Numerical expressions for viscosity, surface tension and density of biodiesel: analysis and experimental validation

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The purpose of this work was to test the accuracy and predictive power of different numerical methods in order to compute reliable values of viscosity, surface tension and density of biodiesel in a wide range of temperature. Available formulae in literature were used to compute the mentioned properties in the temperature ranges in which they were developed. To validate the numerical expressions we have used experimental measurements of viscosity, surface tension and density performed in our laboratory and published in the literature.

In this article, the results obtained by the application of different expressions are shown and possible sources of discrepancy between measured and predicted values are mentioned. The method that predicts the best results is identified for each property. In order to achieve a better fitting to the experimental data, corrections in the expression of the temperature-dependent properties were made when they were necessary.

Keywords: numerical expressions; viscosity; surface tension; density; biodiesel

1. Introduction

The energy crisis that many countries face, the increase of the consumption of fossil fuels and the increase of greenhouse gases concentration produced by their combustion, the decline of the oil reserves, the validity of the Kyoto Protocol and legislation increasingly demanding the control and reduction of pollutant emissions are some reasons to promote, develop and use renewable and environmentally friendly energy resources as soon as possible.

Biodiesel is produced from vegetable oils or animal fats and an alcohol by an alkali catalysed transesterification. The most used alcohol is methanol, which creates a mixture of fatty acid methyl esters. This liquid biofuel can be used mixed with petrodiesel or alone in a diesel engine. Due to the worldwide increase in the production and use of this biofuel, it is extremely important to be able to estimate and predict the dependence of its physicochemical properties with the temperature. The values of these properties depend on

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the proportion of the alkyl esters in the biodiesel, and so they vary with the origin of the oils or fats that were used to produce the fuel.

The study of the variation, with the temperature, of the viscosity, surface tension and density is a key topic in permanent development [1–4] because these properties have influence on the economic, technical and environmental aspects of the fuel use. The knowledge and the prediction of the values of these properties in a wide range of temperatures are fundamental in the performance study of biodiesel as fuel. This can include temperatures below 0°C at which the biofuel can be eventually stored [5], to the temperature of combustion; also important are the intermediate temperatures, such as those of injection and atomisation [6–8]. The atomisation process depends on the geometry of the injection system and the physicochemical properties of the fuel, especially viscosity, surface tension and density [6]. In order to evaluate this process for different injectors, it is necessary to know the values of these properties in a vast range of temperatures.

There are different methods and programs available in the literature which can be used to determine physicochemical properties in petrofuels, but the information for biodiesel is reduced considerably. In order to estimate the temperature-dependent viscosity, surface tension and density of biodiesel, general methods to deduce these properties for pure liquids and their mixtures at different temperatures can be used. Also, specific expressions for the alkyl esters comprised in the biodiesel are developed under particular conditions [5,7,8,9–13]. The validity of these expressions depends on the experimental values used, and therefore they should not be extrapolated out of the development condition, because the fitting coefficients depend on the set of measurements used in their determination – not on the molecular structure of their components and the characteristics of the mixture. On the other hand, although the general formulae do not take into account many characteristics of the compounds (presence of isomers, branching, impurities, etc. [7,12]) they provide a way to establish a relation between the properties and the chemical structure and proportion of components in the mixture. Moreover, they do not depend on specific experimental values and can be used even in cases which lack experimental information.

In this work, the agreement between the results obtained for temperature-dependent viscosity, surface tension and density can be computed using different expressions and experimental values (from our laboratory and from literature). Their results are evaluated. Some sources of discrepancy between experimental and computed values are found. A solution to improve the agreement between the estimated properties and the experimental values (when they are available) is proposed. Therefore, the estimations related to the fuel efficiency based on these properties will be more realistic.

2. Methodology

Any study requiring the values of physicochemical properties of a substance must be based on the reliability of these values, being they measured or computed. When they are computed, the predictive power of the used formulae should be evaluated and analysed in comparison with other expressions for the same property in the same conditions, to estimate accuracy and, if it corresponds, stability or tendency. For this reason, a computational program was operated by our group to compute different expressions developed by several authors from observations of certain regularities (related to the structure of the considered substances) in several temperature-dependent properties. The program also compares the results of the estimated property in the selected range of

temperatures with data measurements, computing differences and presenting the information in graphical form.

The expressions tested (Equations (2), (3), (4), (12) and (13) below) are approximate empirical formulae that relate to the values of some properties of interest to the temperature. They all take into account some characteristics of the internal structure of the substances for which the property is computed, a situation reflected through the model parameter. This feature characterises them as general expressions in contrast with particular ones, originated in data fitting of a set or sets of measurements, that can only be applied to the group of data for which they were developed, still when they correspond to complete series of substances [7–10,12,13]. These particular expressions are a good reference to improve the estimations in the case of insufficient data to validate the formulae, and also (knowing the origin and the conditions of the substances under consideration) they can be used to infer the influence of the molecular structure on the properties of interest [12].

In the first part of this section, several techniques used to compute temperature-dependent viscosity, surface tension and density of pure, non-polar liquids are presented. Then, the mixing rules recommended in the literature are analysed. Finally, the experimental conditions under which these properties were measured in our laboratory are described.

2.1. *Physicochemical properties of pure, non-polar liquids*

2.1.1. *Viscosity*

The viscosity is a property of relevance in the characterisation of fuel and for quality control. For this reason, when the fuel is a mixture of substances, knowledge of the viscosity of its components and their influence in the fuel viscosity are of great importance. The study of performance, waste and deposits in engines as well as the formation of pollutants due to the characteristics of the combustion, requires the values of fuel viscosity in a wide range of temperatures. As the amount of articles about properties of biodiesel and its constituents is scarce compared with those on the same topics for diesel fuel, the development and validation of estimation formulae, relating viscosity and temperature for these substances, is needed.

It is widely accepted that the expressions linking viscosity of pure, non-polar liquids with temperature have the form stated in the Equation (1):

$$\eta = A e^{B/T}, \tag{1}$$

where

η is the dynamic viscosity, mPa.s, or the kinematic viscosity, $mm^2 s^{-1}$,
T is the absolute temperature, K, and
A and B are constants.

The previous equation is known as the equation of Andrade [2,14,15].

