

AN EMPIRICAL APPROACH FOR PREDICTING BIODIESEL FUELS DYNAMIC VISCOSITY FROM THEIR FATTY ACID ESTER COMPOSITION AT VARIOUS TEMPERATURES

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Summary

The purpose of this work was to develop an empirical model for predicting temperature dependent dynamic viscosities of biodiesel, based on their fatty acid ester composition. The Vogel equation [1] was used to describe the viscosity-temperature relationship of pure fatty acid esters (FAME-Fatty acid methyl ester/FAEE-Fatty acid ethyl ester) commonly present in biodiesel fuels, and a modified mass fraction based mixing equation was used to predict viscosity of 47 biodiesel mixtures based on their FAME/FAEE composition. The accuracy of this simple method was better than the other mass-based semilog blending equation reported in the literature.

Key words: Biodiesel, viscosity, prediction, empirical approach, dynamic viscosity.

1. Introduction

The stringent emissions law, the depletion of fossil fuels and the interrelation of fossil fuels with politics have forced the world to find alternatives to fossil fuels [2]. Biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel is one of the renewable and environmentally friendly alternative biofuels that can be used in a diesel engine with little or no modification in the engine. It is an oxygenated fuel that is essentially sulfur-free and biodegradable, significantly reducing particulate matter, hydrocarbon, carbon monoxide and life-cycle net carbon dioxide emissions from combustion sources. Because of these advantages, biodiesel has gained considerable attention in recent years. However, engine manufacturers are concerned about biodiesel's higher viscosity compared with diesel fuel because a high viscosity could cause excessive fuel injection pressures during engine warm-up [2].

Viscosity is one of the most important fuel properties as it impacts the performance of fuel injection system. The effect of viscosity can also be seen in the quality of atomisation and combustion as well as engine wear. Different publications showed that the higher viscosity of biodiesel could increase fuel penetration in the chamber, consequently affecting combustion and emissions from the engine; fuels with high viscosity tend to form larger droplets upon injection, which may result in poor fuel atomisation during spray, increases in engine deposits, greater energy demands for the fuel pump and wear in fuel pump elements and injectors [2 - 4]. On the other hand, fuels with

low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear [5, 6]. In the synthesis process, the knowledge of physical properties including viscosity is of great importance. Design of pipes, reactors, pumps, mixers, settlers and other equipment involved in unity operations related to alkyl esters and/or biodiesel production is highly dependent on this property. Biodiesel's characteristics strongly depend on various plant feedstock. Among the biodiesel's properties, viscosity, density and heating value are the most important parameters that affect the engine performance and the emission characteristics [7].

Reliable biodiesel viscosity data as well as accurate viscosity models that incorporate the dependence on temperature are very important in the development of combustion models [8, 9]. Apart from that, viscosity models are also very useful for design purposes, as well as for simulation and optimisation of process equipment such as heat exchangers, reactors, mixing vessels and process piping [10]. Some researchers have experimentally measured viscosity for some biodiesel fuels and their diesel blends [11 - 18]. These measurements, however, are for specific biodiesel fuels. Because there are numerous biodiesel source materials and the composition of each type of material may vary substantially, it is impractical to determine experimentally the viscosity of fuels produced from each material source. The aim of the present work is to improve the accuracy in the prediction of biodiesel dynamic viscosity for wide ranges of temperature and composition, by using a simple equation and a limited

number of adjustable parameters. In this way, it will be possible to predict with acceptable accuracy the viscosity of biodiesels blends.

According to Krisnangkura et al. [28] viscosity may be considered the integral of the interaction forces of molecules. Viscosity increases with carbon chain length and decreases with the number of double bonds of fatty compounds [19]. The Andrade equation [20] can be considered as the most well-known empirical correlation for the viscosity of the liquids and is given by:

$$\ln(\mu) = A + \frac{B}{T} \quad (\text{Eq. 1})$$

Although the correlation was proposed empirically based on observation, the form of the correlation and the description of the parameters were later suggested by the less rigorous semi-theoretical reaction rate theory by Eyring [21]. Nonetheless, the Andrade correlation is most commonly used by regression of the constants to experimental liquid viscosity data. Several modifications of Andrade equation were made to extend the temperature range. For example, the three-parameter Vogel equation, by adding a third variable parameter as shown:

$$\ln(\mu) = A + \frac{B}{T+C} \quad (\text{Eq. 2})$$

Many authors tried to generalise the parameters of the Andrade and Vogel equations to make the equations predictive rather than completely correlative. The developments were mostly correlations of the parameters to the structure of the molecules based on group contributions. Van Velzen et al. [22] method requires complicated calculations of the group contributions and commonly predicts the viscosity of the lighter compounds of the homologous series with an average deviation of 15%. Orrick and Erbar [23] developed another group contribution method to estimate the parameters of the Andrade equation using the molecular weight and density at 20°C, with overall average deviation of 15% compared to experimental data.

