EFFECT OF n-BUTANOL ADDITION ON DENSITY AND VISCOSITY OF BIODIESEL

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Experimental density and viscosity data of biodiesel + n-butanol mixtures over the entire composition range and for temperature ranging from 293.15 to 323.15 K are reported and compared to diesel fuel standard requirements. Density and viscosity data of pure biodiesel and pure n-butanol can be used to predict the density and viscosity of their mixtures. A linear equation can be recommended to calculate the dependence of density on temperature whereas an exponential type equation correlates the viscosity of biodiesel + n-butanol mixtures with temperature.

Keywords: n-butanol, biodiesel, density, viscosity, refractive index

1. Introduction

A renewed focus on biofuels was registered in the last years as a result of the fluctuating price of crude oil and the concern regarding environment pollution. Some biofuels like biodiesel and bioethanol have been penetrated the fuel market, their production and use increasing significantly. The growing demand of biodiesel and bioethanol has led to important problems regarding food security, deforestation, and soil erosion.

Needs of fuel in transport sector are constantly growing, so that the market demand for biofuels is expected to increase in the near future. To satisfy this demand, besides the diversification of feedstock sources for biodiesel and bioethanol production, with nonedible raw materials, the use of alternative biofuels like n-butanol, could be a sustainable solution.

n-Butanol has some advantages over alcohols with lower hydrocarbon chain (methanol and ethanol), when it is blended with diesel fuel: higher miscibility, less hydrophilicity and physicochemical properties more similar to this fossil fuel [1]. Moreover, the cold flow properties of biodiesel are improved by the addition of n-butanol [2, 3], resulting that n-butanol could be a best choice when considering another replacement for diesel fuel. There are relatively few

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studies on properties of diesel fuel + n-butanol, biodiesel + n-butanol and diesel fuel + biodiesel + n-butanol mixtures regarding distillation curves or low temperature properties [1, 3, 4] and, to the best of our knowledge, no studies have been conducted on volumetric and viscometric properties of these mixtures.

Regarding the distillation curves of diesel fuel and biodiesel mixtures containing up to 20% n-butanol it was found [1] that they are quite similar to the step-like curve of diesel fuel: there is an initial temperature plateau around 120 ^{o}C, followed by a sharp temperature increase which then reaches to the distillation curve of the base fuel (diesel fuel or biodiesel). The same behavior was registered when n-butanol was blended with a mixture of 70 % diesel fuel + 30% biodiesel by volume [1] or in the case of a mixture of 40 % 1-butanol + 48 % diesel fuel + 12 % methyl esters by mass [4]. It was shown [3] that butanol has a positive effect on the low temperature properties of biodiesel. Thus, the cloud point and the cold filter plugging point of biodiesel decrease with the addition of n-butanol, extending the range of temperature at which it can be used. The addition of butanol to diesel fuel + rapeseed biodiesel lowers the cold filter plugging point at about -5^{o}C [5].

Detailed studies are dedicated to the diesel engine performance and exhaust emissions composition when diesel fuel+n-butanol blends are used [6-12]. It was shown that diesel fuel mixed with up to 30 % n-butanol by volume can be successfully used in a diesel engine without any modifications [11]. According to Rakopoulos et al. [6], the combustion behavior during diesel engine starting is affected mostly by using the biodiesel + diesel fuel blend and less by the diesel fuel + butanol blend. The same conclusions were drawn from a study performed on a bus fuelled with diesel fuel + n-butanol mixture [7]. Yao et al. [13] also concluded that blends of diesel fuel with up to 15 %v/v n-butanol reduce the soot and CO emissions. It was reported that the addition of n-butanol to blends of diesel fuel + biodiesel made from cottonseed oil has reduced the emissions of NO_x, hydrocarbons and CO [14].

Continuing our previous works on physicochemical properties of biofuels [15, 16], in this study we present experimental density and viscosity data for biodiesel + n-butanol mixtures, over the entire composition range. The data cover the temperature range from 293.15 to 323.15 K. Optical properties (refractive index) of biodiesel + n-butanol mixtures are also reported. The knowledge of the physicochemical properties is important for the formulation of a fuel with characteristics within the required specifications. The effect of n-butanol addition to biodiesel properties (density and viscosity) was examined and compared with diesel fuel standard requirements (EN 590).

Also, another objective of the study was to evaluate the capacity of different models to predict the density and viscosity of pseudo-binary mixtures of biodiesel with n-butanol. The accuracy of some equations used to calculate the

density and viscosity of diesel fuel + biodiesel mixtures was also evaluated for biodiesel + n-butanol mixtures. Modelling the experimental properties data as density and viscosity, that are not so complex, easy to be used as empirical and semi-empirical equations can be useful for density and viscosity estimation for manufacturing, transportation and distribution domains and for simulation of the behavior of these fuels mixtures in internal combustion engine.

2. Experimental

2.1. Materials

Biodiesel used in this study was synthesized in the laboratory from rapeseed oil and methanol as described elsewhere [16]. n-Butanol was purchased from Chimopar Company (mass fraction > 0.97) and was used without further purification. Some properties of these fuels are presented in Table 1. For n-butanol, the comparison of experimental data with literature proves the quality of own measurements.