In the book of Reid *et al.* [14], different techniques are referred to estimate the variation of the viscosity in the so-called 'low-temperatures range', $T < 0.75\ T_c$ (T_c: critical temperature). In the present work, two of them were analysed: the technique of Orrick and Erbar, and the one of Van Velzen, Cardozo and Langenkamp.

The parameters of the Orrick and Erbar's technique are sensitive to the compound structure. The suggested expression is Equation (2):

$$\ln\left(\frac{\eta_l}{\rho_l M}\right) = A + \frac{B}{T},\tag{2}$$

where

η_l is the dynamic viscosity of the liquid, mPa.s,
ρ_l is the density of the liquid at 20°C, g cm^{-3},
M is the molar mass, g mol^{-1}, and
T is the temperature, K.

The values of the parameters A and B are computed from the contribution of the structural groups of the liquid (using the values of Table 9.9 in Reid *et al.* [14]). The reported errors for the method vary, being the average deviation for organic liquids, ~15%.

Another expression to evaluate the evolution of the dynamic viscosity with the temperature is the method of Van Velzen, Cardozo and Langenkamp, based on Equation (3):

$$\log \eta = B\left(T^{-1} - T\mathrm{o}^{-1}\right),\tag{3}$$

where

η is the dynamic viscosity, mPa.s,
T is the absolute temperature, K, and
T_o and B   are constants.

These constants are computed, as in the previous technique, from the contribution of structural groups (with the values of Table 9.10 in Reid *et al.* [14]). In the comparison with the measured values of time-dependent viscosity for general organic liquids, large errors were reported and special care is suggested in the selection of the internal parameters. Nevertheless, as can be seen below, the application of this technique in the case of the viscosity of the fatty acid methyl esters here involved gives better results than those obtained by the previous technique.

Expressions developed for fatty acid methyl esters were presented by Gouw *et al.* [16] and by Krisnangkura *et al.* [15]. All of them are valid in a more restricted range of temperatures (20°C < T < 80°C), and they require experimental values to calibrate the parameters. The formula developed in the first article for saturated methyl esters (from C12:0 to C19:0) is the following:

$$H = A + S\theta,\tag{4}$$

where

$$H = \log(1.200 + \log \eta),\tag{5}$$

η is the dynamic viscosity, mPa.s,
A is a constant depending of the carbon number, and

S is the slope index,

$$\theta = -\log\left(1 + \frac{T}{135}\right),\tag{6}$$

T is the temperature, °C.

The authors compute the value of S for the mentioned homologous series. As it is based on measured values, it is valid for temperatures between 20 and 70°C. No expressions for temperatures-depending viscosity for unsaturated fatty acid methyl esters are developed there in, but there are experimentally measured values for viscosity at 20, 40 and 70°C for C18:1, C18:2 and C18:3, among others.

Krisnangkura *et al.* [15] deduced relationships for the kinematic viscosity of saturated fatty acid methyl esters. These expressions relate the natural logarithm of the kinematic viscosity with the temperature and the carbon number of the compound, starting from Andrade's formula and through thermodynamic considerations. The parameter calibration of the model is performed using data of literature. To best fit the data, the homologous series is divided in two parts: the subseries with low carbon number to (from C6:0 to C12:0) and the one with high carbon number (from C12:0 to C18:0). The presented relationships are the following:

Viscosity for short-chain methyl esters:

$$\ln \mu = -2.915 - 0.158z + 492.12/T + 108.35z/T\tag{7}$$

Viscosity for long-chain methyl esters:

$$\ln \mu = -2.177 - 0.202z + 403.66/T + 109.77z/T\tag{8}$$

where

μ is the kinematic viscosity, $\mathrm{mm^2\,s^{-1}}$,
T is the temperature, K,
z is the carbon number.

In the case of unsaturated fatty acid methyl esters, only linear correlations between the natural logarithm of the kinematic viscosity and the inverse of the absolute temperature are stated. For the purpose of the present work, the following expressions are considered:

$$\ln \mu_{18:1} = -5.03 + \frac{2051.5}{T}\tag{9}$$

$$\ln \mu_{18:2} = -4.51 + \frac{1822.5}{T}\tag{10}$$

$$\ln \mu_{18:3} = -4.18 + \frac{1685.5}{T}\tag{11}$$

2.1.2. *Surface tension*

The surface tension also plays an important role in the evaluation of fuel performance. In spite of this, we did not find published information about its variation with temperature for the case of biodiesel and its constituent fatty acid methyl esters.

To estimate the variation of the surface tension of pure, non-polar liquids with the temperature, two methods are discussed in Reid et al. [14]. In the present work, the technique of MacLeod and Sugden was analysed. It needs the value of a parameter, called parachor [P] (independent of the temperature but depending on the structural groups of the molecules of the liquid) that relates the surface tension to the vapour and liquid densities of the substance. The values for its computation are mentioned in Allen et al. [8], Reid et al. [14] and Perry et al. [17]. The resulting expression (using correlation between temperature and vapor and liquid densities) is shown in Equation (12).

$$\sigma = ([P]\rho_{lb})^4 \left\{ \frac{(1 - T_r)}{(1 - T_{br})} \right\}^{4n}, \tag{12}$$

where

σ is the surface tension, $dyn\,cm^{-1}$,
$[P]$ is the parachor,
ρ_{lb} is the liquid density at the normal boiling point, $mol\,cm^{-3}$,
T_r is the reduced temperature,
T_{br} is the reduced boiling point, and
$n = 0.31$ for organic compounds.

2.1.3. Density

To convert dynamic viscosity into kinematic viscosity, values of liquid density in the complete range of temperature here considered were needed. To better fulfill this task, the modified Rackett's technique [14,18] was used to estimate the density of the fatty acid methyl esters, using published values for the reference density. The formula is

$$\rho = \frac{\rho_R}{(Z_{RA})^\phi}, \tag{13}$$

where

ρ is the density, $kg\,l^{-1}$,
ρ_R is the experimental density at the reference temperature T_R, $kg\,l^{-1}$, and
Z_{RA} is an unique constant for each substance, evaluated with the following equation:

$$Z_{RA} = 0.29056 - 0.08775 \cdot \omega. \tag{14}$$

ϕ is computed using the formula

$$\phi = \left(1 - \frac{T}{T_c}\right)^{2/7} - \left(1 - \frac{T_R}{T_c}\right)^{2/7}, \tag{15}$$

where

T is the temperature, K,
T_R is the reference temperature, K, and
T_c is the critical temperature, K.

