INSTITUTO SUPERIOR DE ENGENHARIA DO PORTO
MESTRADO EM ENGENHARIA QUÍMICA

Simulação da produção de biodiesel a partir de um óleo ácido baseado em parâmetros cinéticos experimentais

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Simulation of biodiesel production from an acid oil based on experimental kinetic parameters

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DISSERTAÇÃO APRESENTADA AO INSTITUTO SUPERIOR DE ENGENHARIA DO PORTO COMO REQUISITO PARCIAL PARA OBTENÇÃO DO GRAU DE MESTRE EM ENGENHARIA QUÍMICA NO RAMO ENERGIA E BIORREFINARIA

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Resumo

No presente trabalho foi realizada uma simulação computacional em ambiente Aspen Plus V8.4 da produção de biodiesel a partir de uma alimentação de óleo com elevado teor de ácidos gordos livres em solução. A conversão em biodiesel foi determinada pela cinética química, com recurso a dados cinéticos obtidos na literatura, sendo que as espécies eletrolíticas participantes do processo também foram levadas em conta nas etapas reacionais.

O processo simulado é composto por três etapas. As duas primeiras constituem a etapa reacional, sendo a terceira etapa relativa à separação e purificação. A etapa reacional foi dividida na esterificação ácida e na transesterificação alcalina. Na primeira, os ácidos gordos livres em solução são convertidos em biodiesel e na segunda, a corrente de óleos, agora com um teor residual de ácidos gordos livres, é convertida em biodiesel. Na última etapa o biodiesel é purificado, diminuindo-se o seu teor em água e metanol. Nesta etapa também se procede à separação e recuperação do metanol e glicerol utilizados em diferentes pontos do processo.

Assim, foram alimentados ao processo uma corrente de 1000 kg/h de óleo, com 25% em massa de ácidos gordos livres. A conversão desta corrente resultou em 952 kg/h de uma corrente de biodiesel com uma pureza mássica de 97,36%. Para além dos óleos, foram também alimentados ao processo 670 kg/h de metanol, 10 kg/h de ácido sulfúrico concentrado (98%), 5 kg/h de hidróxido de sódio sólido, 100 kg/h de glicerol e 500 kg/h de água para lavagem. Do metanol alimentado ao processo foram consumidos cerca de 16% em massa nas etapas reacionais e recuperados, cerca de 63%, da corrente de alimentação, no final do processo, com uma pureza mássica de 96%. O processo de transesterificação alcalina produz cerca de 76% do glicerol alimentado, sendo este recuperado praticamente na totalidade no final do processo com uma pureza mássica de cerca de 80%.

A conversão dos ácidos gordos livres na etapa de esterificação ácida foi de 98,89%. Relativamente aos óleos, a conversão obtida para os mesmos na etapa de transesterificação alcalina, foi de 96.41%.

A potência térmica consumida para se purificar o biodiesel produzido e recuperar o metanol e glicerol, foi de 202 kW.

Palavras Chave: Biodiesel, Produção de Biodiesel, óleo com elevado teor de ácidos gordos livres, Simulação da Produção de Biodiesel em Aspen Plus V8.4.

Abstract

In the present work a computer simulation was performed in Aspen Plus V8.4 environment, for the production of biodiesel using an oil feed with a high content of free fatty acids in solution. The conversion to biodiesel was determined by chemical kinetics using literature data and the electrolytic species involved in the process were also taken into account in the reaction stages.

The simulated process consists of three steps. The first two constitute the reactional step, the third stage being the separation and purification phase. The reaction step was divided into acid esterification and alkaline transesterification. In the former, the free fatty acids in solution were converted to biodiesel, and in the second, the oil stream, now with a residual content of free fatty acids, is converted into biodiesel. In the last step the biodiesel is purified, reducing its content in water and methanol. This step also separates and recovers methanol and glycerol used at different points in the process.

Thus, a stream of 1000 kg/h of oil, with 25% by weight of free fatty acids, was fed into the process. The conversion of this stream resulted in 952 kg/h of a biodiesel stream with a mass purity of 97.83%. 670 kg/h of methanol, 10 kg/h of concentrated sulfuric acid (98%), 5 kg/h of solid sodium hydroxide, 100 kg/h of glycerol and 500 kg/h of water for washing, were also fed into the process. From the methanol fed to the process, about 16% by mass was consumed in the reaction steps and about 63% of the feed stream was recovered at the end of the process, with a mass purity of 96%. The alkaline transesterification process produces about 76% of the fed glycerol, which is recovered substantially at the end of the process with a mass purity of about 80%.

Conversion of the free fatty acids in the acid esterification step was 98.89%. Regarding the oils, the conversion obtained for them in the alkaline transesterification step was 96.41%.

The thermal power consumed to purify the produced biodiesel and recover the methanol and glycerol, was 202 kW.

Keywords: Biodiesel, Biodiesel production, oil with high free fatty acid content, Simulation of Biodiesel Production in Aspen Plus V8.4.

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1 Introduction

The Diesel engine is an efficient internal combustion engine in which air and fuel are compressed inside a cylinder, resulting in the oxidation of the fuel with the oxygen present in the chamber when the inflammability temperature is reached. The combustion and the expansion of the gases of this reaction act on a piston generating the movement of the same. The movement of the piston can be communicated to wheels, allowing the displacement of vehicles or machines as well as the generation of electric energy (Proctor and Armstrong, 2017).

For years, the high availability of fossil fuels obtained at low cost has led to other possibilities in terms of energy sources being little or nothing exploited. However, given the current environmental scenario, efforts have been made in recent decades to reverse the current trend of extreme dependence of society on fossil fuels (Canakci and Van Gerpen, 2001).

The fuel whose production is estimated in this study is biodiesel. This fuel began to be studied in the 70's when, due to the oil crisis, it began to show academic interest as an alternative source of fuel. Initially vegetable oils were pointed out as an alternative to mineral diesel in diesel engines, however, the high viscosity and low volatility of the same leads to numerous problems in the engine, reason why they were disregarded. However, the deleterious effects of high viscosity and low volatility can be minimized or even eliminated by transesterification of vegetable oils into the formation of methyl esters or ethyl esters of the fatty acids, both also known as biodiesel (Canakci and Van Gerpen, 2001).

In the last decades the attention given to biodiesel has increased, since it presents itself as an alternative source, non-toxic, biodegradable and renewable to petroleum diesel. Nevertheless, one of the challenges to replace petroleum diesel by biodiesel is reducing costs in production and a strategy to reduce costs is the use of low-cost waste materials such as used fried oils and waste animal fats. The disadvantages for these raw materials when compared with refined vegetable oils are some, the main one being the need to add a pre-treatment step, since they cannot be used directly for the production of biodiesel (Canakci and Van Gerpen, 2001).

Thus, the objective of the present work is to develop a computer simulation in environment Aspen Plus V8.4, which estimates the production of biodiesel from a stream of residual oils with a high content of free fatty acids in solution. The conversion to biodiesel must be determined by chemical kinetics, with the kinetic parameters being obtained through data published in literature. The simulation predicts the liquid-liquid equilibrium phases by a thermodynamic model that calculate non-electrolyte activity coefficients. The simulation must also take into account the behavior of the electrolytes and the ionic species in equilibrium that are part of the process matrix.

2 Biodiesel

Biodiesel can be defined as a mixture composed of mono-alkyl esters of saturated or unsaturated long chain fatty acids and which must meet several physical and chemical requirements specified by different standards (depending on geographical location) which regulate and specify the criteria's for the biodiesel produced for commercial purposes. In the European Union, the standard drawn up for this purpose is standard 14214, drafted by the European Committee for Standardization (Rutz and Janssen, 2006). In the United States the equivalent standard is given by ASTM D6751 (American Standards for Testing and Materials) (Chang and Liu, 2010).

2.1 Reaction, Reagents and Products

The reaction of biodiesel production is called transesterification. This name is due to the fact that the process is based on the conversion of esters into different types of esters by the exchange with an organic group of an alcohol. Thus, in a transesterification reaction, (mostly) triglycerides (tri-esters) react with an excess of a small chain alcohol to form biodiesel (mono fatty acid esters) and glycerol (Biodiesel, 2017). There are three reactional mechanisms (to be highlighted) to produce biodiesel from vegetable oils (form or type of fat). These are the transesterification of oils in an acid or alkaline medium, resulting in biodiesel and the conversion of fats into fatty acids and subsequent esterification (conversion of a non-ester compound into an ester) of the fatty acids into monoalkyl esters of fatty acids (EUBIA, 2017).

Figure 2.1 shows the reactions that convert triglycerides and alcohol into biodiesel and glycerol in the presence of a catalyst. A triglyceride molecule reacts with three molecules of methanol, in the presence of catalyst, giving rise to three molecules of biodiesel and one of glycerol. The intermediate steps of this process are the conversion of triglycerides into diglycerides and monoglycerides. The difference between the three is in the number of fatty acids (or esters) in the molecule. By reacting, the triglycerides release the fatty acid and replace it by a hydroxide group, forming a diglyceride and biodiesel. It goes through the same process, forming a monoglyceride and biodiesel. Finally, the monoglyceride is converted into glycerol and biodiesel (Chang and Liu, 2010).

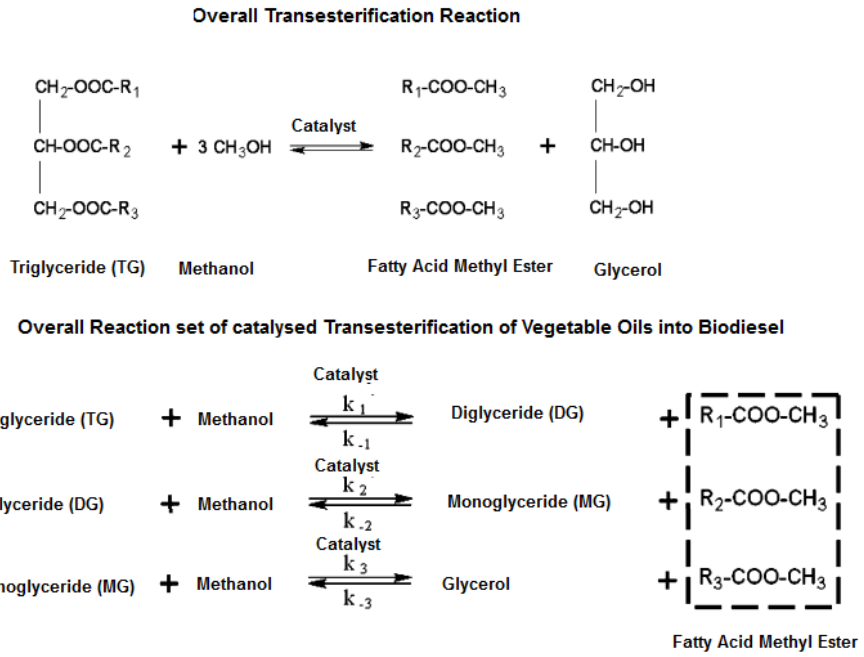

Figure 2.1 - Transesterification reaction of fats in biodiesel (Chang and Liu, 2010).

A fatty acid is a monocarboxylic group attached to a hydrocarbon chain of variable length and which may or may not have double bonds. The fatty acids in figure 2.1 are represented by the groups R, R 'and R ''. For a given triglyceride these groups may all be the same, or combinations of two or three different fatty acids. In this way, the resulting biodiesel will also verify this difference in the fatty acid groups. Thus, depending on the type of oil used as raw material, the resulting biodiesel will also reflect different properties caused by the variety in the fatty acids that make up the biodiesel (Biodiesel, 2017).

2.2 Raw Material

Chemically, the main raw material used in the production of biodiesel are fats or triglycerides. Despite this, the processes of transformation of the triglycerides into biodiesel and the physicochemical characteristics required for biodiesel, impose restrictions on the quality of the raw material to be processed. Parameters such as water and the levels of free fatty acids in solution should be carefully monitored, since their presence above threshold levels compromises the viability of the production process. In addition, to ensure the viability of the use of biodiesel in diesel engines, any biodiesel placed on the market must present several of physico-chemical characteristics such as cloud point that ensure that it is a standard product.

In this way its effect on the diesel engine is predictable, and therefore controllable (EUBIA, 2017).