Yaws [24] used the following extension of the Andrade equation to represent the liquid viscosity of hundreds of hydrocarbons and non-hydrocarbons with tabulated regressed parameters:

$$\ln(\mu) = A + \frac{B}{T} + C \ln T + DT^E \quad (\text{Eq. 3})$$

In 1992, Liew et al. [25] proposed a function of temperature on kinematic viscosity as:

$$\log(\mu) = A + (B \times T) \quad (\text{Eq. 4})$$

In 1999, Tat and Van Gerpen [4] modified Andrade equation to determine the viscosity of the biodiesel at different temperatures. They concluded that the kinematic viscosities of biodiesel blends were well fit by equation as shown below:

$$\ln(\mu) = A + \frac{B}{T} + \frac{C}{T^2} \quad (\text{Eq. 5})$$

In 1999, by considering the carbon number, Krisnangkura et al. [18] proposed different equations to determine viscosity of biodiesels with long and short carbon structure at different temperatures. In 2006, Krisnangkura et al. [9] presented two different equations based on thermodynamic parameters, which use two and four adjusted parameters in the determination of unsaturated and saturated kinematic viscosity of pure methyl esters, respectively. The large relative deviations in relation to experimental data were 9.2%.

In 2007, Ceriani et al. [26] developed a group contribution model to predict viscosity as a function of temperature and chemical compound formula. In 2011, these authors [8] applied this group contribution method to predict the viscosity of fatty compounds, the relative deviations in relation to experimental data ranging up to 16.43 % were obtained on pure fatty alkyl esters.

More recently, in 2013, Ramirez-Verduzco [27] proposed an empirical model with four adjustable parameters (A, B, C, D) to predict the dynamic viscosity of FAMES.

$$\ln(\mu) = A + B \cdot \ln(M) + C \cdot N + \frac{D}{T} \quad (\text{Eq. 6})$$

His model had the advantage of being a single equation for saturated and unsaturated species. However, this model exhibited some significant deviations between experimental and calculated viscosities. The author reported minimum, maximum and average absolute deviations of 0.09%, 29.63% and 6.04%, for 259 data points corresponding to samples of fifteen methyl ester at different temperatures.

Most of the empirical correlations described above are dependent on some constants and vary with type of biodiesel and percentage of blends. It is very important to have a simple, stable and reliable estimation method of viscosity as a function of weight/molar fraction and temperature of biodiesel. In all of the above equations, μ is the kinematic viscosity expressed in and T is the temperature; A, B, C, D, E, N are regression coefficients specific for each compounds.

2. Mixing rule for predicting the viscosity of biodiesel

Empirical viscosity methods for liquid mixtures are either interpolative mixing rules or pure component viscos-

ity models where the parameters of the model are calculated using mixing rules applied to the parameters of the mixture constituents. Although, viscosity is an important factor for biodiesel, methods for estimation of biodiesel viscosities are few [28] compared to those for petroleum. In addition, biodiesels are marketed mostly as the blends for uses in diesel engines and the methods for estimation of the viscosity of biodiesel blends are even fewer [29].

The first proposed mixing rules were mole, mass, or volume averages of a function of the viscosity of the pure components [30] which is widely used [4, 31] to calculate the viscosity of a mixture. It is formulated as:

$$\ln(\mu_{mix}) = \sum_i z_i \ln(\mu_i) \quad (\text{Eq. 7})$$

Molar fractions instead of mass fractions can also be used in this equation and this does not have a significant effect on the prediction of biodiesel viscosity, according to Ramirez-Verduzco [27]. Irving [32] reviewed more than 75 liquid viscosity equations including the above and other developed methods and evaluated them against experimental data for binary mixtures. He found that the simple predictive interpolative methods in the form of equation eq. 7 are only effective for the mixtures of the similar components with the viscosities of the same magnitude. Among the other mixing rules with adjustable constants, Irving [32] concluded that the most effectual yet simple methods are the additive parabolic equations with one adjustable constant. This is why the Grunberg - Nissan [33] equation, which considers the interactions among components, is usually recommended to calculate the viscosity of a mixture.

$$\ln(\mu_{mix}) = \sum_i z_i \ln(\mu_i) + \frac{1}{2} \sum_i \sum_j z_i z_j G_{ij} \quad (\text{Eq. 8})$$

The values of the adjustable parameters, G_{ij} depend on the binary compounds and are generally considered to be pressure or components and/or temperature dependent and this is very difficult to specify. Isdale et al. [34] proposed a complex group contribution method to estimate the G_{ij} values at 298 K. They found that the binary interaction parameter is slightly temperature dependent.

Another method of predicting viscosity of biodiesel based on its fatty acid ester composition was first studied by Allen et al. [17], who measured viscosities of some pure fatty acid esters and applied a mixing rule to predict viscosities of biodiesel fuels based on their component composition. This method was reasonably accurate but only applicable to the viscosity at 40°C. Similar alternatives to the Grunberg and Nissan method are the predic-

tive UNIFAC-VISCO method (Chevalier et al. [35]; Gaston-Bonhomme et al. [36]), the multi-parameter McAllister [37] mixing rule, and the mixing rule of Teja and Rice [38].

