}{dt} = \frac{m_{v12} \cdot h_{v12} + m_{v19} \cdot h_{v19} - m_{v12,gas} \cdot h_{v12} - m_{v19,gas} \cdot h_{v19} - \left(\frac{h_{v12} \cdot m_{gas,out} \cdot y_6}{m_{tot,gas}} \right) - \left(\frac{h_{v19} \cdot m_{gas,out} \cdot y_7}{m_{tot,gas}} \right)}{\frac{c_{p12,gás} \cdot y_6}{1,4} + \frac{c_{p19,gás} \cdot y_7}{1,4}} \tag{17}$$

Total moles of C_{12} in the gas:

$$\frac{dy_6}{dt} = \frac{m_{v12} - m_{v12,gas} - m_{gas,out} \cdot y_6}{m_{tot,gas}} \tag{18}$$

Total moles of C_{19} in the gas:

$$\frac{dy_7}{dt} = \frac{m_{v19} - m_{v19,gas} - m_{gas,out} \cdot y_7}{m_{tot,gas}} \tag{19}$$

Plate temperature:

$$\frac{dy_8}{dt}=\frac{\left[m_{v12,gas}\cdot h_{v12}+m_{v19,gas}\cdot h_{v19}-\dfrac{c_{p12,liq}\cdot m_{gas,out,liq}\cdot y_9}{m_{tot,liq}}-\dfrac{c_{p19,liq}\cdot m_{gas,out,liq}\cdot y_{10}}{m_{tot,liq}}\right]}{y_9\cdot c_{p12,liq}+y_{10}\cdot c_{p19,liq}} \tag{20}$$

$$\frac{dy_9}{dt}=\frac{m_{v12,gas}-m_{gas,out,liq}\cdot y_9}{m_{tot,liq}} \tag{21}$$

$$\frac{dy_{10}}{dt}=\frac{m_{v19,gas}-m_{gas,out,liq}\cdot y_{10}}{m_{tot,liq}} \tag{22}$$

Temperature at the top of the column:

$$\frac{dy_{11}}{dt}=\frac{\dfrac{h_{v12}\cdot m_{gas,out}\cdot y_6+h_{v19}\cdot m_{gas,out}\cdot y_7-h_{v12}\cdot m_{gas,out}\cdot y_{12}-h_{v19}\cdot m_{gas,out}\cdot y_{13}}{m_{tot,gas}}}{\dfrac{c_{p12,gás}\cdot y_{12}}{1,4}+\dfrac{c_{p19,gás}\cdot y_{13}}{1,4}} \tag{23}$$

Total moles of C_{12} in the gas:

$$\frac{dy_{12}}{dt}=\frac{m_{gas,out}\cdot y_6-m_{gas,out}\cdot y_{12}}{m_{tot,gas}} \tag{24}$$

Total moles of C_{19} in the gas:

$$\frac{dy_{13}}{dt}=\frac{m_{gas,out}\cdot y_7-m_{gas,out}\cdot y_{13}}{m_{tot,gas}} \tag{25}$$

The method was programmed in MATLAB® (developed by MathWorks inc.) language for solutions of differential equations. Table 1 shows the initial conditions used in the model.

Table 1. Initial conditions of the model.

Description	**Dodecane**	**Nonadecane**
Cp_{liquid} ($J.mol^{-1}.K^{-1}$)	376.00	602.60
Cp_{gas} ($J.mol^{-1}.K^{-1}$) (Jobacks Method)	406.83	781.39
h_{vap} ($J.mol^{-1}$)	61,100	96,400
Density (kg/m^3)	750.00	820.00
A (Antoine)	4.12285	4.14020
B (K) (Antoine)	1639.270	1932.800
C (K) (Antoine)	181.840	137.600
ka ($mol.s^{-1}$)	0.05	0.05
ka_{gas} ($mol.s^{-1}$)	0.000005	0.000005
Molar Mass ($g.mol^{-1}$)	130.33	268.51
$m_{tot,gas}$ (mol)	0.00072	0.00072
$m_{tot,liq}$ (mol)	0.004	0.004

2.2 Thermodynamic Optimization

To carry out the thermodynamic optimization of the process, the model developed and validated experimentally will be used. An exergetic analysis will be added to the model, which will allow computing the entropy generation (2nd Law of Thermodynamics) to identify the thermodynamic losses that occur in the process, in order to minimize them. Next, it will be necessary to identify the existing constraints for the system, formulate them mathematically and add them to the model. The objective function will be to maximize the distillation of the sample in order to maximize the production and purification of the compounds of interest. will be certain optimal geometric parameters for maximum fractionation of the sample, such as the geometric configuration of the distillation dishes and the size of the column.