The main source of triglycerides used in the production of biodiesel are refined vegetable oils from oilseed crops such as rapeseed, sunflower, peanut, soybean, palm, etc. After the cultivation and harvesting of the seeds, the oil is extracted by processes such as solvent extraction or mechanical pressing of the seeds, and subsequent harvesting of the released oil, due to the pressing process (EUBIA, 2017). Certain sources of raw material, although not ideal, can also be used to produce biodiesel, even though they require a pre-treatment in order to make the process viable. These are the fried oil discarded after several uses and unused animal fats (Canakci and Van Gerpen, 2001).

Thus, a vegetable oil or a fat, consists of a mixture of many components, where most of them are triglycerides, ie a glycerol molecule esterified with three fatty acids. Even so, the composition in terms of triglycerides varies according to the type of seed and the growing conditions. In addition to triglycerides, other components are also found in solution, albeit in much smaller quantities, such as diglycerides, monoglycerides, free fatty acids and residual amounts of water. What distinguishes triglycerides from one another are fatty acid chains. Thus the characterization of the oil is given depending on the type and amount of fatty acid in the oil (Chang and Liu, 2010). A particular fatty acid is characterized by two parameters, the number of carbons and the number of double bonds. Thus, a myristic acid (14: 0) has fourteen carbons and zero double bonds in the chain. In turn, an oleic acid (18: 1) has eighteen and one double bond (Biodiesel, 2017). Table 2.1 shows the mass percentage composition of fatty acid for various types of vegetable oils.

Table 2.1. Composition (mass percentage) of vegetable oils from different sources (Ramos et al., 2009)

Fatty Acid	ID	Palm	Olive	Soy	Sunflower	Almond	Corn
Lauric	**C12:0**	0,10	0,00	0,00	0,00	0,00	0,00
Myristic	**C14:0**	0,70	0,00	0,00	0,00	0,00	0,00
Palmitic	**C16:0**	36,70	11,60	11,30	6,20	10,40	6,50
Palmitoleic	**C16:1**	0,10	1,00	0,10	0,10	0,50	0,60
Stearic	**C18:0**	6,60	3,10	3,60	3,70	2,90	1,40
Oleic	**C18:1**	46,10	75,00	24,90	25,20	77,10	65,60
Linoleic	**C18:2**	8,60	7,80	53,00	63,10	7,60	25,20
Linolenic	**C18:3**	0,30	0,60	6,10	0,20	0,80	0,10

Analyzing table 2.1 it is possible to verify how palmitic, oleic and linoleic acid are those that are verified in greater quantity for the different sources presented.

2.3 Biodiesel Production

The most widely applied and widespread reaction mechanism for biodiesel production is alkaline transesterification, ie the reaction of a vegetable oil with an alcohol in excess, in the presence of an alkaline catalyst, such as sodium hydroxide or potassium hydroxide, to give biodiesel and glycerol. The advantages that lead to the preference of this to other processes are the fact that this is a process at low pressure and temperature, which makes it safer and cheaper. It presents a high yield (> 98%), with few lateral reactions and of small extension (if the raw material quality is secured) and presents a direct conversion of reagents into final product, without intermediates (EUBIA, 2017).

The alkaline transesterification may be carried out in a closed system at a pressure of about 1.4 bar and at a temperature between 50 and 65 °C, the maximum temperature chosen limited by the boiling point of the solvent. Excess alcohol is used to ensure the maximum possible conversion of oils into biodiesel. Being the ratios of 1 to 6 or 1 to 12, moles of oil to moles of alcohol, examples of molar ratios found in the literature (EUBIA, 2017). The first step in the process is the blending of a strong base with a small chain alcohol. The dissolution of the hydroxide in the alcohol leads to the formation of an alkoxide (conjugate base of an alcohol) (Chemistry, 2017). This is the ionic species responsible for the catalytic process. Expression (1) shows this equilibrium when the alcohol used is methanol (Eze et al., 2014):

$$\mathrm{CH_3OH + OH^- \leftrightarrow CH_3O^- + H_2O} \qquad (1)$$

The mixture is then fed to the reactor, and the vegetable oil stream is then added. The residence time may vary from 1 to 8 hours. After being withdrawn from the reactor, the mixture is neutralized in order to interrupt the reaction and then decanted. Decantation results in two distinct phases, the lighter, corresponding to biodiesel and the heavier phase, composed mostly of glycerol, methanol and some water. The biodiesel obtained by decantation will still be subjected to a purification process which may include washing with water and subsequent distillation, in order to remove as much alcohol as still exists in solution. Concerning the heavy phase, methanol is first removed by distillation. The resulting glycerol is then purified to obtain glycerin, which consists of glycerol having a purity above 95% by mass. Figure 2.2 shows a simplified diagram of a biodiesel production process from vegetable oils (EUBIA, 2017):

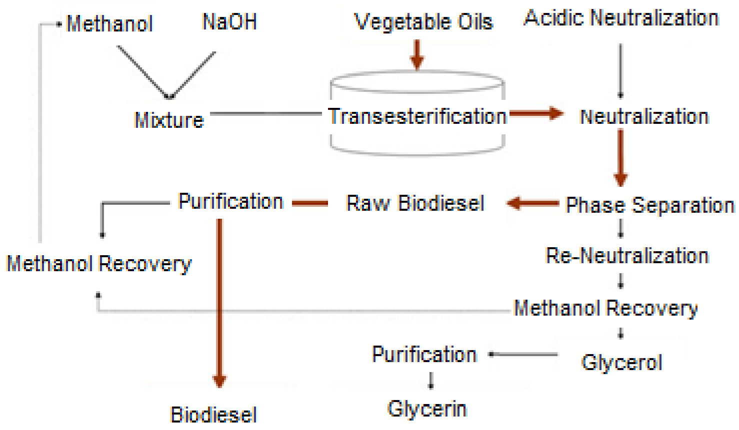

Figure 2.2 - Simplified scheme of the Alkaline Transesterification process (EUBIA, 2017).

One of the limitations of the alkaline transesterification process is the sensitivity of the process to the presence of water and free fatty acids in solution. The presence of water under alkaline conditions leads to saponification of the esters, ie both tri, di and mono glycerides, as well as biodiesel react with sodium hydroxide (dissolved) to form soaps. The free fatty acids also react to form soap and more water. The formation of soap is irreversible, consuming both catalyst and biodiesel itself, reducing the reaction yield. Another problem associated with the formation of soaps are the emulsions caused by their presence in the reaction mixture, leading to problems in the separation and purification steps. Thus, for any alkaline transesterification process, dehydrated refined oil with a fatty acid level below 0.5% by mass should be used. Also the alcohol and the alkaline catalyst must be in anhydrous conditions (Zhang et al., 2003).

In addition to the process of alkaline transesterification of refined vegetable oils, it is also possible to perform alkaline transesterification using residual oils from the hotel and food industry. The problem with these oils lies in the levels of free fatty acids that are well above 0.5% by mass. Thus, in order to reduce the level of fatty acids to acceptable levels an initial acid esterification step is added so as to convert the free fatty acids into biodiesel. Thus, free fatty acids react with an excess of an alcohol (1: 6 moles of fatty acids to moles of alcohol) in acidic medium to give biodiesel and water. The catalyst used is a strong acid, such as sulfuric acid, being added in an amount of 1% by mass of oil. After the acid esterification, the water formed must be withdrawn before the reaction mixture is fed to the alkaline transesterification step, from which point the process follows the path shown in figure 2.2. Although in an acid medium, the oils (tri, di and monoglycerides) also react with methanol to give biodiesel. Even so, the speed of these reactions are much lower when compared to the rate of reaction of the fatty acids to give biodiesel (Sendzikiene et al., 2004).

2.4 Specifications imposed on produced biodiesel

The produced biodiesel must comply with a series of physico-chemical characteristics in order to ensure the best possible operation in diesel engines. Table 2.2 shows the parameters imposed on biodiesel produced for commercial purposes in the European Union, supplied under standard 14214 (Rutz and Janssen, 2006).

By analyzing table 2.2 it is possible to verify the requirements imposed on biodiesel. Of those presented, the following should be highlighted: the purity level of the FAMEs should be higher than 96.5% by mass; The levels of triglycerides, diglycerides and monoglycerides are each below 1% by mass; The density at 15 ºC should be between 860 and 900 kg/m^3. The acidity, ie the free fatty acid content in solution should be less than 0.5 mg KOH / g oil, which corresponds to a value of about 1% by mass of fatty acids per mass of oil. The water content must not exceed 500 mg per kg of oil.

Table 2.2. General requirements applied to Biodiesel in the European Union and respective test methods (Rutz and Janssen, 2006).

Property	Unit	Minimum	Maximum	Testing Standard
Esters Content	% (m/m)	96.5	-	pr EN 14103
Density (15 ºC)	kg/m^3	860	900	EN IS0 3675 EN IS0 12 185
Viscosity (40 ºC)	mm^2	3.5	5	
Flash Point	ºC	ABOVE 101	-	IS0 / CD 3679
Sulphur Content	mg/kg		10	-
Carbon Residue	%(m/m)	-	0.3	EN IS0 10370
Cetane Number	-	51.0	-	EN IS0 5165
Ash content Sulfated	%(m/m)	-	0.02	IS0 3987
Water Content	mg/kg	-	500	EN IS0 12937
Total Contamination	mg/kg	-	24	EN 12662
Cooper Strip Corrosion	rating	Class 1	Class 1	EN IS0 2160
Thermal Stability	-	-	-	-
Stability at Oxidation (T = 110 ºC)	hr	6		prEN 14112
Acidity	mg KOH/g	-	0.5	pr EN 14104
Iodine Number	-	-	120	pr EN 14111
Methyl Esters of Linolenic Acid Content	%(m/m)	-	12	pr EN 14103
Methyl Esters Polyunsaturated Content	%(m/m)	-	1	-
Methanol Content	%(m/m)	-	0.2	pr EN 14110
Monoglyceride Content	%(m/m)	-	0.8	pr EN 14105
Diglycerides Content	%(m/m)	-	0.2	pr EN 14105
Triglyceride Content	%(m/m)	-	0.2	pr EN 14105
Free Glycerol	%(m/m)	-	0.02	pr EN 14105 pr EN 14106
Total Glycerol	%(m/m)	-	0.25	pr EN 14105
Alkaline metals (Na + K)	mg/kg	-	5	pr EN 14108 pr EN 14109
Phosphorus Content	mg/kg	-	10	pr EN 14107

3 Computer Simulation – Aspen Plus V 8.4

3.1 Thermodynamic Models

A chemical process simulator consists of software capable of reproducing the behavior of chemical processes. A chemical process can be analyzed as a thermodynamic system in which phenomena such as chemical reaction, mass transfer, heat transfer and energy transformations occur (Labvirtual, 2017). Thermodynamics is the science that studies energy and its transformations. More specifically, classical thermodynamics deals with equilibrium situations and energy phenomena verified at the macroscopic level. In thermodynamic sense a system can be defined as a part of the universe delimited for study. The delimitation constitutes the frontier, which is only imaginary. This boundary may also be mobile or not and coincide with physical barriers. The system may be closed or opened, depending on whether there is mass transfer across the frontier and the system can be isolated, depending on whether there are heat exchanges between the system and the neighborhood. In this way, in the system and between the system and its vicinity can occur phenomena of chemical reaction and transfer of mass and heat, resulting in a chemical process. In a simulation environment a unit operation constitutes a system in which chemical processes are verified. The choice of the type of process to be simulated is therefore dependent on the chosen unit operation (Aspentech, 2001).

The characterization of a given unit operation and its input and output streams is done through properties or quantities. These quantities that characterize the system thermodynamically can be divided in so-called intensive and extensive system properties. The former, such as pressure, temperature, density, among others, do not depend on the extent of the system. For the latter, the opposite is true, that is, they depend on the extension of the system, such as mass and volume. The intensive and extensive system properties can also be characterized as thermodynamic state variables or functions. In order to generate results, it is necessary to determine the physical properties that characterize the system, divided in thermodynamic properties such as fugacity coefficients, enthalpy, entropy, Gibbs free energy, molar volume and transport properties, such as viscosity, thermal conductivity, etc. The properties directly linked to the mathematical models of unit operations are designated by major properties. This property may depend on other property which is also a major property or it can also depend on other property that is not a major property. These properties that do not constitute major properties can be divided into subordinate properties and intermediate properties. A subordinate property may depend on another major, intermediate, or subordinate property, however they are not directly necessary for calculating the mathematical models for the different unit operations. Intermediate properties, on the other hand, depend neither on the major properties nor on the subordinate properties (Aspentech, 2001).

The calculation of major and subordinate properties is performed by a method. An intermediate property is calculated by model evaluation (Aspentech, 2001).