In 1998, Graboski and McCormick [39] pointed out that kinematic viscosity of the blend was lower than would be predicted from a linear combination model (eq. 7), because dissolution of biodiesel minimised intramolecular interactions. The underpredictions led us to hypothesise that components with higher viscosities contributed more than predicted in a mixture using their pure value, thus leading to underpredicted viscosities, this hypothesis was inspired by Allen et al. [17]. The exact mechanism of the more significant effect of the higher-viscosity components on mixture viscosity is unknown, however, it is generally accepted that the interactions between non-associated components always exist. Therefore, when non-associated components are mixed, in this case biodiesel, their interaction makes the internal friction larger than accounted for by equation (eq. 7). On the contrary, in 2005, Yuan et al. [40] reported that the kinematic viscosities of biodiesel blends estimated by equation (eq. 7) were generally lower than the measured values. Hence, a correction parameter should be used for prediction of the kinematic viscosity of biodiesel blend.

Although biodiesel fuels are non-associated liquids that are composed of mixtures of fatty acid esters with similar structures, interactions among the esters do exist, since we expect that the polar interactions are strong enough. Our observations showed that, if the correction factor was neglected, mixture viscosity was always underestimated. Inspired by the conclusion of Allen et al. [17], in this work, a correction factor (or *binary interaction parameter*) was introduced to correct the difference between experimental and predicted values and the equation took the form:

$$\ln(\mu_{mix}) = \sum_i (1-w_i) z_i \ln(\mu_i) \quad (\text{Eq. 9})$$

w_i is the correction factor. To account for the effect of the higher viscosity component, biodiesel, in this study, the correction factor was determined empirically by minimising the difference of measured and predicted data, the value for different type of fatty acid compounds were reported in Table 1.

3. Results and discussion

Many of the scientific publications relating to biodiesel have reported the FAME/FAEE profile on a mass base [13, 14, 41 - 45]. In this work, we have chosen the

mass fraction as it is the most common way to report the concentration of biodiesel in the literature, the prediction of the biodiesel viscosity is indistinguishable to the use of the mol fraction or mass fraction, as it has been previously observed by Ramirez-Verduzco et al. [41]. The newest experimental data of dynamic viscosity of the ethyl and methyl esters here studied are reported in Table 1.

As expected, the viscosity of all esters increases with the ester chain length and decreases with its level of unsaturation. The ethyl esters also present a higher viscosity than the corresponding methyl ester of the equivalent fatty acid.

The development of the proposed model was performed as follows.

- The Vogel equation was chosen to describe the experimental viscosities as a function of temperature;

the equation's constants were estimated using an optimisation algorithm based on the least squares method. The values of the parameters and the average absolute deviations (AAD) of the regression are reported in Table 1, Figures 1, 2 and 3. The results show that the Vogel equation provides an excellent description of the experimental data of viscosity with a maximum value of AAD of 0.77% and an average deviation of 0.22%, this is comparable to the uncertainty of experimental data.

- The modified mass fraction mixing equation (eq. 9) is used to determine the correction factor. This unique value is used to predict viscosity of all biodiesel mixtures considered in this work.

To assess the predictive ability of the model, the average absolute deviations (AAD) between the predicted and the experimental data of the dynamic viscosity were calculated at different temperatures according to:

Table 1. Parameter values to calculate the dynamic viscosity of pure FAMES/FAEEs that are commonly present in biodiesel fuels using Vogel equation and correction factor, w in equation (eq. 9) to predict mixture's dynamic viscosity

