STUDY ON THE DENSITY OF DIESEL FUEL+ISOPROPANOL AND BIODIESEL+ISOPROPANOL PSEUDO-BINARY SYSTEMS

Georgiana-Raluca SANDU[1], Irina NITA[2]*, Sibel OSMAN[3], Olga IULIAN[4]

The densities of diesel fuel+isopropanol, biodiesel+isopropanol and diesel fuel+biodiesel pseudo-binary systems have been measured on the whole composition range for temperature varying from 293.15 K to 323.15 K. A nonlinear dependency of density on composition was observed for diesel fuel and biodiesel systems with isopropanol. The density of studied systems can be calculated with a good accuracy using mixing rules or empirical equations. The density dependence on temperature was observed to be of linear nature on the studied domain.

Keywords: isopropanol, biodiesel, density, diesel fuel

1. Introduction

Biofuels have a lot of advantages over fossil fuels because they are made from renewable feedstocks everywhere spreaded, are biodegradable, and contribute to the reduction of environment pollution.

Mixtures of bioalcohol with diesel fuel or biodiesel are interesting systems from a theoretical point of view due to their complexity, taking into account that diesel fuel and biodiesel are multicomponent systems. More than that, blends of bioalcohols with fossil fuels can contribute to a better combustion in the diesel engine and to the emissions reduction. Alcohols with 1 to 5 carbon atoms in the molecule can be used in small quantities blended with fossil fuels, to feed the internal combustion engines without the need of engine modification.

In order to reduce fossil fuels utilisation in the transport sector, bioalcohols can be added to diesel fuel or diesel fuel+biodiesel blends [1,2]. In the last years, the improved miscibility of higher alcohols (C>3) with diesel fuels compared to lower ones has led to the research intensification regarding diesel engine behavior

[1] PhD student, Dept.of Inorganic Chemistry, Physical Chemistry & Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: stoica_raluka@yahoo.com
[2] Assoc.Prof., Dept. of Chemistry and Chemical Engineering, University OVIDIUS of Constanta, Romania, e-mail: inita@univ-ovidius.ro correspondent author
[3] Lecturer, Dept. of Chemistry and Chemical Engineering, University OVIDIUS of Constanta, Romania, e-mail: sibel_o@yahoo.ro
[4] Emeritus Prof., Dept. of Inorganic Chemistry, Physical Chemistry & Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: olgaiulian@yahoo.com

fuelled with this kind of blends [3-7]. Only few studies refer to n-propanol and isopropanol utilisation in transportation, and engine behavior and the emissions level were the issues of the investigations [8-10].

The thermophysical properties of fuels mixtures must be known in order to develop models for fuel combustion in internal combustion engine. Density and viscosity are one of the most important properties needed to estimate diesel engine behavior, and especially the combustion process. Engine power and fuel consumption are affected by the density of the fuels blend that are dependent on the blend composition and temperature. An increase in fuel density can affect the injection system as a result of the increase of the quantity of fuel directed to the combustion chamber because this quantity is measured by a volume basis [11].

The study of the properties of diesel fuel+isopropanol and biodiesel+isopropanol blends is interesting from theoretical and practical point of view, in order to understand the thermodynamic properties of these blends with alcohol, useful for future applications in transportation sector.

As a continuation of our experimental work on mixtures of fossil fuels with biofuels [4, 12-14], the main aim of this paper is to report the density of diesel fuel+isopropanol and biodiesel+isopropanol mixtures on the whole composition range and for temperature varying between 293.15 K and 323.15 K. After our knowledge, similar data for these systems have not been published. Taking into account that the experimental measurement of the density necessitates time and performant equipments, the accuracy of different equations used to calculate the density of these fuels mixtures was assessed.

2. Experimental part

The density of diesel fuel+isopropanol, biodiesel+isopropanol and diesel fuel+biodiesel binary systems was determined for the whole composition range and for temperature between 293.15 K and 323.15 K. Diesel fuel+biodiesel system was used as reference for the behavior of diesel fuel and biodiesel each mixed with isopropanol. These systems are named binary systems but in fact, they are pseudo-binary systems because diesel fuel and biodiesel are complex mixtures of hydrocarbons and of monoalkyl esters of fatty acids, respectively.

Diesel fuel and biodiesel samples used in measurements were obtained from specialized producers and fulfill quality standard requirements, EN 590 and EN14214, respectively.

Diesel fuel and biodiesel were characterized by the means of some specific physicochemical properties and by their mean molar mass determined using the cryoscopic method. Benzene that has a cryoscopic constant of 5.12 kg.K/mol and a melting point of 5.4 ^{o}C was used as solvent. The mean molar mass of biodiesel was calculated according to its chemical composition chromatographically

determined using a Clarus 500 GC equipment with a FID detector and a SGE BPX70 capillary column of high polarity. Hydrogen at a 20 mL/min flow rate was the carrying gas.

