

Database creation for modeling and simulation of biodiesel production from predict methods of thermophysical properties

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ABSTRACT :Adequate knowledge of biodiesel's physical properties is necessary to simulate and optimize its process obtaining, mainly the chemical reactor. The objective of this work was to evaluate predictive models of physical properties of components of vegetable oils, methyl and ethyl esters that compose biodiesel to model reactor. Although some experimental data are available, their determination for all the existing biodiesel components can be expensive and complex. Thus, this work investigated the performance of group contribution and approach by fragments in the calculation of these properties. The properties evaluated in this study were: normal boiling temperature, critical temperature, critical pressure, critical volume, acentric factor, saturation pressure, enthalpy and Gibbs energy of formation, viscosity, cetane number, cold flow properties and flash point. For each property evaluated was recommended of the most feasible model by comparing estimated values to experimental data available in the literature. Therefore, a database of these properties was created to use in engineering applications.

KEYWORDS FAME, FAEE, fatty acids, triacylglycerol, physical properties, group contribution, simulation.

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I. INTRODUCTION

The decline in available oil reserves and stricter environmental regulations has motivated global interest in studies for the discovery and improvement of renewable energy sources. Biodiesel is produced from renewable biological sources, such as vegetable oils and animal fats, and presents technical and environmental information that encouraged its use as an alternative fuel or as a mixing component of diesel from petroleum (del Río et al., 2016).

Biodiesel production costs 1.5 to 3 times higher than conventional diesel, being the main disadvantage of its commercialization (Do Carmo et al., 2015). In this way, there is a growing interest in the design and optimization of processes to obtain this fuel. This demand points to a need for data on the physical and chemical properties of related components such as methyl esters, ethyl esters, fatty acids, and triglycerides. However, there are no experimental data available in the literature (Evangelista et al., 2017a, 2018; García et al., 2012; Su et al., 2011) for some properties of fatty acid methyl esters (FAMES) and ethyl fatty acid esters (FAEES) (e.g. critical properties). One of the reasons is that these components are available primarily as constituents of complex mixtures and are difficult to obtain in pure form.

Group Contribution (CG) methods have been used in recent years to estimate some physicochemical properties of organic substances, such as normal boiling point, critical properties and acentric factors (Evangelista et al., 2017b; García et al., 2012; Wallek et al., 2013). The GC considers that the properties of molecules depend on the nature of atoms and the types of chemical bonds within molecules (Do Carmo et al., 2015). In addition to GC, methods with the principle of contributor fragments have been used for calculations that consider that the properties of molecules are established from the contributions of their functional groups (Poling et al., 2001). These methodologies need only small amounts of information about the substances to obtain a reliable estimate. Although there are many methods in the literature, each of them has built-in premises and practical limits that must be applied.

Knowledge of normal boiling temperature (T_b) can be used in vapor-liquid equilibrium calculations (Do Carmo et al., 2015). Critical properties are commonly used as coordinates of the critical point of a substance. The acentric factor (ω) is input parameters for many state equations (Nannoolal et al., 2008).

Properties such as density, viscosity, thermal conductivity, surface tension, vapor pressure, vaporization enthalpy, critical properties and acentric factor are essential for the precision of a biodiesel simulation process, as well as can be used to evaluate the characteristics of spraying, atomization and combustion in engines (Evangelista et al., 2018).

Therefore, this work aimed to make a comparison of methods of contribution of groups and approach by fragments to determined T_b , temperature, pressure and volume critical, ω , enthalpy of formation (ΔH_f^0), Gibbs energy formation (G_f^0), density (ρ), of triacylglycerols, fatty acids, and viscosity (ν), number of cetane (NC), cold flow properties and flash point for methyl and ethyl esters. Thus, it was described the appropriate models when experimental data is lacking and created a database so that it can be used in engineering calculations, especially in simulations of biodiesel procurement reactions.

II. METHODOLOGY

2.1 Predicting thermophysical properties

For the application of the methods of estimating properties, the molecules of the compounds of interest were drawn and, then, the functional groups identified and quantified.

Example: A molecule of triacylglycerol PLO, formed by the junction of palmitic fatty acids (P), linoleic (L) and oleic (O) in a glycerol molecule. Its chemical formula is represented by $C_{55}H_{100}O_6$. Fig. 1 represents the triacylglycerol PLO molecule.

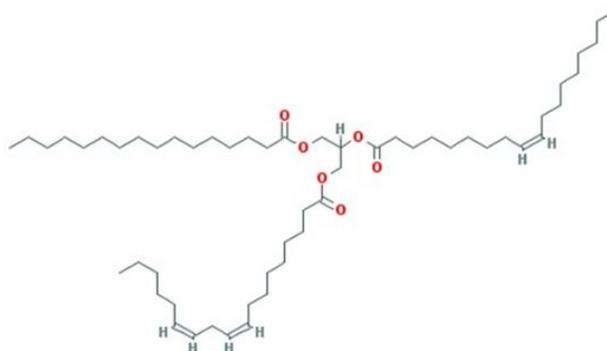


Fig. 1. Chemical structure of triacylglycerol PLO.

The groups present in the molecular structure represent in Fig. 1 were counted for the methods of contribution of groups showed in Table 1, JOBACK (Joback and Reid, 1987) and GANI (Constantinou et al., 1994).

Table 1. Occurrence of the groups for the JOBACK and GANI method for the PLO triacylglycerol.

JOBACKgroups	Score	GANIgroups	Score
CH ₃	3	CH ₃	3
>CH ₂	42	>CH ₂	40
>CH-	4	>CH-	1
-COO-	3	-CH ₂ -COO-(C)	2
=CH-	3	-COO-	1
		-CH=CH-	3

Each of these groups has a contribution value depending on the property to be calculated and method used. Thus, it is possible to use the equations of the methods safely to predict the properties.

2.1.1 Normal boiling temperature (T_b)

T_b is the temperature at which the vapor pressure equals the external or atmospheric pressure. Constantinou and Gani (Constantinou and Gani, 1994) developed an advanced method of group contribution based on the groups of the thermodynamic model Universal Functional Activity Coefficient (UNIFAC). In addition, the authors added the so-called "second order" contributions that allow differentiating molecules from isomers, molecules that have the same groups, located together or not, resonance structures, among others (Poling et al., 2001). The equations of the JOBACK and GANI models for T_b estimation are represented by equations 1 and 2.

JOBACK:

$$T_b = 198 + \sum_k N_k(T_{bk}) \quad (1)$$

GANI:

$$T_b = 204.359 \times \ln \left(\sum_k N_k T_{bk} \right) \quad (2)$$

where N_k represents the number of groups of type k and T_{bk} the contribution to the normal boiling temperature of groups k .

The semi-empirical approach of Ceriani and Meirelles (2004); Zong et al. (2010a) was also used to calculate of T_b of TAGs, DAGs and MAGs is implemented the basis of fragments of the constituents. A relationship between the boiling temperature of each of the fragments of the TAGs (fatty acids and glycerol) and pressure was applied. Therefore, the experimental data of (DDB, 2019; Matricarde Falleiro et al., 2012) on the temperature of each of the fragments were adjusted to Equation 3.