	Compound	A	B	C	AAD (%)	Npt	T _{min} (K)	T _{max} (K)	Correction factor, w	Ref. data
Fatty acids methyl esters (FAME)										
C8:0	methyl-caprylate (C ₉ H ₁₈ O ₂)	-3.47	856.42	69.39	0.05	15	283	353	-0.04	[46]
C10:0	methyl-caprate (C ₁₁ H ₂₂ O ₂)	-3.32	814.90	93.34	0.19	19	278	372	-0.04	[29, 46]
C12:0	methyl-laurate (C ₁₃ H ₂₆ O ₂)	-3.30	857.10	100.84	0.17	16	283	372	-0.04	[29, 46]
C14:0	methyl-myristate (C ₁₅ H ₃₀ O ₂)	-3.09	823.48	114.17	0.08	13	298	372	-0.04	[46]
C16:0	methyl-palmitate (C ₁₇ H ₃₄ O ₂)	-3.09	880.48	113.61	0.05	12	308	363	-0.04	[46]
C16:1	methyl-palmitoleate (C ₁₇ H ₃₂ O ₂)	-3.04	818.87	109.26	0.51	18	278	363	-0.04	[44]
C18:0	methyl-stearate (C ₁₉ H ₃₈ O ₂)	-3.61	1173.32	87.97	0.37	14	313	513	-0.04	[29, 46]
C18:1	methyl-oleate (C ₁₉ H ₃₆ O ₂)	-2.78	778.85	125.41	0.09	16	283	363	-0.04	[29, 46]
C18:2	methyl-linoleate (C ₁₉ H ₃₄ O ₂)	-3.03	904.55	97.92	0.38	16	278	353	-0.04	[29, 46]
C18:3	methyl-linolenate (C ₁₉ H ₃₂ O ₂)	-3.12	962.63	84.70	0.73	20	278	373	-0.04	[44]
C20:0	methyl-arachidate (C ₂₁ H ₄₂ O ₂)	-2.76	824.91	132.98	0.02	11	323	373	-0.04	[44]
C20:1	methyl-gadoleate (C ₂₁ H ₄₀ O ₂)	-2.55	737.30	136.72	0.07	20	278	373	-0.04	[44]
C22:0	methyl-behenate (C ₂₃ H ₄₆ O ₂)	-2.56	781.24	143.37	0.03	9	333	373	-0.04	[44]
C22:1	methyl-erucate (C ₂₃ H ₄₄ O ₂)	-2.51	753.18	138.80	0.30	18	278	363	-0.04	[44]
C24:0	methyl-lignocerate (C ₂₅ H ₅₀ O ₂)	-2.54	809.36	144.42	0.07	8	338	373	-0.04	[44]
Fatty acids ethyl esters (FAEE)										
C10:0	ethyl-caprate (C ₁₂ H ₂₄ O ₂)	-3.57	954.79	76.71	0.11	16	278	353	+0.05	[46]
C12:0	ethyl-laurate (C ₁₄ H ₂₈ O ₂)	-3.24	859.64	100.52	0.10	15	283	353	+0.05	[46]
C14:0	ethyl-myristate (C ₁₆ H ₃₂ O ₂)	-3.14	866.33	108.57	0.14	15	283	353	+0.05	[46]
C16:0	ethyl-palmitate (C ₁₈ H ₃₆ O ₂)	-3.42	1045.30	95.11	0.57	18	298	513	+0.05	[46]
C18:0	ethyl-stearate (C ₂₀ H ₄₀ O ₂)	-3.04	920.00	115.98	0.01	11	313	363	+0.05	[46]
C18:1	ethyl-oleate (C ₂₀ H ₃₈ O ₂)	-2.65	761.20	126.97	0.10	18	278	363	-0.09	[46]
C18:2	ethyl-linoleate (C ₂₀ H ₃₆ O ₂)	-2.64	754.47	119.01	0.44	18	278	363	-0.09	[44]
C18:3	ethyl-linolenate (C ₂₀ H ₃₄ O ₂)	-2.68	800.68	100.87	0.05	20	278	373	-0.09	[44]
C20:0	ethyl-arachidate (C ₂₂ H ₄₄ O ₂)	-2.96	933.05	119.32	0.17	12	318	373	+0.05	[44]

$$AAD = \frac{\eta_{cal} - \eta_{exp}}{\eta_{exp}} \times 100 \quad (\text{Eq. 10})$$

The overall average absolute deviation (OAAD) was calculated as a summation of the modulus of AAD over N_p experimental data points. The OAAD was calculated by:

$$OAAD = \frac{\sum AAD}{n_{exp}} \quad (\text{Eq. 11})$$

3.1. Viscosity of individual FAMES

Viscosities of FAME commonly present in biodiesel fuels were correlated to temperatures by the Vogel equation. The Vogel equation constants in Eq.2 for dynamic viscosity are given in Table 1.

The experimental data published in the literatures was compared for the same systems. The relative deviations for the FAMES and FAEEs are within 3%, at high temperatures that show large deviations when compared from different authors.

3.2. Viscosity of biodiesel fuels

The proposed mass fraction mixing rule in this work was applied to predict the viscosity of 47 biodiesel mixtures whose FAME/FAEE compositions at different temperatures were taken from the literature. The FAME/FAEE compositions of these fuels are listed in Tables 2 and 3.

Using Vogel equation constants and correction factor (listed in Table 1), viscosities of biodiesel fuels at a given temperature can be easily calculated. Prediction of dynamic viscosity at different temperatures for 47 biodiesel mixtures is given in Tables 4 and 5 and Figure 4 for some samples. For these 47 biodiesels, minimum and maximum absolute deviations between experimental and predicted values of 0.58 - 9.48% were obtained respectively (except for 3 mixtures).

In most of the cases, predicted values for biodiesel mixtures are in close agreement with the measured data, with prediction errors of less than 4% in the temperature range of 293 - 373K. However, at high temperature (higher than 373K, up to 393K) for the three biodiesel fuels (BioD 32, 33, 34), maximum errors were underestimations of around 12 - 18% compared to experimental data. Figure 4 shows the dynamic viscosity of some sample biodiesels as obtained in the present study.

These results indicate that viscosity prediction of FAMES/FAEEs biodiesel can be performed with good accuracy from the empirical approach proposed in this

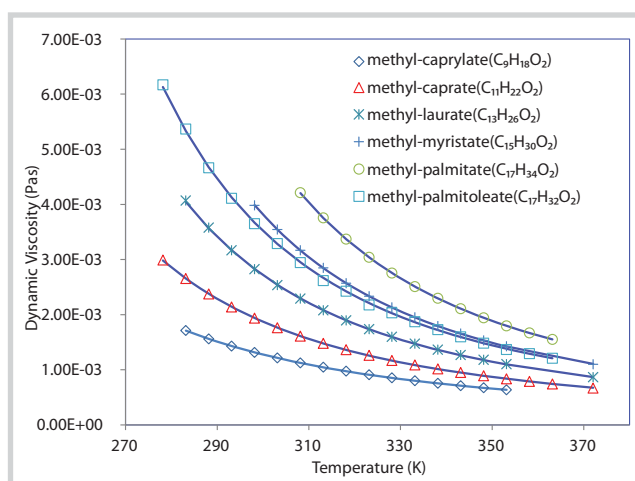


Figure 1. Dynamic viscosity of FAMES as a function of temperature. Experimental data (symbols) gathered from the literature (Table 1) and calculated values (lines) obtained in this work