Table 1 presents the fatty acid methyl ester profile of biodiesel and physicochemical characteristics of diesel fuel and biodiesel are shown comparatively with European standards requirements in Table 2. Isopropanol of 99.7 % purity was purchased from Merck.

Table 1

The fatty acid methyl ester profile of biodiesel

Fatty acid	Typical formula	M (g/mol)	Composition (% w/w)
Lauric (C12:0)	$C_{13}H_{26}O_2$	214.344	-
Miristic (C14:0)	$C_{15}H_{30}O_2$	242.398	-
Palmitic (C16:0)	$C_{16}H_{32}O_2$	270.456	3.47
Stearic (C18:0)	$C_{18}H_{36}O_2$	298.510	1.32
Arachidic (eicosenoic) (C20:0)	$C_{20}H_{40}O_2$	326.563	0.38
Palmitoleic (C16:1)	$C_{16}H_{30}O_2$	268.440	-
Oleic (C18:1)	$C_{18}H_{34}O_2$	296.494	39.22
Linoleic (C18:2)	$C_{18}H_{32}O_2$	294.478	39.52
Linolenic (C18:3)	$C_{18}H_{30}O_2$	292.462	-
11-Octadecenoic (11-vacenic) (C19:2)	$C_{19}H_{34}O_2$	282.461	15.09
Gadoleic (11-eicosenoic) (C20:1)	$C_{21}H_{40}O_2$	324.541	0.75

Table 2

Physicochemical characteristics of diesel fuel and biodiesel

Property	Unit	EN 590	Diesel fuel	EN 14214	Biodiesel
Density at 15 °C	Kg/m^3	820.0 - 845.0	840.5	860.0 – 900.0	883.8
Viscosity at 40 °C	mm^2/s	2.0 – 4.5	2.6791	3.5 – 5.0	4.4189
Flash Point	°C	>55	64	>120	175
Mean molar mass	g/mol	-	210.01	-	295.18

The studied diesel fuel+isopropanol, biodiesel+isopropanol and diesel fuel+biodiesel mixtures were prepared on a mass basis with a precision of ±0.0001 g. The density was determined using an Anton Paar densymeter 4500 series. The equipment is provided with a tube of "U" shaped form as cell for density measurement. The cell filled with the sample is exposed to an electromagnetic field. The tube will vibrate in the electromagnetic field with a frequency proportional to the sample density. The uncertainty of density measurement was ± 0.00005 g/cm^3.

3. Equations for calculating the density of the studied mixtures

Experimental density data were used to asses the accuracy of different equations to estimate the density of the studied binary systems. Equations from

the thermodynamics of molecular mixtures, empirical equations or equations used in chemical engineering specifically applied to fuels blends were employed to calculate the density of the studied mixtures. Appling different mixing rules, predictive equations allow the calculation of the density of the binary systems from the density of the pure components without the need of experimental data. Correlative equations can be used to verify the quality of the experimental data and to calculate mixture's property. These equations contain one or more correlation parameters obtained from experimental data using regression analysis.

The composition of the studied binary systems was expressed by mass fraction or molar fraction.

Correlation with composition

Kay's mixing rule was used for the prediction of the density. This rule is utilized in the field of petroleum products and in the last years it was applied for fossil fuels + biofuels blends density estimation [15-18]:

$$\rho = w_1\rho_1 + w_2\rho_2 \tag{1}$$

where ρ is the density of the mixture, ρ_1 and ρ_2, w_1 and w_2 are the densities and mass fractions, respectively of the mixture's components.

From petroleum products a predictive equation was applied [19]:

$$\rho = \frac{x_1M_1 + x_2M_2}{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}} \tag{2}$$

where M_1 and M_2, x_1 and x_2 are the molar masses and molar fractions, respectively of mixture's components.

An empirical equation proposed by Alptekin and Canaki [20] to correlate the experimental density data of diesel fuel+biodiesel blends was used:

$$\rho = aw_2 + b \tag{3}$$

An empirical polynomial equation that describes well the density dependence on mixture composition for biofuels mixtures with organic component was also tested:

$$\rho = aw_2^2 + bw_2 + c \tag{4}$$

where a, b and c from Eqs. (3) and (4) are regression parameters.

Correlation with temperature

To express the density dependence on temperature, the equation proposed by Yuan [21] and applied by Tesfa [22] was utilised:

$$\rho = aT + b \tag{5}$$

where T represents the temperature (K), a and b are regression parameters.

