Full Length Article

Kinematic viscosity of soybean biodiesel and diesel fossil fuel blends: Estimation from permittivity and temperature

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HIGHLIGHTS

- Kinematic viscosity and permittivity of diesel fuel/biodiesel blends were determined.
- The kinematic viscosity of the blends depends exponentially on composition.
- The activation energy of the viscosity of blends depends linearly on composition.
- The viscosity of blends was modelled as a function of permittivity and temperature.
- The model parameters depend only on the properties of the pure fuels.

ARTICLE INFO

ABSTRACT

Kinematic viscosity and relative permittivity were determined in blends of soybean biodiesel with diesel fossil fuel in the full range of composition at temperatures between 298 K and 318 K (±0.1 K).

The kinematic viscosity as a function of temperature fits very satisfactorily to an Arrhenius dependence at all the compositions. The activation energy of this process depends linearly on blend composition. Also, at constant temperature, the kinematic viscosity increases exponentially with biodiesel content.

From the analysis of the experimental data, a model is proposed to estimate the kinematic viscosity of blends of unknown composition as a function of permittivity and temperature. Interestingly, the model parameters depend only on the properties of the pure fuels. The fitting to experimental data is very satisfactory; the RMS uncertainty is lower than 0.02 mm^2 s^{-1}.

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1. Introduction

Biodiesel (BD) is an alternative biofuel used in Diesel engines, normally blended with diesel fossil fuel (DF) [1–3]. The accurate knowledge of the physical and chemical properties of DF/BD blends is very important for the optimization of engine performance. In particular, the determination of the fuel kinematic viscosity is necessary to achieve a proper fuel atomization; this impacts directly on the combustion efficiency and consequently in the engine power [1,4,5]. The standard method of fuel viscosity measurements [6] provides highly accurate results but requires long measurement times and it is not suitable for online measurements. Therefore, alternative or indirect methods that avoid these limitations are of technological interest.

The kinematic viscosity of DF/BD blends strongly depends on temperature and composition, and several numerical models that attempt to describe the viscosity of blends of known composition as a function of temperature are found in the literature [7–11]. However, the determination of the composition of DF/BD blends is not straightforward.

In recent works [12,13], the authors studied in detail the dependence of the permittivity of DF/BD blends on composition and temperature to accurately estimate their composition. Dielectric spectroscopy [2,14,15] is a low cost, non-destructive technique, that is fast, adaptable to online measurements and requires no special training. It has been used to characterize BD [2,16], and fatty

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acid methyl esters (FAME) [17], vegetable oils [18,19], to estimate the composition of DF/BD blends [12,13,20–22], to monitor the biodiesel purification process [23], to distinguish between vegetable oils and biodiesel [24] and to detect contaminants in the final product [25].

In this work, a systematic study of the kinematic viscosity of DF/BD blends was carried out as a function of temperature, composition and permittivity. From these results, a model of kinematic viscosity estimation is proposed with very good fitting to experimental data. This is of interest for the implementation of multiparametric sensors and control strategies.

2. Theory

Several numerical models have been proposed to describe the dependence of viscosity of liquids with temperature. Among them, those based on the exponential dependence that follows from the pioneer works of Andrade and Eyring [26,27] are particularly interesting. Therefore, in this work, we propose that, at a given a composition, kinematic viscosity, η, of DF/BD blends follows an Arrhenius law

$$\eta(T) = Ae^{\frac{E_a}{kT}} \tag{1}$$

where η and A are in mm^2 s^{-1}, T is the absolute temperature (K), E_a is the activation energy in electron volts (eV) and k is the Boltzmann constant (8.617332×10^{-5} eVK^{-1}). This a very reasonable assumption for temperatures well above the pour point and the cold filter plugging point (CFPP).

Furthermore, at each temperature, the kinematic viscosity has been numerically fitted to an exponential dependence on biodiesel content, Bx. Therefore, at a given temperature, the kinematic viscosity of a blend is modeled as

$$\eta(Bx) = Ce^{DBx} \tag{2}$$

where C and D are fitting parameters, and C is given in mm^2 s^{-1} and D in %$^{-1}$. Eq. (2) is similar to one of the empirical models proposed in [8].