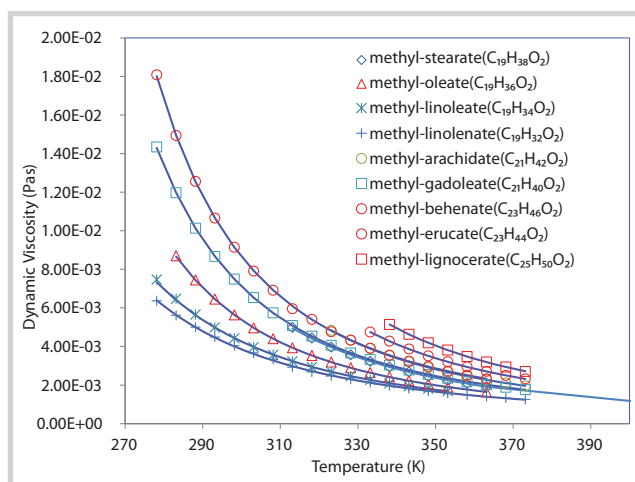


Figure 2. Dynamic viscosity of FAMES as a function of temperature. Experimental data (symbols) gathered from the literature (Table 1) and calculated values (lines) obtained in this work

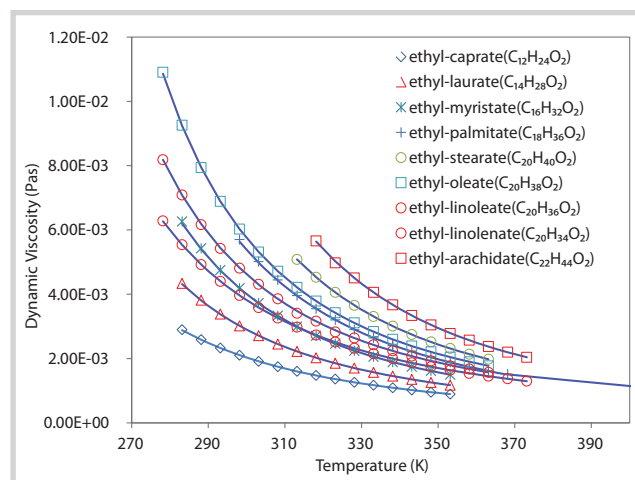


Figure 3. Dynamic viscosity of FAEEs as a function of temperature. Experimental data (symbols) gathered from the literature (Table 1) and calculated values (lines) obtained in this work

work. The results obtained for the complete data sets of biodiesels are summarised in Tables 4 and 5, in which AADs are compared with the corresponding values obtained for previously reported models.

Various studies were conducted to estimate viscosity of different biodiesel mixtures at various temperatures. The effect of the biodiesel blends' fraction and temperature on the dynamic viscosity of