The accuracy of tested equations was assesed by the means of average relative deviation (ARD) and correlation coefficient (R^2) values:

$$ARD = \frac{100}{n}\sum_{i=1}^{N}\left|\frac{\rho_{\exp,i} - \rho_{cal,i}}{\rho_{\exp,i}}\right| \quad (7)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(\rho_{\exp,i} - \rho_{cal,i}\right)^2}{\sum_{i=1}^{N}\left(\rho_{mean} - \rho_{cal,i}\right)^2} \quad (8)$$

where $\rho_{exp,i}$ and $\rho_{cal,i}$ represent experimental and calculated density, respectively, ρ_{mean} is the mean value of the density, N is the number of experimental points.

4. Results and discussions

Experimental data

The experimental density data of diesel fuel+isopropanol, biodiesel+isopropanol and diesel fuel+biodiesel systems are presented in Table 3.

In order to point out the influence of composition and temperature on the density of the binary systems with isopropanol compared to diesel fuel+biodiesel system, Fig.1 presents the tridimensional graphical representation of the experimental data. It can be seen that the density variation with alcohol content or biodiesel, (w_2), respectively, for the reference diesel fuel+biodiesel system, is monotonous without extreme points. The density of diesel fuel+isopropanol and biodiesel+isopropanol systems is decreasing with the increase of alcohol content in contrast to diesel fuel+biodiesel system, for which an increase in density is registered with the increase in biodiesel content. The dependence of the density on system composition is almost linear for diesel fuel+biodiesel system (Fig.1c), while a nonlinear dependency can be observed (Fig.1a,b) for diesel fuel+isopropanol and biodiesel+isopropanol systems, the experimental data points being well correlated by polynomial curves.

Isopropanol is the most sensible on temperature from the three studied fuels taking into account that, for the studied temperature range the greatest density variation correspond to alcohol (0.770 g/cm^3 to 0.800 g/cm^3) followed by diesel fuel (0.820 g/cm^3 to 0.840 g/cm^3) and biodiesel (0.860 g/cm^3 to 0.880 g/cm^3).

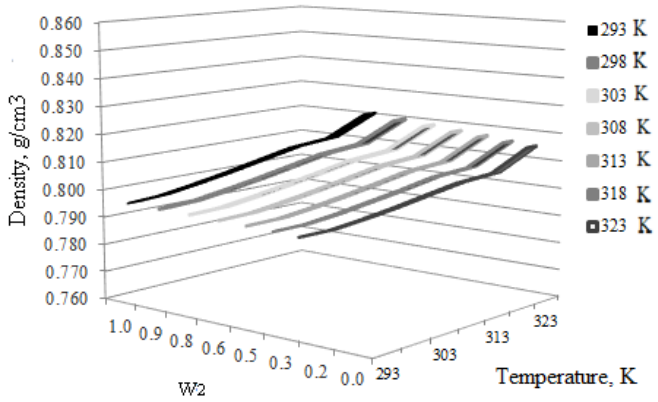
Table 3

Density of diesel fuel(1) + isopropanol(2), biodiesel(1) +isopropanol(2) and diesel fuel(1) + biodiesel(2) mixtures at different compositions and temperatures