ZONG

$$T_b^a = a \times \ln(P) + b \quad (3)$$

where a and b are the adjustment parameters of each fragment, T_{ba} is the boiling temperature of fragment a (K) and P is the vapor pressure (mmHg). Knowing the value of T_b^a for each of the fragments, it was possible to calculate the value of T_b^{TAG} using Equation 4:

$$T_b^{\text{TAG}} = \frac{\sum N_{\text{Frag},a} \times T_b^a}{3} \quad (4)$$

T_b^{TAG} represents normal boiling temperature of triacylglycerol (K) and N_{Frag} number of fragments of a .

2.1.2 Critical properties (P_c , V_c and T_c)

Pressure (P_c), volume (V_c), temperature (T_c) and compressibility factor (Z_c) critical are parameters used in many volumetric, thermodynamic and transport correlations based on the theory of corresponding states to estimate gas and liquid properties. According to Poling et al. (2001), the experimental determination of these properties is difficult, as chemical degradation can occur at high temperatures, especially for long chain components.

The estimation methods evaluated in this study were: Ambrose (1980); Constantinou and Gani (1994); Joback and Reid (1987); Lydersen (1955). The first method requires only information on the structure of the compound, while the other methods require values of molar mass and boiling temperature. The methods are represented by Equation 5 to Equation 16.

JOBACK

$$T_c = T_b \left[0.584 + 0.965 \sum_k N_k(T_{ck}) - \left(\sum_k N_k(T_{ck}) \right)^2 \right]^{-1} \quad (5)$$

$$P_c = \left[0.113 + 0.0032 N_{at} - \sum_k N_k(P_{ck}) \right]^{-2} \quad (6)$$

$$V_c = 17.5 + \sum_k N_k(V_{ck}) \quad (7)$$

GANI

$$T_c = 181.28 \times \ln \left(\sum_k N_k T_{ck} \right) \quad (8)$$

$$P_c = \left(\sum_k N_k P_{ck} + 0.10022 \right)^{-2} + 1.3705 \quad (9)$$

$$V_c = \left(\sum_k N_k(V_{ck}) - 0.00435 \right) \times 1000.0 \quad (10)$$

AMBROSE:

$$T_c = T_b \left[1 + \left(1.242 + \sum_k N_k(T_{ck}) \right)^{-1} \right] \quad (11)$$

$$P_c = M_M \left[0.339 + \sum_k N_k(T_{ck}) \right]^{-2} \quad (12)$$

$$V_c = 40 + \sum_k N_k(V_{ck}) \quad (13)$$

LYDERSEN:

$$T_c = \frac{T_b}{0.567 + \sum N_k(T_{ck}) - (\sum N_k(T_{ck}))^2} \quad (14)$$

$$P_c = \frac{M_M}{(0.34 + \sum N_k(P_{ck}))^2} \quad (15)$$

$$V_c = 40 + \sum_k N_k(V_{ck}) \quad (16)$$

T_{ck} , P_{ck} and V_{ck} represent the contributions of each functional group and that vary numerically depending on the method of contribution of groups. N_k is the number of times the group "k" appears in the molecule. T_c is given in Kelvin, P_c in bar and V_c in cm^3/mol .

2.1.3 Acentric factor (ω)

The acentric factor was introduced by Kenneth Sunborn Pitzer in 1955. It's associated with the sphericity of the molecule force field and polarity (Poling et al., 2001). Originally defined by Equation 17:

$$\omega = -\log \left[\lim_{\left(\frac{T}{T_c}\right)=0.7} \left(\frac{P_{vp}}{P_c} \right) \right] - 1.0 \quad (17)$$

where P_{vap} is vapor pressure, T_c critical temperature and P_c critical pressure.

The definition of the equation (Equation 17) arose because monoatomic gases (Air, K-r, Xe) have $\omega \sim 0$, except for noble gases (He, Ne) and some others (e.g. Rn). All other species have positive values up to 1.5. To obtain ω values is necessary to know the constants T_c , P_c , and the property P_{vap} at reduced temperature, $T/T_c = 0.7$.

Pitzer rule (PITZER) and Kesler-Lee (LEE) were selected in this work to determined ω . Equation 18 was presented by Pitzer (1955) for ω calculation:

$$Z_c = 0.291 - 0.080\omega \quad (18)$$

2.1.4 Enthalpy formation and Gibbs free energy of formation in the standard state

The knowledge of standard enthalpy of formation (ΔH_f^0) is important to provide the enthalpy reaction for the formation of a mol of a substance from the chemical elements that constitute it, in its reference states.

The Gibbs free energy formation (G_f^0) is defined as Gibbs' energy reaction for the formation of a mol of a substance from the chemical elements that constitute it in its reference states. According to Atkins et al. (2017), Gibbs free energy can be obtained from calorimetric data (enthalpy and entropy, from calorific capacities), equilibrium constants in chemical reactions, electrochemical measurements and spectroscopy data, when in the gas phase.

Methods of contributions groups such as Joback and Reid (1987), Benson et al. (1969); Constantinou and Gani (1994) and others, have been of great help in predicting reliable estimates of values of formation

enthalpy, absolute entropy and Gibbs free energies. Groups contribution to G_f (298.15 K) and H_f (298.15 K) were obtained by Constantinou and Gani (1994) through equations (Equation 19 and Equation 20).

GANI

$$H_f^0 = 10.835 + \sum_k N_k (H_{fk}) \quad (19)$$

$$G_f^0 = -14.828 + \sum_k N_k (G_{fk}) \quad (20)$$

N_k represents the number of groups and H_{fk} and G_{fk} the group's contribution to enthalpy and Gibbs energy, respectively.

The method of Benson et al. (1969) can also be used to estimate formation enthalpy and absolute entropy of chemical compounds in the gas phase, considering the standard state. In this method, contributions are given only to atoms with valence greater than one. Groups are linked to key atoms with specific nomenclature (Equation 21, Equation 22, and Equation 23). For example, group C-(C)(H)₃ is a reference to the carbon atom (key atom) bound to another carbon and three hydrogens.

BENSON

$$\Delta H_f^0(298,15K) = \sum_k N_k (\Delta H_{fk}^0) \quad (21)$$

$$\Delta G_f^0(298,15K) = \Delta H_f^0(298,15K) - 298,15 \Delta S_f^0 \quad (22)$$

$$\Delta S_f^0(298,15K) = \sum_k N_k (\Delta S_{fk}^0) - R \ln \sigma + \ln \eta \quad (23)$$

where σ is the symmetry of the molecule and η the number of isomers. R is the universal constant of gases.

The Joback method (Joback and Reid, 1987) is an extension of the Lydersen (Lydersen, 1955). It is a method that uses additive contributions and no contribution to interactions between groups. According to the authors, it is not a high-precision method, but works well for many chemical species. Among these properties, those of interest for this work are Gibbs free energy estimates of standard formation and enthalpy of standard formation. Equation 24 and Equation 25 are used by this method to estimate these two properties.