A method (in Aspen context) is an equation used to calculate physical properties based only on universal scientific principles, such as thermodynamics or transport methods. The equation may contain assumptions, as well as the need for state properties and variables but will not depend on correlation parameters to calculate a specific property. A model (Aspen context) consists of one or more equations used to determine a property and includes state variables, universal parameters, and correlation parameters as input variables. In this way the value of each property required for a given method is obtained by another method or another model. The calculation of the top properties is dictated by the property name, associated method, major and subordinate properties, name of the model associated with each intermediate property. This information constitutes a route. Note that it is not mandatory for a method to have a major or subordinate associated property, however, if it does, the route will depend on sub-level routes. The number of levels that can exist in a route is variable, however each level depends on the information listed in the previous level to be completely defined. In this way an information tree is formed which ends in the model, since this one does not depend on lower level information (Aspentech, 2001).

In order to produce results that do not change over time it is necessary to achieve the equilibrium state, namely phase equilibrium. In terms of chemical equilibrium, this can be achieved however, for irreversible reactions the composition of the system will depend on the chemical kinetics, thus not assuming the chemical equilibrium (Aspentech, 2001).

The phase equilibrium state means that the composition of the components that make up the different phases do not change over time. All of the irreversible processes that occur at constant pressure and temperature are in the direction of decreasing Gibbs Free energy, ie (Pimenta, 2015):

$$(dG)_{P,T} \leq 0 \qquad (2)$$

Equation (2) shows that for a closed system the equilibrium state is that for which Gibbs Free energy is minimal, so in equilibrium (Pimenta, 2015):

$$(dG)_{P,T} = 0 \qquad (3)$$

This is the general criterion of equilibrium that can be applied to both phase equilibrium and chemical equilibrium (Pimenta, 2015).

Another possible way of representing phase equilibrium, namely a liquid vapor equilibrium, is that expressed in equation (4), which dictates the equality between the fugacity of a component *i* in the vapor phase (f_i^v) and the fugacity of this same component *i* in the liquid phase (f_i^l) (Aspentech, 2001):

$$f_i^v = f_i^l \qquad (4)$$

Applied thermodynamics provides two distinct ways for calculating fugacities in a phase equilibrium situation, as a function of measurable variables. These are the determination through an equation of state method, or through a method for determining the liquid phase activity coefficients (Aspentech, 2001).

For an equation of state method (Aspentech, 2001):

$$f_i^v = \varphi_i^v y_i p \qquad (5)$$

$$f_i^l = \varphi_i^l x_i p \qquad (6)$$

Being that φ consists of the fugacity coefficient of the liquid phase (l) or the vapor phase (v). The molar fraction of the component *i* in the vapor phase is given by y_i and in the liquid phase is given by x_i. p is the system's pressure, wich can be replaced by an equation of state. The equation of state is then used to determine the coefficients of fugacity (Aspentech, 2001).

Regarding the the activity coefficient method (Aspentech, 2001):

$$f_i^v = \varphi_i^v y_i p \qquad (7)$$

$$f_i^l = x_i \Upsilon_i f_i^{*,l} \qquad (8)$$

Where Υ_i is the liquid activity coefficient of component *i* e $f_i^{*,l}$ the liquid fugacity of pure component *i*, at the temperature of the mixture. Again, for equation (7) the coefficient of fugacity for the vapor phase is calculated using an equation of state. However, for equation (8) it is necessary to determine the liquid activity coefficient for the different components (Aspentech, 2001).

Each property method in Aspen is based either on an equation of state method or on an activity coefficient method to perform vapor-liquid equilibrium description. The method for determining the phase equilibrium determines how other properties will be calculated, such as enthalpy or molar volume. So if an equation of state method is used, all the properties can be derived from the equation of state, for both phases. Using an activity coefficient method, the properties of the vapor phase are calculated using an equation of state and the properties of the liquid phase are determined by summing the properties of the pure components, at the temperature of the mixture, to which is added a mixing or excess term (Aspentech, 2001).

An equation of state consists of a constitutive equation that describes the (P, T, V) (Pressure, Temperature, Volume) of pure components and mixtures, and is usually explicit in relation to pressure (Aspentech, 2001).

Regarding to models, these can also be divided into equation of state models and activity coefficient models (Aspentech, 2001).

The simplest equation of state consists of the ideal gas equation. The ideal gas law assumes that molecules have no size and do not interact with each other. Nevertheless, an ideal equation of state is only valid for certain conditions. In other situations another type of equation of state should be used, such as the cubic equation of state and the virial equations of state. Still, it should be remembered that the concept of ideality described applies to gases, being the concept of ideality very different when it comes to a liquid. In an ideal solution, the components present in the solution are all the same size and are randomly distributed. This assumption is valid for mixtures whose components are of identical size and have poor molecular interactions. If the opposite occurs, ie a multicomponent liquid system, with the components varying greatly in size and polarity type, then one would expect a marked deviation from the ideal behavior caused by size and energy asymmetry. The deviation from ideality for a liquid solution is quantified by the coefficient of activity Υ_i. The more this value deviates from unity the larger is the deviation from ideal solution behavior (Aspentech, 2001).

In this way, being the components that constitute the production of biodiesel, different both in size and in polarity character it is presumed to be a mixture with a significant deviation from ideality, caused by the already mentioned asymmetries of energy and size. In addition to these, the influence of electrolytes in solution must be taken into account, which further aggravate the effects of non-ideality. In this way, the first thermodynamic model adopted account for the simulation was the ElecNRTL model. This thermodynamic model fits into the activity coefficient models for the liquid phase. It is a suitable model for electrolytic solutions of any strength and is also suitable for solutions with various solvents (Aspentech, 2001).

Since, during the use of the ElecNRTL model, difficulties were detected in the phase separation step, this model was used only in the reaction stage, and the UNIFAC model was adopted for the separation phase (Aspentech, 2001).

The UNIFAC model also fits into the liquid-phase activity coefficient models, forming part of the subgroup of the so-called group-contribution models. This is a predictive model for non-electrolyte solutions which can be applied for the evaluation of liquid-vapor and liquid-liquid equilibria (Aspentech, 2001).

3.2 Process description

The overall biodiesel production process is shown in Figure 3.1. In the current work, two simulations were developed and performed, each of them constituting an executable file. Thus, the process illustrated in Figure 3.1 consists of the overlapping of these two simulated processes. The first executable file, or the first simulation, uses the thermodynamic model ElecNRTL and is used to model the chemical reaction. The unit blocks belonging to it correspond to the three reactors: ACIDICST1, ACIDICST2, ALKALTR1. In the second simulation, the UNIFAC thermodynamic model was used for the modeling carried out in relation to the decanting and flash separations (distillation). Apart from chemical reactors, all other units belong to the second simulation.

The beginning of the process can be seen in the upper left corner of Figure 3.1. The first stage of the process, the acid esterification, is composed of the first two reactors: ACIDICST1 and ACIDICST2. The OIL1 stream consists of the raw material, oil with high content of free fatty acids (25% w/w). This stream is fed to the ACIDICST1 reactor, together with an excess of methanol and the catalyst, concentrated sulfuric acid. After the first reactor the PROD1 mixture is decanted into DEC1, from which two phases result, the light, LTPHASE, and the heavy, HEPHASE. The light phase comprising of oil and biodiesel is fed to a second reactor in order to increase the conversion of the fatty acids. Methanol in excess, MET2 is also fed into the reactor. After reduction of the free fatty acid content the reaction mixture is again decanted now in DEC2, where a stream of glycerol is also added to remove as much water as possible. From this decanter, two phases result. The oil phase plus biodiesel, LTPHASE2 is then conducted to the alkaline transesterification step, ALKALTR1. In this reactor the excess methanol and the catalyst are also admitted, sodium hydroxide dissolved in a stream of methanol resulting in the equilibrium of the methylate ion. After the chemical reaction step, separation and purification are followed. Biodiesel mixed with methanol and glycerol, PROD3, is decanted in the third decanter, DEC3, from which two streams exit. The lightest one is biodiesel with methanol and small amounts of soap and water. The heavier stream is composed mostly of the excess methanol used in the reaction step and the glycerol formed also in this step. Biodiesel is now fed to a flash drum, FLASHSP2, further reducing its content in methanol and water. From this stage leaves the final biodiesel, FAME, and a small amount of methanol and water, METREC2. HEPHASE 1, HEPHASE2 and AQPHASE streams are also distilled so as to separate and recover methanol, METREC1, from glycerol, GLYREC, in FLASHSP1. HEPHASE 4 is not added to this drum because it contains a lot of water, so it would make no sense to add water to the other fed streams to FLASHSP1, just to separate it again further down the process line.

Table 3.1 compiles the process streams and presents a brief description of each. Table 3.2 shows the same type of information regarding the unit blocks of the simulation.

Table 3.1. Process streams and their description.

Stream	Short Description
OIL1	Oil with high content of free fatty acids. Initial raw material.
MET1	Excess methanol fed to ACIDICST1 reactor.
SULFAC1	Sulfuric acid catalyst used in the ACIDICST1 reactor.
PROD1	ACIDICST1 reactor products. Vegetable oils plus biodiesel converted from the free fatty acids..
LTPHASE1	Lighter phase of decanter DEC1. Mostly vegetable oils and biodiesel.
HEPHASE1	Heavier phase of decanter DEC1. Methanol plus water from esterification reaction.
MET2	Excess methanol fed to ACIDICST2 reactor
PROD2	ACIDICST2 reactor products. Increased conversion of free fatty acids.
GLYCEROL	Glycerol fed to decanter DEC2 to promote separation of water.
LTPHASE2	Lighter phase of decanter DEC2. Mostly vegetable oils and biodiesel.
HEPHASE2	Heavier phase of decanter DEC2. Glycerol plus methanol and water.
MET3	Excess methanol fed to the ALKALTR1 reactor.
NAOHYMET	Catalyst, sodium hydroxide dissolved in methanol, resulting in the equilibrium of the methylate ion, which is the catalytic species of the alkaline transesterification reaction, taking place at ALKALTR reactor.
PROD3	Products of the ALKALTR reactor. Biodiesel, methanol, glycerol, small amounts unreacted oils, soap and water.
OILPHASE	Mostly biodiesel.
AQPHASE	Glycerol plus methanol, water, soaps, among others.
WATER	Water for washing, with an acidity level in order to reduce the alkalinity of biodiesel.
LTPHASE4	Biodiesel with a small fraction of methanol and water.
HEPHASE4	Mostly water.
METREC1	Methanol flashed from glycerol.
GLYREC	Recovered Glycerol Stream.
METREC2	Small amount of methanol and water flashed from biodiesel (LTPHASE4).
FAME	Biodiesel.
FAMEREC	Small amount of biodiesel separated from glycerol and methanol.

Table 3.2. Brief description of the unit blocks used in the simulation.

Block	Short Description
ACIDICST1 **ACIDICST2**	First and second reactor of acid esterification. CSTR Reactor - "Continuous Stirred Tank Reactor".
ALKALTR1	Alkaline transesterification reactor. CSTR reactor.
DEC1, DEC2 **DEC3, DEC4**	Decanters.
FLASHSP1 **FLASHSP2**	Flash Drums.

Thus, the overall process is composed of three chemical reactors, four decanters and two flash drums. Chemical reactors are modeled in the process by the "Continuous Stirred Tank Reactor" model. This type of model corresponds to a reactor for which perfect agitation and therefore uniformity of properties throughout the reactor, namely concentration, temperature, pressure, reaction rate, etc., is assumed.

Decantation processes are modeled in decanters units. In this block, liquid-liquid calculations are performed assuming the formation of only two liquid phases.

Single stage separators are modeled in knock-out drums FLASHSP1 and FLASHSP2. In the first a vapor-liquid-liquid equilibrium is assumed for stage calculations and in the second, a vapor-liquid equilibrium is assumed for the same purpose as the former one.

There are twenty-three streams, the main components of the simulation being vegetable oil, methanol, biodiesel, sodium hydroxide, sulfuric acid, their respective electrolytes and soap.