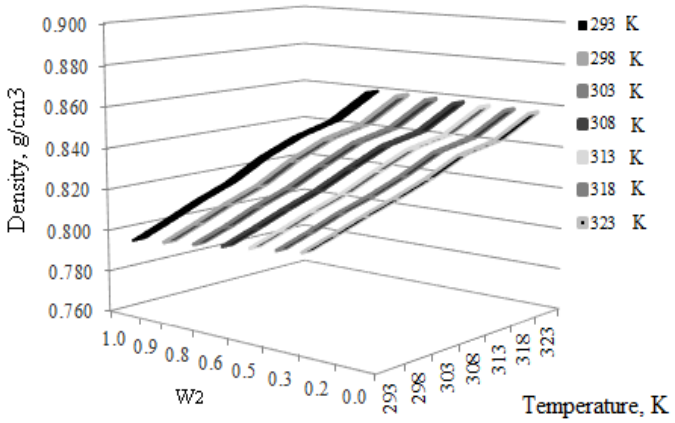
Diesel fuel (1)+ Isopropanol (2)		**Biodiesel (1)+ Isopropanol (2)**		**Diesel fuel (1)+ Biodiesel (2)**	
w_2	Density (g/cm^3)	w_2	Density (g/cm^3)	w_2	Density (g/cm^3)
293.15 K					
1.0000	0.7953	1.0000	0.7953	1.0000	0.8785
0.8434	0.7998	0.8369	0.8071	0.8561	0.8714
0.6893	0.8053	0.6787	0.8193	0.7102	0.8662
0.5375	0.8110	0.5253	0.8305	0.5621	0.8596
0.3879	0.8170	0.3764	0.8442	0.4118	0.8534
0.2406	0.8230	0.2318	0.8556	0.2593	0.8469
0.1437	0.8275	0.1378	0.8645	0.1564	0.8431
0.0000	0.8365	0.0000	0.8785	0.0000	0.8365
298.15 K					
1.0000	0.7909	1.0000	0.7909	1.0000	0.8749
0.8434	0.7954	0.8369	0.8028	0.8561	0.8677
0.6893	0.8010	0.6787	0.8150	0.7102	0.8626
0.5375	0.8068	0.5253	0.8263	0.5621	0.8560
0.3879	0.8129	0.3764	0.8403	0.4118	0.8498
0.2406	0.8190	0.2318	0.8522	0.2593	0.8433
0.1437	0.8237	0.1378	0.8606	0.1564	0.8396
0.0000	0.8329	0.0000	0.8749	0.0000	0.8329
303.15 K					
1.0000	0.7865	1.0000	0.7865	1.0000	0.8712
0.8434	0.7910	0.8369	0.7981	0.8561	0.8642
0.6893	0.7967	0.6787	0.8108	0.7102	0.8590
0.5375	0.8027	0.5253	0.8222	0.5621	0.8524
0.3879	0.8088	0.3764	0.8355	0.4118	0.8462
0.2406	0.8150	0.2318	0.8482	0.2593	0.8398
0.1437	0.8198	0.1378	0.8568	0.1564	0.8360
0.0000	0.8294	0.0000	0.8712	0.0000	0.8294
308.15 K					
1.0000	0.7820	1.0000	0.7820	1.0000	0.8676
0.8434	0.7866	0.8369	0.7940	0.8561	0.8606
0.6893	0.7924	0.6787	0.8064	0.7102	0.8554
0.5375	0.7984	0.5253	0.8181	0.5621	0.8488
0.3879	0.8047	0.3764	0.8314	0.4118	0.8426
0.2406	0.8111	0.2318	0.8442	0.2593	0.8363
0.1437	0.8160	0.1378	0.8529	0.1564	0.8325
0.0000	0.8258	0.0000	0.8676	0.0000	0.8258
313.15 K					
1.0000	0.7775	1.0000	0.7775	1.0000	0.8639
0.8434	0.7821	0.8369	0.7895	0.8561	0.8570
0.6893	0.7879	0.6787	0.8021	0.7102	0.8518

0.5375	0.7941	0.5253	0.8137	0.5621	0.8452
0.3879	0.8005	0.3764	0.8273	0.4118	0.8391
0.2406	0.8071	0.2318	0.8402	0.2593	0.8327
0.1437	0.8121	0.1378	0.8490	0.1564	0.8289
0.0000	0.8224	0.0000	0.8639	0.0000	0.8224
318.15 K					
1.0000	0.7728	1.0000	0.7728	1.0000	0.8603
0.8434	0.7775	0.8369	0.785	0.8561	0.8534
0.6893	0.7834	0.6787	0.7978	0.7102	0.8482
0.5375	0.7898	0.5253	0.8094	0.5621	0.8416
0.3879	0.7962	0.3764	0.8221	0.4118	0.8355
0.2406	0.8030	0.2318	0.8362	0.2593	0.8291
0.1437	0.8081	0.1378	0.8453	0.1564	0.8254
0.0000	0.8187	0.0000	0.8603	0.0000	0.8187
323.15 K					
1.0000	0.7681	1.0000	0.7681	1.0000	0.8567
0.8434	0.7728	0.8369	0.7804	0.8561	0.8498
0.6893	0.7789	0.6787	0.7931	0.7102	0.8446
0.5375	0.7853	0.5253	0.8052	0.5621	0.8381
0.3879	0.7921	0.3764	0.8179	0.4118	0.8319
0.2406	0.7988	0.2318	0.8322	0.2593	0.8255
0.1437	0.8041	0.1378	0.8413	0.1564	0.8219
0.0000	0.8152	0.0000	0.8567	0.0000	0.8152

a)



b)



c)