ω is the acentric factor, computed with the following formula:

$$\omega = -\log P_{vpr} - 1.00, \tag{16}$$

where

P_{vpr} is the reduced vapor pressure of the liquid (at reduced temperature $T_r = 0.7$).

2.2. *Physicochemical properties of mixtures of non-polar, non-associated liquids*

The estimation of the properties of a mixture depends on the constituent substances profile (in this case, the mass fraction of the methyl esters and other substances), the adopted mixing rule, and the value of the property (known or computed) for each component. If the estimation is made considering only the methyl ester contribution, a source of error is associated with the quality of the source (different composition, regional factors) and with the characteristics of the production (technological factors), as the influence of the other components is masked [2,11]. Taking into account that in the case of the present work, the mixing rules are simple (see below), the taken values for the properties of each one of the methyl esters has great incidence in the final result. The techniques presented in Section 2.1. establish a fixed value for the considered property (according to the selected parameters for each method), for each value of temperature and each constituent of the mixture. Therefore, the evolution of the property values with the temperature for the biodiesel will depend on the mixing rule and the proportion of the comprising substances considered. This will justify the election of a correction factor affecting the complete relationship, to adapt the values of the property when they deviate from the data measured on some particular production (for which it is of interest to evaluate the behaviour even in the range of temperatures where data are not available). As the shape of the curve representing the evolution of the property with the temperature is the correct one, the adjusted values will be reliable in the complete range.

Knowledge of acceptable values for those properties under similar conditions [1,2] is of central importance to develop and validate expressions that allow the estimation of the evolution of these properties under conditions in which the measurements are difficult or impossible.

2.2.1. *Viscosity*

For reduced temperatures <0.7, the viscosity of liquids is very sensitive to the structure of their constituent molecules. For this reason, Reid *et al.* [14] recommend computing the mixture viscosity with an expression that takes into account the interactions among molecules of the constituent liquids, as it is the case of the method of Grunberg–Nissan whose expression is shown in the Equation (17):

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \sum_{i \neq j} \sum_j x_i x_j G_{ij}, \tag{17}$$

where

η_m is the dynamic viscosity of the mixture, mPa.s,
x_i is the molar fraction of the ith component,

η_i is the dynamic viscosity of the ith component, mPa.s, and
G_{ij} is an interaction parameter.

In the case of biodiesel, the comprising methyl esters are non-polar, non-associated liquids at the temperatures of interest. Therefore, Allen *et al.* [7] suggest taking all the interaction parameters, G_{ij}, equal to zero. The previous suggestion, made for a fixed temperature of 40°C, is extended by Krisnangkura [15] to the interval between 20 and 80°C. In both articles the authors used mass fractions instead of mole fractions. Applying this suggestion to the present study, the simple rule was used to compute temperature-dependent kinematic viscosity of biodiesel through kinematic viscosities of its fatty acid methyl esters computed with the rules of Orrick and Erbars, VanVeltszen, Cardozo and Langenkamp, and Krisnangkura *et al.* The final mixing rule is shown in Equation (18):

$$\ln \mu_{\mathrm{m}} = \sum_i y_i \ln \mu_i, \tag{18}$$

where

μ_{m} is the kinematic viscosity of the the mixture, $\mathrm{mm^2\,s^{-1}}$,
y_i is the mass fraction of the ith component, and
μ_i is the kinematic viscosity of the ith component, $\mathrm{mm^2\,s^{-1}}$.

In the literature, there are data-fitting relationships linking viscosity of the biodiesel with the temperature [10,12], based on the measurements carried out for specific productions in a certain range of temperature. The resulting curves for biodiesel produced with soy oil were compared with the data from our production, having similar fatty acid methyl esters profiles (Table 1).

In Tat and Van Gerpen [10], Equation (19) is used to relate kinematic viscosity with temperature:

$$\ln \mu = 0.7883 - 1638/T + 582500/T^2, \tag{19}$$

where

μ is the kinematic viscosity, $\mathrm{mm^2\,s^{-1}}$, and
T is the temperature, °C.

The range of validity of Equation (19) is $0°C < T < 100°C$.

Table 1. Mass fraction (%) of the methyl esters comprising in soy oil-based biodiesel.

Methyl ester	Col. I (%)	Col. II(%)	Col. III(%)	Col. IV(%)	Col. V(%)
Methyl palmitate (16:0)	9.27	10.83	10.2	12	10.2
Methyl estearate (18:0)	3.77	4.31	4.6	3	3.7
Methyl oleate (18:1)	22.83	24.22	22.2	23	22.8
Methyl linoleate (18:2)	57.46	54.67	54.6	55	53.7
Methyl linolenate (18:3)	6.67	6.78	8.2	6	8.6
References	Our production	Tat and Van Gerpen [10]	Allen *et al.* [7,8]	Clements [4]	Ma and Hanna [3]

In Tate *et al.* [12] a similar equation is found. It is the following:

$$\ln \mu = 0.076 - 1078/T + 469.741/T^2, \tag{20}$$

where

μ is the kinematic viscosity, $mm^2 s^{-1}$, and
T is the temperature, K.

The range of validity of the expression is $0°C < T < 300°C$.

2.2.2. Surface tension

The surface tension of a liquid mixture is not a simple function of the surface tensions of its pure components [14] because, in the mixture, the composition of the surface is not (necessarily) the same as the bulk.

Allen *et al.* [8] suggest the use of the following empiric expression:

$$\sigma_m = \sum_i w_i y_i \sigma_i, \tag{21}$$

where

σ_m is the surface tension of the mixture, $dyn\,cm^{-1}$,
y_i is the mass fraction of the *i*th component,
σ is the surface tension of the *i*th component, $dyn\,cm^{-1}$, and
w_i are weighting factors.

They determined the values of the weighting factors at 40°C. We decided to consider all of them equal to one ($w_i = 1$, for all the liquid components of the mixture) due to the lack of information to select their values and to decide their trend of variation with the temperature.