JOBACK

$$H_f^0 = 68.29 + \sum_k N_k (H_{fk}) \quad (24)$$

$$G_f^0 = 53.88 + \sum_k N_k (G_{fk}) \quad (25)$$

N_k represents the number of groups, H_{fk} contribution to enthalpy formation and G_{fk} contribution to Gibbs free energy of formation of groups k.

The highlight the similarity of Equation 21 and Equation 25, for the calculation of the enthalpy of formation in the GANI and JOBACK methods, respectively. The main difference in these equations lies in the identification of group k. It is known that the GANI method considers second-order interactions, consequently, the groups identified by this method may be different from that obtained by JOBACK. Similarly, it happens in Equation 20 and Equation 25 for Gibbs energy calculation.

2.1.5 Vapor pressure (p_{vap})

The fragment-based method Zong et al. (2010a) and the Clausius-Clapeyron equation were applied to estimate vapor pressures of TAGs using Equation 29. As it wasn't possible to find experimental data for vapor pressures of unsaturated TAGs, then was considered that the chains of saturated and unsaturated fatty acids have identical vapor pressures when they have the same number of carbon atoms for the fragment approach.

ZONG

$$\log P(T) = \frac{-\Delta G_{\theta}^{vap}}{R\theta \ln 10} + \frac{\Delta H_{\theta}^{vap}}{R\theta \ln 10} \left(\frac{1}{\theta} - \frac{1}{T} \right) \quad (26)$$

where P is the vapor pressure (Pa), T is the absolute temperature (K), R is the constant of the gases, θ is the reference temperature ($\theta=298.15$ K), ΔH_{θ}^{vap} is the vaporization enthalpy at the reference temperature θ , and ΔG_{θ}^{vap} is the Gibbs energy of vaporization at the reference temperature θ .

Ceriani et al. (2013) proposed a group contribution method to estimate vapor pressure and heats of vaporization as a function of the temperature of organic liquids found in the oil and biofuel industries. The regression of the parameters was based on an extensive database, composed of fatty acids, esters of methyl,

ethyl, propyl and butyl, tri- di- and monoacylglycerols and hydrocarbons. This methodology improved the predictions obtained by Ceriani and Meirelles (2004) method, due to the inclusion of new experimental data of esters and glycerides and critical points. Then, the equation 27 was used to calculated of P_{vap} . The pressure is in Pa and temperature in K.

CERIANI

$$\ln(P_{vap}) = A + \frac{B}{T} + C \cdot \ln(T) \quad (27)$$

$$A = \sum_k N_k (A_{1k} + M_M \cdot A_{2k}) + (s_0 + N_{Cs} \cdot s_1) + \alpha(f_0 + N_C \cdot f_1)$$

$$B = \sum_k N_k (B_{1k} + M_M \cdot B_{2k}) + \beta(f_0 + N_C \cdot f_1)$$

$$C = \sum_k N_k (C_{1k} + M_M \cdot C_{2k})$$

where N_k is the number of k groups in the molecule, MM is the molecular mass of the component, N_{Cs} is the number of carbons of the alcoholic part of methyl and ethyl esters (N_{Cs} equals 1 and 2, respectively), N_C is the total number of carbon atoms in the molecule. A_{1k} , B_{1k} , C_{1k} , A_{2k} , B_{2k} , C_{2k} , α , β , s_0 , s_1 , f_0 and f_1 are the parameters obtained by regression.

2.1.6 Enthalpy of vaporization (H_{vap})

Ceriani et al. (2009) was developed a model to predict vaporization heat from the Clausius-Clapeyron equation (Equation 28) and the group contribution method of Ceriani and Meirelles (2004) (Equation 29). After substitution and manipulating in the Clausius-Clapeyron equation, an equation for ΔH_{vap} was obtained as a function of temperature (Equation 30).

$$\frac{dP_i^{vap}}{dT} = \frac{P_i^{vap} \Delta H_i^{vap}}{RT^2} \quad (28)$$

$$P_i^{vap} = \exp\left(A_i + \frac{B_i}{T^{1.5}} - C_i \ln T - D_i T\right) \quad (29)$$

$$\Delta H_i^{vap} = -R \left(\frac{1.5B_i}{\sqrt{T}} + C_i T + D_i T^2 \right) \quad (30)$$

R represents the universal constant of gases and B_i , C_i and D_i are the parameters of the same contribution group used to estimate the vapor pressure in Ceriani and Meirelles (2004). In high temperature and high vapor pressure conditions, the ideal gas condition made in the equation (Equation 30) is not valid. Therefore, Ceriani et al. (2009) included a correction term, which originated Equation 31.

$$\Delta H_i^{vap} = -R \left(\frac{1.5B_i}{\sqrt{T}} + C_i T + D_i T^2 \right) \left(1 - \frac{T_c^3 P_i^{vap}}{T^3 P_c} \right)^{0.5} \quad (31)$$

P_i^{vap} is the vapor pressure of component i and T_c and P_c are critical temperature and critical pressure, respectively.

A linear equation to estimate heat of vaporization was used by Pitzer (1955). ΔH_{vap} , as a function of reduced temperature (T_r) and acentric factor ω . Su et al. (2011) derived this expression in an analytical equation, through an approximation of the correlation of $0.6 < T_r < 1.0$ (Equation 32).

$$\frac{\Delta H_{vap}}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456} \quad (32)$$

Basařová and Svoboda (1995) applied another group contribution method to estimate vaporization heat for several substances as a function of reduced temperature (Equation 33).

$$\Delta H_{vap} = A(1 - T_r)^\alpha \exp(\beta(1 - \alpha T_r)) \quad (33)$$

ΔH_{vap} represents vaporization heat, T_r at reduced temperature, and A and α are contributing parameters of the group.

Zong et al. (2010a) used Equation 26 to predict vaporization enthalpy. The vaporization heat appears from the correlation of vapor pressure by Antoine's equation. Temperature dependence with vaporization heat was not evaluated.

2.2 Properties for characterization of FAMES and FAEE biodiesel

2.2.1 Viscosity (ν)

According to biodiesel regulatory standards (United States, ASTM 6751; Europe, EN14214; Brazil, ANP 45), viscosity at 40°C is a fundamental property for the standardization of biodiesel. It is known that the high viscosities of vegetable oils or fats can lead to operational problems of mechanical engines.

Allen et al. (1999) applied the simplified Grunberg-Nissan equation (Equation 34) to predict the viscosity of biodiesel mixtures. The Grunberg-Nissan equations:

$$\ln \mu_m = \sum_{i=1}^n y_i \ln \mu_i \quad (34)$$

where μ_m is the average viscosity of the mixture (Pa.s); μ_i is the viscosity of the pure i component (Pa.s); y_i are the mass fractions of component i . The method should not be used for the esters of C20:0, C20:1, C22:1 and C24:0, because the authors did not find experimental data available for these compounds for the validation of the method.