Table 1

Properties of biodiesel and n-butanol, respectively

Property	Biodiesel	n-Butanol	
		experimental	Literature
Density at 20 °C g/cm^3)	0.8787	0.8102	0.8101[17] 0.8115[18] 0.8098[19]
Sulfur content (mg/kg)	0	0	
Methylic esters of fatty acids (% w/w)	97.0	0	
Kinematic viscosity at 40 °C (mm^2/s)	4.5934	2.2362	2.2216[18]* 2.23[20] 2.24[21]
Flash point (°C)	170	33	35[22]

*derived from density and dynamic viscosity values at 40 °C.

2.2. Mixtures preparation

Biodiesel and diesel fuel are miscible with n-butanol and can be blended in any proportion to create a stable mixture [1, 23, 24]. The preparation techniques of fuels blends in industry, as splash blending, in-tank blending and in-line blending, are based on volume. In this work, in order to estimate the behavior of the mixtures at different temperatures, the pseudo-binary mixtures biodiesel with n-butanol were prepared by weighting at mass fractions covering the entire composition range (w_2 - alcohol mass fraction), using an electronic balance with a precision of $\pm 10^{-4}$ g. The experimental uncertainty in mass fractions was estimated to be less than ±0.0002. The samples were stored in glass bottles tightly sealed with Teflon stoppers. Filling was carried out so that the volume of the samples to be near to the volume of the bottles. Pre-cautionary measures were taken to avoid exposure to air and evaporation.

2.3. Density and viscosity measurements

The density and viscosity of the pseudo-binary mixtures were measured at atmospheric pressure using an Anton Paar SVM 3000 viscometer which is equipped with a density measurement cell based on the "U" vibrating tube method and a rotational viscometer cell. This device dedicated to petroleum products was manually calibrated with dry air and ultra-pure water at atmospheric pressure, according to the operating manual. The measurements were carried out from 293.15 K to 323.15 K at 5 degrees intervals. The temperature of the samples was maintained constant within ±0.02 K, using a built-in Peltier thermostat. The precision of density measurements was ± 0.0005 g/cm^3. The accuracy of viscosity measurements was ± 0.35 %. Triplicate measurements of the mixture properties were performed for each sample and the results were averaged. The repeatability in the viscosity measurement is ±0.1%,and its reproducibility is <0.5%, according to the manufacturer.

2.4. Models for density and viscosity estimation

The density and viscosity of liquid mixtures depend on the composition, temperature and nature of the components. The dependence on the pressure is usually neglected. Different approaches were proposed in literature to estimate the density and viscosity of diesel fuel + biodiesel blends: equations that correlate the mixtures properties with composition, and equations that express the properties as temperature function. In this study, we have used equations that have already been verified for diesel fuel + biodiesel mixtures. As density and viscosity are important properties of a fuel, regression analysis was performed in order to develop equations to estimate these properties from the refractive index data of the mixture [15], easier to be determined. Table 2 summarizes these equations together with their computational performances.

Equations (1) and (6) shown in Table 2, frequently used for diesel fuel + biodiesel blends, can calculate the density and viscosity of mixtures from properties of pseudo-pure components. Grunberg-Nissan one parameter equation (Eq. 7) and its simplified form (Eq. 6) applied with good results to diesel fuel + biodiesel and oil + n-butanol blends, were selected to represent the viscosity-composition relationship.

Taking into account that n-butanol has polar molecules, both Grunberg-Nissan type equations can be tested to estimate the viscosity of biodiesel + n-butanol mixtures. Empirical equations, as linear (Eq. 2) and polynomial (Eq. 3) for density, and polynomial for viscosity (Eq. 7) were also tested. For property - temperature relationship, according to literature, only a linear equation (Eq. 4) for density and an exponential type equation (Eq. 8) for viscosity were applied. In all equations, the mass fractions, w_i, were utilized to express the mixtures composition.

Table 2

Equations used in this study for density and viscosity estimation

Equation*	Type	Parameters	Computational performances
Density			
Kay's: $\frac{1}{\rho} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}$ (1)	predictive		0.09-0.15 % [25] errors for diesel fuel + biodiesel blends
Linear regression: $\rho = aw + b$ (2)	correlative-predictive	*a, b*	0.01-0.42 %[26] errors for diesel fuel + biodiesel blends, and 0.8%[27] error and 0.9984-0.9998[25] R^2 correlation coefficient values, respectively, for rapeseed oil + n-butanol blends
Polynomial regression: $\rho = aw^2 + bw + c$ (3)		*a, b, c*	better than 0.997[28] R^2 values for diesel fuel + biodiesel blends
Linear regression: $\rho = aT + b$ (4)		*a, b*	0.9989-0.9997[29] and 0.9943-0.9977[25] R^2 values for diesel fuel + biodiesel blends, and 0.9982-0.9987[30] R^2 values for soybean oil + n-butanol blends
Viscosity			
Grunberg-Nissan simplified: $\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2$ (5)	predictive		0.07-2.25 %[26] and 0.64-1.07%[16] errors for diesel fuel + biodiesel blends
Grunberg-Nissan one parameter: $\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 + w_1 w_2 G_{12}$ (6)	correlative-predictive	G_{12}	0.12-0.51%[15] errors for diesel fuel + biodiesel blends, and 4.38–5.10 %[30] errors for soybean oil + n-butanol blends
Polynomial regression: $\eta = aw^2 + bw + c$ (7)	correlative-predictive	*a, b, c*	0.01–1.58 %[26] errors and 0.9983–0.9998[26] R^2 values for diesel fuel + biodiesel blends
Andrade equation: $\eta = \exp(a/T + b)$ (8)		*a, b*	0.9623–0.9891[25] R^2 values for diesel fuel + biodiesel blends