As shown in a previous work [13], the permittivity of the blends may be accurately estimated from the permittivity of pure DF and BD:

$$\varepsilon_r(Bx, T) = a + bT + cBx + dTBx \tag{3}$$

where ε'_r is the relative permittivity, T is the absolute temperature, and a, b, c and d are obtained from the permittivites of DF and BD as a function of temperature, as explained in [13].

3. Materials and methods

3.1. Materials

Commercial soybean BD and ultra low sulfur content DF samples were provided by local producers. The samples of BD and DF complied with EN 14214 [28] and ASTM D975-15c [29], respectively. DF/BD blends were prepared in the full range of composition, in 10% steps. In this work, the composition of the blends is given as BD percentage, x, in volume (V/V). For instance, B10 indicates a 10% of BD in the blend.

3.2. Methods

Kinematic viscosity of blends and relative permittivity of pure DF and BD were measured between 298 K and 318 K. The temperature of the samples was controlled within ±0.1 K with a thermostat (Lauda).

Kinematic viscosity measurements were carried out according to ASTM D445 [6] with a Canon Fenske viscometer (Size No. 50). Measurement uncertainty was below 0.1%.

Relative permittivity of pure DF and BD was measured with an RLC meter (Tonghui TH2822C), at the frequencies of 1 kHz, 10 kHz and 100 kHz. Since the differences in the measured permittivity values at the three frequencies were below 1%, the reported results correspond to 100 kHz. From pure BD and DF permittivities, the model of Eq. (3) was applied to estimate the permittivity of their blends ($10\% \leq Bx \leq 90\%$) [13]. The permittivity measurement system is also described in detail in [13]. The calibration uncertainty of the system was below 1%.

4. Results and discussion

4.1. Kinematic viscosity, composition and temperature

Fig. 1 shows experimental data of kinematic viscosity, η, as a function of the temperature, T, and composition, Bx, of all the studied samples. It can be seen that the experimental data define a smooth and regular surface.

Fig. 2 shows the plot of kinematic viscosity data as a function of the temperature, $1/T$. The symbols indicate the experimental values and the curves correspond to the fitting of Eq. (1). In Figs. 1 and 2 the limits of the uncertainty bands are not drawn since they are very small in comparison with the symbols.

Table 1 shows the fitting parameters of Eq. (1), A and E_a, their uncertainties, ΔA and ΔE_a, the RMS uncertainty of the estimation,
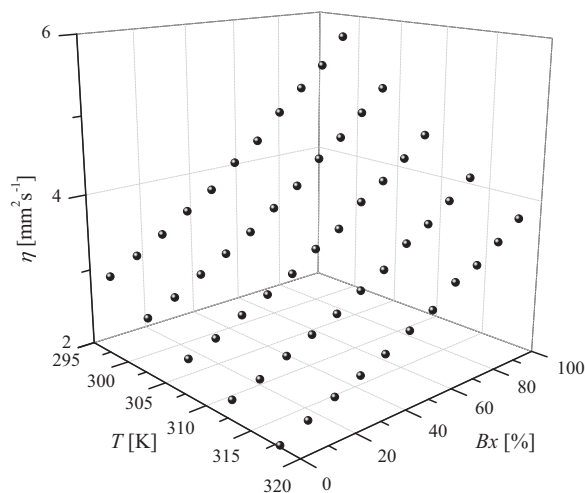

Fig. 1. Kinematic viscosity results, η, as a function of the temperature, T, and composition, Bx.
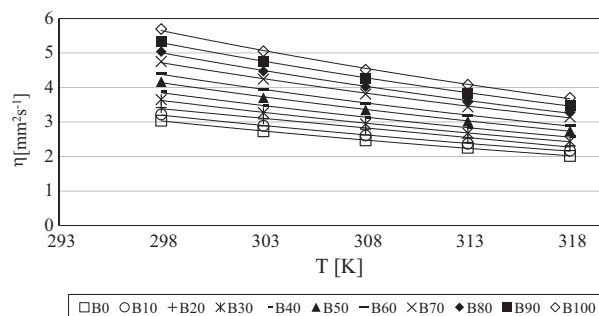

Fig. 2. Kinematic viscosity, η, versus temperature, T. Symbols: experimental values. Curves: fitting of Eq. (1).