2.2.3. Density

Yuan *et al.* [19] did not use mixing rules for the temperature-dependent density of biodiesel. They directly applied the Rackett expression to compute biodiesel density as function of temperature. In this case, the values for the reference density, the constant Z_{RA} and the critical temperature were those of the biodiesel. The results they obtained were in good agreement with the experimental values of Tat and Van Gerpen [9].

The formulae used in the mentioned article (that we have also used) are the following:

$$\rho_m = \frac{\rho_{Rm}}{(Z_{RA_m})^\phi}, \tag{22}$$

where

ρ_m is the density, $kg\,L^{-1}$, and
ρ_{Rm} is the experimental density at the reference temperature T_{Rm}, $kg\,L^{-1}$.

$$Z_{RAm} = \sum_i x_i Z_{RAi} \tag{23}$$

where

x_i is the mole fraction of the ith component,

Z_{RAi} is a constant of the ith component, and

ϕ is computed from Equation (24).

$$\phi = \left(1 - \frac{T}{T_{c_m}}\right)^{2/7} - \left(1 - \frac{T_{Rm}}{T_{c_m}}\right)^{2/7}, \tag{24}$$

where

T is the temperature, K,

T_{Rm} is the reference temperature of the mixture, K, and

T_{c_m} is the critical temperature of the mixture, K.

3. Experimental measurements

3.1. *Composition of the samples*

Biodiesel was obtained in our laboratory through transesterification of vegetable oils with methanol, at 60°C, using sodium hydroxide as catalyst [1,3,20,21]. The composition of different productions was determined by chromatographic analysis and the mean values were computed (Table 1, column I). The mass fractions of the fatty acid methyl esters comprising this biodiesel were similar to those reported in the literature for soy oil based biodiesel, as can be seen in Table 1. In this table, profiles of specific productions are placed in columns II and III and generic ones in columns IV and V.

3.2. *Viscosity*

The measurements were made according to the standard test method ASTM D 445 (to determine kinematic and dynamic viscosity of opaque and transparent liquids) with a Cannon Fenske (series 50 N° 255) glass viscosimeter (capillary type) maintaining the sample in a thermostatic bath (Awards heater type B) for each temperature. Kinematic viscosity data were collected between 10 and 85°C.

3.3. *Surface tension*

The measurements of surface tension were made according to the standard method ASTM D 1331 (to determine the surface tension of liquid products from petroleum) with a Krüss K8 Interfacial Tensiometer with a De Nuoy ring (mean range ±90 mN m^{-1}, precision 0.1 mN m^{-1}, resolution 0.05 mN n^{-1}). The thermostatic bath used is mentioned above. The measurements were carried out between 20 and 70°C.

3.4. *Density*

The density was measured according to the standard test ASTM D 1298 (to determine density and relative density of liquid products from petroleum) with a glass hydrometer calibrated at 15°C, maintaining the sample at constant temperature in a thermostatic bath

Awards RHS 20 (range −5 at 100°C, precision ±0.25°C). The measurements were carried out between 10 and 70°C. The correction for temperature was applied, according to the standard test.

4. Results and discussion

The literature data for soy oil-based biodiesel (mass fraction of the fatty acid methyl esters comprised in it; predicted, adjusted and measured values for the properties of interest) and the values obtained by chromatographic analysis of the biodiesel produced in our laboratory enabled us to establish comparisons. With the values (composition and properties) obtained for our biodiesel, those computed with our program and those published, we tested the formulae explained in Section 2.

To verify the influence of the mass fraction on the values for the properties and to estimate the discrepancy that could be attributed to other causes (methyl esters not included due to their low proportion, impurities, incomplete methylation, structural characteristics not taken into account, regional factors, seasonal factors inside a region, etc.) information was sought for biodiesel with similar composition. The range of temperature for which the properties were studied was limited to a maximum reduced temperature of 0.7. Then, the results were computed for temperatures between 0 and 300°C.

Relevant information for the present work included in the literature is provided below:

Tat and Van Gerpen [9,10] presented measurements of viscosity and specific gravity of soy oil-based biodiesel and its blends with diesel fuel for temperatures between 0 and 100°C. The composition of the biodiesel that they used is shown in Table 1, column II. We compared the data they presented for biodiesel with those of other sources, and we extrapolated their (non-linear and linear) regression equations to see the tendencies of the curves out of the range they were developed.

The articles of Allen *et al.* [7,8] showed results on viscosity and surface tension at 40°C for biodiesel produced by transesterification from different oils and for biodiesel which is prepared by mixing the fatty acid methyl esters in definite proportions (referred by the authors as 'simulated biodiesel'). We included (as a reference) the values of the reported properties for soy oil-based biodiesel in some of the graphics. As these authors informed the detailed composition of several biodiesel (one of them is placed in Table 1, column III), these data were used in predictions with the formulae of the section 2.

Tate *et al.* [12,13] measured the viscosity and density of biodiesel at temperatures between 0 and 300°C with special devices. No data on detailed composition of the fuels were mentioned in the articles. Fitting data curves were included. We used the fitting expressions for the properties of interest corresponding to soy oil-based biodiesel in our comparisons.

Krisnangkura *et al.* [15] developed expressions for the viscosity of methyl esters, calibrated their parameters with published data and tested the formulae with measurements. As they did not include soy oil-based biodiesel in the tests, we only used the technique developed there to compute methyl esters viscosities.

Gouw *et al.* [16] found a relationship characterising the viscosity of saturated fatty acid methyl esters and measured viscosities for saturated and unsaturated methyl esters at 20, 40 and 70°C. The values of the measured viscosities were used in this study.

Table 2. Kinematic viscosity ($mm^2 s^{-1}$) of methyl esters at $40°C$ (published values).

References	Viscosity of methyl esters ($mm^2 s-1$)				
	16:0	18:0	18:1	18:2	18:3
Knothe [11]	4.38	5.85	4.51	3.65	3.14
Gouw *et al.* [16]	4.32	5.61	4.45	3.64	3.27
Allen *et al.* [7]	4.39	5.62	4.31	3.45	2.98
Swern ([7] and references therein)	4.58	5.79	4.47	3.59	3.19

Knothe *et al.* [11] analysed the influence of the compound structure on the values of viscosity at $40°C$, remarking the incidence of isomery and branching on the measured values. The published values for methyl esters viscosity were included in our study.