*ρ, ρ_1, ρ_2 are the density of the mixture and components 1 and 2, respectively; w, w_1, w_2 – mass fraction of mixture and components, respectively; η, η_1, η_2 – kinematic viscosity of the mixture and components, respectively; G_{12} - interaction parameter; *a, b, c* - regression coefficients, *T*-temperature; errors were shown in the biocombustible literature

The accuracy of different models for predicting mixtures density and viscosity was evaluated by the means of both average relative deviation (*ARD*) calculated with the equation:

$$ARD = \frac{100}{n}\sum_{i=1}^{n}\frac{\left|P_{\exp,i} - P_{cal,i}\right|}{P_{\exp,i}} \quad (9)$$

and standard deviation (σ):

$$\sigma = \sum_{i=1}^{n}\sqrt{\frac{\left(P_{\exp,i} - P_{cal,i}\right)^2}{n-m}} \quad (10)$$

where P_{exp} and P_{cal} are the experimental and calculated properties, respectively; n - the number of experimental data points; m – the number of model parameters.

3. Results and Discussion

The experimental densities and kinematic viscosities of biodiesel + n-butanol mixture over the entire composition range expressed by butanol mass fraction (w_2) are presented in Table 3. As liquid fuels motion and fuel injection processes are of interest in practice, the kinematic viscosity was extensively investigated.

Table 3

Experimental density, kinematic viscosity and refractive index of biodiesel mixtures with n-butanol

Temperature (K)	Composition (w_2*)						
	0.0000	0.1997	0.4001	0.5999	0.8001	0.9001	1.0000
density (g/cm^3)							
293.15	0.8787	0.8633	0.8490	0.8357	0.8224	0.8164	0.8102
298.15	0.8750	0.8595	0.8452	0.8318	0.8186	0.8126	0.8063
303.15	0.8714	0.8557	0.8414	0.8280	0.8147	0.8087	0.8024
308.15	0.8678	0.8520	0.8375	0.8241	0.8108	0.8048	0.7985
313.15	0.8641	0.8482	0.8336	0.8202	0.8069	0.8009	0.7946
318.15	0.8606	0.8444	0.8298	0.8162	0.8029	0.7970	0.7907
323.15	0.8569	0.8406	0.8259	0.8123	0.7990	0.7930	0.7867
kinematic viscosity (mm^2/s)							
293.15	7.3117	5.3276	4.4600	3.9583	3.7016	3.6303	3.6059
298.15	6.4929	4.7393	3.9744	3.5320	3.2845	3.2274	3.1976
303.15	5.7440	4.2117	3.5386	3.1424	2.9140	2.8578	2.8286
308.15	5.1180	3.7670	3.1662	2.8087	2.5955	2.5407	2.5087
313.15	4.5934	3.3887	2.8485	2.5217	2.3223	2.2674	2.2362
318.15	4.1458	3.0661	2.5746	2.2745	2.0857	2.0320	1.9959
323.15	3.7617	2.8030	2.3391	2.0599	1.8848	1.8241	1.7886

*w_2 – mass fraction of n-butanol

3.1. Density

From Table 3 it can be seen that the density of pseudo-binary mixture of biodiesel with n-butanol decreases with the increase of alcohol content in the mixture. The density of all mixtures decreases with temperature increasing. These

results are consistent with results from literature regarding diesel fuel + ethanol [31] and soybean oil+n-butanol blends [30]. The experimental density data were utilized to test Kay's mixing rule (Eq. 1) and correlative equations (2) and (3). The calculation results regarding regression coefficients *a*, *b* and *c* from Eq.(2) and Eq.(3) determined by least square regression together with the statistical parameters ARD and correlation coefficient, R^2 are summarized in Table 4.

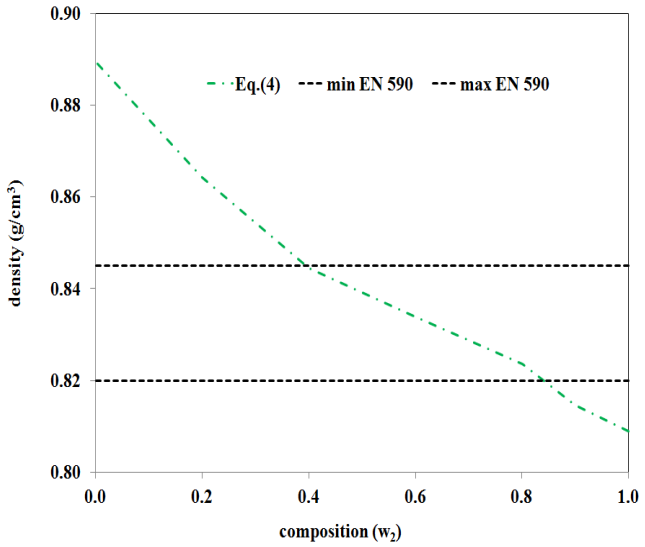

Fig. 1 Calculated density of biodiesel(1) + n-butanol(2) mixtures versus composition at 288.15 K and limit values of density as required by diesel fuel standard (EN 590)