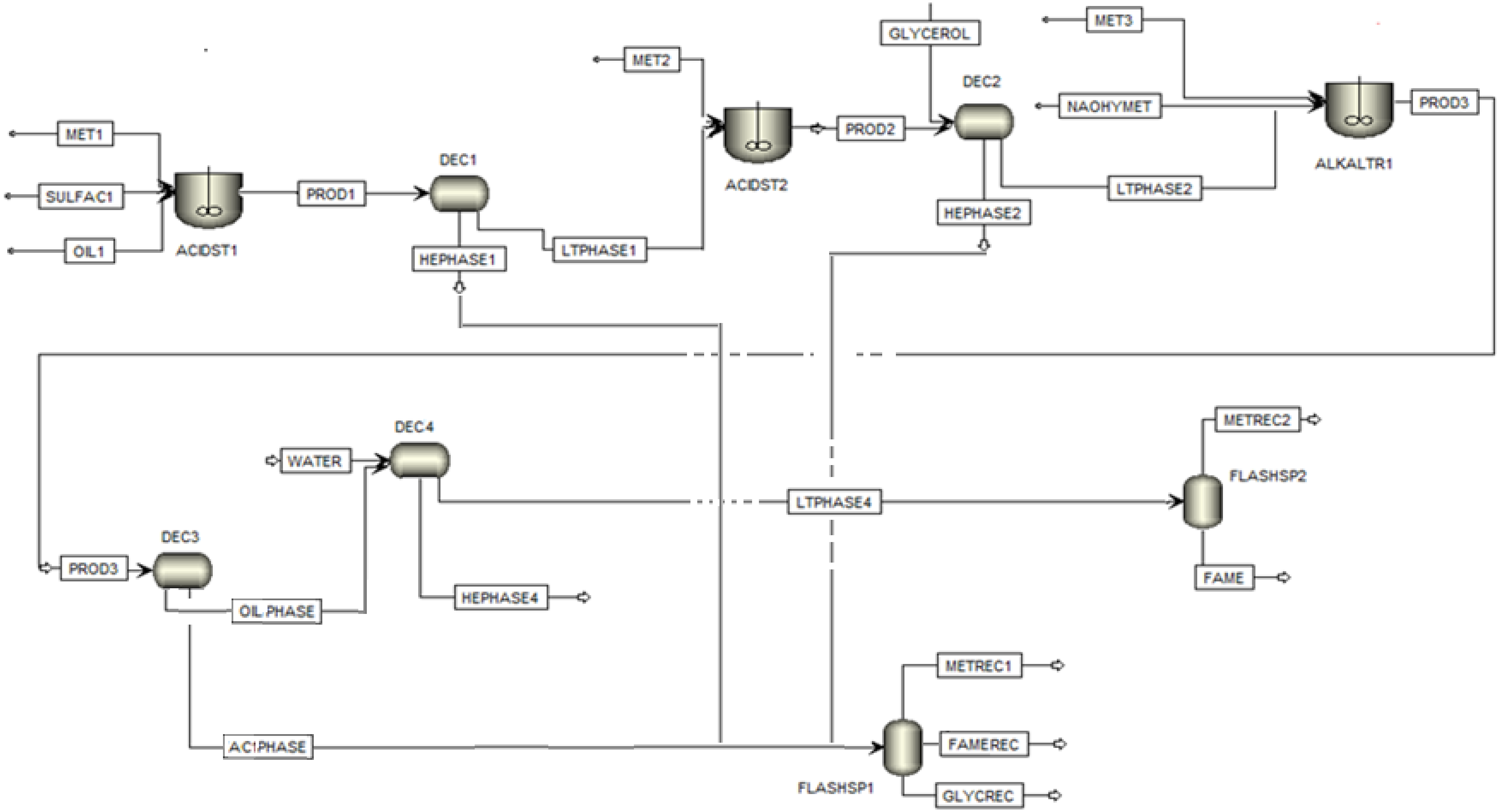

Figure 3.1 – Global Simulation of biodiesel production.

3.3 Input List

The input list performed in the two simulations is presented here using the sequence of the process presented in Figure 3.1. Table 3.3 shows the complete list of components used. This differs between the two simulations since the second simulation does not include the electrolytes, NaOH and H_2SO_4, ions, nor the electrolytic equilibria (acid-base reactions, formation / dissociation of salts, etc).

Table 3.3. List of Components used in the simulation.

Component ID	**Component Name**	**Chemical formula**	**Thermodynamic Model***	**Aspen Database**
TG	Triolein	$C_{57}H_{104}O_6$	ElecNRTL ; UNIFAC	APV84.PURE28
DG	Diolein	$C_{39}H_{72}O_5$	ElecNRTL ; UNIFAC	APV84.PURE28
MG	2-Monoolein	$C_{21}H_{40}O_4$	ElecNRTL ; UNIFAC	APV84.BIODIESEL
FFA	Oleic Acid	$C_{18}H_{34}O_2$	ElecNRTL ; UNIFAC	APV84.PURE28
FAME	Methyl Oleate	$C_{19}H_{36}O_2$	ElecNRTL ; UNIFAC	APV84.PURE28
SOAP	Sodium-Oleate	$C_{18}H_{33}NAO_2$	ElecNRTL ; UNIFAC	NISTV84.NIST-TRC
METHANOL	Methanol	CH_4O	ElecNRTL ; UNIFAC	APV84.PURE28
GLYCEROL	Glycerol	$C_3H_8O_3$	ElecNRTL ; UNIFAC	APV84.PURE28
WATER	Water	H_2O	ElecNRTL ; UNIFAC	APV84.PURE28
CH3NaO	Sodium-Methylate	CH_3NaO	ElecNRTL ; UNIFAC	APV84.PURE28
NaOH	Sodium-Hydroxide	NaOH	ElecNRTL	APV84.PURE28
H_2SO_4	Sulfuric-Acid	H_2SO_4	ElecNRTL	APV84.PURE28
Na^+	Sodium ion	Na^+	ElecNRTL	APV84.AQUEOUS
H^+	Hydrogen ion	H^+	ElecNRTL	APV84.AQUEOUS
NaOH(S)	Sodium Hydroxide Solid	NaOH	ElecNRTL	APV84.SOLIDS
NaOH:(S)	Hydrated Sodium Hydroxide Solid	NaOH*H2O	ElecNRTL	APV84.SOLIDS
SODIU(S)	Sodium-Sulfate Solid	$NaSO_4$	ElecNRTL	APV84.SOLIDS
OH^-	Hydroxide ion	OH^-	ElecNRTL	APV84.AQUEOUS
HSO_4^-	Hydrogen Sulfate	HSO_4^-	ElecNRTL	APV84.AQUEOUS
SO_4^{--}	Sulfate	SO_4^{--}	ElecNRTL	APV84.AQUEOUS

Thus, as already mentioned in subchapter *2.2 - Raw Material*, an oil is a compound with several molecular elements. The common feature is the existence of a glycerol molecule whose hydroxyl groups will be esterified with a minimum of one, up to a maximum of three, fatty acid chains, which may or may not be the same as one another. A common simplification, carried out in such a way as to model the behavior of an oil, is to assume that the oil is constituted only by one of the components that form part of its constitution. This component is a triglyceride called Triolein. This is composed by the same fatty acids, with eighteen carbons and one double bond named oleic acid (Chang and Liu, 2010). In addition to Triolein (three), Diolein and Monolein were also introduced. These consist of the diglyceride and monoglyceride molecules associated with triolein, each consisting of two and one oleic acid, respectively. In this way, the other components associated, directly or indirectly, with the oil, have the oleic acid in its constitution. That is, the FFAs, or free fatty acids in the oil, are modeled using oleic acid. FAMEs, or methyl esters of fatty acids, are modeled using methyl oleate, which corresponds to biodiesel formed by the reaction of an oil, composed of oleic acid, with methanol. The soap corresponds to the sodium oleate. Again, an oil composed by oleic acid, reacts with sodium ion to form the soap, SOAP.

As already mentioned in subchapter *2.3 Biodiesel production*, the ionic species that catalyzes the alkaline transesterification, corresponds to the conjugated base of the alcohol used in the reaction. Thus, in this situation, the catalytic species corresponds to the methylate ion (CH_3O^-). This species was not found in any database presented in Table 3.3. The other known alternative was the introduction of the compound in the simulation, however, the amplitude of the work required to make an adequate characterization in terms of the properties and parameters of the compound needed by the methods and models used in the simulation was unknown. So, this option was not followed. Although the methylate ion has not been found, a compound that already exists in an Aspen database is sodium methylate. This compound corresponds to the methylate salt in aqueous phase. In this way, the sodium methylate compound was chosen, so as to be a species resulting from an electrolytic equilibrium to catalyze the transesterification reaction in the simulation. Thus, reaction (1), presented in *chapter 2.2*, becomes:

$$\mathrm{CH_3OH + Na^+ + OH^- \leftrightarrow CH_3NaO + H_2O} \quad (10)$$

In fact, instead of reaction (10) reaction (1) should be placed as well as the formation / dissociation equilibria of the sodium methylate salt in water and methanol. In these three reactions would be present the methylate ion, which should be the one, instead of the salt, to be defined as the catalytic species of the transesterification reaction.

The ionic species presented, resulting from the dissociation of sulfuric acid and sodium hydroxide, are automatically generated by the simulation. It includes the solids shown: sodium hydroxide, hydrated sodium hydroxide and sodium sulfate.

Tables 3.4 and 3.5 present the variables and their scalar arbitrated / introduced with respect to stream variables and block variables (unit operation). These variables constitute the degrees of freedom of the system (simulation), and the imposition of values for each of these variables constitutes the minimum number of variables to be defined, so that the system of equations that characterize the process is possible and determined. Each cell in the table that has a “-“ mark represents a variable whose value is determined by the simulation. Cells that contain DESIGNSPEC refer to variables that have been defined by design specification. This means that its value is determined by some type of expression or equality, thus enabling the value of the variable to be defined in terms of another variable or variables. The variables defined in this way were the molar flows of methanol fed to the two first reactors and the mass flow rates of the catalysts in the acidic esterification step. In addition to the design specification, an optimization was also performed in order to obtain the molar flow rate of methanol and sodium hydroxide to be fed to the third reactor in order to maximize production.

Table 3.4. Stream variables specifications.

Stream ID	Temperature (ºC)	Pressure (bar)	Mass Flow (kg/h)	Mass Percentage Compositon	Thermodynamic Model
OIL1	60	1	1000	TG - 70; DG - 4; MG - 1; FFA - 25	ELECNRTL
MET1	60	1	DESIGN-SPEC1	Methanol -100	ELECNRTL
SULFAC1	60	1	DESIGN-SPEC3	H_2SO_4 - 98 ; Water - 2	ELECNRTL
PROD1	-	-	-	-	ELECNRTL; UNIFAC
LTPHASE1	-	-	-	-	ELECNRTL; UNIFAC
HEPHASE1	-	-	-	-	UNIFAC
MET2	60	1	DESIGN-SPEC2	Methanol -100	ELECNRTL
PROD2	-	-	-	-	ELECNRTL; UNIFAC
GLYCEROL	60	1	100	Glycerol - 100	UNIFAC
LTPHASE2	-	-	-	-	ELECNRTL; UNIFAC
HEPHASE2	-	-	-	-	UNIFAC
MET3	60	1	OPTIMIZATION1	Methanol -100	ELECNRTL; UNIFAC
NAOHYMET	60	1	OPTIMIZATION1	NaOH – 90; Methanol - 10	ELECNRTL; UNIFAC
PROD3	-	-	-	-	ELECNRTL; UNIFAC
LTPHASE3	-	-	-	-	UNIFAC
HEPHASE3	-	-	-	-	UNIFAC
WATER	10	1	500	Water - 100	UNIFAC
LTPHASE4	-	-	-	-	UNIFAC
HEPHASE4	-	-	-	-	UNIFAC
METREC1	-	-	-	-	UNIFAC
GLYREC	-	-	-	-	UNIFAC
METREC2	-	-	-	-	UNIFAC
FAME	-	-	-	-	UNIFAC

As can be seen in Table 3.4, the inputs are relative to the input streams of the blocks, the value of the output stream variables being obtained by calculation of the simulation. For the blocks or unit operations the operating conditions that fulfill the degrees of freedom are defined and the simulation provides results that vary depending on the specific block.

Table 3.5. Block specifications.

Block ID	Block Type	Temperature (ºC)	Pressure (bar)	Valid Phases	Residence Time (min)
ACIDICST1	Reactor CSTR	60	1	Liquid (One Phase)	15
ACIDICST2	Reactor CSTR	60	1	Liquid (One Phase)	15
ALKALTR1	Reactor CSTR	60	1	Liquid (One Phase)	90
DEC1	Decanter	60	1	Liquid (Two Phases)	-
DEC2	Decanter	60	1	Liquid (Two Phases)	-
DEC3	Decanter	60	1	Liquid (Two Phases)	-
DEC4	Decanter	10	1	Liquid (Two Phases)	-
FLASHSEP1	Flash Drum	90	0.7	Vapor-Liquid-Liquid	-
FLASHSEP2	Flash Drum	95	0.7	Vapor-Liquid (One Phase)	-

The temperature remains virtually unchanged throughout most of the process. This corresponds to 60 ºC and is the optimum temperature of the biodiesel production reaction for both acid and alkaline esterification (Sendzikiene et al., 2004). The operating pressure throughout the process equals atmospheric pressure, with the exception being the flash drums, wich operate at about 0.7 bar.