Table 1
Fitting parameters of Eq. (1), A and E_a, and their uncertainties, ΔA and ΔE_a.

Sample	A [mm^2 s^{-1}]	ΔA [mm^2 s^{-1}]	E_a [eV]	ΔE_a [eV]	$\Delta \eta$ [mm^2 s^{-1}]	R^2
B0	0.0062	0.0006	0.159	0.003	0.02	0.999
B10	0.0060	0.0004	0.161	0.001	0.01	>0.999
B20	0.0065	0.0001	0.161	0.001	<0.01	>0.999
B30	0.0061	0.0004	0.164	0.002	0.01	>0.999
B40	0.0060	0.0003	0.166	0.001	0.01	>0.999
B50	0.0056	0.0005	0.169	0.002	0.01	>0.999
B60	0.0056	0.0003	0.171	0.002	0.01	>0.999
B70	0.0066	0.0007	0.169	0.003	0.01	0.999
B80	0.0052	0.0003	0.176	0.002	0.01	>0.999
B90	0.0061	0.0002	0.174	0.001	0.01	>0.999
B100	0.0060	0.0006	0.176	0.002	0.02	0.999

$\Delta\eta$, and the determination coefficient of the fittings, R^2, in the full range of blend composition.

From Fig. 2 and Table 1 it can be seen that the model of Eq. (1) fits the experimental data very satisfactorily ($R^2 > 0.999$). In the work of Franco et al. [30] it is proposed that the activation energy of the dynamic viscosity of vegetable oil/diesel fossil fuel blends may be obtained as a linear combination of the activation energies of the two pure components. Then, it is not surprising that the activation energy of the kinematic viscosity of the DF/BD blends may also be obtained in the same way. Therefore, in this work it is proposed that the activation energy at a given composition, $E_a(Bx)$, may be estimated with very good accuracy by means of a linear combination of the activation energies of pure DF ($E_a(DF)$) and pure BD ($E_a(BD)$),

$$E_a(Bx) = E_a(DF) + [E_a(BD) - E_a(DF)]\frac{Bx}{100} \tag{4}$$

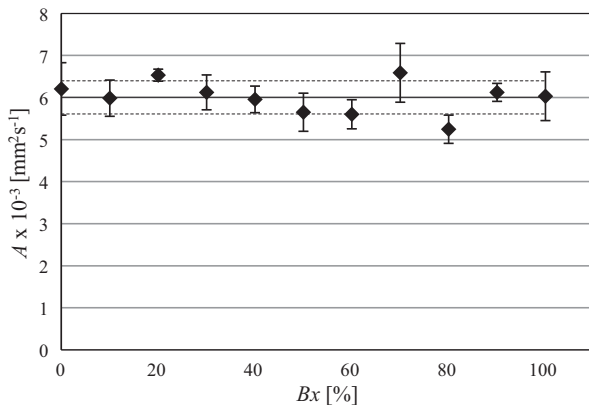In fact, Eq. (4) fits the values of E_a in Table 1 with an RMS error below 1%.

It is important to remark that the pre-exponential factor in Table 1, may be considered as a constant, A^*, within the experimental uncertainty, in the full range of composition, as it may be seen in Fig. 3.

From the above, the kinematic viscosity of the DF/BD blends in the full range of composition and temperature studied in this work is given by

$$\eta(T, Bx) = A^* e^{\frac{E_a(DF) + [E_a(BD) - E_a(DF)]\frac{Bx}{100}}{kT}} \tag{5}$$

where A^* is (0.0060 ± 0.0004) mm^2 s^{-1}.

At each composition Eq. (5) simplifies to Eq. (1), and at constant temperature it reduces to Eq. (2).