Table 4

Regression parameters of density–composition relationship for Eq. (2) and statistical parameters ARD and R^2 for Eqs. (1), (2) and (3)

Temperature (K)		293.15	298.15	303.15	308.15	313.15	318.15	323.15
Eq. (1)	ARD (%)	0.0916	0.0951	0.0718	0.0985	0.1053	0.1089	0.1210
	R^2	0.9987	0.9986	0.9985	0.9984	0.9983	0.9980	0.9979
Eq. (2)	*a* (g/cm^3)	-0.0681	-0.0683	-0.0685	-0.0688	-0.0690	-0.0693	-0.0696
	b (g/cm^3)	0.8773	0.8736	0.8699	0.8663	0.8625	0.8589	0.8551
	R^2	0.0530	0.0526	0.0574	0.0639	0.0688	0.0823	0.0837
Eq. (3)	*a* (g/cm^3)	0.0090	0.0092	0.0095	0.0101	0.0105	0.0114	0.0116
	b (g/cm^3)	-0.0773	-0.0776	-0.0782	-0.0790	-0.0796	-0.0890	-0.0814
	c (g/cm^3)	0.8786	0.8749	0.8712	0.8676	0.8639	0.8604	0.8567
	ARD (%)	0.0164	0.0176	0.0187	0.0202	0.0208	0.0215	0.0213
	R^2	1.0000	1.0000	0.9999	0.9999	0.9999	0.9999	0.9999

As seen from Table 4, the density of biodiesel + n-butanol mixtures is predicted with a good accuracy by a simple mixing rule (Eq. 1), the error (ARD, %) in density estimation being less than 0.09 %.

The minimum and maximum set limit values for density as requested by diesel fuel standard (EN 590) are 0.820 g/cm^3 and 0.845 g/cm^3, respectively, at

288.15 K. The density of biodiesel + n-butanol mixture at different compositions at 288.15 K was estimated using Eq. (4) (regression parameters are presented in Table 5) and graphically represented (Fig.1), together with the set limit values imposed by EN 590 (the horizontaly lines). It can be seen from Fig. 1 that mixtures of biodiesel with n-butanol, with mass fraction of alcohol varying approximately between 0.4 and 0.8, were within the diesel fuel standard limits.

The accuracy of Eq. (4) for density calculation at different temperatures is good for all studied systems (Table 5). The same behavior was observed by Tat and van Gerpen [32] for diesel fuel+biodiesel mixtures.

Table 5

Regression parameters of density-temperature relationship for Eq. (4)

Composition (w_2*)	0.0000	0.1997	0.4001	0.5991	0.8001	0.9001	1.0000
a (g/cm^3·K)	-0.0007	-0.0008	-0.0008	-0.0008	-0.0008	-0.0008	-0.0008
b (g/cm^3)	1.0912	1.0848	1.0750	1.0644	1.0516	1.0451	1.0395
ARD (%)	2.6243	1.6060	1.0757	0.7482	0.7005	0.7697	0.6898
R^2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

*w_2 – mass fraction of n-butanol

3.2. Viscosity

The addition of n-butanol to biodiesel (viscosities shown in Table 3) decreases the resistance to flow, which is beneficial for the combustion process of the mixtures. The decrease of the viscosity of pseudo-binary mixtures biodiesel and n-butanol with the increasing alcohol content is due to the difference in the viscosity of the mixture components at the same temperature: n-butanol < biodiesel. These results are in good agreement with similar results regarding diesel fuel + alcohol blends [31].

Viscosity variation with temperature of combustible mixtures is important and should be known, especially at low temperatures that may increase viscosity to unacceptable values. According to the data shown in Table 3, the kinematic viscosity of biodiesel + n-butanol mixtures decreases nonlinearly with temperature. The sensibility of the mixtures viscosity with temperature decreases with temperature increasing.

In the following, viscosity experimental data were utilized to analyze viscosity-composition and viscosity-temperature relationships applying Eqs. (5-7 and 8), respectively. The Grunberg-Nissan one parameter and simplified equations (Eqs. 5 and 6), as well as polynomial equation (Eq. 7) were used to predict the viscosity of the mixtures from the viscosities of the pure components and to correlate the experimental data. The interaction coefficients G_{12} from Grunberg-Nissan one parameter equation were determined by fitting the equation to the experimental viscosity values with a least-squares type algorithm. The values of interaction coefficients G_{12} from Eq. (6), and of regression parameters a,

b and *c* from Eq. (7) determined by least square regression, together with statistical parameters values corresponding to Eqs. (5-7) are listed in Table 6.