3. RESULTS AND DISCUTION

Figure 2 shows the behavior at the top of the column, C_{12} (dodecane) evaporates first because it is lighter, when it reaches its maximum mass fraction its mass decreases and C_{19} (nonadecane) increases, as it is a compound the heavier the tendency is for it to come out in greater quantity when the C_{12} starts to decrease with time.

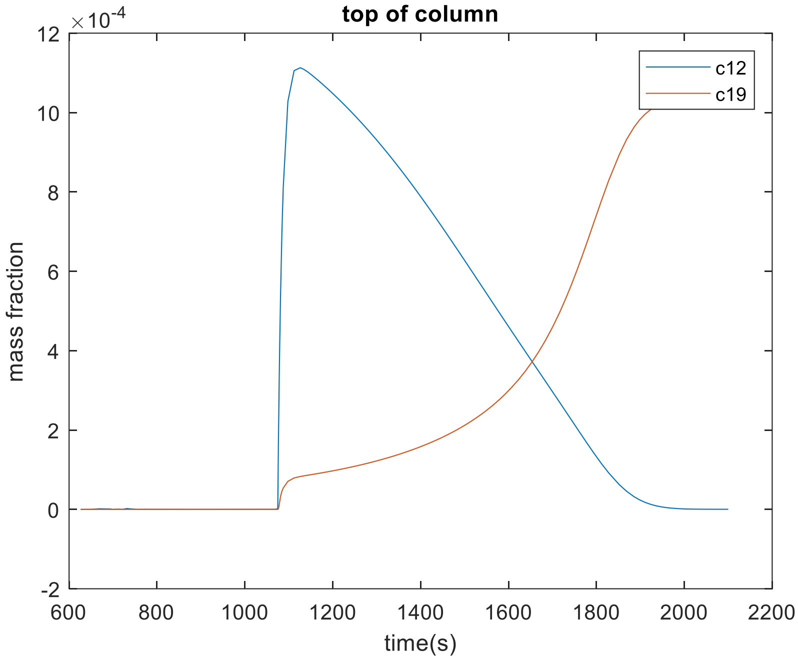

Figure 2. Top of column.

Figure 3 shows the balloon bottom initially at 300K. As time goes on, the temperature increases, until it reaches the point where the lighter compound will start to evaporate, as it will reach its boiling temperature.

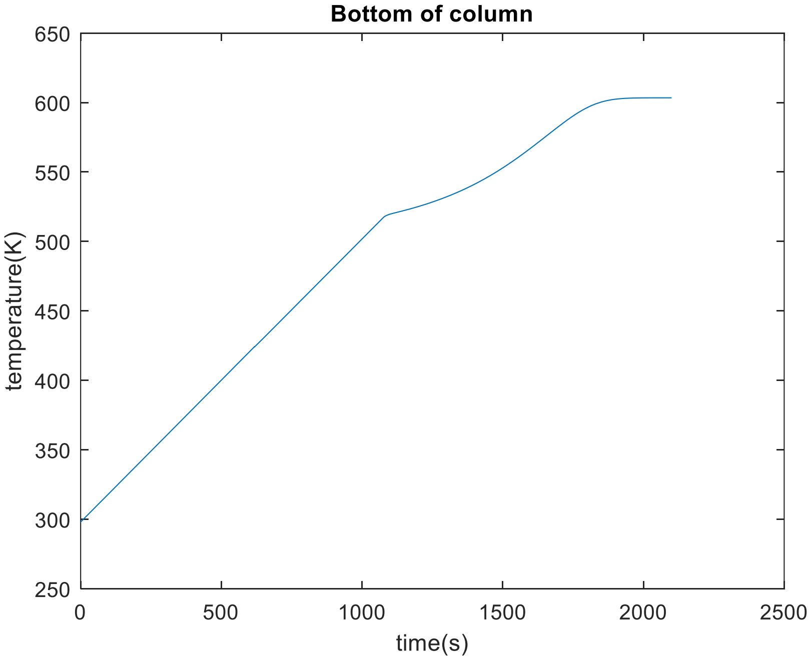

Figure 3. Bottom of column.