4.1. *Viscosity*

There is a real need for information on the evolution with the temperature of the fatty acid methyl ester viscosity. Published data at $40°C$ are very similar, as can be seen in Table 2 for the fatty acid methyl esters comprising in soy oil-based biodiesel. This could not be the case for other temperatures, where the lack of information does not allow the comparison.

In Table 3, the literature values corresponding to measured viscosities at $40°C$ for the methyl esters of interest for three values of temperatures and the computed values from the Equations (2), (3), (8), (9) and (10), for the same temperatures can be seen. The values computed with the estimation techniques described in Section 2 provide dissimilar results. Therefore, as stated previously, the estimation of the biodiesel viscosity will be strongly influenced by the values computed for the viscosity of its fatty acid methyl esters components.

To analyse the variation of the values of biodiesel viscosity and to compare the capacity of estimation of the formulae based on structural characteristics of its fatty acid methyl esters, the values at $40°C$ measured in Knothe [11] and Allen *et al.* [7] the average measured values of our production and the fitting curves of the experimental data presented in Tat and Van Gerpen [10] and Tate *et al.* [12] were put together in Figure 1.

For biodiesel based on the same type of oil, the incidence of the mass fraction variations in the estimation of the mixture viscosity (using the techniques described in Section 2.2.1) is not shown graphically, because the curves computed for the composition corresponding to the columns I, II and III of the Table 1 overlap, being the maximum difference among the values equal to 1.54%.

For the same composition, the application of different expressions to compute temperature-depending viscosity of biodiesel (using the same mixing rule, Equation (18)) provides little different results, as it can be seen in Figures 2, 3 and 4, for the mass fractions in columns I, II and III of the Table 1, respectively.

The Orrick and Erbar technique (Equation (2)) overestimates the values of viscosity below $100°C$ for the three computed cases, as it can be seen in Figures 2, 3 and 4 (fact reported by Yuan *et al.* [19] in relation with the data of Tat and Van Gerpen [10]) while the three techniques provide similar values of viscosity for temperatures $>100°C$.

Table 3. Kinematic viscosity ($mm^2 s^{-1}$) of methyl esters (published and measured values).

| Temperature	Reference	Computation method	Kinematic viscosity ($mm^2 s^{-1}$)				
			C16:0	C18:0	C18:1	C18:2	C18:3
20°C	Gouw *et al.* [16]	–	–	–	7.023	5.50	4.84
		Equation (2)	7.807	11.123	10.332	9.595	8.912
		Equation (3)	5.570	7.415	6.607	6.977	6.505
		Equation (8)	7.093	10.105	–	–	–
	–	Equation (9)	–	–	7.157	–	–
		Equation (10)	–	–	–	5.512	–
		Equation (11)	–	–	–	–	4.804
40°C	Allen *et al.* [7]		4.39	5.62	4.31	3.45	2.98
	Knothe [11]	–	4.38	5.85	4.51	3.65	3.14
	Gouw *et al.* [16]		4.32	5.61	4.45	3.64	3.27
		Equation (2)	4.839	6.603	6.225	5.919	5.606
		Equation (3)	3.579	4.632	4.111	4.103	3.731
		Equation (8)	2.660	5.963	–	–	–
	–	Equation (9)	–	–	4.577	–	–
		Equation (10)	–	–	–	3.706	–
		Equation (11)	–	–	–	–	3.328
70°C	Gouw *et al.* [16]	–	2.50	3.11	2.60	2.25	2.09
		Equation (2)	2.636	3.401	3.304	3.203	3.110
		Equation (3)	2.041	2.547	2.248	2.088	1.842
		Equation (8)	2.424	3.068	–	–	–
	–	Equation (9)	–	–	2.581	–	–
		Equation (10)	–	–	–	2.228	–
		Equation (11)	–	–	–	–	2.078
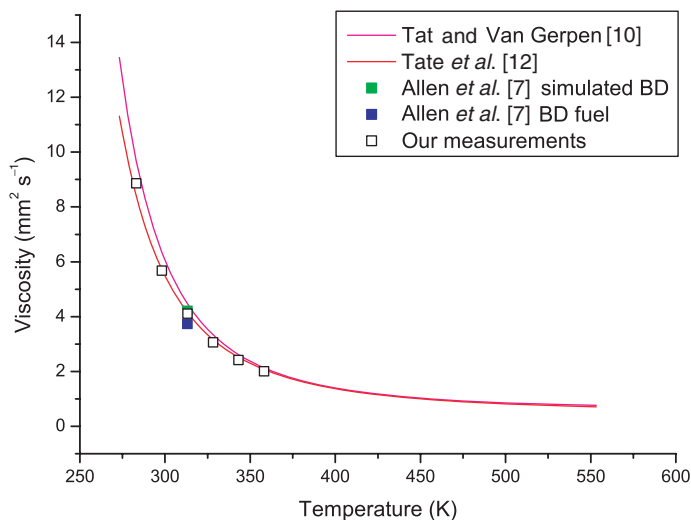
Figure 1. Reported and own values of temperature-dependent viscosity for soy oil-based biodiesel (BD).
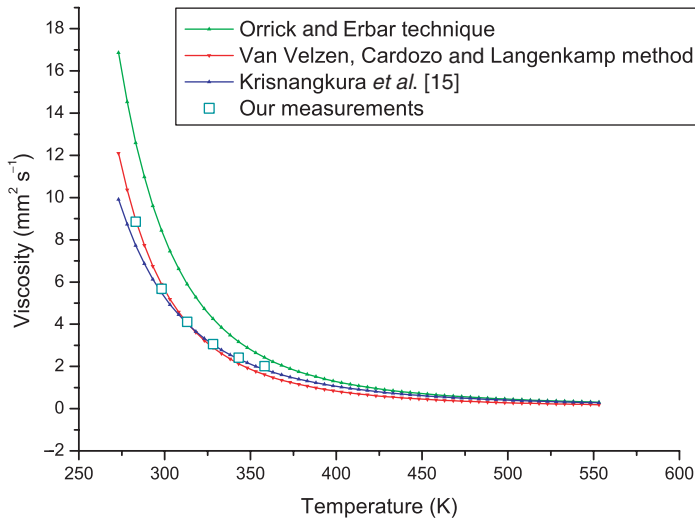
Figure 2. Estimations for temperature-dependent viscosity for soy oil-based biodiesel for the mass fraction in column I, Table 1.
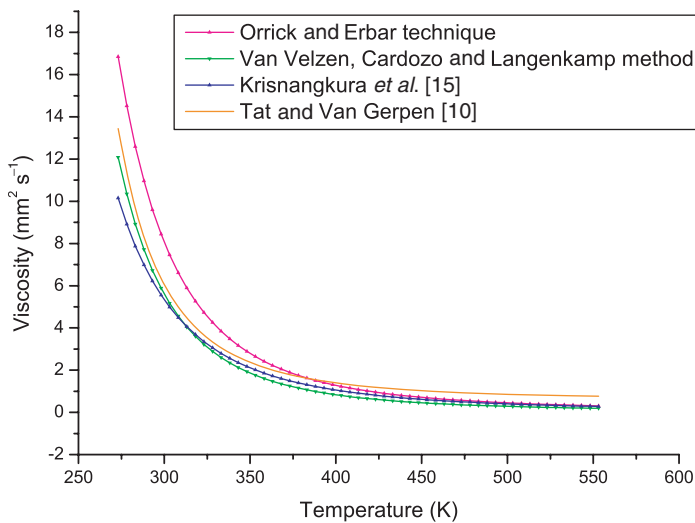