Ceriani et al. (2011) developed a refined methodology for the forecast of this transport property. In this method, experimental data from Pratas et al. (2010) were used to make regression for methyl esters and ethyl esters and values for radical diacylglycerol and glycerol.

$$\ln(\mu_i) = \sum_k N_k \left(A_{1k} + \frac{B_{1k}}{T + C_{1k}} \right) + \left[M_i \sum_k N_k \left(A_{2k} + \frac{B_{2k}}{T + C_{2k}} \right) \right] + Q \quad (35)$$

In Equation 4, N_k represents the number of k groups in molecule i ; M is the molecular mass of the component that multiplies; A_{1k} , B_{1k} , C_{1k} , D_{1k} , A_{2k} , B_{2k} , C_{2k} and D_{2k} are parameters obtained from the regression of the experimental data; k represents the component groups i ; Q is a correction term; T temperature in K.

Su et al. (2011) described the correlation (Equation 36) for viscosity calculation.

$$\mu = 0.235N_C - 0.468N_{double} \quad (36)$$

where N_C is the number of carbon atom and N_{double} the number of double bonds.

2.2.2 Cetane number

The number of cetane depends directly on the ignition delay of the engines. The higher the number of cetane, the lower the ignition delay and the higher the quality of the diesel. However, very high cetane number values are indicative that combustion may occur before fuel and air are properly mixed, resulting in incomplete combustion and smoke emission.

The compound n-hexadecane, also known as cetane, represents the standard fuel for the maximum value of the high cetane number, being assigned its value equal to 100. Diesel engine manufacturers recommend that the number of cetane be between 40 and 50 (Knothe, 2014). Clements (1996) demonstrated that the simple mixing rule can predict the cetane number of fuels by Equation 37.

$$CN_{mixture} = \sum_i x_i CN_{pure} \quad (37)$$

where x_i is the mass fraction and pure CN is the cetane number of the pure ester. There are no experimental data for C20:0, C20:1, C22:0, C24:0, and C24:1. Thus, it is not possible to estimate CN of biodiesel originated these fatty acids use the equation cited above.

Gopinath et al. (2009) created a correlation to estimate the cetane number of biodiesels from their compositions (Equation 38). To extend the prediction of a mixture of methyl esters, they proposed a multiple linear regression model based on the following biodiesel mass compositions: La [C12:0], M [C14:0], P[C16:0], S [C18:0], O [C18:1], L [C18:2], and Ln [C18:3].

$$CN_{mixture} = 62.2 + (0.017 La) + (0.074 M) + (0.115 P) + (0.177 S) - (0.103 O) - (0.279 L) - (0.366 Ln) \quad (38)$$

where La, M, P, S, O, L and Ln are percent concentration of lauric, myristic, palmitic, stearic, oleic, and linoleic acids in methyl esters, respectively.

Chang and Liu (2010) presented a linear correlation for predicting the cetane number of biodiesels based on the weighted average of the number of carbon atoms and double bonds (Equation 39).

$$CN_{biofuel} = 4.201N_C - 20.077N_{double} + 2.005 \quad (39)$$

2.2.3 Flash point

The flash point (T_f) of a liquid is the temperature at which the substance emits enough vapor to form a flammable mixture with air under experimental conditions. It's one of the main parameters used to determine the risks of fire and explosion of liquids Chang and Liu (2010).

There are many approaches in the literature for predicting flash point. Stefanis et al. (2004) developed a group contribution method to determine the flash point of organic compounds (Equation 40). According to Su et al. (2011) existing methods aren't applicable to ester mixtures or are complex to use.

$$T_f = \sum_i n_i P_i + \sum_j n_j S_j + 216 \quad (40)$$

where P_i is the contribution of first-order groups of type i and S_j is the contribution of second-order groups of type j , n the number of times the group appears in the molecule. T_f is given in Kelvin.

The method of Su et al. (2011) is based on the relationship of the flash point with of average number of carbon atoms and double bonds in biodiesel samples (Equation 41).

$$T_f = 23.362N_C + 4.854N_{double} \quad (41)$$

where N_C is the number of carbon atoms a N_{double} is the number of double bonds.

2.2.4 Cloud point (CP), Pour point (PP) and Cold filter plugging point (CFPP)

At low temperatures, biodiesel tends to partially solidify or lose fluidity, leading to interruption of fuel flow and clogging of the filtration system, causing problems in engine ignition.

The cloud point (CP) is the temperature of the fuel, in a cooling process, where the formation of the first crystals is observed. Cold filter plugging point (CFPP), is the temperature at which the fuel loses filterability when cooled. Fluidity point (pour point - PP), is the lowest temperature at which fuel oil flows when subjected to cooling under certain test conditions. These properties are important for establishing the handling and storage conditions of the product.

Sarin et al. (2009) indicated the correlations (Equation 42, 43 and 44) when the effects of unsaturation were evaluated for the determination of CP, PP and CFPP:

$$CP(^{\circ}C) = -0.576(X) + 48.255 \quad (42)$$

$$PP(^{\circ}C) = -0.626(X) + 45.594 \quad (43)$$

$$CFPP(^{\circ}C) = -0.561(X) + 43.967 \quad (44)$$

where X is the mass fraction of unsaturated esters.

Su et al. (2011) determined the equations for predicting the properties of esters at low temperatures, which are Equation 45, 46 and 47:

$$CP(K) = 18.134N_C - 0.790(N_{doubles}) \quad (45)$$

$$PP(K) = 18.880N_C - 1.000(N_{doubles}) \quad (46)$$

$$CFPP(K) = 18.019N_C - 0.804(N_{doubles}) \quad (47)$$

2.3 Characterization of vegetable oils

To evaluate the methods of prediction of properties correctly, one should make the choice of consistent data, that is, the composition of the studied oil sample should be as real as possible, in order to ensure that the conclusions are effective.

For soybean, sunflower and palm oil, which were used as raw material in this work, the composition used in triacylglycerols was that obtained by Cunha and Oliveira (2006); Dunkle et al. (2012); Ma and Hanna (1999), respectively. These authors determined the oil profile in TAGs by high performance liquid chromatography (HPLC). For macauba oil, as the composition in TAGs, DAGs and MAGs was not found in the literature, two characterization methodologies were proposed. The first is an approach in which oil is represented by a mixture of Mixed TAG, either by (A) high resolution gas chromatography or (B) computational methodology proposed by Antoniosi Filho et al. (1995). The second approach characterizes vegetable oil as a mixture of fatty acids.

2.3.1 High Performance Gas Chromatography Analysis (GC)

The sample of macauba pulp oil was diluted in toluene at the final concentration of 0.7%. GC analysis was performed without derivatization on a thermo stabilized fused silica capillary column of TG-5 HT from

Thermo brand of 15 meters x 0.25 mm x 0.10 micrometers. The analysis was performed with hydrogen flow from 1.5 mL to 50°C under constant pressure. The initial temperature of the column was 50°C, with a temperature increase schedule of 15°C/minute to 180°C, with ramps of 7°C/minute up to 230°C and up to 350°C with programming of 10°C/min, remaining at this temperature for another 25 minutes. The injector was maintained at 320°C, in the flow division mode of 1:50 and 1 microliter of solution was injected. The detector was maintained at 380°C. Internal normalization was performed to quantify triacylglycerols. Standards of palmitic acid, linoleic, monoolein, monopalmitin, diolein, dipalmitin, tripalmitin and triolein from Sigma and Nu Chek brands were used for identification. They were dissolved in toluene PA.