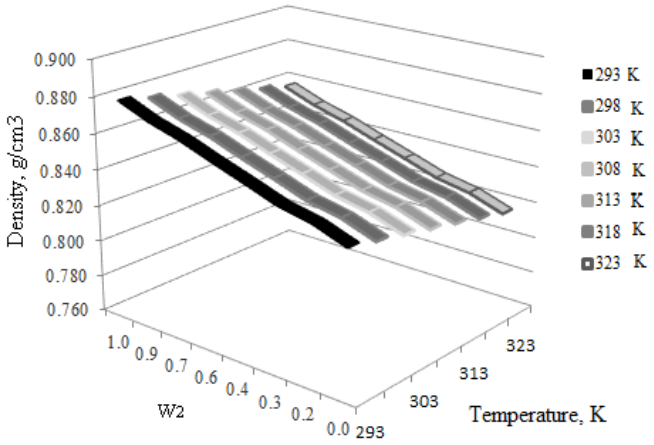


Fig. 1. Density versus composition and temperature for binary systems: a) diesel fuel(1)+isopropanol(2), b)biodiesel(1)+isopropanol(2), c) diesel fuel(1)+biodiesel(2)

As a result, the domain of density variation with temperature is greater for the systems with isopropanol compared to diesel fuel+biodiesel system. The influence of temperature on density is more pronounced for biodiesel+isopropanol system.

The determination of density dependence on composition and temperature is important especially from practical point of view because this information is needed to establish the possibility of diesel fuel+isopropanol and

biodiesel+isopropanol mixtures utilisation as fuels for internal combustion engine and to evaluate the possibility of transportation fuels quality improvement by mixing with bioalcohols.

To the best of our knowledge, density data for diesel fuel+isopropanol and biodiesel+isopropanol systems are not available in literature to be compared with experimental data obtained in this study. Experimental density data obtained for diesel fuel+biodiesel reference system are in accordance with data presented in literature [18, 22, 23].

Experimental density data modeling

Experimental density data were used to test the accuracy of different equations for density correlation with composition.

Table 4

Regression parameters from Eq.(3) and Eq.(4) and correlation coefficient R^2 values at different temperatures

Eq.		Temperature (K)						
		293.15	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
		Diesel fuel(1) + Isopropanol(2)						
(3)	*a*	-0.0403	-0.0411	-0.0419	-0.0428	-0.0438	-0.0448	-0.0458
	b	0.8336	0.8301	0.8264	0.8227	0.819	0.8152	0.8114
	R^2	0.9893	0.9886	0.9876	0.9873	0.9856	0.9853	0.9841
		Biodiesel(1) + Isopropanol(1)						
(3)	*a*	-0.0825	-0.0834	-0.0842	-0.0849	-0.0857	-0.0866	-0.0877
	b	0.8759	0.8724	0.8685	0.8647	0.861	0.8571	0.8534
	R^2	0.9971	0.9971	0.9969	0.9967	0.9965	0.9958	0.9956
		Diesel fuel(1) + Biodiesel(2)						
(3)	*a*	0.0416	0.0416	0.0415	0.0414	0.0413	0.0412	0.0411
	b	0.8364	0.8328	0.8293	0.8257	0.8222	0.8186	0.8151
	R^2	0.9994	0.9993	0.9995	0.9994	0.9995	0.9995	0.9994
		Diesel fuel(1) + Isopropanol(2)						
(4)	*a*	0.0141	0.0148	0.0156	0.0163	0.0177	0.0183	0.0193
	b	-0.0544	-0.056	-0.0576	-0.0591	-0.0616	-0.063	-0.0652
	c	0.8358	0.8322	0.8286	0.825	0.8215	0.8178	0.8142
	R^2	0.9988	0.9988	0.9985	0.9986	0.9985	0.9983	0.9980
		Biodiesel(1) + Isopropanol(2)						
(4)	*a*	0.0148	0.015	0.0163	0.0168	0.0175	0.0193	0.0200
	b	-0.0973	-0.0984	-0.1004	-0.1016	-0.1031	-0.1059	-0.1076
	c	0.8780	0.8745	0.8708	0.8671	0.8634	0.8598	0.8562
	R^2	0.9997	0.9997	0.9998	0.9998	0.9998	0.9997	0.9997
		Diesel fuel(1) + Biodiesel(2)						
(4)	*a*	0.0015	0.0015	0.0015	0.0014	0.0015	0.0013	0.0014
	b	0.0401	0.0400	0.0399	0.0399	0.0397	0.0399	0.0397
	c	0.8366	0.8330	0.8295	0.8259	0.8225	0.8188	0.8153
	R^2	0.9995	0.9994	0.9996	0.9995	0.9996	0.9996	0.9995

The density of the studied systems was calculated using predictive (Eq.(1) and Eq.(2)) and correlative equations (Eq.(3) and Eq. (4)). Table 4 presents the values of regression parameters from Eq. (3) and Eq. (4) determined based on experimental data by regression, using the least-square method, and correlation coefficient (R^2) values. Table 5 presents the average realative deviation values (ARD, %) for density calculation of the pseudo-binary fuels mixtures, using Eqs. (1)-(4). It results from Table 4 that the density of diesel fuel+biodiesel system is well correlated with a linear equation (R^2 = 0.9993-0.9995) (Eq.3), while the density of systems with isopropanol is well correlated with a polynomial equation (Eq.4) (R^2 = 0.9980-0.9998) for the whole studied temperature range.