Figure 4 shows the bottom of the flask in amount of substance (moles) of C_{12} and C_{19}. Over time, the tendency is for the bottom of the flask to be heated, thus, the amount of substance of C_{12} is decreasing at the bottom of the flask, it is understood that at the top of the column the C_{12} is increasing in amount of substance, because is being distilled. This serves analogously for C_{19}, where after C_{12} starts to decrease at the top of the column, the tendency is for C_{19} to increase, until it is fully distilled.

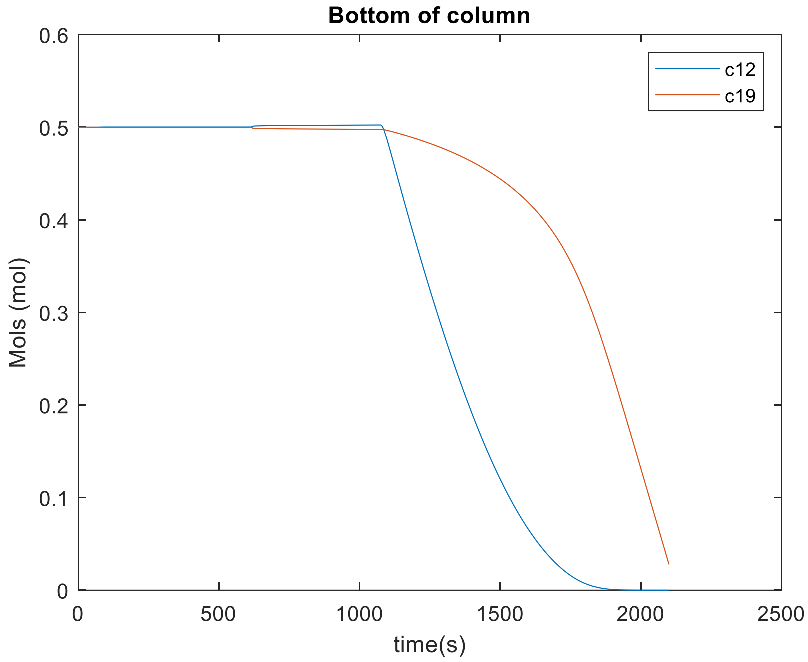

Figure 4. Bottom of column.

Figure 5 shows the behavior at the top of the column, that is, the temperature remains constant for a certain time and then starts to increase, because the bottom of the balloon is already quite heated, so the top of the column can already feel this increase in temperature. because of the initial evaporation of the sample.

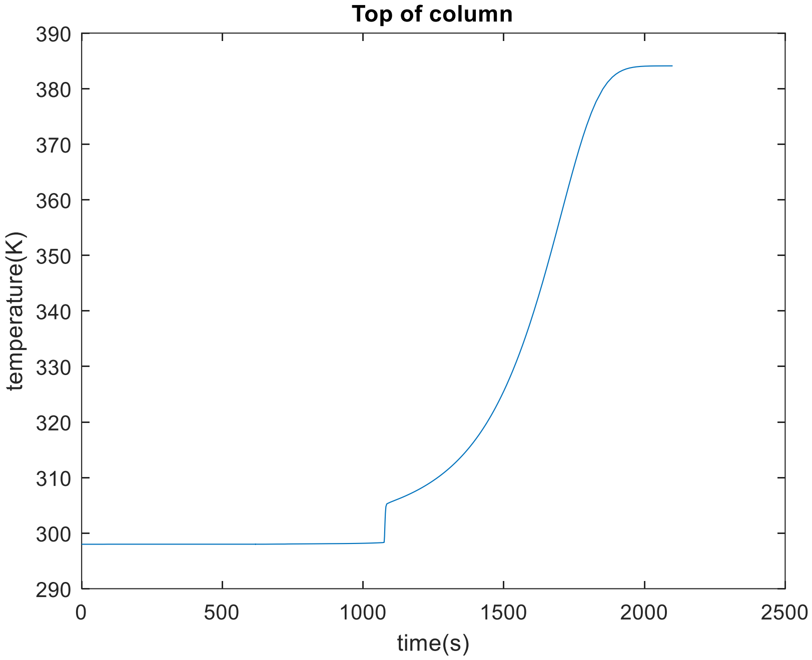

Figure 5. Top of column.