It can be seen from Table 6 that correlative Eqs. (6) and (7) give better results than the predictive Eq. (5). Eqs. (6) and (7) can represent with the best results (ARD less than 1.4 %) the dependency of viscosity on composition, based on experimental data, which is better expressed than for other oil + n-butanol mixtures from literature [30]. The accuracy of simplified Grunberg-Nissan equation (Eq. 5) is not too good (ARD between 9.7 % and 11.8 %) proving that biodiesel + n-butanol system has not an ideal behavior. Eq. (5) can be utilized only to estimate with a relative accuracy the viscosity of the mixtures, from pure components values. Simplified Grunberg-Nissan equation gives best results if applied to mixtures with components having similar chemical structure, as is the case of diesel fuel + biodiesel mixtures.

Table 6

G_{12} interaction parameter from Eq. (6), regression parameters from Eq. (7) and statistical parameters for Eqs. (5-7)

Temperature (K)	Eq.(5)	Eq.(6)			Eq.(7)				
	ARD (%)	G_{12} (mm^2/s)	σ_{G12}	ARD (%)	*a* (mm^2/s)	*b* (mm^2/s)	*c* (mm^2/s)	ARD (%)	R^2
293.15	11.7710	-0.8546	2.0277	1.3659	5.3256	-8.8747	7.1414	2.8725	0.9850
298.15	11.5257	-0.8379	2.0424	1.3778	4.6637	-7.6879	6.4316	2.8607	0.9850
303.15	11.1764	-0.8136	1.9876	1.3273	4.0396	-6.7215	5.6129	2.7746	0.9856
308.15	10.8081	-0.7887	1.9479	1.3009	3.5280	-5.9332	5.0034	2.7223	0.9862
313.15	10.5361	-0.7695	1.9000	1.2554	3.1168	-5.2946	4.4921	2.6674	0.9868
318.15	10.1459	-0.7435	1.8834	1.2559	2.7611	-4.7506	4.0557	2.6547	0.9874
323.15	9.6787	-0.7118	1.6853	1.1519	2.4489	-4.2849	3.6857	2.5403	0.9892

Diesel fuel is a mixture of a large number of hydrocarbons, especially paraffinic and naphthenic hydrocarbons, and biodiesel is composed by numerous straight chain monoalkylesters of fatty acids. Yuan et al. [33] consider that the structure of biodiesel is close to the structure of diesel fuel, due to the hydrogen-carbon chain of the esters from biodiesel, similar to that of unbranched alkanes from diesel fuel. The second component of the studied pseudo-binary mixture, n-butanol, is a pure non-branched alcohol. Diesel fuel and biodiesel are liquids made up of large molecules bound by weak (van der Waals) forces, while n-butanol is made up of small molecules connected by hydrogen bounds. Like most alcohols, n-butanol is a polar and self-associated liquid. As a result of their structure, the interactions between n-butanol molecules and biodiesel molecules are probably weak, but different from the interactions from pure mixture components, therefore the interaction parameter G_{12} should not be neglected when estimating biodiesel + n-butanol viscosity using Grunberg-Nissan equation. From Table 6 it can be observed that interaction parameters (G_{12}) from Grunberg-Nissan one parameter equation (Eq. 6) are negative, showing that the interactions between unlike molecules are weak. Negative but smaller values for interaction parameter G_{12} were also reported in literature for biodiesel + diesel fuel blends

[34]. Andrade equation (Eq. 8) was tested to represent viscosity-temperature dependence for the studied mixture (Table 7).

Table 7

Regression parameters of kinematic viscosity - temperature relationship for Eq. (8)

Composition (w_2)	a (K·mm^2/s)	b (mm^2/s)	ARD (%)	σ (mm^2/s)
0.0000	2109.4177	-5.2080	0.3025	0.4062
0.1997	2042.3290	-5.2969	0.3804	0.4969
0.4001	2045.7830	-5.4840	0.1654	0.2260
0.5999	2071.4415	-5.6886	0.1271	0.1743
0.8001	2139.3419	-5.9880	0.1132	0.1434
0.9001	2180.2955	-6.1440	0.1735	0.2620
1.0000	2220.5833	-6.2878	0.2215	0.2939

The values of parameters *a* and *b* from Eq. (8) were obtained with the least square method, by fitting the equation to the experimental values. Eq. (8) represents well the viscosity variation with temperature correlating the viscosity data with ARD of maximum 0.38 %. Given the simplicity of Eq. (8), it can be recommended for viscosity of biodiesel + n-butanol mixtures calculation, between 293.15 and 323.15 K. Experimental and calculated viscosity versus composition of biodiesel + n-butanol mixtures was graphicaly represented at 313.15 K (Fig. 2), the reference temperature for viscosity measurement according to diesel fuel standard (EN 590). The symbols and lines indicate the experimental and calculated values, respectively. The minimum and maximum set limit values for kinematic viscosity as requested by diesel fuel standard (EN 590) are 2 mm^2/s and 4.5 mm^2/s, respectively. It can be observed that all the mixtures of biodiesel with n-butanol comply with these standard requirements. Figure 2 clearly shows the better accuracy of Grunberg-Nissan one parameter equation (Eq. 6) for biodiesel + n-butanol mixtures viscosity prediction, compared to simplified Grundberg-Nissan equation (Eq. 5).