2.3.2 Computational Analysis

Fatty acid profile obtained by del Río et al. (2016) was used to construction of the oil profile studied in TAGs (33 triacylglycerol molecules with 99 fatty acid radicals), and the number of each radical in these 33 molecules was proportional to the percentage of composition. These FA radicals were randomly distributed among the 33 molecules of TAGs.

Thus, the thermophysical properties were estimated for each mixed TAG by applying the specific prediction method and then the mixing rule was used to estimate the oil property.

2.4 Characterization of FAME and FFAE biodiesel

Normally, the compositions and properties of the compounds present in a mixture are used to estimate the properties, using the ideal mixing rule (Equation 48).

$$P_{mixture} = \sum_{i=1}^n x_i P_{pure,i} \quad (48)$$

This method is used to estimate a property of a mixture with known composition from the properties of the pure substance, in which $P_{mixture}$ is property of the mixture, x_i is the molar fraction or mass fraction of component i , and $P_{pure,i}$ is the value of the corresponding property of the pure compound.

III. RESULTS AND DISCUSSIONS

Three statistical parameters have been used to determine the accuracy of the performed predictions: absolute deviation (AD), relative deviation (%RD) and absolute average relative deviation (%AARD):

$$Absolute\ deviation\ (AD) = |x_{exp,i} - x_{calc,i}| \quad (49)$$

$$\%RD = \frac{|x_{exp,i} - x_{calc,i}|}{x_{exp,i}} \quad (50)$$

$$\%AARD = \frac{1}{n} \sum_i^N \frac{|x_{exp,i} - x_{calc,i}|}{x_{exp,i}} \quad (51)$$

X is the property to be evaluated, n is the number of experimental data, and the subscripts "exp" and "calc" indicate the experimental and calculated property, respectively.

3.1 Estimation of thermodynamic properties

3.1.1 Normal boiling temperature (T_b)

First, normal boiling temperatures for triacylglycerols were estimated, whose experimental data were found in the literature. The contribution methods of JOBACK and GANI groups, and the method based on ZONG fragments were evaluated and the estimated data are represented in Fig. 2.

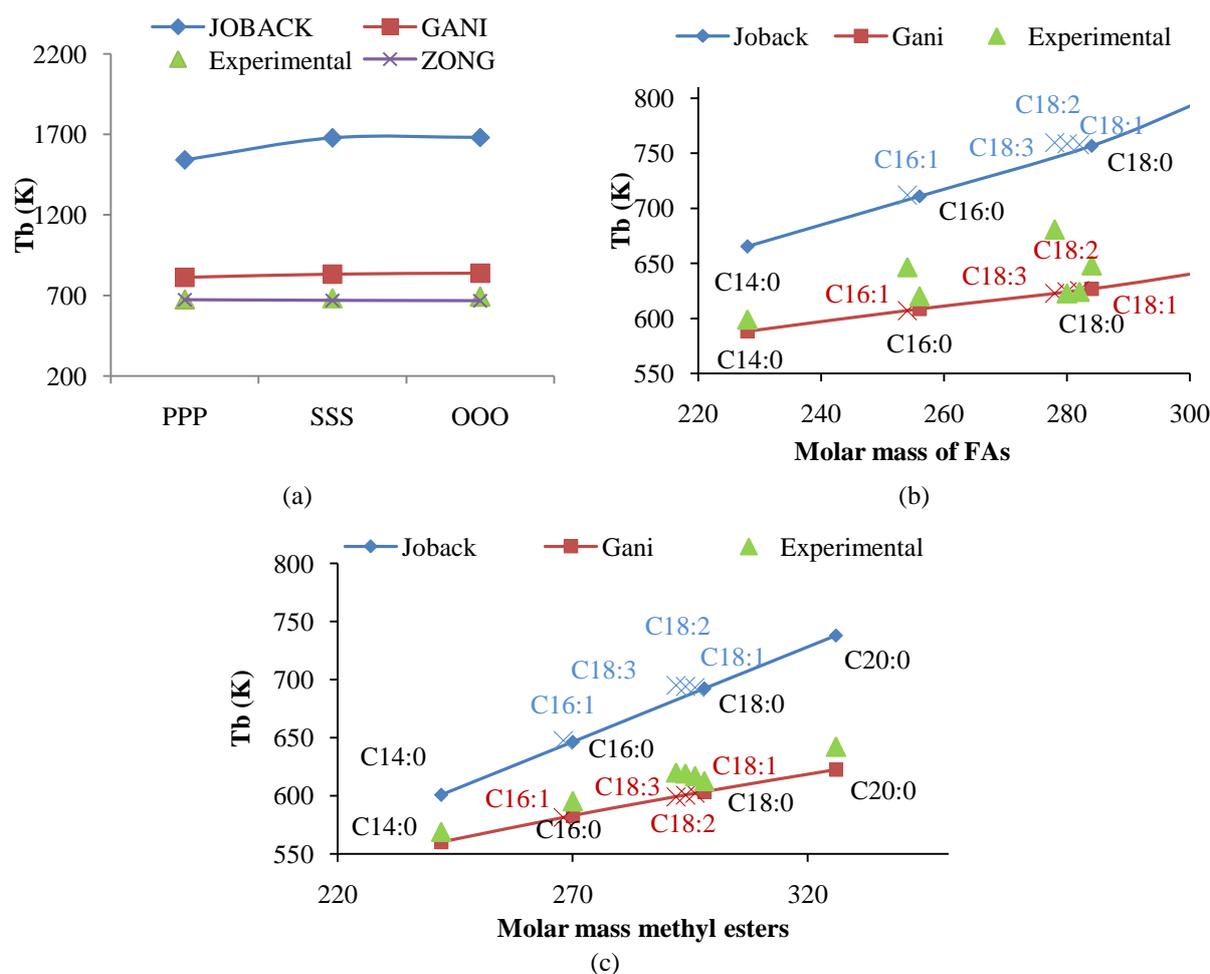


Fig. 2. Normal boiling temperatures (K) estimated for (a) Simple triacylglycerols, (b) fatty acids and (c) methyl esters. X represents unsaturation forms.

However, between the two methods studied to estimate the boiling temperature of methyl and ethyl esters, GANI presented the highest precision in the face of experimental data. Thus, the method was chosen to be used in the calculations of this work.

3.1.2 Critical properties (P_c , V_c and T_c)

It's important to mention that only critical temperature data from some AGs were found (NIST, 2019). No values were available for TAGs, DAGs and MAGs. The AARD obtained for the predicted critical temperatures for the AGs compared to the experimental data are 3.31%, 0.52%, 3.57% and 2.40%, respectively, for the JOBACK, GANI, LYDERSEN and AMBROSE methods.

It is noted that the GANI method presented an average of the smaller relative deviations for fatty acids (AARD=0.52%). In addition, this method is the only one among those evaluated that requires, as input, only the molecular structure (TECH, 2019). Thus, this was chosen to predict the critical properties of the components of oils.