Figure 3. Estimations for temperature-dependent viscosity for soy oil-based biodiesel for the mass fraction in column II, Table 1 [11].

As it was said in section 2.2.1, the Equations (19) and (20) are modified Andrade equations. They differ from the Andrade equation, used in the expressions developed for methyl esters (Equations (2), (3) and (7) to (13)), in the functional dependence with the temperature. These last expressions have a physical base for the linear dependence of the viscosity logarithm (natural or decimal) with the inverse of the temperature for pure substances, because they are based in an Arrhenius-type equation. In Figure 5,
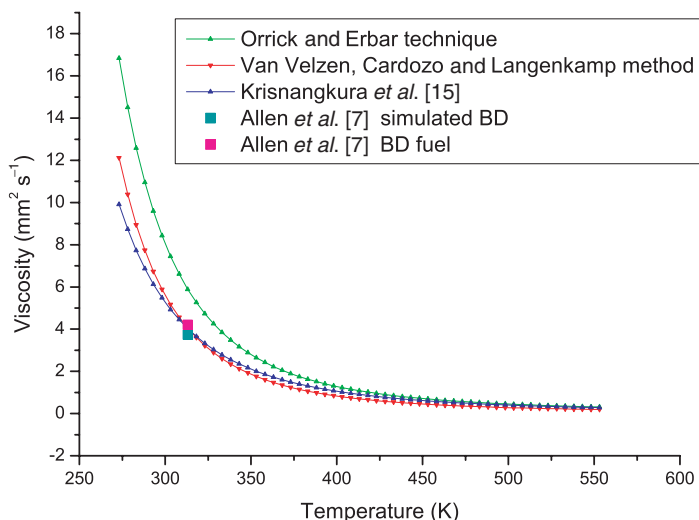
Figure 4. Estimations for temperature-dependent viscosity for soy oil-based biodiesel (BD) for the mass fraction in column III, Table 1, and values at 40°C [7].
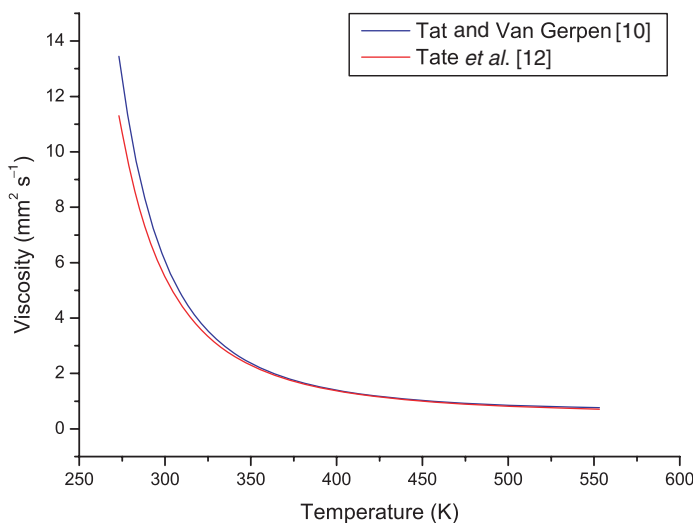

Figure 5. Fitting curves from literature: modified Andrade equation for temperature-dependent viscosity for soy oil-based biodiesel.

the data-fitting curves of Tat and Van Gerpen [10] and Tate *et al.* [12] are compared. The formula of Tat and Van Gerpen [10] was extrapolated out of the measurement range to facilitate the comparison. The major differences between these curves are registered in the range of temperature below 100°C, where they must fit the corresponding measured values. As both expressions have the same functional form, they approach asintotically for temperatures above 100°C.
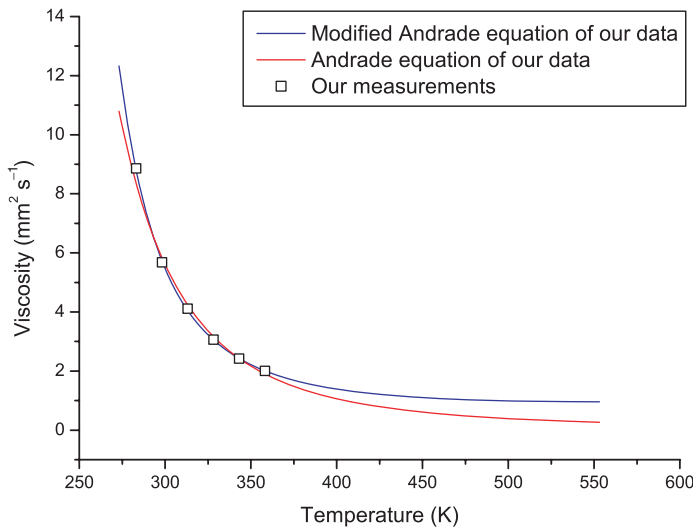
Figure 6. Fitting curves of our measurements: Andrade equation and modified Andrade equation for temperature-dependent viscosity for our production.