Deviation in viscosity depends on the molecular interactions and on the size and shape of the molecules of a liquid mixture. To better understand the behavior of biodiesel + n-butanol mixture, the deviation in viscosity, $\Delta\eta$, was calculated using equation:

$$\Delta\eta = \eta - (w_1\eta_1 + w_2\eta_2) \tag{12}$$

The values of $\Delta\eta$ were correlated by Redlich-Kister polynomial equation:

$$\Delta\eta = w_1 w_2 \sum_k A_k (w_1 - w_2)^k \tag{13}$$

where A_k are the polynomial coefficients, k is the degree of polynomial.

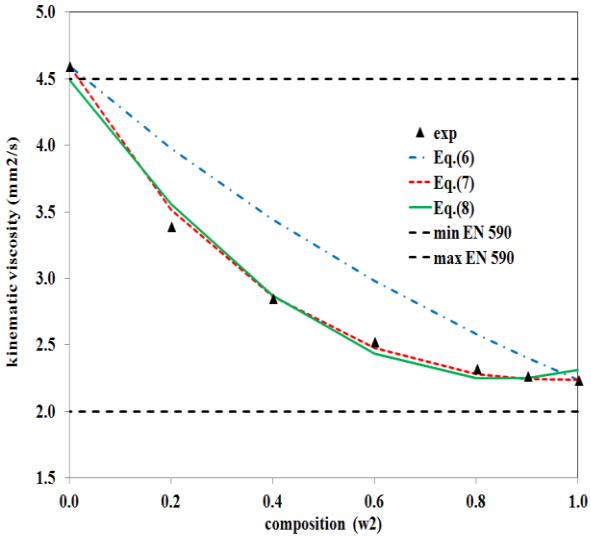

Fig.2. Experimental and calculated kinematic viscosities of biodiesel(1) + n-butanol(2) mixtures versus composition at 313.15 K and limit values of viscosity as required by diesel fuel standard (EN 590)

The values of the parameters A_k were obtained by fitting the equation to the experimental viscosity values, with the least-squares method. Table 8 summarizes the values of the A_k coefficients along with the corresponding values of standard deviation. Deviation in viscosity for biodiesel + n-butanol mixture was found to be negative over the whole composition range and for all investigated temperatures (Fig. 3). It was found that Redlich-Kister equation correlates well the experimental data, standard deviation being smaller than 0.0075 mm^2/s. The negative deviation in viscosity values are consistent with negative parameter values G_{12}, showing weak interactions in biodiesel + n-butanol mixture.

Table 8

Values of Redlich-Kister coefficients (Eq. 13) and corresponding standard deviation

Correlation parameters	Temperature (K)						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
A_0	-5.1109	-4.4654	-3.8658	-3.3759	-2.9815	-2.6417	-2.3585
A_1	-2.5232	-2.2155	-1.9142	-1.6785	-1.4837	-1.3245	-1.2100
A_2	-2.2744	-2.0902	-1.8467	-1.6146	-1.4485	-1.2677	-0.9626
A_3	-1.5217	-1.3995	-1.2073	-1.0408	-0.9046	-0.8044	-0.4544
σ (mm^2/s)	0.0075	0.0015	0.0016	0.0009	0.0013	0.0006	0.0023

The absolute value of deviation in viscosity decreases with temperature decrease. Negative but smaller values for deviation in viscosity for diesel fuel + biodiesel mixture were reported in our previous research [35] indicating a smaller deviation from ideality in this system than in biodiesel + n-butanol mixture, in agreement with Benjumea's structural considerations [25].

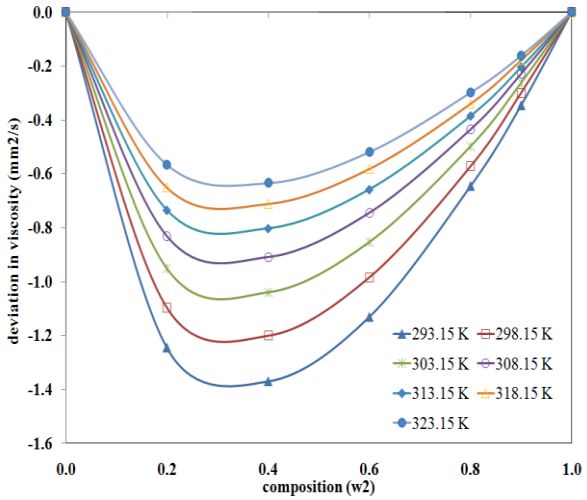

Fig.3 Deviation in viscosity versus composition for biodiesel(1) + n-butanol(2) mixtures (points are experimental values, lines comes from fitting with Redlich-Kister equation)

4. Conclusions

The influence of n-butanol addition to biodiesel properties was examined in respect to density and viscosity and compared to diesel fuel standard requirements. Experimental data of density and viscosity for biodiesel + n-butanol mixtures were presented on the whole composition range and at temperatures from 293.15 K to 323.15 K. The conclusions arising from this study are:

- biodiesel properties can be improved by blending with n-butanol which decreases the viscosity and density of mixture;
- as in the case of diesel fuel + biodiesel mixtures, density and viscosity data of pure biodiesel and butanol can be used to predict the density (Eq. 1) or viscosity (Eq. 6) of the pseudo-binary mixtures of these fuels. Only the full form of the Grunberg-Nissan equation (Eq. 6) proved to give accurate results for estimating mixtures viscosity. Regression equations of second degree polynomial type (Eq. 3) for density and Eq. (7) for viscosity) can also be recommended to calculate the density and viscosity, respectively, when experimental data of biodiesel mixtures with n-butanol are available;
- mixtures of biodiesel + n-butanol with mass fraction varying between 0.4 and 0.8 comply with diesel fuel standard requirements regarding density, and all the mixtures were within diesel fuel standard limits for viscosity;
- a linear equation (Eq. 4) and an exponential type equation (Eq. 8) can be recommended to calculate the dependence of density and viscosity, respectively, on temperature.
- beside bioethanol, (bio)n-butanol has a great potential as a blending component with biodiesel.

REFERENCES

[1] *M. Lapuerta, J. Rodriguez-Fernandez, R. Garcia-Contreras, M. Bogarra*, "Molecular interactions in blends of alcohols with diesel fuels: Effect on stability and distillation", in Fuel, **vol. 139,** 2015, pp. 171-179.

[2] *H. Joshi, B. R. Moser, J. Toler, W. F. Smith, T. Walker*, "Effects of blending alcohols with poultry fat methyl esters on cold flow properties", in Renew. Energ., **vol. 35**, no.10, 2010, pp. 2207-2210.

[3] *V. Makareviciene, K. Kazancev, I. Kazanceva*, "Possibilities for improving the cold flow properties of biodiesel fuel by blending with butanol" in Renew. Energ. **vol. 75**, 2015, pp. 805-807.

[4] *Y. Yoshimoto, E. Kinoshita, L. Shanbu, T. Ohmura*, "Influence of 1-butanol addition on diesel combustion with palm oil methyl ester/gas oil blends", in Energy, **vol. 61**, 2013, pp. 44-51.

[5] *Z. Sahin, O. N. Aksu,* "Experimental investigation of the effects of using low ratio n-butanol/diesel fuel blends on engine performance and exhaust emissions in a turbocharged DI diesel engine", in Renew. Energ. **vol. 77**, 2015, pp. 279-290.

[6] *C. D. Rakopoulos, A. M. Dimaratos, E. G. Giakoumis, D. C. Rakopoulos*, "Study on turbocharged diesel engine operation, pollutant emissions and combustion noise radiation during starting with bio-diesel or n-butanol diesel fuel blends", in Appl. Energ., **vol. 88**, 2011, pp. 3905-3916.

[7] *D. C. Rakopoulos, C. D. Rakopoulos, D. T. Hountalas, E. C. Kakaras, E. G. Giakoumis, R. G. Papagiannakis*, "Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends", in Fuel, **vol. 89**, 2010, pp. 2781-2790.

[8] *D. C. Rakopoulos, C. D. Rakopoulos, E. G. Giakoumis, A. M. Dimaratos, D. C. Kyritsis,* "Effect of butanol-diesel fuel blends on the performance and emissions of high-speed DI diesel engine", in Energ. Convers. Manage., **vol. 51**, 2010, 1989-1997.

[9] *C. D. Rakopoulos, A. M. Dimaratos, E. G. Giakoumis, D. C. Rakopoulos*, "Investigating the emissions during acceleration of turbocharged diesel engine operating with bio-diesel or n-butanol diesel fuel blends", in Energy, **vol. 35**, 2010, pp. 5173-5184.

[10] *O. Dogan*, "The influence of n-butanol/diesel fuel blends utilization on a small diesel engine performance emissions", in Fuel, **vol. 90**, no. 7, 2011, pp. 2467-2472.

[11] *J Campos-Fernádez, J.M. Arnal, J. Gómez, M.P. Dorado*, "A comparison of performance of higher alcohols/diesel fuel blends in a diesel engine", in Appl. Energ., **vol. 95**, 2012, pp. 267-275.

[12] *S. Kumar, J. H. Cho, J. Park, I. Moon,* "Advances in diesel_alcohol blends and their effect on the performance and emissions of diesel engine", in Renew. Sust. Energ. Rev., **vol. 22**, 2013, pp. 46-72.

[13] *M. Yao, H. Wang, Z. Zheng, Y. Yue*, "Experimental study of n-butanol additive and multi-injection on HD diesel engine performance and emissions", in Fuel, **vol. 89**, no. 9, 2010, pp. 2190-2201.

[14] *S. Altun, C. Oner, F. Yasar, H. Adin,* "Effect of n-butanol blending with a blend of diesel and biodiesel on performance and exhaust emissions of a diesel engine", in Ind. Eng. Chem. Res., **vol. 50**, no. 15, 2011, pp. 9425-9530.

[15] *I. Nita, S. Geacai, O. Iulian*, "Measurements and correlations of physico-chemical properties to composition of pseudo-binary mixtures with biodiesel" in Renew. Energ., **vol. 36**, no. 12, 2011, pp. 3417-3423.

[16] *S. Geacai, O. Iulian, I. Nita*, "Measurement, correlation and prediction of biodiesel blends viscosity", in Fuel, **vol. 143**, 2015, pp. 268-274.