An et al. (2013) estimated critical properties using the methods of Ambrose (1980) and Joback and Reid (1987). According to the authors, in these two methods the critical temperature estimation is dependent on the normal boiling temperature. Therefore, the critical temperature was also evaluated by the authors by Fedors (1982), in which the critical temperature is independent of the normal boiling temperature. According to An et al. (2013), the Joback method presented the lowest deviations for critical volume and Ambrose's method presented the smallest deviations from the data available in (NIST, 2019) for critical temperature and pressure. Similarity was observed with the data estimated in this study with those determined by García et al. (2012) and Evangelista et al. (2018).

The AARDs obtained for the predicted critical temperatures for methyl and ethyl esters were <10%. Moreover, the GANI method presented an AARD smaller than methyl esters and ethyl, respectively 3.07% and 4.55%. In addition, this method is the only one among those evaluated that requires, as input, only the molecular

structure (TECH, 2019). Thus, GANI method was chosen for the prediction of the critical properties of FAME and FAEE.

3.1.3 Acentric factor (ω)

The data estimated by Kesler and Lee (1976); Pitzer (1955) showed similar results, with average deviations < 1.0%. In this work, the Pitzer rule was adopted for the determination of the acentric factors of all compounds, as it is the most used method according to (REID; PRAUSNITZ; POLING, 1987).

3.1.4 Enthalpy of formation and Gibbs free energy formation in the standard state (H_f^0 , G_f^0)

The absolute deviations obtained for standard energy of formation for triolein was: $AD_{GANI} = 1.08 < AD_{JOBACK} = 14.41 < AD_{BENSON} = 35.05$ kJ.mol⁻¹; for diolein $AD_{JOBACK} = 14.84 < AD_{GANI} = 16.09 < AD_{BENSON} = 44.92$ kJ.mol⁻¹ and monoolein $AD_{GANI} = 14.68 < AD_{JOBACK} = 15.34 < AD_{BENSON} = 45.66$ kJ.mol⁻¹. It is noted that the evaluated methods presented relative mean deviations below 3%. The lowest AARD was observed when GANI (0.75%) was used, followed by JOBACK (0.95%). However, the GANI method requires normal boiling temperature as input. Thus, to avoid the error associated with a previously estimated measurement, the method chosen in this work was JOBACK. This requires as input only the molecular structure of the compounds. The Gibbs free energies also were calculated by JOBACK for TAGs, DAGs and MAGs.

For the FAs and esters, only data of stearic acid, methyl ester oleate and ethyl ester oleate were obtained for enthalpy of formation. The AADR found for the methods of JOBACK, GANI and BENSON, respectively, were 13.42%, 16.10% and 37.86%. Therefore, the first method was chosen to predict the formation energy for fatty acids. For Gibbs free energy, the method chosen for fatty acids and esters was BENSON (Reid et al., 1987). According to (TECH, 2019), this is more accurate in estimating this property compared to GANI and JOBACK methods, considering the effects of neighboring atoms on calculations.

3.1.5 Vapor pressure (P_{vap})

The vapor pressure was initially evaluated for simple TAGs by the group contribution method (Ceriani et al., 2013) and fragment-based method (Zong et al., 2010a, b). Fig. 3 compares the estimated P_{vap} data compared to experimental data for tristearin (SSS) and tripalmitin (PPP), obtained in (Perry et al., 1949).

The methods evaluated showed similar predictions for TAGs as shown in Fig.3. The means of the deviations of the estimated steam pressures, in the temperature range of 230 to 313°C, for the simple triacylglycerols tripalmitin (PPP) and tristearin (SSS) were respectively 15.01 and 20.04 for ZONG and 6.63 and 19.58 for CERIANI. This resulted in AARDs for the ZONG method of 17.52% and for CERIANI 13.11%. By the analysis of the AARDs, the method of Ceriani et al. (2013) showed higher accuracy, so it was pointed to the estimation of steam pressure for TAGs.

Moreover, according to Ceriani et al. (2013), the proposed method can represent any number of fatty and hydrocarbon compounds with the lowest number of parameters and can extrapolate the temperature (critical point), by correctly describing the vapor pressures and vaporization heats.

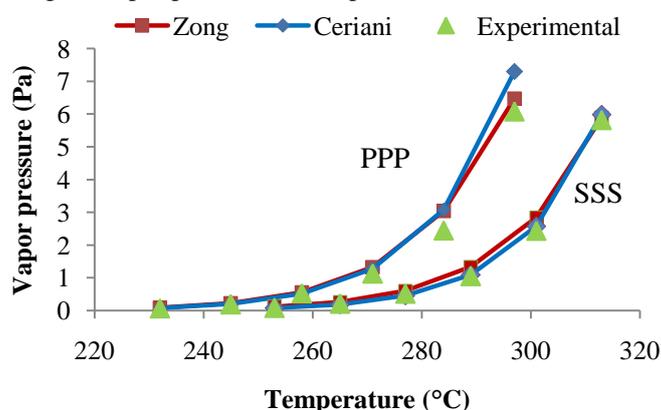


Fig. 3. Experimental and estimated vapor pressure (Pa) data for tripalmitin (PPP) and tristearin (SSS).

3.1.6 Enthalpy of vaporization (H_{vap})

Estimated values for enthalpy of vaporization were compared to data obtained from NIST (2019). According to the analysis of AARD, the lowest AARD was observed for the Basarova method (2.68%),

followed by Ceriani (10.05%) and Pitzer (25.55%). It is noteworthy that, for the methods of Pitzer (1955) and Basařová and Svoboda (1995), it is necessary to inform the critical temperatures and pressures, and the acentric factors of the TAGs.

Su et al. (2011) indicated Basarova and Svoboda method to predict enthalpy of vaporization values when the Ceriani and Meirelles (2004) method was used. In turn, Ceriani et al. (2013) corrected the temperature limitations of the previously proposed method Ceriani and Meirelles (2004). So, the method adopted in this study to predict ΔH_{vap} of TAGs, DAGs, MAGs, FAME and FFAE was Ceriani et al. (2013).

3.2 Properties of characterization of FAME and FFAE

3.2.1 Viscosity (ν)

Viscosity estimates were calculated in the temperature range from 5 to 90°C. Fig.4 shows the relative deviations (DR) obtained between the experimental and estimated values.

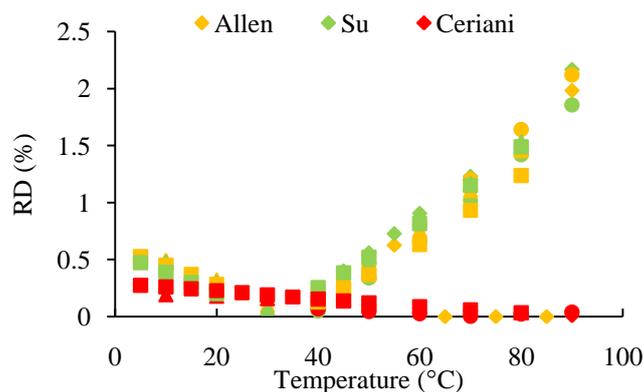


Fig. 4. Relative deviations (%) viscosities estimated for FAME (\blacklozenge C16:0, \bullet C18:0, \blacktriangle C18:1, \blacksquare C18:2). Points in orange were obtained by the method of Allen et al. (1999), green Su et al (2011) and red by Ceriani et al. (2007).