The values of viscosity measured in our laboratory were fitted with an Andrade equation and a modified Andrade equation, obtaining the following formulae:

Andrade equation fitting ($R^2 = 0.9937$):

$$\mu = \exp\left(1998.153/T - 4.936\right), \tag{25}$$

modified Andrade equation fitting ($R^2 = 0.9998$):

$$\mu = \exp(7.225/T^2 - 2572.039/T + 2.244). \tag{26}$$

In the expressions above, μ is the kinematic viscosity in $mm^2\,s^{-1}$ and T the temperature in K.

As expected, both curves are similar in the region of experimental data, because they are built to fit them, but their trend is far different from the measured values. These features are shown in Figure 6.

Even when it seems that the tendency for temperature-dependent viscosity for biodiesel is better represented by a modified Andrade equation, no theoretical base is developed to favour this option.

4.2. *Surface tension*

The estimation of temperature-dependent surface tension is insensitive to little differences in mass composition, as those placed in Table 1, similarly to the same fact observed for temperature-dependent viscosity. The expressions (12) and (21), applied to the range of temperatures of interest for mass compositions of columns I, II and III of Table 1 overlap. Figure 7 shows our experimental, the prediction curve for our production and the corresponding values for surface tension at 40°C for two soy oil-based biodiesel (reported in Allen *et al.* [8]).
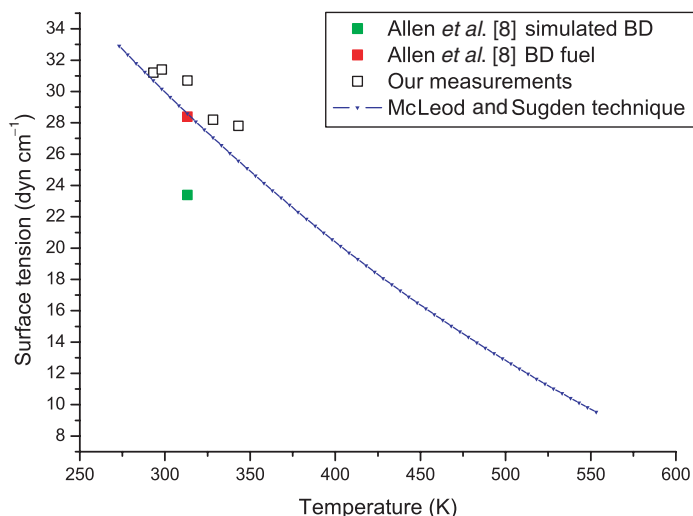
Figure 7. Reported and own values of temperature-dependent surface tension for soy oil-based biodiesel (BD) and the prediction curve.

The values of surface tension of our production at 40°C were higher than both reported by Allen *et al.* [8] at the same temperature. The values of surface tension obtained by these authors in the biodiesel produced by transesterification is bigger than the corresponding one for the biodiesel prepared as a fatty acid methyl esters mixture, being the first value close to our measurement. This suggests that the difference in the values of surface tension could be related with the presence of other substances in the oil, since our biodiesel was also produced by transesterification.

A linear regression equation for our data fits well in the region of the experimental points, but it deviates from the estimation expression out of this range. This is expected because it is observed in pure liquids that 'surface tension decreases with the temperature at a rate somewhat exceeding that predicted by a linear relation' [14]. This trend transfers to the mixture when the mixing rule is a Dalton-type one.

The linear fit ($R^2 = 0.908$) is shown in Equation (27) and was extrapolated for the sake of comparison in Figure 8:

$$\sigma = -0.079 \cdot T + 54.74, \tag{27}$$

where σ is the surface tension in dyn cm^{-1} and T is the temperature in K.

4.3. *Density*

The conversion of dynamic viscosity into kinematic viscosity needs the values of density for the complete range of temperatures. The Equation (13) was used to compute the fatty acid methyl esters for temperatures between 0 and 300°C. The density of biodiesel was computed with the Equation (22). By using data of Tat and Van Gerpen [9] and our own data of biodiesel density, the results were checked. It is insensitive to the difference in mass composition, so estimation curves computed with the mass fractions of column I, II and III (Table 1) overlap.

In Figure 9 is our experimental data: the prediction curve for our biodiesel and the linear fits reported by Tat and Van Gerpen [9] and Tate *et al.* [13] for soy oil-based biodiesel.

Between 0 and 100°C, the trend of the density can be very well fitted with a linear expression. Equation (28) below was obtained by linear regression of our measurements and it is similar to that reported in Tat and Van Gerpen [9] that is placed in Equation (29).
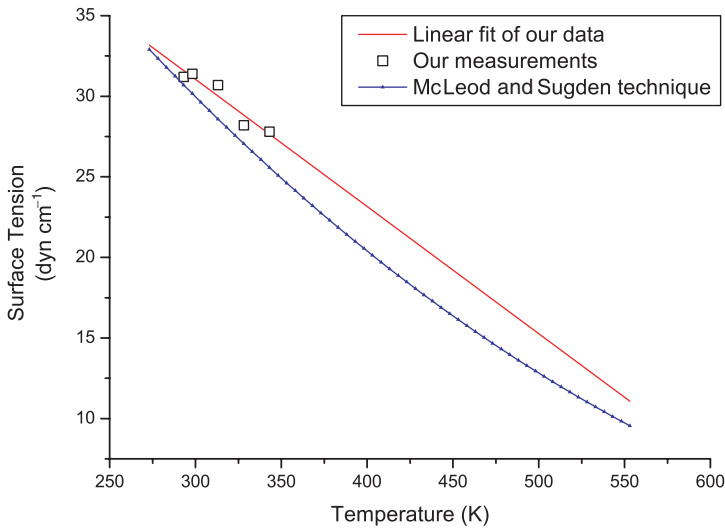

Figure 8. Linear fit, estimation curve and experimental data of temperature-dependent surface tension of our production.
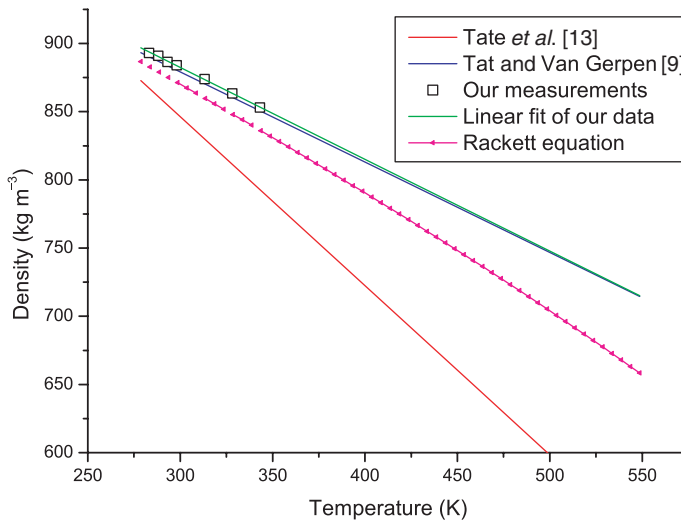

Figure 9. Reported and own values of temperature-dependent density for soy oil-based biodiesel and prediction curve.