Eq. (5) estimates the viscosity of DF/BD blends with an RMS uncertainty of 0.07 mm^2 s^{-1} in the full range of studied compositions and temperatures.

As a check, parameters A^*, $E_a(DF)$ and $E_a(BD)$ were also independently obtained by means of a non-linear multiple regression performed on Eq. (5) using all the experimental data.

With the parameters listed in Table 2, the RMS uncertainty of the estimation of Eq. (5) is 0.01 mm^2 s^{-1}.
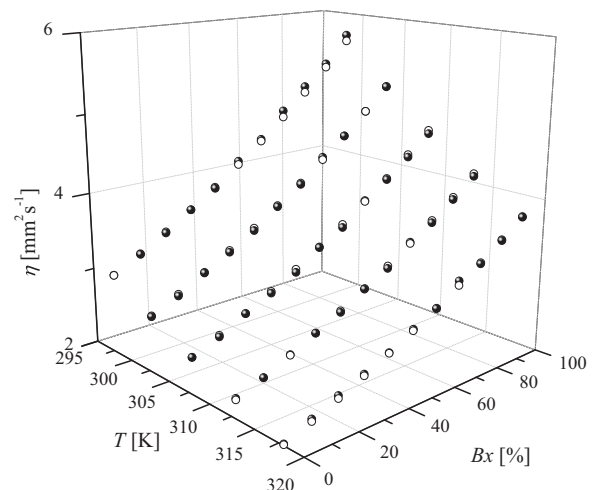
From the comparison of Tables 1 and 2, it can be seen that the agreement between the parameters is very good. Particularly, the value of the pre-exponential factor in Table 2, A^*, agrees very well with that calculated as the average value of the pre-exponential factors in Table 1.

It is remarkable that kinematic viscosity of pure DF and BD estimated from Eq. (5) with the parameters of Table 2 has an RMS uncertainty of 0.02 mm^2 s^{-1}, in a very good agreement with the measurements of pure fuels.

Fig. 4 shows the experimental values of kinematic viscosity of the DF/BD blends (black symbols) and the values estimated from

Table 2
Parameters A^*, $E_a(DF)$ and $E_a(BD)$ from Eq. (5) obtained by a multiple non-linear regression.

Parameter	Value
A^* [mm^2 s^{-1}]	0.0060
$E_a(DF)$ [eV]	0.160
$E_a(BD)$ [eV]	0.176

Fig. 3. Fitted values of the pre-exponential factor, A, in Table I (symbols). Average value, A^* (continuous line). Limits of one standard deviation (dashed lines).

Fig. 4. Experimental values (black symbols) and estimated values (white symbols) of kinematic viscosity as a function of the temperature, T, and composition, Bx, with the parameters in Table 2.

Eq. (5), with the parameters of Table 2 (white symbols). It can be seen that the estimation is very good.

As a check of the model of Eq. (5), the dependence of kinematic viscosity on composition was analysed.

From the comparison between Eqs. (2) and (5), it can be seen that the exponent, D, in Eq. (2), is given by

$$D = \frac{[E_a(BD) - E_a(DF)]}{100kT} \tag{6}$$

Therefore, Eq. (2) may be written as

$$\eta(T, Bx) = \eta_{DF}(T)e^{\frac{[E_a(BD)-E_a(DF)]}{kT}\frac{Bx}{100}} \tag{7}$$

where $\eta_{DF}(T)$ is the kinematic viscosity of pure DF at temperature T.

4.2. Kinematic viscosity, permittivity and temperature

Given the relations between kinematic viscosity and composition, on one hand, and permittivity and composition on the other, as explained in a previous work [13], it is interesting to examine the relation between permittivity and kinematic viscosity of DF/BD blends.

Fig. 5 shows a 3D plot of the measured values of kinematic viscosity as a function of permittivity and temperature of DF/BD blends.

As in Fig. 1, the surface in Fig. 5 is smooth and regular, so it can be described in terms of simple analytical functions of permittivity and temperature.