Table 5

Absolute relative deviation (ARD, %) of density calculation using Eqs.(1) – (4)

Eq.	Temperature (K)						
	293.15	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
Diesel fuel(1) + Isopropanol(2)							
(1)	0.2805	0.2962	0.3169	0.3285	0.3596	0.3596	0.4006
(2)	0.0692	0.0761	0.0889	0.0935	0.1161	0.1219	0.1395
(3)	0.1335	0.1486	0.1590	0.1636	0.1791	0.1870	0.1981
(4)	0.0486	0.0493	0.0560	0.0562	0.0594	0.0640	0.0725
Biodiesel(1) + Isopropanol(2)							
(1)	0.2675	0.2715	0.2948	0.3035	0.3168	0.3388	0.3565
(2)	0.0978	0.0972	0.1163	0.1198	0.1282	0.1438	0.1550
(3)	0.1382	0.1435	0.1473	0.1575	0.1659	0.1828	0.1903
(4)	0.0534	0.0508	0.0383	0.0404	0.0441	0.0498	0.0491
Diesel fuel(1) + Biodiesel(2)							
(1)	0.0379	0.0410	0.0364	0.0365	0.0353	0.0350	0.0372
(2)	0.0232	0.0263	0.0226	0.0243	0.0221	0.0252	0.0263
(3)	0.0329	0.0359	0.0328	0.0326	0.0325	0.0323	0.0336
(4)	0.0265	0.0317	0.0256	0.0274	0.0248	0.0277	0.0285

From Table 5 it can be observed that all the tested equations give good results for density estimation (ARD < 0.40 %), the greater accuracy corresponding to diesel fuel+biodiesel system (ARD < 0.04 %). Predictive Eq.(1) and Eq.(2) give good results for density of pseudo-binary systems with isopropanol estimation, but the more complex Eq.(2) gives better results (ARD < 0.15 %) than the simple Kay's mixing rule (Eq.1) (ARD < 0.35 %). Correlative equations represent well experimental data density – composition, polynomial Eq. (4) being more accurate (ARD < 0.06 %) than linear Eq.(1) (ARD < 0.04 %). Experimental density data of diesel fuel+biodiesel system are well represented with all equations (Eqs.(1)-(4)), which are either predictive or correlative (ARD < 0.04 %).

Finally, it can be said that Eqs. (1) - (4) can be used for density calculation for all investigated binary systems with excellent and good results.

The better accuracy recorded for diesel fuel + biodiesel system, especially in respect of the Kay's rule, shows a practical ideal behavior of this system. Diesel fuel is a complex mixture of nonpolar hydrocarbons (C_{12}-C_{20}), and biodiesel is a mixture of low polar monoalkylesters with high molecular weights. The pseudo-binary system is, probably, a mixture of the molecules of the two components without or with very weak interactions between molecules.

Table 6

Regression parameters from Eq.(5) and correlation coefficient R^2 values for pure components and studied binary systems at different compositions

Parame-ters	w_2							
	0.0000	**0.1437**	**0.2406**	**0.3879**	**0.5375**	**0.6893**	**0.8434**	**1.0000**
	Diesel fuel(1) + Isopropanol(2)							
a	-0.0007	-0.0008	-0.0008	-0.0008	-0.0009	-0.0009	-0.0009	-0.0009
b	0.8507	0.8432	0.8391	0.8337	0.8282	0.8230	0.8179	0.8136
R^2	1.0000	0.9999	0.9999	0.9999	0.9998	0.9999	0.9998	0.9998
	w_2							
	0.0000	**0.1378**	**0.2318**	**0.3764**	**0.5253**	**0.6787**	**0.8369**	**1.000**
	Biodiesel(1) + Isopropanol(2)							
a	-0.0007	-0.0008	-0.0008	-0.0009	-0.0008	-0.0009	-0.0009	-0.0009
b	0.8931	0.8799	0.8717	0.8621	0.8475	0.8368	0.8249	0.8136
R^2	1.0000	1.0000	0.9960	0.9991	0.9999	0.9998	0.9998	0.9998
	w_2							
	0.0000	**0.1564**	**0.2593**	**0.4118**	**0.5621**	**0.7102**	**0.8561**	**1.0000**
	Diesel fuel(1) + Biodiesel(2)							
a	-0.0007	-0.0007	-0.0007	-0.0007	-0.0007	-0.0007	-0.0007	-0.0007
b	0.8507	0.8573	0.8612	0.8677	0.8739	0.8806	0.8857	0.8931
R^2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