3.2.2 Number of cetane

To analyze number of cetane estimated was used the experimental data determined by , Knothe et al. (2005) and McCormick et al. (2001) and . The evaluated methods estimated presented with good approximation, indicated by the low AARDs (<11%). It is noteworthy that the methodology proposed by Clements (1996) has the restriction of considering only a few methyl esters, ignoring the rest. A neglected example is the ester derived from palmitoleic acid (C16:1).

The Gopinath et al. (2009) method showed the lowest mean of relative deviations ($AARD_{\text{GOPINATH}} = 3.40\%$) compared to the others evaluated ($AADR_{\text{CLEMMENTS}} = 4.36\%$ and $AADR_{\text{CHANGELIU}} = 10.88\%$). So, this method was adopted for the calculation of cetane numbers for methyl and ethyl esters.

3.2.3 Flash point

The relative deviations of the estimated flash points were determined using experimental data from Kimura et al. (2010). This study recommends the methodology of Stefanis et al. (2004) for the determination of the flash point of methyl and ethyl esters, for presented the lowest absolute average relative deviations ($AARD_{\text{STEFANIS}} = 3.0\% < AARD_{\text{SU}} = 10.3$).

3.2.4 Cloud point (CP), Pour Point (PP) and Cold Filter Plugging Point (CFPP)

The method of Su et al. (2011) was chosen for the calculation of these properties of methyl and ethyl esters, for presenting smaller relative deviations than Sarin method. For FAMEs determined $DR_{\text{C14:0}} = 10.02\%$, $DR_{\text{C16:0}} = 6.20\%$ and $DR_{\text{C18:0}} = 6.89\%$ to SARIN and $DR_{\text{C14:0}} = 6.89\%$, $DR_{\text{C16:0}} = 1.86\%$ and $DR_{\text{C18:0}} = 6.49\%$ SU methods. In addition, the calculations for this method are simple based only on the size of the carbon chain and the number of double bonds.

3.3 Characterization of vegetable oils

3.3.1 High Performance Gas Chromatography Analysis (GC)

The results of chromatographic analysis can be seen in Table 2. As in this technique a non-polarized capillary column was used, the analysis is qualitative and simplified.

Table 2. Composition of macauba pulp oil obtained by GC

Sample	Macauba pulp oil		
	Rep. 1	Rep. 2	Examples of possible TAGs
C48	0.77924	0.80121	PPP
C50	9.96296	9.79972	PPS, PPO, PPL, PPLn
C52	42.1804	41.928	SSP
C54	47.077	47.471	SSS, OOO, LLL

Note: No exist differentiation between C18:0, C18:1 e C18:2

A more refined separation of TAGs occurs when a polarized column is used in chromatographic analysis. So, in a polarized column, separation of TAGs, such as POO and PLS, which are TAGs with the same number of carbons and degree of unsaturation, but with different polarity, can be achieved. In both non-polar and polarized columns, there is no discrimination between isomeric triglycerides such as POO and OPO (Antoniosi Filho et al., 1995).

3.3.2 Computational Analysis

The identification of triacylglycerols by groups with different numbers of carbon atoms and by different combinations of saturated and unsaturated fatty acids were made by comparing the percentage data obtained from the GC with those provided by the program created on the computer. It can be observed that the proportions of each component calculated by the computer (PC) are close to the average obtained by chromatographic analysis (GC). The composition of macauba oil in triacylglycerol determined to PC technique was: C50=10%, C52=44% and C54=46% and for GC methodology C48=0.79%, C50=9.88%, C52=42.05% and C54=47.27%.

Thus, the list of triacylglycerols presented in Table 3, obtained by the computer program, will be considered as the composition of the macauba pulp oil for this present study. Since the mixed triacylglycerol approach is closer to reality, and the results of chromatographic analysis show that the program used for the distribution of mixed TAGs meets the data obtained experimentally.

Table 3. Characterization of macauba pulp oil in TAGs

Groups	TAGs	%m/m	Groups	TAGs	%m/m	Groups	TAGs	%m/m
C50:1	POP	8.0	C52:3	PLO	2.0	C54:3	OOO	26.0
C50:1	PPoS	2.0	C52:4	LOP _o	6.0	C54:4	OOL	14.0
C52:2	POO	28.0	C52:4	PLnO	4.0	C54:5	OLL	2.0
C52:3	OP _o O	4.0	C54:2	SOO	4.0			

3.4 Properties of vegetable oils

The representation of temperature-dependent thermophysical properties, such as vaporization enthalpy (H_{vap}) and vapor pressure (P_{vap}) is shown in Fig.5 (a) and Fig.5 (b), respectively.

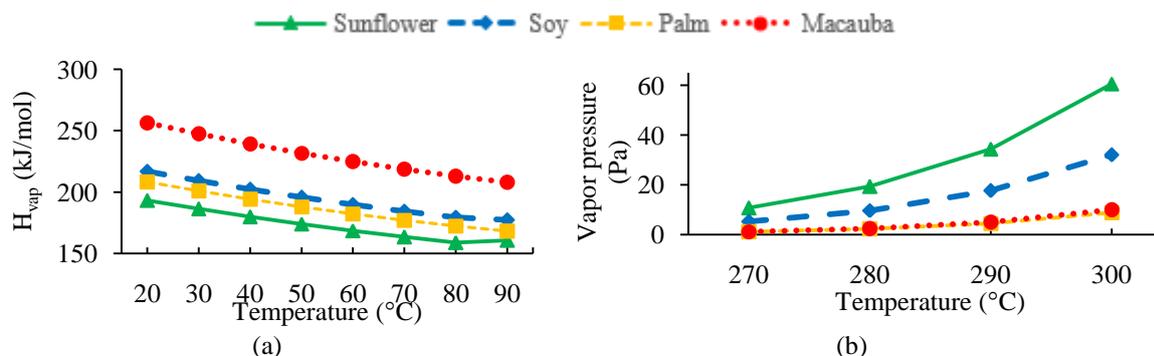


Fig. 5. Estimated properties dependent on temperature (a) Vaporization enthalpy and (d) vapor pressure for sunflower (▲), palm (■), soybean (◆) and macauba pulp (●) oil

By the analysis of Fig.5 (a), it is observed that the enthalpy of vaporization of vegetable oils decreases with increasing temperature. Heat of vaporization for soybean oil was determined by Hammond et al. (2005),

$H_{\text{vap}}=184.9$ kJ/mol. The predicted value for soybean oil in this study was in the range of 216 to 174 kJ/mol, showing that there is agreement of the predicted given with the experimental.

Vapor pressure of various vegetable oils was determined by Murata et al. (2010). The authors found vapor pressures for soybean oil in the range of 2.6kPa to 73.5kPa, ranging from 250-330°C. Similar values were observed, as can be seen in Fig.5 (b).