The imposition of only one liquid phase in the reactors is due to the fact that these correspond to the CSTR model. Thus, with perfect agitation, only one phase is assumed and the volume to be taken into account when calculating the concentration of the components should be the total volume of the reactor.

The residence time in the reactional blocks is another variable to be introduced by the user. Relative to the acid esterification step this value was 15 minutes. This period is the time for which the kinetic model of the acid esterification part is valid (Sendzikiene et al., 2004). Thus the maximum residence time allowed for a reactor in the acid esterification step is only 15 minutes.

3.4 Design-Specification

The sizing specifications were three. The first two were named DESIGNSPEC1 and DESIGNSPEC2 and aimed to define the methanol feed to the ACIDICST1 and ACIDICST2 reactors. The methanol feed to the former reactor was given as six times the molar flow rate of free fatty acids (FFAs) in the OIL1 stream, only 80% of which is fed to the first reactor. The remaining 20% are fed to the second, thus defining the molar (and / or mass) flow rate of methanol to be fed to the two acid esterification reactors.

DESIGNSPEC3 defines the mass flow rate of sulfuric acid to be fed to the acid esterification reactor. The mass flow rate of concentrated sulfuric acid fed to the reactor was defined as 1% (w/w) of the oil flow fed to the first reactor (OIL1).

3.5 Optimization

The flow rate of the stream MET3 and NAOHYMET, and the residence time of the ALKALTR reactor, were obtained by optimization. The objective of the optimization was to maximize the production of FAMES, varying the flow rate of MET3 and NAOHYMET as well as the residence time of the third reactor. The range of variation for the mass flow rates was 150 to 500 kg/h (MET3) and 1 to 20 kg/h (NAOHYMET). The residence time was varied between 1 and 90 minutes. This optimization was subjected to a soap production restriction. This way the mass percentage of soaps in the PROD3 stream should never exceed 0.5% (w/w).

3.6 Reactions

In this simulation three sets of reactions can be defined. Two of them defined by the author, and the third by the electrolytic chemistry wizard of the simulator. The reactions defined by the author correspond to reactions of biodiesel production, both in acidic and alkaline media and also include some unwanted lateral reactions. The third set of reactions corresponds to electrolytic equilibria which include acid-base reactions and formation / dissociation of salts. These reactions are automatically generated by the simulation, depending on the chosen components and the thermodynamic model used. The three sets of reactions were applied to the three reaction blocks.

3.6.1 AcidicST

This set consists of only one reaction, the reaction of free fatty acids (FFA) with methanol to form biodiesel and water. This reaction occurs in the first two reactors due to the acid content of the medium.

Table 3.6. Acid esterification reaction and other parameters (Sendzikiene et al., 2004).

Acid Esterification	
Reaction	**FFA + METHANOL ----> FAME + WATER**
Reaction Phase	Liquid (One Phase)
Kinetic term	k.[FFA]
Rate Basis	Reactor Volume
Kinetic Factor, k (min^{-1})	$k_0 . T^n . e^{-E/RT}$
k_0 (min^{-1})	1,27
N	0
E (kJ/mol)	13,3
[C_i] Basis	Molarity

In Table 3.6 it is possible to consult the reaction of acid esterification and parameters of interest in the analysis of the reaction kinetics. Thus, the reaction medium is liquid, with only one phase. The reaction velocity is shown in terms of reactor volume. The kinetic factor is given by Arrhenius's Law, where k_0 is the pre-exponential factor, E is the activation energy of the reaction, T is the temperature of the medium and R is the ideal gas constant. The concentration of the species present in the kinetic term is given in terms of molarity (M), and only the presence of FFAs is taken into account in the kinetic term, since methanol is in excess and, therefore, is assumed constant throughout the residence time of the reactor.

3.6.2 AlkalineTR

Regarding the alkaline transesterification process, ten different reactions were taken into account. These can be seen in Table 3.7 and include the reactions between oils and methanol as well as the reactions that result in the formation of soaps. The reaction phase is liquid with only one phase. The reaction rate is given in terms of reactor volume.

Table 3.7. Kinetic parameters of alkaline transesterification (Eze et al., 2014).

Alkaline Transesterification	
Reaction	1 to 10 (Table 3.8)
Reacion Phase	Liquid (One phase)
Rate Basis	Reactor Volume
Kinetic constant k_i	$k_0 . T^n . e^{-E/RT}$
N	0
[C_i] Basis	Molarity

Table 3.8. Reactions taken into account in the alkaline transesterification model (Eze et al., 2014).

Alkaline Transesterification				
	Reaction	**k_0 (L^2 /(mol^2.s))**	**E (kJ/mol)**	**Kinetic Term**
1	**TG + METHANOL ----> DG + FAME**	7,10E+07	58,74	k_1.[TG].[MET].[CH_3NaO]
2	**DG + FAME ----> TG + METHANOL**	71730	44,93	k_2.[DG].[FAME].[CH_3NaO]
3	**DG + METHANOL ----> MG + FAME**	3,627E+09	67,146	k_3.[DG].[MET].[CH_3NaO]
4	**MG + FAME ----> DG + METHANOL**	1,09E+08	58,184	k_4.[MG].[FAME].[CH_3NaO]
5	**MG + METHANOL ----> GLYCEROL + FAME**	10447	30,01	k_5.[MG].[MET].[CH_3NaO]
6	**GLYCEROL + FAME ----> MG + METHANOL**	329200	46,009	k_6.[GLY].[FAME].[CH_3NaO]
7	**TG + 3OH^- + 3Na^+ ----> 3SOAP + GLYCEROL**	2,12E+09	69,104	k_7.[TG].([OH^-])
8	**FAME + OH^- + Na^+ ----> SOAP + METHANOL**	3,27E+08	61,16	k_8.[FAME].[OH^-]
9	**FFA + OH^- + Na^+ ----> SOAP + WATER**	10230	31,394	k_9.[FFA].[OH^-]
10	**FFA + CH_3NaO ----> SOAP + METHANOL**	613600	31,394	k_{10}.[FFA].[CH_3NAO]

3.6.3 Electrolytic Equilibria

The electrolytic reactions taken into account in the reaction stage of acid esterification and alkaline transesterification are presented in Table 3.9. The equilibrium constant value was determined by the simulation for all reactions except for the equilibrium found between the sodium hydroxide dissolved in methanol and the methylate ion plus water. However, as already mentioned in subchapter *3.3 Input List*, since, on the one hand the methylate ion was not found in any of the available databases and, on the other hand, it was not possible to create and carry out the characterization of the compound in terms of thermodynamic properties, the sodium methylate compound was introduced as an alternative to the methylate ion. It corresponds to the salt formed between the methylate anion and sodium cation. This compound is found in the simulation (and therefore in the reaction) in the aqueous phase. The equilibrium constant at 60 ° C is 3.2 (Eze et al., 2014).

The remaining reactions correspond to the equilibrium between aqueous sulfuric acid and the corresponding electrolytes, the electrolytic equilibrium of the water and the dissolution of solids in solution. In terms of solids dissolved in solution, these are sodium sulfate, sodium hydroxide and sodium hydroxide monohydrate. Once again, all these reactions were automatically generated by the simulation through the tool *Electrolyte Wizard*.

Table 3.9. Electrolytic reactions taken into account for the modeling of the acid esterification and alkaline transesterification processes

	Reaction
1	$H_2SO_{4\ (aq)}$ <---> $H^+_{(aq)}$ + $HSO_4^-{}_{(aq)}$
2	$HSO4^-{}_{(aq)}$ <---> $H^+_{(aq)}$ $SO4^{--}{}_{(aq)}$
3	WATER(l) <---> $H^+_{(aq)}$ + $OH^-_{(aq)}$
4	$METHANOL_{(l)}$ + $NA^+_{(aq)}$ + $OH^-_{(aq)}$ <---> $CH_3NaO_{(aq)}$ + $WATER_{(l)}$
5	$Na_2SO_{4(S)}$ <---> $Na^+_{(aq)}$ + $SO_4^{--}{}_{(aq)}$
6	$NaOH.H_2O_{(S)}$ <---> $Na^+_{(aq)}$ + $OH^-_{(aq)}$ + $H_2O_{\ (aq)}$
7	$NaOH_{(S)}$ <---> $Na^+_{(aq)}$ + $OH^-_{(aq)}$

4 Simulation Results

In this subchapter the results of the simulation are presented. This presentation is divided into topics, and a summary of the results is given in Table 4.21, which can be found at the end of the chapter. The topics are four, three of which correspond to key points in the process. Thus, in the first place, the results obtained in the conversion of the free fatty acids in biodiesel are presented. This constitutes the acid esterification step, to which the alkaline transesterification step follows. Here are the oils to be converted into biodiesel. At this point the reaction stage related to the production of biodiesel ends, passing to the washing and purification part. At the last point, the same results are presented but varying the temperature. This analysis is performed block (unit process operation in the simulation) by block.

To facilitate the reading of the results, the chaining of the same streams between different tables is made with the aid of colors. That is, consider the first example. The output stream, PROD1, of the first acid esterification reactor (ElecNRTL simulation) is shown in light blue in table 4.1. This stream will then be the stream given as input in the DEC1 decanter (UNIFAC simulation), whose representation can be seen, also in light blue, in table 4.3. This color-based chaining takes place until the end of the process and follows the same chaining logic. Y-color stream, shown in table 4.i, output of block X, gives entry to block W, whose representation is in table 4.j, in color Y.

4.1.1 Acid Esterification

The process part for acid esterification is given in Figure 4.1. In this zone are the reactors ACIDICST1 and ACIDICST2, as well as the decanters DEC1 and DEC2.

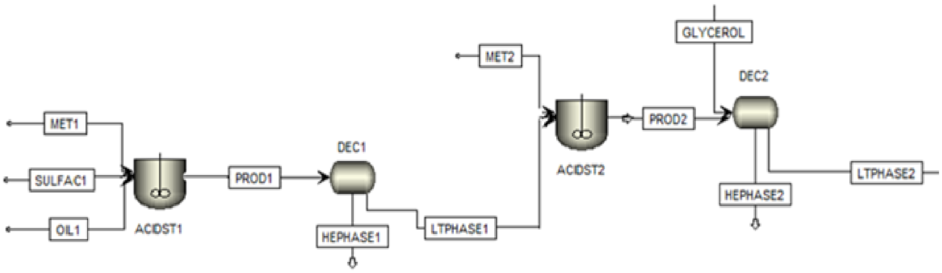

Figure 4.1. Acid esterification step.

The results for the first reaction block are presented in Table 4.1. A 1000 kg/h oil (OIL1) stream is fed to the reactor, together with a flow rate of 98% w/w concentrated sulfuric acid (SULFAC 1) and methanol (MET 1). The flow rate of sulfuric acid corresponds to 1% of the oil flow, and the methanol feed corresponds to 80% of a stream with six times the molar flow of the FFAs in the oil stream. After 15 min (residence time) the PROD1 stream is obtained. By analyzing the results, it can be seen that FFA levels fall from 250 kg/h to about 24 kg/h. Associated with the decrease of FFAs is the formation of FAMEs, which see their value go from 0 in the feed, to about 237 kg/h at the exit.

As already mentioned in subchapter *3.3 Input List*, the imposition of 15 min for residence time is due to the validity of the kinetic model being applicable only for this duration in time. In this way the volume of the reactor and the conversion of FFAs into FAMEs are also defined. The level of FFAs in the stream fed to the alkaline transesterification reactor should be below the limit of 0.5% (w/w). The violation of this threshold will result in a significant amount of soap and the consequent formation of emulsions will hinder the separation step. Thus, as in the first reactor output stream, this level (0.5%) is not reached, a second reaction block was added in the acid esterification part. The output stream of the first reactor is decanted and then fed to a second reactor, in which the conversion of the remaining FFAs is started. It should be noted that the division into two reactors is due only to the fact that the kinetic model of the acid esterification step, is valid only for the first 15 minutes. Therefore, it should not be assumed that the acid esterification step actually requires two reactors. In a real situation it is conceivable that there is only a need to increase the residence time in the first reactor in order to achieve the desired conversion. This possibility will depend on the value of the kinetic constants of the reactions in play, after the first 15 minutes.