The density correlation with temperature was realised with Eq. (5). The regression parameters from Eq. (5) and correlation coefficient R^2 values are listed in Table 6. It can be observed that the linear equation correlates well the density of all investigated mixtures, diesel fuel and biodiesel, respectively, with isopropanol, and the reference system, diesel fuel+biodiesel, the value of correlation coefficient (R^2) being higher than 0.999. The slope of the line that correlates the density with temperature (parameter *a* from Eq.(5)) is slightly increasing with alcohol content increase for systems with isopropanol while, for the reference system diesel fuel+biodiesel, the slope does not vary with system composition.

Table 7 lists the average relative deviation values (ARD, %) for density calculation of the pseudo-binary fuels mixtures, using Eqs. (5). The errors are between 0.01% and 0.17%, demonstrating the good accuracy of linear correlation for all investigated systems.

Table 7

Absolute relative deviation (ARD, %) of density calculation with Eq.(5) at different compositions

Diesel fuel(1) + Isopropanol(2)								
w_2	0.0000	0.1437	0.2406	0.3879	0.5375	0.6893	0.8434	1.0000
ARD (%)	0.0379	0.0753	0.0108	0.1200	0.1759	0.0807	0.0127	0.0257
Biodiesel(1) + Isopropanol(2)								
w_2	0.0000	0.1378	0.2318	0.3764	0.5253	0.6787	0.8369	1.0000
ARD (%)	0.1025	0.1043	0.0460	0.0679	0.1701	0.1151	0.0490	0.0257
Diesel fuel(1) + Biodiesel(2)								
w_2	0.0000	0.1564	0.2593	0.4118	0.5621	0.7102	0.8561	1.0000
ARD (%)	0.0379	0.0331	0.0494	0.0580	0.0605	0.0718	0.0626	0.1035

6. Conclusions

Experimental density data for diesel fuel+isopropanol, biodiesel+isopropanol and diesel fuel+biodiesel systems were reported. The accuracy of different equations used to calculate the density of these systems was evaluated. It was observed that the densities of diesel fuel+isopropanol and biodiesel+isopropanol systems decrease with alcohol content increasing. The density of the studied systems with isopropanol can be calculated with good accuracy at different temperatures in the range of 273.15 K and 323.15 K using Kay's mixing rule, a predictive equation used for petroleum products or an empirical second order polynomial equation. A linear dependence of density on temperature was found.

Higher bioalcohols (C>3) could become competitive in the next future on the biofuel market due to their improved miscibility with fossil fuels compared to lower alcohols and as they can be obtained with improved yield due to recent developments. Density data of fuel systems with isopropanol could be of interest not only for manufacturing process of fuels with improved characteristics, but also for modeling and simulation of internal combustion engine behavior.

R E F E R E N C E S

[1]. *X.C. Lu, Z. Huang, W.G. Zhang and D.G. Li*, "The influence of ethanol additives on the performance and combustion characteristics of diesel engines", in Combust. Sci. Technol., **vol. 176**, no.8, 2004, pp. 1309–1329.

[2]. *X.C. Lu, J.G. Yang, W.G. Zhang and Z. Huang*, "Effect of cetane number improver on heat release rate and emissions of high speed diesel engine fueled with ethanol– diesel blend fuel", in Fuel, **vol. 83**, 2004, pp. 2013–2020.