Linear fit for our values ($R^2 = 0.99938$):

$$\rho = -0.673 \cdot T + 1084.23s. \tag{28}$$

Linear fit from Tat and Van Gerpen [9] ($R^2 = 0.9989$):

$$\rho = -0.662 \cdot T + 1077.82. \tag{29}$$

In both equations, ρ is the density in $kg\,m^{-3}$ and T is the temperature in K. The measurements were made with similar devices. All the straight lines are extrapolated to the complete range of temperatures of interest.

From 0 to 300°C, Tate *et al.* [13] measured (with a special equipment) density of different biodiesel. For soy oil-based biodiesel, the reported linear fit is placed in Equation (30).

Linear fit from Tate *et al.* [13] ($R^2 = 0.9872$):

$$\rho = -1.24 \cdot T + 1218.42, \tag{30}$$

where

ρ is the density in $kg\,m^{-3}$, and
T is the temperature in K.

The equation of Rackett (revised by Spencer and Danner [18]) predicts with precision the density of a great quantity of liquids until temperatures close to the critical one.

It has the proper functional form to describe the smooth, almost linear, behaviour of the density in the low reduced temperature range, and a sharp decrease in density near the critical point [18]. For this reason, the use of this expression is recommended outside the range of the experimental information.

In the case of our prediction, the curve produced by the Rackett equation for the temperature-depending density differs in 1.14% from the value measured by us at 15°C. A correction factor can be applied to the Equation (22) to better fit the data, preserving the functional form. The graphic representation for the new expression is shown in Figure 10
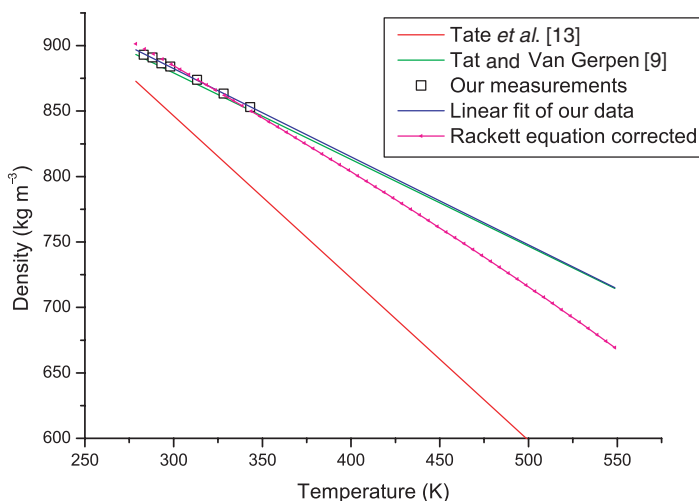
Figure 10. Reported and own values of temperature-dependent density for soy oil-based biodiesel and corrected estimation curve.

together with the data of our biodiesel and the linear fits of Tat and Van Gerpen [9] and Tate *et al.* [13].

Conclusions

In this work, different prediction techniques for temperature-dependent viscosity, surface tension and density of soy oil-based biodiesel were compared in order to select the method that best estimates the values in the range of temperatures of interest.

The Van Velzen, Cardozo and Langenkamp method, with the indicated mixture rule for methyl esters, gives a good fit for the experimental values and correctly represents the tendency of variation for the viscosity as a function of temperature (between 0 and 300°) for the studied type of biodiesel. Krisnangkura's equations (developed specifically for fatty acid methyl esters) with the indicated mixing rule, can give a good agreement with experimental data (depending on the the values used to calibrate the parameters) and the extrapolated curve can provide a good variation trend (even out of the range of temperatures for which the expressions are valid). The use of this technique is less general that the previous one. The Orric and Erbar technique for methyl esters, with the indicated mixing rule, overpredicts the values of viscosity for biodiesel and its use should not be justified in this case (even when a correcting factor could be applied) taking into account that there are other, more accurate expressions for temperature-dependent viscosity. Fitting data curves are a good solution to interpolate values (having been built with enough reliable data), being their extrapolation is a matter for decision in each particular case. When the fit is non-linear (as the case of the temperature-dependent viscosity of liquids) the functional type selected is, also, a matter of decision that can depend on the theoretical base for the functional form or on the need of accurate intermediate values. In this work, for estimations of temperature-dependent viscosity, no correcting factor was necessary.

In the study of the variation of surface tension with the temperature, the lack of data prevents us from establishing accuracy in the estimation. Having few available measured data, and inferring that substances other than fatty acid (and their proportions) in the base oil, have an important influence on the measured values, the expression of McLeod and Sugden with a Dalton-type mixing rule, gives acceptable values compared with those measured in our laboratory. This technique provides the trend of variation stated in the literature, and it is therefore preferable to the linear fit to estimate values out of the range of the measurements. Again, the use of correction factors was not necessary.

In this work, the prediction of the variation of density with the temperature for different fatty acid methyl esters and biodiesel was only necessary to convert the values of dynamic viscosity into kinematic viscosity. The (obtained and reported) accuracy of the Rackett's expression is enough for the use in this work. The density behaves non-linearly with the temperature and the Rackett equation reflects this trend. In this case a correcting factor was needed to prevent greater errors in the computed kinematic viscosities.

The use of general techniques or fitting data methods, for the temperature-dependent properties studied here, is conditioned by the temperature range for which the properties are needed (e.g. for the deposits generation prediction or to estimate the characteristics of atomisation).

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