Table 4.1. ACIDICST1 reactor input and output streams.

Reactor 1 – Acid Esterification				
Stream	**OIL1**	**SULFAC1**	**MET1**	**PROD1**
Component	**Mass Flow Rate kg/hr**			
TG	700	0	0	700
DG	40	0	0	40
MG	10	0	0	10
FFA	250	0	0	24,06
FAME	0	0	0	237,16
SOAP	0	0	0	0
METHANOL	0	0	136,12	110,49
GLYCEROL	0	0	0	0
WATER	0	0,20	0	14,61
CH_3NaO	0	0	0	0
NaOH	0	0	0	0
H_2SO_4	0	0	0	0,11
NA^+	0	0	0	0,0
H^+	0	0,10	0	0,10
NaOH(S)	0	0	0	0
NaOH:(S)	0	0	0	0
SODIU(S)	0	0	0	0
OH^-	0	0	0	0
HSO_4^-	0	9,68	0	9,59
SO_4^{--}	0	0,02	0	4,79E-05
Total	1000	10	136,12	1146,12
pH		-3,00		-2,83

Returning to the analysis of the first reactor output stream, it is verified that another product of the FFA conversion into FAMEs is water. About 15 kg/h of water leaves the reactor. The oils remain unchanged between the inlet and the outlet. The pH at the outlet and therefore in the reactor was close to -3, which corresponds to an extremely acidic medium.

Table 4.2 compiles the results of the sizing obtained for the ACIDICST1 reactor. The value of 438L was obtained for the reactor volume. The cooling duty of this isothermal reactor was 5.19 kW

Table 4.2. Results of the dimensioning of the ACIDICST1 Reactor.

Reactor	**ACIDICST1**
T_{OUT} (ºC)	60
P_{OUT} (bar)	1
Vapor Fraction	0
Heat Duty (kW)	-5,19
Net Duty (kW)	-5,19
Reactor Volume (L)	438
Residence Time (min)	15

The PROD1 stream is then fed to the first settler, which operates at the same pressure and temperature conditions as the first reactor. Table 4.3 shows the results of the separation, which results in two phases. The values presented in Table 4.3 correspond to the mass flow rates of the two phases leaving the settler and the respective components. Table 4.4 shows the molar composition, under equilibrium conditions, of each component by the two phases.

Table 4.3. Input and output mass flow rate of block DEC1.

DEC 1 - 60 ºC			
Stream	**PROD1**	**LTPHASE1**	**HEPHASE1**
Component	**Mass Flow Rate kg/hr**		
TG	700,00	699,99	0,01
DG	40,00	39,78	0,22
MG	10,00	3,87	6,13
FFA	24,06	23,55	0,51
FAME	237,16	236,19	0,97
SOAP	0,00	0	0
METHANOL	110,49	61,55	48,94
GLYCEROL	0,00	0	0
WATER	14,61	4,48	10,13
CH_3NaO	0,00	0	0
Total	1136,32	1069,41	

By the analysis of Table 4.3 it is possible to verify the formation of two phases. The heaviest phase is composed essentially of methanol, water and small amounts of oils and biodiesel. The lighter phase is composed of oils, biodiesel, free fatty acids, methanol and a small amount of water. It should also be mentioned that in relation to oils the exception occurs in the monoglyceride, MG, since this appears in greater quantity in the heavy phase, unlike the other fats and biodiesel, which have more affinity to the light phase than rather to in the heavy phase.

In terms of the distribution of each component between the phases, it is possible to verify that for the TG, DG, FFA and FAME, the equilibrium molar fraction is significantly higher in the first phase, or in the light phase. The MG, as already mentioned, is distributed in greater proportion in the heavy phase. It is assumed that this behavior is linked to the existence of only one fatty acid chain, the ends of the glycerol being simply bound to OH groups. Thus the non-polar character of the molecule decreases, which makes it less prone to this medium, and more prone to mixing in a polar medium, such as a mixture composed of methanol and/or water.

Table 4.4. Equilibrium molar fractions of the inlet and outlet of DEC1 decanter.

DEC1				
Component	**F**	**X1**	**X2**	**K**
TG	0,13	0,20	7,02E-06	3,48E-05
DG	0,01	0,02	1,65E-04	0,01
MG	4,65E-03	2,78E-03	0,01	2,93
FFA	0,01	0,02	8,50E-04	0,04
FAME	0,13	0,20	1,55E-03	0,01
METHANOL	0,57	0,49	0,72	1,47
WATER	0,13	0,06	0,27	4,19

F - Molar composition of the feed to the Decanter.

X1 - Mole fraction of each component in phase 1 under liquid equilibrium conditions.

X2 - Mole fraction of each component in phase 2 under liquid equilibrium conditions.

K - Constant liquid-liquid equilibrium, k = X2 / X1

After decantation, the LTPHASE1 stream is fed to the ACIDICST2 reactor for a further reaction step. Thus, stream LTPHASE1, now identified by OIL2 in Table 4.5, goes from about 25 kg/h in FFAs to just over 2 kg/h in the output stream, PROD2. At this point the first objective in the process is achieved, that is, the conversion of free fatty acids into biodiesel is completed.

Table 4.5. ACIDICST2 reactor input and output streams.

Reactor 2 – Acid Esterification			
Stream	**OIL2**	**MET2**	**PROD2**
Component	**Mass Flow Rate kg/hr**		
TG	699,99	0	699,99
DG	39,78	0	39,78
MG	3,87	0	3,87
FFA	23,55	0	2,27
FAME	236,19	0	258,53
SOAP	0,00	0	0,00
METHANOL	61,55	34,03	93,16
GLYCEROL	0,00	0	0,00
WATER	4,48	0	5,84
CH_3NaO	0,00	0	0
NaOH	0	0	0
H2SO4	0,35	0	0,33
NA^+	0	0	0
H^+	0,03	0	0,03
NaOH(S)	0	0	0
NaOH:(S)	0	0	0
SODIU(S)	0	0	0
OH^-	0	0	0
HSO_4^-	2,63	0	2,64
SO_4^{--}	0	0	0,00
Total	1072,41	34	1106
pH	-3,17	-	-3,08

The second reactor operates at 60 °C at atmospheric pressure. In this reactor it was needed to dissipate around 370 W of thermal power, in order to ensure isothermal conditions. The residence time was maintained at 15 min and the reactor volume was equal to 423 L.

Table 4.6. Results of dimensioning of the ACIDICST2 reactor.

Reactor	**ACIDICST2**
T_{OUT} (ºC)	60
P_{OUT} (bar)	1
Vapor Fraction	0
Heat Duty (kW)	-0,37
Net Duty (kW)	-0,37
Reactor Volume (L)	423
Residence Time (min)	15

The reaction mixture is again decanted (DEC2). At this point in the process, the concern is for the removal of the water, since the presence of this enables the dissolution of hydroxide ions. These are fed in the next step, the alkaline transesterification, in the form of sodium hydroxide dissolved in methanol. Thus, hydroxide ions in aqueous media react with FFAs, FAMEs, and oils present in solution to produce soaps (Zhang et al., 2003). Any of these reactions is irreversible, which decreases the yield of the process, thus justifying the importance of removing the water present in the feed to the transesterification step. To this settler is also fed a stream of glycerol. This glycerol stream can be obtained from the process, since glycerol is a by-product in the production of biodiesel. Thus glycerol is added for two reasons. Firstly, because glycerol helps in the removal of water. Second, because the acid stream from the esterification step must have its pH neutralized. Thus, glycerol is added, since it has an alkaline content, being a byproduct of alkaline transesterification. Since the decanting is simulated using the UNIFAC model, it is not possible to model the behavior of electrolytes. Thus, at this point it was assumed that the glycerol stream has a sodium hydroxide content equal to that needed to neutralize the acidity of the ACIDICST2 reactor output stream.

Table 4.7. Mass flow rate of the DEC2 settler inlet and outlet.

DEC2 - 60 ºC				
Corrente	**PROD2**	**GLYCEROL**	**LTPHASE2**	**HEPHASE2**
Componente	**Mass Flow Rate kg/hr**			
TG	699,99	0	699,99	7,66E-06
DG	39,78	0	39,78	1,69E-03
MG	3,87	0	3,33	0,55
FFA	2,27	0	2,25	0,02
FAME	258,53	0	258,37	0,17
SOAP	0,00	0	0	0
METHANOL	93,16	0	27,64	65,52
GLYCEROL	0,00	100,00	0,16	99,84
WATER	5,84	0	0,40	5,44
CH_3NaO	0,00	0	0	0
Total	1103,44	100	1032	172

The distribution obtained in the second settler follows what was expected, with reference to the results obtained in the first settling, except for the monoglyceride, MG, which, this time, showed more affinity to the lighter phase. Thus, the oils and FAMES leave the decanter in the light phase, whereas glycerol, methanol and water comprise the three main components in the heavy phase. The equilibrium molar distribution can be found in Table 4.8.

Table 4.8. Equilibrium molar fractions of the inlet and outlet of the decanter DEC2.

DEC2				
Component	**F**	**X1**	**X2**	**K**
TG	0,13	0,30	2,52E-09	8,38E-09
DG	1,06E-02	0,02	7,93E-07	3,26E-05
MG	1,79E-03	3,55E-03	4,48E-04	0,13
FFA	1,32E-03	3,03E-03	1,73E-05	5,72E-03
FAME	0,14	0,33	1,62E-04	4,89E-04
METHANOL	0,48	0,33	0,60	1,82
GLYCEROL	0,18	6,44E-04	0,32	490,65
WATER	0,05	8,39E-03	0,09	10,49

After the decantation stage, the LTPHASE2 stream is fed to the alkaline transesterification reactor in order to convert the oils into biodiesel. This stream is identified as OIL3 in Table 4.9.

4.1.2 Alkaline Transesterification

In Figure 4.2 the flowsheet of alkaline transesterification step is shown. It consists of only one reactor, ALKALTR, and three inputs and one output streams.

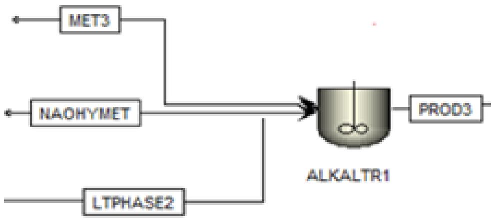

Figure 4.2. Alkaline transesterification step.

The LTPHASE2 (or OIL3) stream consists of the raw material, now with the reduced fatty acid content. The methanol is fed in MET3 and the catalyst, sodium hydroxide dissolved in methanol to form the methylate ion in NAOHYMET. Methanol is added to this stream since it is not possible to add solids (such as sodium hydroxide) in a stream, unless they are in solution. Sodium hydroxide could be added together with the stream MET3, however, it is performed separately only for the sake of presentation. Still, since it is not possible to include it in a stream that is not dissolved in solution or crystallized (also in a solution), the NAOHYMET stream has a fraction in methanol. In

Table 4.9 it is possible to consult the result of the equilibrium formation of the methylate ion, here represented by the sodium methylate compound.

Table 4.9. Input and output streams of the ALKALTR reactor.

Reactor 3 – Alkaline Transesterification				
Stream	**OIL3**	**MET3**	**NAOHYMET**	**PROD3**
Component	**Mass Flow Rate kg/hr**			
TG	699,99	0	0	7,76
DG	39,78	0	0	4,69
MG	3,33	0	0	7,53
FFA	2,25	0	0	9,91E-04
FAME	258,37	0	0	980,76
SOAP	0,00	0	0	5,50
METHANOL	27,64	500	0,005	446,56
GLYCEROL	0,16	0	0	76,27
WATER	0,40	0	0,32	2,55
CH_3NaO	0,00	0	0,95	6,03
NaOH	0	0	0	0
H_2SO_4	0	0	0	0
NA^+	0	0	0,20	3,14E-04
H^+	0	0	5,65E-20	2,07E-18
NaOH(S)	0	0	4,07	0
NaOH:(S)	0	0	0	0
SODIU(S)	0	0	0	0
OH^-	0	0	0,15	2,32E-04
HSO_4^-	0	0	0	0
SO_4^{--}	0	0	0	0
Total	1032	500	5,69	1537,66
pH	7,28	-	15,78	14,41

In this way, a flow rate of 500 kg/h in methanol, equivalent to about 18 moles of methanol for each mole of oil (nTG + nDG + nMG) fed to the reactor was obtained for the current MET3. Relative to the catalyst flow rate, this amounts to about 5.69 kg/h (90% NaOH). These values can be found in Table 4.9 which compiles the input and output streams of the ALKALITR reactor.