At each temperature, the kinematic viscosity of the blends depends exponentially on biodiesel content (Eq. (2)) whereas the relative permittivity depends linearly on Bx (Eq. (3)). Therefore, it

is reasonable to propose an exponential relation between kinematic viscosity and permittivity,

$$\eta(T, \varepsilon'_r) = \eta_o(T)e^{\frac{\varepsilon'_r}{\epsilon(T)}} \tag{8}$$

where η_o and $\epsilon(T)$ are fitting parameters. Their values are shown in Table 3 together with their uncertainties; the unit of η_o is mm^2 s^{-1} and $\epsilon(T)$ is dimensionless.

It can be seen from Table 3 that the fitting of Eq. (8) to experimental data is very satisfactory ($R^2 \geq 0.999$).

Fig. 6 shows the plot of the kinematic viscosity, η, as a function of the permittivity, ε'_r, in the full range of measured temperature, together with the fitting to Eq. (8).

In a previous work [13], it was shown that biodiesel content, Bx, may be estimated as a function of temperature and permittivity,

$$Bx(\varepsilon'_r, T) = \frac{\varepsilon_r - a - bT}{c + dT} \tag{9}$$

The values of the constants a, b, c and d of Eq. (9) for the samples studied in this work were calculated as explained in [13] and they are listed in Table 4.

Therefore, Eq. (9) can be introduced in Eq. (7) to estimate the kinematic viscosity in terms of the permittivity and temperature

$$\eta(T, \varepsilon'_r) = \eta_{DF}(T)e^{\frac{[E_a(BD)-E_a(DF)]}{100kT}\left(\frac{\varepsilon'_r-a-bT}{c+dT}\right)} \tag{10}$$

As shown in Fig. 7, the agreement between experimental data and Eq. (10) is very good. The RMS uncertainty of fitting of Eq. (10) to kinematic viscosity experimental data, using the parameters from Tables 2 and 4, is 0.02 mm^2 s^{-1}.
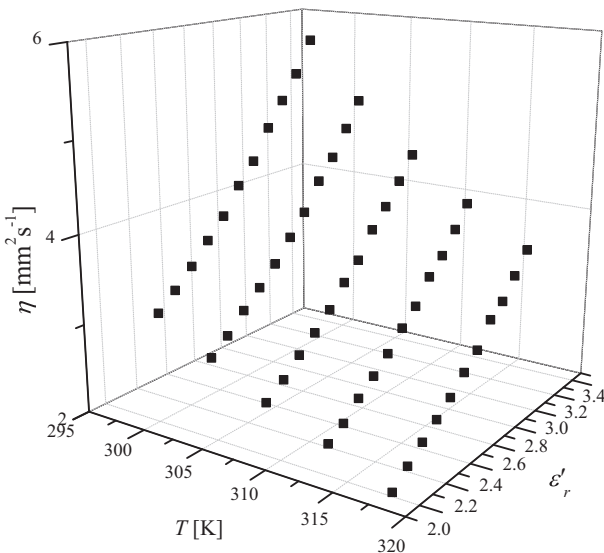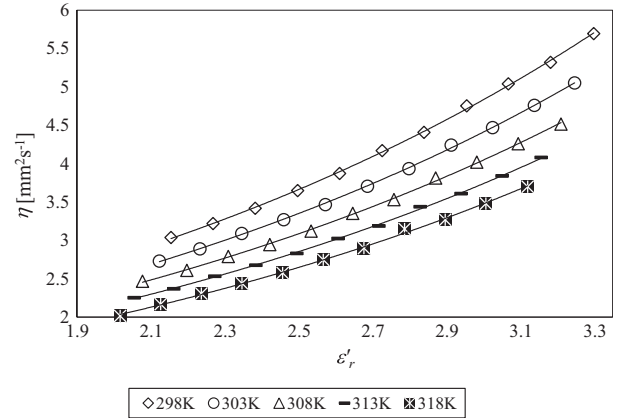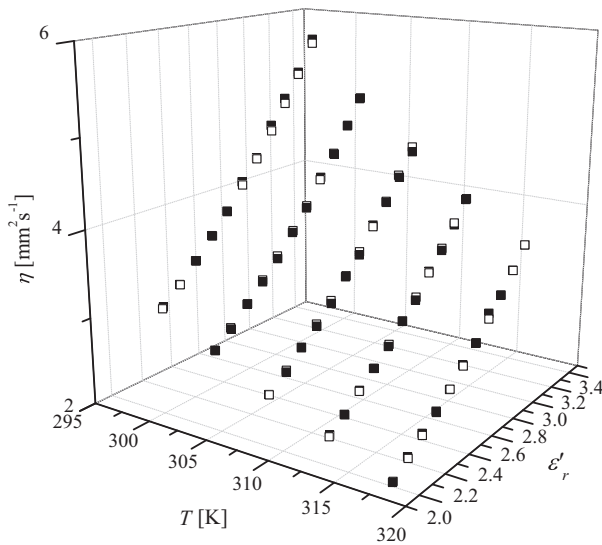