Table 2. Composition of the biodiesel studied, FAME in mass fraction

Mixture	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1	C24:0	Ref data
BioD-1	-	-	-	-	0.1129	-	0.0396	0.1998	0.5839	0.0586	-	-	0.0052	-	-	[12]
BioD-2	-	-	-	-	0.4150	-	0.0490	0.4010	0.1350	-	-	-	-	-	-	[13]
BioD-3	-	0.0010	-	0.0010	0.1510	0.0090	0.0710	0.4470	0.3140	0.0020	0.0020	-	0.0020	-	-	[13]
BioD-4	-	0.0460	0.2533	0.2303	0.1500	-	0.0493	0.2071	0.0578	0.0058	-	-	0.0005	-	-	[12]
BioD-5	-	0.0359	0.1976	0.1797	0.1419	-	0.0472	0.2055	0.1734	0.0174	-	-	0.0015	-	-	[12]
BioD-6	-	0.0304	0.1675	0.1523	0.1375	-	0.0460	0.2046	0.2359	0.0237	-	-	0.0021	-	-	[12]
BioD-7	-	0.0254	0.1403	0.1275	0.1335	-	0.0450	0.2038	0.2925	0.0294	-	-	0.0026	-	-	[12]
BioD-8	-	0.0201	0.1110	0.1010	0.1292	-	0.0439	0.2030	0.3533	0.0355	-	-	0.0031	-	-	[12]
BioD-9	-	0.0100	0.0551	0.0501	0.1210	-	0.0417	0.2014	0.4695	0.0471	-	-	0.0042	-	-	[12]
BioD-10	-	0.0050	0.0278	0.0253	0.1170	-	0.0407	0.2006	0.5261	0.0528	-	-	0.0047	-	-	[12]
BioD-11	-	0.0425	0.2344	0.2142	0.1685	-	0.0463	0.1995	0.0946	-	-	-	-	-	-	[12]
BioD-12	-	0.0410	0.2260	0.2067	0.1711	-	0.0455	0.1980	0.1117	-	-	-	-	-	-	[12]
BioD-13	-	0.0358	0.1971	0.1810	0.1801	-	0.0430	0.1928	0.1704	-	-	-	-	-	-	[12]
BioD-14	-	0.0358	0.1971	0.1810	0.1801	-	0.0430	0.1928	0.1704	-	-	-	-	-	-	[12]
BioD-15	-	0.0161	0.0888	0.0850	0.2135	-	0.0334	0.1734	0.3898	-	-	-	-	-	-	[12]
BioD-16	-	0.0099	0.0548	0.0548	0.2240	-	0.0304	0.1672	0.4588	-	-	-	-	-	-	[12]
BioD-17	-	0.0051	0.0281	0.0311	0.2322	-	0.0281	0.1625	0.5129	-	-	-	-	-	-	[12]
BioD-18	-	0.0510	0.2811	0.2556	0.1541	-	0.0504	0.2079	0.0000	-	-	-	-	-	-	[12]
BioD-19	0.0002	-	-	0.0008	0.1049	0.0012	0.0427	0.2420	0.5136	0.0748	0.0036	0.0028	0.0040	0.0007	0.0014	[14]
BioD-20	-	-	-	0.0170	0.1947	-	0.1438	0.5467	0.0796	0.0069	0.0025	0.0052	0.0021	-	-	[14]
BioD-21	0.0920	0.0640	0.4870	0.1700	0.0770	-	0.0220	0.0540	0.0220	-	-	-	-	-	-	[14]
BioD-22	-	-	-	-	0.4060	-	0.0510	0.4280	0.1100	0.0050	-	-	-	-	-	[14]
BioD-23	-	-	-	-	0.0420	-	0.0170	0.5680	0.2170	0.1570	-	-	-	-	-	[14]
BioD-24	-	-	-	0.0062	0.2409	-	0.0256	0.1574	0.5699	-	-	-	-	-	-	[12]
BioD-25	-	-	-	-	0.1618	-	0.0382	0.2880	0.5046	-	-	-	-	-	-	[15]
BioD-26	-	-	-	0.0007	0.1078	0.0007	0.0395	0.2302	0.5366	0.0703	0.0038	0.0023	0.0080	-	-	[15]
BioD-27	-	-	-	0.0180	0.0470	0.0470	0.0190	0.7113	0.0989	-	0.0589	-	-	-	-	[15]
BioD-28	-	-	0.0002	0.0007	0.0641	0.0009	0.0423	0.2393	0.6425	0.0012	-	0.0003	0.0077	0.0008	-	[15]
BioD-29	-	0.0001	0.0004	0.0007	0.0526	0.0020	0.0163	0.6249	0.2094	0.0699	0.0060	0.0123	0.0135	0.0019	-	[15]
BioD-30	-	0.0003	0.0025	0.0057	0.4252	0.0013	0.0403	0.4199	0.0981	0.0009	0.0036	0.0015	0.0009	-	-	[15]
BioD-31	-	-	0.0002	0.0013	0.1057	0.0013	0.0266	0.4105	0.3667	0.0710	0.0044	0.0067	0.0045	0.0012	-	[15]
BioD-32	-	0.0001	0.0004	0.0007	0.1076	0.0007	0.0394	0.2296	0.5353	0.0702	0.0038	0.0023	0.0080	0.0024	0.0022	[16]
BioD-33	-	-	0.0003	0.0007	0.0522	0.0020	0.0162	0.6211	0.2107	0.0695	0.0060	0.0135	0.0035	0.0019	-	[16]
BioD-34	-	-	-	0.0009	0.0890	0.0015	0.0276	0.4182	0.3751	0.0702	0.0046	0.0068	0.0046	0.0012	-	[16]
BioD-35	0.0750	0.0600	0.5330	0.1710	0.0730	-	0.0190	0.0550	0.0140	-	0.0020	-	-	-	-	[17]
BioD-36	-	-	-	-	0.1050	0.0040	0.0270	0.4660	0.3010	0.0100	0.0130	0.0140	0.0240	-	0.0350	[17]
BioD-37	-	-	-	-	0.0580	0.0080	0.0170	0.6000	0.1990	0.0960	0.0070	0.0160	-	-	-	[17]
BioD-38	-	-	0.0040	0.0130	0.4810	0.0030	0.0400	0.3730	0.0800	0.0020	0.0030	0.0010	-	-	-	[17]
BioD-39	-	-	-	-	0.0420	0.0040	0.0200	0.5740	0.2130	0.1120	0.0120	0.0210	0.0010	-	-	[17]
BioD-40	-	-	-	-	0.0580	0.0080	0.0160	0.6000	0.1990	0.0960	0.0070	0.0160	-	-	-	[17]
BioD-41	0.0750	0.0600	0.5330	0.1710	0.0730	-	0.0190	0.0550	0.0140	-	-	-	-	-	-	[17]
BioD-42	-	-	0.0040	0.0130	0.4810	0.0030	0.0400	0.3730	0.0800	0.0020	0.0030	0.0010	-	-	-	[17]
BioD-43	-	-	-	-	0.0420	0.0040	0.0200	0.5740	0.2130	0.1120	0.0120	0.0210	0.0010	-	-	[17]