In the stream PROD3 the produced biodiesel reaches close to 981 kg/h. The amount of soap formed comes close to 5.5 kg/h and the levels of all oils fall below 8 kg/h. The FFAs are completely consumed, as can be seen, by their residual value in the output stream of the reactor. After the transesterification step, it is necessary to remove the excess methanol used in the reaction and the glycerol formed therein. The content of water, pH and others, must have the respective levels set, in order to comply with the normative values foreseen for biodiesel. Nevertheless, the present work analyzes only the removal of methanol, glycerol and water, in order to purify the produced biodiesel.

Again, the operating temperature was 60 °C at atmospheric pressure. In order to maintain isothermal conditions about 10.5 kW had to be dissipated. The volume of the reactor was about 7 times the volume of the reactors used in the esterification. This is assumed to be expected since the excess methanol is almost 4 times the mass of the excess used in the first step and also the material to be treated is 3 times the mass of the material treated in the first step and the residence time increased 6 times when compared to the former reactors values. The volume obtained for the reactor was then 3093 L.

Table 4.10. Results of the dimensioning of the ALKALTR reactor.

Reactor	ALKALITR
T_{OUT} (ºC)	60
P_{OUT} (bar)	1
Vapor Fraction	0
Heat Duty (kW)	-10,45
Net Duty (kW)	-10,45
Reactor Volume (L)	3093
Residence Time (min)	90,0

After alkaline transesterification, the PROD3 stream is fed to the DEC3 decanter, where by decanting a fraction of methanol and glycerol is withdrawn. The results obtained can be found in Table 4.11.

The stream names exiting DEC3 had to be changed, because this time the simulator identified the lighter phase as being the aqueous phase. This was caused by the amount of excess methanol used in transesterification reaction which results in an aqueous phase having mostly methanol. Methanol, fame and oils have similar mass per unit of volume, and since the glycerol in the AQPHASE stream only accounts for a small fraction of the stream, the AQPHASE and the OILPHASE end up by having very similar values of densities.

Table 4.11. Mass flow rate of the DEC3 decanter inlet and outlet.

DEC3 - 60 ºC			
Stream	**PROD3**	**OILPHASE**	**AQPHASE**
Component	**Mass Flow Rate kg/hr**		
TG	7,76	7,76	1,27E-03
DG	4,69	4,60	0,09
MG	7,53	2,13	5,40
FFA	0,00	8,52E-04	1,39E-04
FAME	980,76	952,88	27,88
SOAP	5,50	4,73	0,77
METHANOL	446,56	100,12	346,44
GLYCEROL	76,27	0,24	76,03
WATER	2,55	0,19	2,36
CH_3NaO	6,03	1,35	4,68
Total	1537,66	1074,00	463,66
MASS per unit of VOLUME. (gm/cc)	0,8206	0,8308	0,8296

Using decantation, it is possible to remove about 77% of all the methanol present in the PROD3 stream and practically all of the glycerol. The oils TG and DG are mostly distributed in the oil phase, unlike the MG, which is distributed more by the aqueous phase. The distribution between the oil and aqueous phase can also be evaluated in terms of molar composition, in Table 4.12. Thus, after the third decanter the oil phase is now composed of about 50% (molar fraction) in biodiesel and 49% (molar fraction) in methanol, so it is necessary to remove the remaining methanol until it reaches the minimum point of purity required for biodiesel (above 96.5%).

Table 4.12. Equilibrium molar fractions of the inlet and outlet of DEC3 decanter.

DEC3				
Component	**F**	**AQPHASE**	**OILPHASE**	**K**
TG	4,77E-04	1,20E-07	1,37E-03	11417,53
DG	4,11E-04	1,26E-05	1,15E-03	91,75
MG	1,15E-03	1,26E-03	9,33E-04	0,74
FFA	1,91E-07	4,11E-08	4,70E-07	11,45
FAME	0,18	7,86E-03	0,50	63,76
SOAP	1,06E-03	2,28E-04	2,61E-03	11,45
METHANOL	0,76	0,90	0,49	0,54
GLYCEROL	0,05	0,07	4,09E-04	0,01
WATER	7,71E-03	0,01	1,64E-03	0,15
CH_3NaO	6,08E-03	7,24E-03	3,90E-03	0,54

4.1.3 Separation and Purification

In Figure 4.3 the scheme of the separation and purification steps is shown. It consists of the DEC4 decanter and the FLASHSP1 and FLASHSP2 flash drums. At this stage, the oil and aqueous streams, resulting from the third settler, are fed.

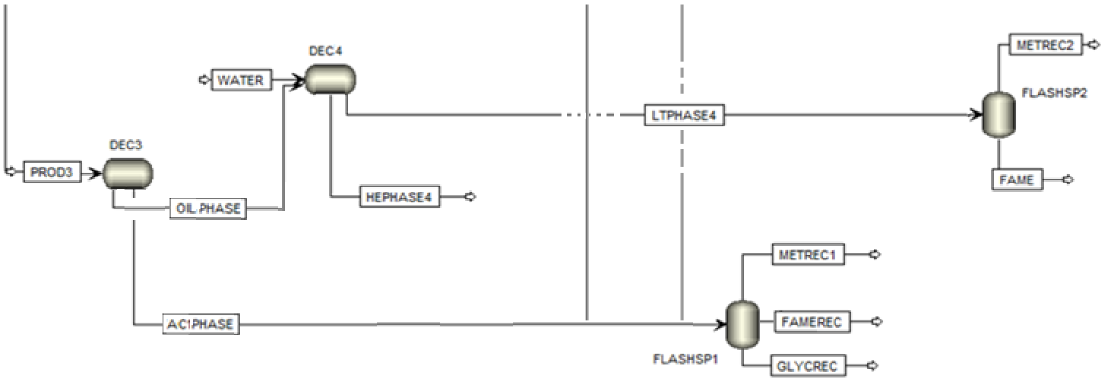

Figure 4.3. Separation and purification step.

Thus, in order to see its methanol content reduced, the stream of FAMEs (oil phase), is fed to the DEC4 decanter. The results of the decantation in terms of inlet and outlet mass flow rates can be found in Table 4.13. Relative to the molar fractions of each component under equilibrium conditions, these are presented in table 4.14.

The DEC4 decanter operates at 10 °C. In this, a stream of water is mixed with the oil stream, in order to drag the methanol. Since modeling is performed using UNIFAC, it is not possible to predict the behavior of electrolytes in solution. Nevertheless, if it were possible to do so, a weak acid, such as phosphoric acid, should be dissolved in the water in order to neutralize the medium, so the reaction could be stopped and also in order to prevent the formation of more soaps (Zhang et al., 2003).

The mass flow rate was defined to remove most of the methanol, thus reaching 500 kg/h of water. Analyzing Table 4.13 it is possible to conclude that about 94% of methanol is entrained by water. The light stream also absorbs some amount of water, about 3 kg/h. Thus, the molar fraction of FAMEs in the light stream goes from 50% in the outlet of DEC3 decanter, to 90%, at the exit of the fourth decanter. Even so, its water content rises to 5% and the present methanol still accounts for 4% of the total blend (molar percentages). In this way, the light stream LTPHASE4, which leaves the fourth decanter, is fed to FLASHSP2 drum.

Table 4.13. Mass flow rate of the DEC4 settler inlet and outlet.

	DEC4 - 10 ºC			
Stream	**OILPHASE**	**WATER**	**LTPHASE4**	**HEPHASE4**
Component		**Mass Flow Rate kg/hr**		
TG	7,76	0	7,76	6,646E-19
DG	4,60	0	4,60	5,93E-12
MG	2,13	0	2,13	5,37E-04
FFA	8,52E-04	0	8,52E-04	2,67E-09
FAME	952,88	0	952,88	1,07E-04
SOAP	4,73	0	4,73	1,48E-05
METHANOL	100,12	0	5,00	95,12
GLYCEROL	0,24	0	4,91E-06	0,24
WATER	0,19	500	2,94	497,25
CH3NaO	1,35	0	0,07	1,29
Total	1074,00	500	980,10	593,90

Table 4.14. Equilibrium molar fractions of the inlet and outlet of the decanter DEC4.

DEC4				
Component	**F**	**X1**	**X2**	**K**
TG	2,57E-04	2,45E-03	2,45E-23	1,00E-20
DG	2,17E-04	2,07E-03	3,12E-16	1,51E-13
MG	1,75E-04	1,67E-03	4,92E-08	2,94E-05
FFA	8,83E-08	8,45E-07	3,09E-13	3,66E-07
FAME	0,09	0,90	1,18E-08	1,31E-08
SOAP	4,90E-04	4,68E-03	1,71E-09	3,66E-07
METHANOL	0,09	0,04	0,10	2,2219
GLYCEROL	7,67E-05	1,49E-08	8,57E-05	5739,05
WATER	0,81	0,05	0,90	19,78
CH3NaO	7,33E-04	3,50E-04	7,77E-04	2,22

The inlet and outlet mass flows in the FLASHSP2 drum can be found in Table 4.15. Thus, the incoming stream corresponds to the light phase of the fourth settler, which results, after distillation, in a stream of steam and another of liquid. The vapor stream is composed of methanol and water, the liquid being composed of the other components. The need for evaporation at this point in the process is justified by the water content present in the FAME stream. This value should pass from 0.3% (mass percentage), of the feed to the evaporator, to 0.05% (mass percentage) in the stream of FAMEs. The operating conditions set for FLASHSP2 were 0.7 atm and 95 ºC. Temperature was not set higher than 95 ºC in order to prevent biodiesel degradation. The values set for the operating conditions of FLASHSP2 were found to be insufficient to achieve the desired levels, in terms of water and methanol content.

Table 4.15. Mass flow rate of FLASHSP2 flash evaporator inlet and outlet.

FLASHSP2			
STREAM	**LTPHASE4**	**METREC2**	**FAME**
COMP.	**Mass Flow Rate kg/hr**		
TG	7,76	2,26E-04	7,76
DG	4,60	2,89E-06	4,60
MG	2,13	2,24E-14	2,13
FFA	8,52E-04	9,41E-11	8,52E-04
FAME	952,88	4,39E-04	952,88
SOAP	4,73	8,45E-08	4,73
METHANOL	5,00	0,71	4,28
GLYCEROL	4,91E-06	1,31E-08	4,90E-06
WATER	2,94	0,63	2,31
CH3NaO	0,07	0,02	0,05
Total	980,10	1,36	978,74

The analysis of Table 4.16 also shows that after leaving the fourth settler, the FAME content in the light stream had already exceeded the minimum of 96.5%, mass percentage purity, imposed on the produced biodiesel.

Table 4.16. Mass fraction of FLASHSP2 evaporator inlet and outlet streams.

FLASHSP2			
STREAM	**LTPHASE4**	**METREC2**	**FAME**
COMP.	**Mass Frac**		
TG	0,79%	0,02%	0,79%
DG	0,47%	0%	0,47%
MG	0,22%	0%	0,22%
FFA	0%	0%	0%
FAME	97,22%	0,03%	97,36%
SOAP	0,48%	0%	0,48%
METHANOL	0,51%	52,62%	0,44%
GLYCEROL	0%	0%	0%
WATER	0,30%	46,06%	0,24%
CH3NaO	0,01%	1,28%	0,01%

Regarding the heat duty needed, about 50 kW were required to carry out the separation in block FLASHSP2.

In terms of compliance with the standard 14214, the level of triglycerides and diglycerides, are all above the maximum allowable level of 0.2% m/m. The FFA content is residual (0.000087099%), ensuring the acidity of the blend does not exceed 0.5 mg KOH/g oil. The same is true for the residual glycerol content. The water maintains its level well above 0.05% (500 mg/kg oil), reaching the 0.24% in mass. Also the methanol level surpasses its maximum allowable value of 0.2% in mass. The value obtained in the stream of FAMEs is equal to 0.44% in mass.

Table 4.17. Mass flow rate of the FLASHSP1 drum inlet and outlet.