[17] *V. V. E. Prasad, S. B. Agrawal, A. B. Bajaj, D. H. L. Prasad*, "Density and viscosity of methanol plus trichloroethylene, n-propanol plus trichloroethylene and n-butanol plus trichloroethylene mixtures", in Phys. Chem. Liq.: Int. J. **vol. 38**, no. 4, 2000, pp. 433-438.
[18] *E. D. Dikio, S. M. Nelana, D. A. Isabirye, E. E. Ebenso*, "Density, dynamic viscosity and derived properties of binary mixtures of methanol, ethanol, n-propanol, and n-butanol with pyridine at T=(293.15, 303.15, 313.15 and 323.15) K", in Int. J. Electrochem. Sci., **vol. 7**, 2012, pp. 11101-11122.
[19] *T. Walner, S. A. Miers, S. McConnell*, "A comparison of ethanol and butanol as oxygenates using a direct-injection, spark-ignition engine", in J. Eng. Gas Turb. Power., vol. 131, no. 3, 2009, pp. 032802-032811.
[20] *E. Ileri, A. Atmanli, N. Yilmaz*, "Comparative analyses of n-butanol-rapeseed oil-diesel blend with biodiesel, diesel and biodiesel-diesel fuels in a turbocharged direct injection diesel engine", in J. Energ. Institute, 2015, DOI:10.1016/j.joei.2015.06.004.
[21] *P-M. Yang, Y-C. Lin, K. C. Lin, S-R. Jhang, S.-C. Chen, C-C. Wang, Y-C. Lin*, "Comparison of carbonyl compound emissions from a diesel engine generator fueled with blends of n-butanol, biodiesel and diesel", in Energy, **vol. 90**, 2015, pp. 266-273.
[22] *Z. Chen, J. Liu, Z. Hau, B. Dee, Y. Liu, C. Lee*, "Study on performance and emissions of a passanger-car diesel engine fueled with butanol-diesel blends", in Energy, **vol. 55**, 2013, pp. 638-646.
[23] *J. Campos-Fernández, J. M. Arnal, J. Gómez, M. P. Dorado*, "A comparison of performance of higher alcohols/diesel fuel blends in a diesel engine", in Appl. Energ., **vol. 95**, 2012, pp. 267-275.
[24] *A. Atmanli, E. Ileri, B. Yuksel*, "Experimental investigation of engine performance and exhaust emissions of a diesel engine fueled with diesel–n-butanol–vegetable oil blends", in Energ. Convers. Manage., **vol. 81**, 2014, pp. 312-321.
[25] *P. Benjumea, J. Agudelo, A. Agudelo*, "Basic properties of palm oil biodiesel-diesel fuel blends", in Fuel, **vol. 87**, no. 10-11, 2008, pp. 2069-2075.
[26] *E. Alptekin, M. Canakci*, "Determination of the density and the viscosities of biodiesel-diesel fuel blends", in Renew. Energ., **vol. 33**, no. 12, 2008, pp. 2623-2630.
[27] *T. Laza, A. Bereczky*, "Basic properties of rapeseed oil-higher alcohols blends", in Fuel, **vol. 90**, no. 2, 2011, pp. 803-810.
[28] *M. Gulum, A. Bilgin*, "Two-term power models for estimating kinematic viscosities of different biodiesel-diesel fuel blends", in Fuel Process. Technol., **vol. 149**, 2016, pp.121-130.
[29] *M. E. Tat, J. H. Van Gerpen*, "The specific gravity of biodiesel and its blends with diesel fuel", in J. Amer. Oil Chem. Soc., **vol. 77**, no. 2, 2000, pp. 115-119.
[30] *R. Schoo, A. Hoxie*, "Basic properties of refined, bleached and deodorized soybean oil – butanol blends", in Fuel, **vol. 102**, 2012, pp. 701-708.
[31] *E. Torres-Jimenez, M. S. Jerman, A. Gregorc, I. Lisec, M. P. Dorado*, "Physical and chemical properties of ethanol-diesel fuel blends", in Fuel, vol. 90, no. 2, 2011, pp. 795-802.
[32] *M. E. Tat, J. H. Van Gerpen*, "The specific gravity of biodiesel and its blends with diesel fuel", in J. Amer. Oil Chem. Soc., **vol. 77**, no. 2, 2000, pp.115-119.
[33] *W. Yuan, A. C. Hansen, Q. Zhang*, "Vapour pressure and normal boiling point predictions for pure methyl esters and biodiesel fuels", in Fuel, **vol. 84**, no. 7-8, 2005, pp. 943-950.
[34] *S. Geacai, I. Nita, O. Iulian, E. Geacai*, "Refractive indices for biodiesel mixtures", in U.P.B. Sci. Bull., **vol. 74**, no. 4, 2012, pp. 149-159.
[35] *I. Niţă, S. Geacai, O. Iulian*, "Viscosity, refractive index, deviation in viscosity and deviation in refractive index of biodiesel+diesel fuel (or benzene) binary mixtures.", in Rev. Chim. (Bucharest), **vol. 65**, no. 4, 2014, pp. 453-460.