Figure 6 shows the behavior of the sample in the distillation dish. The amount of C_{12} and C_{19} substance increases and decreases as the compounds are distilled.

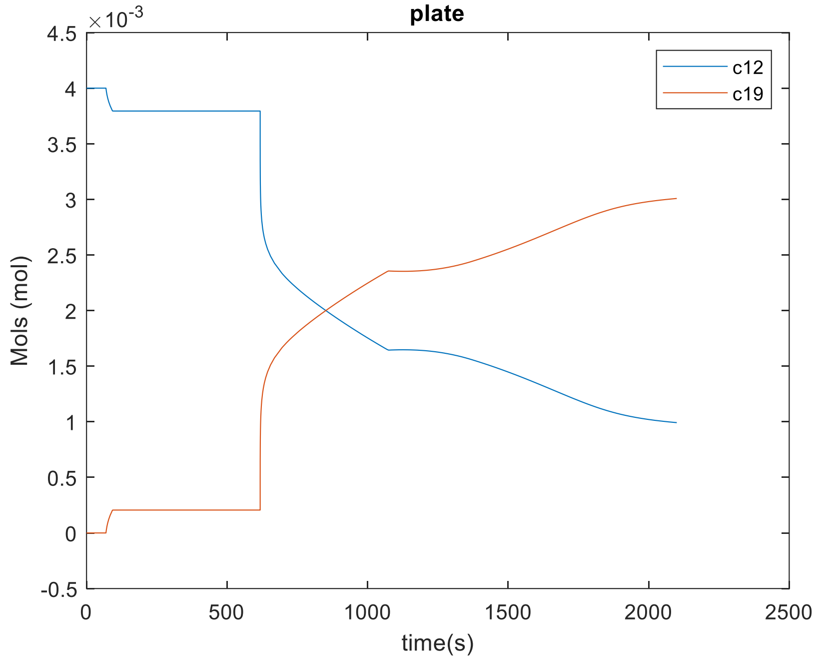

Figure 6. Mols in plate.

Figure 7 analyzes the temperature in the column plate. Initially the temperature remains constant, after a certain time the tendency is for it to increase, because the flask being heated, the heat is dissipated to the column and felt in the column plate.

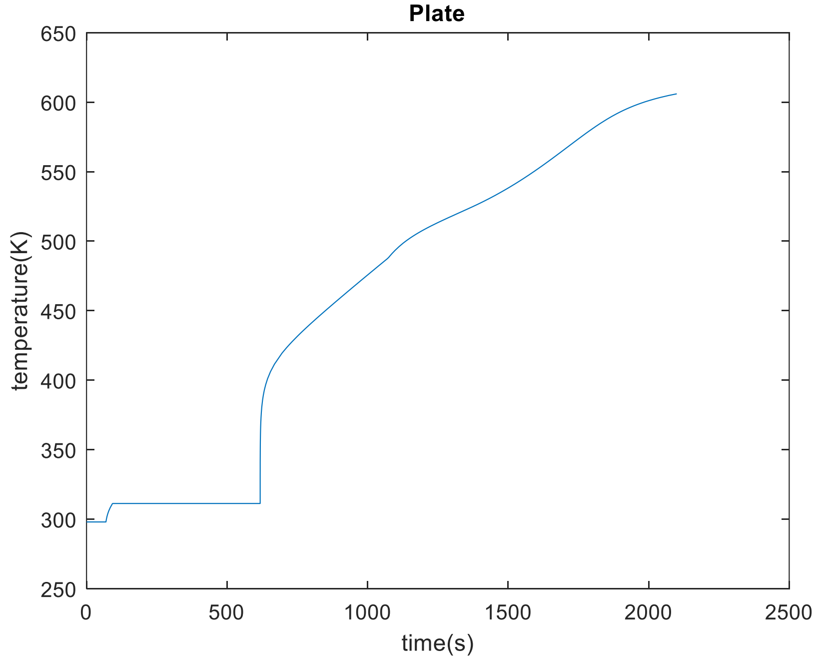

Figure 7. Temperature in plate.

The mathematical model met the objectives of this work, which was to show the fractional distillation of a sample with different compounds (dodecane and nonadecane) and to analyze the behavior of each of them inside the column. More compounds can be added to the model so you can analyze the behavior more accurately. The model must be validated experimentally.

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