Table 4 shows the rest of the thermophysical properties that were estimated for the different vegetable oils under study, which can be able to use as input data for engineering calculations like simulations and optimize process.

Table 4. Estimated properties for vegetable oils by the methods adopted in this work

Properties	Sunflower	Soybean	Palm	Macauba
T_b (K)	583.34	662.40	615.54	739.08
T_C (K)	836.34	950.30	879.71	1051.57
P_C (N/m ²)	2.95x10 ⁵	3.36 x10 ⁵	3.17 x10 ⁵	3.86 x10 ⁵
V_C (m ³ /kmol)	2.80	3.18	2.91	3.48
H_f (J/kmol)	-1.40 x10 ⁹	-1.76 x10 ⁹	-1.84 x10 ⁹	-2.09 x10 ⁹
G_f (J/kmol)	-6.95 x10 ⁷	-2.16 x10 ⁸	-3.99 x10 ⁸	-3.73 x10 ⁸
ω	-0.59	-0.66	-0.62	-0.75

3.4.1 Properties of FAME and FAAE biodiesel

Table 5 analysis shows that the normal boiling points of FAAEs are higher than FAME. Goodrum (2002) experimentally determined the boiling temperature of methyl and ethyl esters obtained from soybean, canola, rapeseed, and animal fat oils. For methyl esters, this author observed 620.80 K (soybean oil) and 642.14 K (rapeseed oil), however for the ethyl esters 628.39 K (soybean oil) and 635.39K (rapeseed oil) were found.

Table 5. Estimated properties for biodiesel composed of methyl and ethyl esters corresponding to the pulp oil of macauba, soybean, sunflower and palm, by the methods adopted in this work

	FAME			
	Sunflower	Soybean	Palm	Macauba
T_b (K)	547.59	593.64	541.50	685.00
T_C (K)	704.99	763.10	697.87	880.85
P_C (N/m ²)	1.02x10 ⁶	1.12 x10 ⁶	1.08 x10 ⁶	1.31 x10 ⁶
V_C (m ³ /kmol)	1.00	1.08	0.97	1.24
H_f (J/kmol)	-5.27 x10 ⁸	-6.06 x10 ⁸	-6.13 x10 ⁸	-7.39 x10 ⁸
G_f (J/kmol)	-5.54 x10 ⁷	-9.09 x10 ⁷	-1.46 x10 ⁸	-1.42 x10 ⁸
ν (cSt)	3.77	4.11	4.47	4.41
CN	43.94	48.46	61.93	54.17
Flash point (K)	449.02	448.60	441.64	447.07
CP (K)	281.35	281.06	281.35	280.30
PP (K)	278.72	278.36	278.72	277.39
CFPP (K)	278.04	277.75	278.04	276.97
	FAAE			
	Sunflower	Soybean	Palm	Macauba
T_b (K)	556.52	603,38	550,79	696,35
T_C (K)	711.99	771,82	706,24	891,04
P_C (N/m ²)	9.67 x10 ⁵	1,06 x10 ⁶	1,02 x10 ⁶	1,24 x10 ⁶
V_C (m ³ /kmol)	1.05	1,14	1,02	1,31
H_f (J/kmol)	-5.46 x10 ⁸	-6.27 x10 ⁸	-6.32 x10 ⁸	-7.63 x10 ⁸
G_f (J/kmol)	-4.77 x10 ⁷	-8.26 x10 ⁷	-1.39 x10 ⁸	-1.33 x10 ⁸
ν (cSt)	3.84	4.19	4.54	4.49
CN	49.74	54.97	64.91	60.10
Flash point (K)	459.83	459.41	452.46	457.88
CP (K)	359.56	357.44	342.89	353.44
PP (K)	291.34	287.14	312.89	279.32
CFPP (K)	290.54	286.83	305.25	279.92

Yuan et al. (2003)determined the critical properties for the methyl esters of soybean oil. The critical temperature, pressure and volume obtained were 785.7 K, 12.08 bar and 1.082 m³/kmol, respectively. The

absolute deviations of these data compared to the data estimated in this study are low (13.9 K; 0.88 bar and $0.02\text{m}^3/\text{kmol}$), showing the accuracy of predictive methods.

Kinematic viscosities determined by Rodrigues (2007) for methyl and ethyl biodiesel from macauba pulp oil, 4.525 cSt and 4.782 cSt, respectively. In this work, 4.41 and 4.49 cSt were obtained, respectively, for the same esters of macauba pulp oil (Table 5).

Knothe et al. (2005) determined that the cetane number of soybean methyl biodiesel is in the range of 48.7 to 55.9. In this work, values of CN similar the experimental data was obtained (48.5), as can be observed in Table 5. The same authors determined for palm ethyl biodiesel CN=56. Compared to the data obtained in this study, a relative deviation of 11% was determined for ethyl palm biodiesel. This deviation is relatively small, so it generates low error when this method is adopted.

According to Yuen et al. (2005), ester pour points range from 6 to 18°C (279 to 291K). The pour point is defined as the lowest temperature that the product can still be poured by gravity. Methyl esters have better cold flow properties when compared to ethyl esters, as can be seen by Table 5.

The cloud point was generally greater than the fluidity points of the same product, ranging from 268K to 359K (Table 5). The flash points of methyl esters were greater than 420 K, a higher value than fuel derived from mineral diesel. According to Yuen et al. (2005), methyl esters obtained from palm oil exhibit a flash point between 438 and 451K, while mineral diesel has a flash point of less than 80°C (353K). Kouame (2011) determined glow points for biodiesel obtained from 393K Jatropha oil versus 448.15K for soybean biodiesel. In this work, the estimated value for the flash point of soybean oil was 448.60K, which presents a low absolute deviation ($AD=0.45\text{K}$), showing that the predictive method adopted is accurate.

Cavalcante et al. (2010) determined the cold clogging point (CFPP) of biodiesel from soybean and palm oil, -2°C and 16°C , respectively. In this work, it was found for this property for the methyl esters of soybean oil, sunflower, palm and macauba, values between 276 and 278K (Table 5). For ethyl esters, the values obtained from CFPP were higher and are in the range of 280 to 305K.

IV. CONCLUSION

This work showed that the modeling of properties of TAGs, DAGs, MAGs, fatty acids, methyl, and ethyl esters is closely linked to the estimation of base parameters, such as normal boiling temperature, properties critical and acentric factor. In addition, it was shown that the use of experimental data to validate the method should be carried out with caution, considering that the nature of many available data is predicted.

Prediction models of properties such as group contribution and fragment approach were evaluated to determine the normal boiling point, critical properties, vapor pressure and vaporization enthalpy of fatty acids, triglycerides, diacylglycerols and monoacylglycerols; and viscosity, number of cetane, flash point, cold flow properties for esters. It was possible to arrive at values similar the experimental values of the properties to vegetable oils and esters with the application of selected methods for each property.

The knowledge of the thermophysical properties of esters is important in engineering calculations, especially in simulations and process optimization. Therefore, identifying the best method of predicting properties is crucial for data to be closer to the real. Thus, in this work a database was created that can be used as input parameters in simulation projects.

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