Fig. 6. Kinematic viscosity, η, as a function of permittivity, ε'_r. Symbols: experimental values. Lines: fittings of Eq. (8).

Table 4
Constants a, b, c and d of Eq. (9).

a	b $[K]^{-1}$	c $[\%]^{-1}$	d $[\%K]^{-1}$
4.203	−0.0069	0.0176	−2.08E−05

Fig. 5. Experimental values of kinematic viscosity versus permittivity and temperature of DF/BD blends.

Table 3
Fitting parameters of Eq. (7), η_o and ϵ with their uncertainties, $\Delta\eta_o$ and $\Delta\epsilon$.

T [K]	η_o [mm^2 s^{-1}]	$\Delta\eta_o$ [mm^2 s^{-1}]	ϵ	$\Delta\epsilon$	$\Delta\eta$ [mm^2 s^{-1}]	R^2
298	0.92	0.01	0.00180	0.00001	0.02	>0.999
303	0.85	0.01	0.00182	0.00001	0.02	>0.999
308	0.80	0.01	0.00184	0.00002	0.02	0.999
313	0.74	0.01	0.00185	0.00001	0.02	0.999
318	0.68	0.01	0.00184	0.00002	0.02	0.999

Fig. 7. Experimental and estimated values of kinematic viscosity as a function of the temperature, T, and permittivity, ε'_r. Black symbols: experimental values. White symbols: estimation of Eq. (10).

Then, Eq. (10) may be used to accurately estimate the kinematic viscosity of DF/BD blends from permittivity and temperature measurements.

It is worth noting that the RMS uncertainty of the model of Eq. (10) is very close to that of Eq. (5). Interestingly, all the parameters in Eq. (10) can be obtained from kinematic viscosity and permittivity measurements of pure DF and BD, as a function of temperature.

These results are relevant for the fast, online and accurate determination of kinematic viscosity of DF/BD blends using dielectric techniques. Applications include automotive sensors [20] to optimize the engine performance in real time.

5. Conclusion

The kinematic viscosity of diesel fossil fuel, biodiesel and their blends was measured in the full range of composition at temperatures between 298 K and 318 K. It was verified that kinematic viscosity fits very satisfactorily to an Arrhenius dependence on temperature and it also depends exponentially on composition. The RMS uncertainty of the fittings was below 0.02 mm^2 s^{-1}. Interestingly, it was also found that the activation energy of the kinematic viscosity of blends may be estimated as a linear combination of those of the pure fuels, with an RMS uncertainty below 1%.

The relative permittivity of the samples of pure diesel fuel and biodiesel was measured in the same range of temperature. Those values were used to estimate the relative permittivity of the blends, according to the model recently published by the authors in this journal.

From the above, a model was proposed to estimate the kinematic viscosity of diesel fossil fuel/biodiesel blends from permittivity and temperature measurements, with very good agreement to experimental data. The RMS uncertainty of the fitting was below 0.02 mm^2 s^{-1}. Remarkably, the kinematic viscosity in the full range of composition can be estimated from experimental values of permittivity and kinematic viscosity of the pure fuels as a function of temperature.

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