Table 3. Composition of the biodiesel studied, FAEE in mass fraction

	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	Ref data
BioD-44	-	-	-	0.0840	0.0303	0.4933	0.3329	0.0595	-	[18]
BioD-45	-	-	-	0.1162	0.0290	0.2695	0.5274	0.0579	-	[18]
BioD-46	-	0.0066	0.0087	0.4029	0.0457	0.4361	0.1000	-	-	[18]
BioD-47	-	-	-	0.4260	0.0470	0.3930	0.1340	-	-	[18]

Table 4. Dynamic viscosity prediction of 47 biodiesel mixtures at different temperatures. Comparison between experimental data reported in literatures and predicted values of this work

Mixture	Npt	T range (K)	OAAD (%)	Ref data	Mixture	Npt	T range (K)	OAAD (%)	Ref data
BioD-1	5	293 - 373	10.19%	[12]	BioD-25	18	278 - 363	1.04%	[15]
BioD-2	14	293 - 358	5.40%	[13]	BioD-26	18	278 - 363	2.26%	[15]
BioD-3	14	293 - 358	7.38%	[13]	BioD-27	18	278 - 363	1.80%	[15]
BioD-4	5	293 - 373	5.53%	[12]	BioD-28	18	278 - 363	1.46%	[15]
BioD-5	5	293 - 373	2.06%	[12]	BioD-29	18	278 - 363	1.57%	[15]
BioD-6	5	293 - 373	1.34%	[12]	BioD-30	18	278 - 363	1.48%	[15]
BioD-7	5	293 - 373	2.23%	[12]	BioD-31	18	278 - 363	2.21%	[15]
BioD-8	5	293 - 373	3.46%	[12]	BioD-32	6	278 - 363	12.59%	[16]
BioD-9	5	293 - 373	7.01%	[12]	BioD-33	6	278 - 363	14.89%	[16]
BioD-10	5	293 - 373	8.73%	[12]	BioD-34	6	278 - 363	18.22%	[16]
BioD-11	5	293 - 373	6.16%	[12]	BioD-35	1	313	0.96%	[17]
BioD-12	5	293 - 373	5.96%	[12]	BioD-36	1	313	9.48%	[17]
BioD-13	5	293 - 373	5.10%	[12]	BioD-37	1	313	6.50%	[17]
BioD-14	5	293 - 373	1.56%	[12]	BioD-38	1	313	3.41%	[17]
BioD-15	5	293 - 373	2.02%	[12]	BioD-39	1	313	5.34%	[17]
BioD-16	5	293 - 373	1.37%	[12]	BioD-40	1	313	6.33%	[17]
BioD-17	5	293 - 373	1.07%	[12]	BioD-41	1	313	0.58%	[17]
BioD-18	5	293 - 373	7.27%	[12]	BioD-42	1	313	3.41%	[17]
BioD-19	5	293 - 373	1.79%	[14]	BioD-43	1	313	5.34%	[17]
BioD-20	5	293 - 373	2.97%	[14]	BioD-44	9	283 - 363	5.32%	[18]
BioD-21	5	293 - 373	1.38%	[14]	BioD-45	9	283 - 363	0.83%	[18]
BioD-22	5	293 - 373	2.45%	[14]	BioD-46	9	283 - 363	3.98%	[18]
BioD-23	5	293 - 373	1.05%	[14]	BioD-47	14	283 - 363	6.18%	[18]
BioD-24	5	293 - 373	1.25%	[12]					

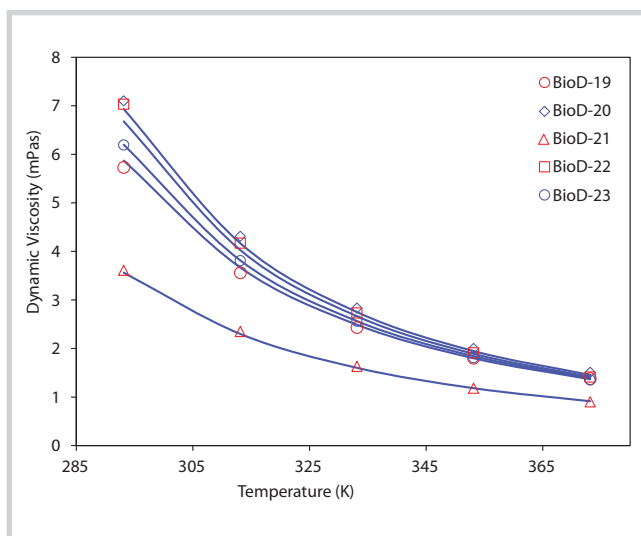


Figure 4. Temperature effects on dynamic viscosity for biodiesel mixtures, symbols are experimental data, line are calculated results in this work

biodiesel was investigated and corresponding models were proposed.

Different empirical correlations have been developed, such as Chavarria-Hernandez [47], do Carmo [48], Yuan [14, 46], Ramirez-Verduzco [27], and Ceriani [26], which relate various performance parameters with viscosity of biodiesel, and compared to deviation obtained

in this work, in most of the cases, the maximum deviation obtained in this work is lower than other models published.

Although only 47 actual biodiesel fuels were tested, the method presented in this study can be extended to any type of methyl ester biodiesel fuel with known ester composition. For the ethyl ester biodiesel fuel, more experimental data is needed to validate the model. The applicable temperature of this method can be extended up to the temperature of 373K of the fuels because of the limitation of the Vogel equation. Below 278K, this method should be used with caution when the temperature is reduced down to the cloud point of the fuel, depending on the components.