FLASHSP1				
STREAM	**IN**	**METREC1**	**GLYREC**	**FAMEREC**
COMP.	**Mass Flow Rate kg/hr**			
TG	0,01	2,73E-03	1,17E-10	0,01
DG	0,31	7,01E-04	1,98E-05	0,31
MG	12,07	1,10E-10	3,47	8,60
FFA	0,52	1,51E-04	0,02	0,50
FAME	29,02	0,06	0,18	28,78
SOAP	0,77	3,94E-05	0,04	0,74
METHANOL	460,91	424,28	35,77	0,85
GLYCEROL	175,87	0,13	175,67	0,07
WATER	17,93	13,97	3,94	0,02
CH_3NaO	4,68	4,50	0,18	0,00
Total	702,11	442,94	219,27	39,89

Regarding the aqueous streams leaving the first, second and third settlers, these are fed to FLASHSP1 drum. The flow rates of the feed and outlets of this block can be found in Table 4.17.

FLASHSP1 drum also operates at 0.7 atm, at a temperature of 90 °C. About 92% of the methanol is vaporized and collected in the stream METREC1. This stream leaves the block with a purity percent close to 96% in methanol. The glycerol leaves the evaporator, via the base stream, in GLYREC, and a small amount of biodiesel and monoglyceride, MG, are also separated, leaving FLASHSP1 via the FAMEREC stream. Also, practically 100% of glycerol is recovered in the stream GLYREC with a purity value of 80%.

The separation required a thermal power of about 152 kW.

4.1.4 Analysis of variation in Operating Temperature

In the present section the influence of the variation in the operating temperature of the different blocks that compose the system, with the exception of the evaporators, is evaluated. First, the results of the variation in the operating temperature of the reaction blocks are presented. The analysis is not performed for the ACIDICST2 block, since it is assumed that the result obtained for the ACIDICST1 block is also valid for the

ACIDICST2 block. The same type of analysis is then presented for the process decanters.

In this way, the values of mass flow of the different components of the output stream of the reactor ACIDICST1 and ALKALTR, for different temperature values, are presented in the Table 4.18 and 4.19. The minimum temperature corresponds to 10 °C, the maximum being 60 °C, limited by the boiling point of the methanol, 65 °C.

Table 4.18. Effect of the temperature on the output stream of the ACIDICST1 reactor.

	Reactor 1 – Acid Esterification			
Stream	**PROD1 - 60 ºC**	**PROD1 - 50 ºC**	**PROD1 - 40 ºC**	**PROD1 - 10 ºC**
Component	**Mass Flow Rate kg/hr**			
TG	700	700	700	700
DG	40	40	40	40
MG	10	10	10	10
FFA	24	27,49	32	49,77
FAME	237	233,56	229,25	210,17
SOAP	0	0	0	0
METHANOL	110	111	111	113,41
GLYCEROL	0	0	0	0
WATER	14,61	14,39	14,13	12,97
CH_3NaO	0	0	0	0
NaOH	0	0	0	0
H_2SO_4	0,10972	0,05129	0,02355	0,00209
NA^+	0	0	0,00	0,00
H^+	0,10	0,10	0,10	0,10
NaOH(S)	0	0	0	0
NaOH:(S)	0	0	0	0
SODIU(S)	0	0	0	0
OH^-	1,15E-18	6,30E-19	3,19E-19	2,34E-20
HSO_4^-	9,59	9,648512	9,68	9,6971
SO_4^{--}	4,79E-05	6,50E-05	8,62E-05	1,73E-04
Total	1146	1146	1146	1146

By the analysis of Table 4.18 the effect on the decrease of the temperature in the conversion of the free fatty acids becomes clear. The decrease in temperature decreases the conversion of the reaction and as such the amount of FFA increases at the exit, unlike the flow of FAMEs, which decreases.

The effect of temperature variation on alkaline transesterification is similar as that of acid esterification. Decrease in temperature causes a decrease in the FAME conversion, although between 40 °C and 60 °C the temperature variation seems to have a small effect on the production of FAMEs. From 60 to 50 ºC, the FAME stream decreased about 0.61%, and dropped 2.14% when production at 60 ºC is compared with production at 40 ºC. This value increases to almost 30% when operating temperature for the process is 10 ºC.

Table 4.19. Effect of the temperature on the output stream of the ALKALTR reactor.

	Reactor 3 – Alcaline Transesterification			
Stream	**PROD3 - 60 ºC**	**PROD3 - 50 ºC**	**PROD3 - 40 ºC**	**PROD3 - 10 ºC**
Component	**Mass Flow Rate kg/hr**			
TG	7,76	14,05	26,71	213,30
DG	4,69	6,84	11,67	87,74
MG	7,53	6,53	5,66	3,38
FFA	9,91E-04	1,34E-03	1,88E-03	6,64E-03
FAME	980,76	974,85	959,06	701,58
SOAP	5,50	3,83	2,99	2,27
METHANOL	446,56	447,08	448,70	476,45
GLYCEROL	76,27	75,56	73,75	43,65
WATER	2,55	2,62	2,67	2,71
CH_3NaO	6,03	6,24	6,39	6,51
NaOH	0	0	0	0
H_2SO_4	0	0	0	0
NA^+	3,14E-04	2,92E-04	2,67E-04	1,55E-04
H^+	2,07E-18	1,25E-18	7,10E-19	6,76E-20
NaOH(S)	0	0	0	0
NaOH:(S)	0	0	0	0
SODIU(S)	0	0	0	0
OH^-	2,32E-04	2,16E-04	1,98E-04	1,15E-04
$HSO4^-$	0	0	0	0
$SO4^{--}$	0	0	0	0
Total	1537,66	1537,60	1537,60	1537,60

The results obtained for the four decantations are presented in Table 4.20, at temperatures of 30 °C and 10 °C. The letters L and H correspond to the light and heavy phases that leave each decanter, except for the decanter DEC3 where the oil phase is given by OILPH and the aqueous phase by AQPH.

In the first decantation the temperature variation does not seem to have a great influence on the distribution of the oils (TG and DG), biodiesel and FFA. These molecules migrate mostly to the light phase. The monoglyceride, MG, is the exception, insofar as it is distributed more to the heavy phase, and the decrease in temperature further promotes the passage of MG from the oil phase to the aqueous phase. The same is true of methanol and water, the main components of the aqueous phase, but which, however, are also distributed in the light phase. However, as can be seen in Table 4.20, the decrease in temperature contributes to the transition of water and methanol from the light phase to the heavy phase. In the second settler the situation is the same as that described for the first settler, except for the second one also involving glycerol. This component is practically distributed throughout the aqueous phase and the temperature variation has little influence on its distribution. Also this time the MG component is distributed mostly in the light phase. Decrease in temperature increases the amount transferred to the heavy phase, but nevertheless MG still verifies appears mostly in the light phase.

Table 4.20. Evaluation of the variation in the operating temperature, in the separation of phases, obtained for the four decanters present in the process.

T_{op} = 30 °C								
Block	**Dec1**		**Dec2**		**Dec3**		**Dec4**	
Stream	**L**	**H**	**L**	**H**	**OILPH**	**AQPH**	**L**	**H**
Comp.	**Mass Flow Rate kg/hr**							
TG	699,98	0,02	699,99	0	7,76	1,07E-03	7,76	6,45E-19
DG	39,66	0,34	39,78	0	4,58	0,11	4,58	3,00E-12
MG	2,32	7,68	3,17	0,70	1,38	6,15	1,38	0,0002
FFA	23,36	0,70	2,25	0,02	8,26E-04	1,65E-04	8,26E-04	1,93E-09
FAME	235,98	1,18	258,39	0,15	953,18	27,58	953,18	8,59E-05
SOAP	0	0	0,00	0	4,58	0,92	4,58	1,07E-05
MET	49,22	61,27	23,19	69,97	74,06	372,50	4,62	69,44
GLY	0	0	0,08	99,92	0,09	76,18	0	0,09
WATER	3,21	11,40	0,28	5,55	0,12	2,43	3,32	496,80
CH_3NaO	0	0	0	0	1,00	5,03	0,06	0,94
Total	1053,74	82,58	1027,14	176,31	1046,75	490,91	979,48	567,27
T_{op} = 10 °C								
Block	**Dec1**		**Dec2**		**Dec3**		**Dec4**	
Stream	**L**	**H**	**L**	**H**	**OILPH**	**AQPH**	**L**	**H**
Comp.	**Mass Flow Rate kg/hr**							
TG	699,98	0,02	699,99	0	7,76	0	7,76	0
DG	39,56	0,44	39,78	0	4,56	0,13	4,56	0
MG	1,54	8,46	3,03	0,84	0,98	6,55	0,98	0,0001
FFA	23,23	0,83	2,25	0,02	0	0	0	0
FAME	235,89	1,27	258,40	0,13	953,87	26,89	953,87	0
SOAP	0	0	0,00	0	4,47	1,03	4,47	0
MET	41,49	69,00	20,17	72,99	59,11	387,45	3,18	55,94
GLY	0	0	0,05	99,95	0,05	76,22	0	0,05
WATER	2,54	12,07	0,22	5,62	0,08	2,47	2,84	497,25
CH_3NaO	0	0	0	0	0,80	5,23	0,04	0,76
Total	1044,24	92,08	1023,88	179,56	1031,68	505,98	977,70	553,99

In the third and fourth decanters, the components are maintained, but the proportions are changed. Now, FAMEs are in greater quantity than oils, and there are also larger quantities of water and methanol. Nevertheless, the trend in the distribution of components does not change to what was described in the previous paragraph. Also, it can be verified that for the decantation DEC4, as expected the increase in temperature, from 10 to 30 ºC slightly increases the amount of water present in the light phase.

4.1.5 Overall Results

Table 4.21 compiles the most significant results regarding the simulation of biodiesel production from a source of oils, with a high content of free fatty acids.

The production capacity of purified biodiesel (98%) was around 953 kg/h for a feed of 1000 kg/h of an oil stream, with 25% w/w of free fatty acids in solution. The amount of methanol fed into the process was 670 kg/h, in the acid esterification step a 1:6 excess (fatty acid: methanol) was used, and an excess of 1:18 was used in the transesterification step. 10 kg/h of a concentrated solution (98%) of sulfuric acid was used in the esterification step and about 8 kg/h of sodium hydroxide must be dissolved in the methanol fed to the alkaline transesterification. The glycerol used for the washing process and separation steps was 100 kg/h, rising to 500 kg/h, for water used for the same purposes.

The conversion of the process is presented under the prism of the conversion of the free fatty acids and the conversion of the oils. Thus, the former found a conversion of 98.89% and the latter of 96.41%.

The energy consumption was evaluated only in the evaporations. The total power consumed by these (FLASHSP1 and FLASHSP2) was 202 kW.

Table 4.21. Summary table of simulation results for biodiesel production.

CAPACITY	953	kg/h
Oils (TG, DG, MG)	750	kg/h
FFA	250	kg/h
METHANOL	670	kg/h
H_2SO_4 (98%)	10	kg/h
$NaOH_{(s)}$	5	kg/h
Glycerol	100	kg/h
Washing Water	500	kg/h
FAME purity	97,36%	%
FFA Conversion	98,89	%
Oil Conversion	96,41	%
Heat Duty$_{\text{FLASH DRUMS}}$	202	kW

5 Conclusions and suggestions for future work

In the present work a computer simulation was performed in Aspen Plus V8.4 environment of the biodiesel production from an oil feed with a high content of free fatty acids in solution. The conversion to biodiesel was determined by chemical kinetics using literature data, and the electrolytic species involved in the process were also taken into account in the reaction stages.

The thermodynamic models used were ElecNRTL and UNIFAC. The first is used in the modeling of the chemical reaction step and the second in the separation and purification step.

Thus, in order to produce a current of 953 kg/h of biodiesel, with a mass purity of 97.36%, a stream of 1000 kg/h of oils, with an initial content of 25% by weight of free fatty acids was required. 670 kg/h of methanol, 10 kg/h of concentrated sulfuric acid (98%), 5 kg/h of solid sodium hydroxide, 100 kg/h of glycerol and 500 kg/h of water for washing were also fed into the process. About 16% in mass of the fed methanol is consumed in the reaction steps and recovered, about 63%, of the total methanol feed stream, at the end of the process, with a mass purity of 96%. The alkaline transesterification process produces about 76% of the fed glycerol, which is recovered substantially at the end of the process with a mass purity of about 80%.

The conversion of the free fatty acids in the acid esterification step was 98.89%, being 96.41% the conversion of the oils in the alkaline transesterification step.

The thermal power consumed to purify the biodiesel produced and recover the methanol and glycerol was 202 kW.

In terms of improvements and suggestions for future work, the need to introduce the methylate component in the simulation, to make a diversified input in terms of triglycerides, diglycerides and monoglycerides and the respective adjustment of the kinetic parameters in the kinetic model. In addition to these, it would also be desirable for the acid esterification step to incorporate the concentration of the acid catalyst in the kinetic law.

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