[3]. *M. Lapuerta, R. García-Contreras, J. Campos-Fernández and M.P. Dorado*, "Stability, lubricity, viscosity and cold-flow properties of alcohol-diesel blends", in Energy Fuels, **vol. 24**, no. 8, 2010, pp. 4497–4502.
[4]. *E. Geacai, I. Nita, S. Osman and O. Iulian,* "Effect of n-butanol addition on density and viscosity of biodiesel", in U.P.B. Sci. Bull., series B, **vol. 79**, no. 1, 2017, pp. 11-24.
[5]. *D. Babu and R. Anand*, "Effect of biodiesel – diesel – n-pentanol and biodiesel – diesel – n-hexanol blends on diesel engine emission and combustion characteristics" in Energy, **vol. 133**, 2017, pp. 761-776.
[6]. *H.K. Imdadul, H.H. Masjuki, M.A. Kalam, N.W.M. Zulkifli, A. Alabdulkarem, M.M. Rashed, Y.H. Teoh and H.G. How*, "Higher alcohol – biodiesel –diesel blends: An approach for improving the performance, emission, and combustion of a light-duty diesel engine" in Energy Convers. Manage., **vol. 111**, 2016, pp. 174 – 185.
[7]. *R. Vallinayaagam, S. Velharaj, W.M. Yang, W.L. Roberts and R.W. Dibble*, "Feasibility of using less viscous and lower cetane (LVLC) fuels in a diesel engine: A review" in Renewable Sustainable Energy Rev., **vol. 51**, 2015, pp. 1166 – 1190.
[8]. *Z.H. Zhang and R. Balasubramanian*, "Investigation of particulate emission characteristics of a diesel engine fueled with higher alcohols/biodiesel blends", in Applied Energy, **vol. 163**, 2016, pp. 71–80.
[9]. *A.K. Singh, C. Mishra, V. Vibhanshu and N. Kumar*, "Performance evaluation and emission studies of a single cylinder diesel engine fueled with isopropyl alcohol and diesel", in SAE Technical Paper Series, 2013 http://dx.doi.org/10.4271/2013-01-1132
[10]. *H. Hazar and M. Uyar*, "Experimental investigation of isopropyl alcohol (IPA) diesel blends in a diesel engine for improved exhaust emissions", in IJAET, vol. 4, **no. 1**, 2015, pp.1 http://dx.doi.org/10.18245/ijaet.67279
[11]. *L. F. Ramirez-Verduzco, B. E. Garcia-Flores and J.E. Rodriguez-Rodriguez*, "Prediction of the density and viscosity in biodiesel blends at various temperatures", in Fuel, **vol. 90**, no. 5, 2011, pp. 1751-1761.
[12]. *I. Nita, O. Iulian, E. Geacai and S. Osman*, "Physico-chemical properties of the pseudo-binary mixture gasoline+1-butanol", in Energy Procedia, **vol. 95**, 2016, pp. 330-336.
[13]. *I. Nita and S. Geacai*, "Study of the density and viscosity for ternary mixtures biodiesel+diesel fuel+bioalcohols" in Ovidius University Annals of Chemistry, **vol 23**(1), 2012, pp. 58-62.
[14]. *I. Nita, E. Geacai, S. Geacai and O. Iulian,* "Volumetric properties of pseudo-binary and ternary mixtures with biodiesel" in Rev. Chim. (Bucharest), **vol. 67** no. 9, 2016, pp. 1763-1768.
[15]. *D.L.Clements*, "Blending rules for formulating biodiesel fuel. Liquid fuels and industrial products for renewable resources", in Proceedings of the Third Liquid Fuels Conf. Am. Soc.Agric. Eng., 1996, pp. 44–53.
[16]. *M..J. Pratas, S.V.D. Freitas, M.B. Oliveira, S.C. Monteiro A.S Lima. and J.A.P Coutinho*, "Biodiesel density: experimental measurements and prediction models", in Energy Fuel, v**ol. 25**, 2011, pp. 2333-2340.
[17]. *M.E. Tat and J.H. Van Gerpen,* "The specific gravity of biodiesel and its blends with diesel fuel", in J. Am. Oil Chem. Soc, **vol.77**, no. 2, 2000, pp. 115-119.
[18]. *E. Alptekin and M.Canakci*, "Determination of the density and the viscosities of biodiesel-diesel fuel blend", in Renew. Energ., **vol. 33**, no. 12, 2008, pp. 2623-2630.
[19]. American Petroleum Institute, Technical data book-Petroleum Refining, API Publishing Services, 1220 L Street, N.W., Washington, D.C. 20005, Sixth edition, april 1997, pp.485.
[20]. *E. Alptekin and M.Canakci*, "Characterization of the key fuel properties of methyl ester-diesel fuel blends", in Fuel, **vol. 88**, no. 1, 2009, pp. 75-80.

[21]. *W. Yuan, A.C Hansen and Q. Zhang*, "Predicting the temperature dependent viscosity of biodiesel fuels", in Fuel, **vol. 88**, 2009, pp. 1120-1126.
[22]. *B. Tesfa, R. Mishra, F. Gua and N. Powles*, "Prediction models for density and viscosity of biodiesel and their effect on fuel supply system in CI engines" in Renew. Energ., **vol. 35**, no.12, 2010, pp. 2752-2760.
[23]. *I. Nita, s. Geacai and O. Iulian*, "Measurement and correlations of physico-chemical properties to composition of pseudo-binary mixtures with biodiesel" in Renew. Energ., **vol.36**, 2011, pp. 3417-3423.