4. Conclusions

Viscosity is one of the most significant properties of biodiesel, because of its major effect on the engine performance. For this reason, reliable mathematical models that accurately describe the dynamic viscosity of biodiesel as a function of temperature are of great interest for the development of combustion models as well as for the design of process equipment. Based on these requirements, this work has been performed to:

Table 5. Comparison of AADs obtained by using equations of this work as well as 7 other different models applied to the same data bank of biodiesel mixtures

Mixture	Npt	T range (K)	Chavarria-Hernandez [47]	do Carmo [48]	Yuan [46]	Ramirez-Verduzco [27]	do Carmo [48]	Yuan [14]	Ceriani [26]	This work	Ref data
BioD-41	1	[313,15]	3.32	0.00	7.49	2.50	6.99	9.65	9.21	0.58	[17]
BioD-36	1	[313,15]	3.44	0.09	2.48	4.54	2.14	0.92	3.67	9.48	[17]
BioD-37	1	[313,15]	0.51	3.13	0.21	2.57	4.59	1.40	2.38	6.50	[17]
BioD-38	1	[313,15]	2.30	9.89	1.95	3.00	11.63	2.84	1.01	3.41	[17]
BioD-39	1	[313,15]	0.79	2.73	0.22	1.42	4.46	1.94	3.23	5.34	[17]
BioD-19	5	[293,373]	2.55	5.43	1.57	2.86	5.67	2.21	11.08	1.79	[14]
BioD-20	5	[293,373]	5.45	12.96	6.79	8.57	13.19	7.92	8.12	2.97	[14]
BioD-21	5	[293,373]	4.22	1.82	7.14	7.42	6.22	9.10	10.62	1.38	[14]
BioD-22	5	[293,373]	5.97	11.47	5.97	7.91	12.50	6.26	7.70	2.45	[14]
BioD-23	5	[293,373]	5.32	2.80	3.67	3.66	2.83	4.68	12.17	1.05	[14]
BioD-18	5	[293,373]	5.45	1.48	0.37	3.01	4.07	1.43	3.56	7.27	[12]
BioD-1	5	[293,373]	12.45	0.40	4.44	13.43	0.65	4.69	11.78	10.19	[12]
BioD-24	5	[293,373]	12.87	6.28	13.52	4.86	6.21	14.01	22.36	1.25	[12]
BioD-25	15	[283,353]	5.71	0.18	4.59	4.71	0.39	5.24	7.78	1.04	[45]
BioD-26	18	[278,363]	2.59	5.38	2.37	2.45	5.78	2.98	8.74	2.26	[45]
BioD-27	15	[283,353]	4.71	10.53	7.30	6.91	9.71	8.08	5.27	1.80	[45]
BioD-28	17	[283,363]	5.29	2.52	5.41	4.03	3.28	6.19	11.29	1.46	[45]
BioD-29	18	[278,363]	3.69	9.72	5.92	5.50	10.77	6.03	6.65	1.57	[45]
BioD-30	16	[288,363]	4.89	11.89	5.48	7.03	13.12	5.94	4.79	1.48	[45]
BioD-31	18	[278,363]	2.50	1.56	2.63	2.72	2.06	3.38	7.27	2.21	[45]
BioD4-BioD10	35	[293,373]	5.16	4.06	7.74	6.98	6.18	8.72	13.39	4.34	[12]
BioD11-BioD17	35	[293,373]	2.88	0.48	2.59	3.03	2.76	3.48	7.40	3.32	[12]

Table 6. Comparison of AADs obtained by using model proposed in this work and other models applied to the same data bank of biodiesel mixtures

Mixture/ Ref data [18]	BioD-44	BioD-45	BioD-46
Model	AAD (%)	AAD (%)	AAD (%)
Ceriani et al. [8]	12.91	6.00	1.30
SRA [49]	16.31	9.16	4.44
NAK model [9]	14.72	8.12	2.18
Restricted NAK model [44]	12.10	6.89	0.81
This work	5.32	0.83	3.98

- Correlate the parameters of the Vogel equation for dynamic viscosity to the “best” experimental data collected in this study; applied to pure fatty acid methyl esters and fatty acid ethyl esters that are commonly present in biodiesel fuels. The maximum average absolute deviation of correlated dynamic viscosities for the alkyl esters was 0.73%, indicating that the Vogel equation closely represented the relationship between dynamic viscosity and the temperature of the alkyl esters;

- Propose modified mixing equation to predict biodiesel dynamic viscosity from their saturated and unsaturated esters composition, and therefore it can be extended to any type of alkyl ester biodiesel fuel with

known ester composition. However, impurities were not considered in the model developed in this study since the model was for mixtures of fatty acid methyl esters mainly.

- Suggest a simple correction factor, independent of temperature incorporated in a simple modified mixing equation that can be applied to all cases in predicting viscosity of variation biodiesel mixtures. The proposed method was used to predict viscosities of 47 biodiesel mixtures, compared with experimentally measured viscosities in the range of 278 - 393K and prediction overall average errors were less than 3.25%. If the considered temperature is outside of regression data, the model would have generated higher prediction errors.

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