Study of the Variation of Kinematic Viscosity and Density of Various Biodiesel Blends with Temperature

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Biodiesel has emerged as a non-toxic and biodegradable fuel for use in transportation sector as well as other applications, such heating and irrigation. Also biodiesel plays an important role in reducing the dependency of petroleum fuels and environmental pollution. Nevertheless, the higher density and viscosity are two important physical properties that affect fuel atomization, spray characteristics and combustion in an unmodified engine. The biodiesel used was produced from sunflower oil and mixed with diesel fuel in different proportions (B10...B100). Kinematic viscosity and density were measured at average climate conditions as 30, 40 and 50°C. Several correlations are proposed to predict the correlation of density and viscosity and compare them with well-known models previously published in literature.

Keywords: biodiesel, fuel spray, density, viscosity

Biodiesel is an attractive alternative fuel mainly due to the actual situation in the word, the depletion of fossil fuels, the stringer emissions laws for reducing the environmental pollution and political decision factors. Currently almost every country has chosen biodiesel as a solution and prepares a policy to produce and use biodiesel in its transport sector [1,2].

In addition an increase in the research of biodiesel storage, production, performance and emission was observed in the last years [3].

Biodiesel can be produced by various sources as vegetable oil, recycled cooking greases or animal fats by a process called transesterification in which is transformed in mono-alkyl esters of long-chain-fatty acids [3-6].

Biodiesel is considered biodegradable, without of sulfur and aromatics, with higher flash point, which improves lubricity of diesel in blends [7].

The characteristics of biodiesel depends of several factors such as soil type, growing climate condition, plant feed stock and plant maturity upon harvest. These factors influence the physical and chemical properties of biodiesel which affects directly the performance and emissions of the engine [8]. Two important properties that influence the engine at low temperatures are density and viscosity [9].

The viscosity is a measure of the internal friction of a fluid to flow and is dependent of temperature. The higher viscosity promote the fuel spray penetration into the combustion chamber compared with diesel fuel but there are more negative effects including poor fuel atomization, increases of engine deposits, excessive fuel injection pressures and incomplete combustion [10, 11].

Engine manufacturers have expressed concern about the biodiesel viscosity especially the viscositytemperature behavior. The kinematic viscosity is established in European standard (EN 14214) with lower limits 3.5–5.0 mm²/s and in US standard (ASTM D6751) at 1.9–6.0 mm²/s [12].

Density of biodiesel is higher than diesel fuel and his variation affects the fuel spray characteristics and power during combustion and fuel injection in cylinder [13].

Several researchers found correlations between density and viscosity in function of pressure and temperature. Ejim et al. [14] investigated different biodiesel blends and found that biodiesel has an impact of 90% in the atomization

process and density only a 2% change. Alptekin and Canakci [15] measured the kinematic viscosity at 313 K and density at 288 K for various biodiesel blends (B2, B5, B10, B20, B50 and B75) using two diesel fuels and six biodiesel samples (canola, corn, cottonseed, sunflower, soybean and palm oil). Density was correlated by a linear equation and viscosity by second order polynomial equation function of biodiesel concentration. Fahd et al. [16] studied heating value, density and viscosity for biodiesel bends of waste cooking palm (B20, B40, B60 and B80) at different temperatures. The density and viscosity was predicted with 1st order and exponential equations function of temperature for each of the fuel blend. Benjumea et al. [17] investigated for five biodiesel concentrations of palm oil (B0, B5, B20, B100) the density and kinematic viscosity at various temperatures (from 289 to 373 K). The density has a linear function of temperature and the kinematic viscosity varied exponentially in all cases. Although literature presents lots of prediction models this approach propose new density and viscosity experimental data for the prediction by equations of different biodiesel blends function of temperature and concentration.

Viscosity. In general viscosity may be viewed as the interaction between molecules. The temperature affects the molecule that at low temperature can then slide over each other very slow and at high temperature they pass very rapidly each other resulting in a liquid less viscous. This parameter is used in the petroleum industries and the best known equation that correlates the viscosity with temperature is Andrade Equation (eq. 1) [18] and is used to predict the viscosity up to normal boiling point.

$$\mu = \mathbf{A}\mathbf{e}_{\mathbf{T}}^{\mathbf{B}} \tag{1}$$

were T- absolute temperature and A, B- constants.

Other equations (eq. 2) to predict the effect of temperature on viscosity was proposed by Liew et al. [19]:

$$= \mathbf{a} + \mathbf{b}\mathbf{T} \tag{2}$$

where *a* and *b* are constants.

logµ

$$\ln \mu = \mathbf{m} + \frac{\mathbf{B}}{\mathbf{T} - \mathbf{T}_0} \tag{3}$$

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Tat and Van Gerpen [21] proposed an equation (eq.4) with three constants A, B and C that varies with biodiesel fraction and type.

$$\ln(\eta) = \mathbf{A} + \frac{\mathbf{B}}{\mathbf{T}} + \frac{\mathbf{C}}{\mathbf{T}^2}$$
(4)

where T is temperature in K and η is the kinematic viscosity $(mm^2/s).$

Depending of the carbon number the equations proposed by Krisnangkura et al. [22]

determines the viscosity of various biodiesels function of long and short carbon structure (eq.5,6).

$$\ln\left(\eta_{C_{12}-C_{18}}\right) = -2.177 - 0.202z + \frac{403.66}{T} + \frac{109.772}{T}z \quad (5)$$

$$\ln\left(\eta_{C_{12}-C_{18}}\right) = -2.915 - 0.158z + \frac{492.12}{T} + \frac{103.35}{T}$$
(6)

where T is temperature in K, $\mathbf{C}_{_{12}}\text{-}\mathbf{C}_{_{18}}$ number of carbon atoms and z is carbon number.

Riazi and Al-Otaibi [23] developed an equation for the prediction of viscosity of petroleum fuels and biodiesel at different temperatures from the refractive index values (I) (eq.7). In this model as input are necessary specific gravity, values of molecular weight, refractive index and boiling temperature.

$$\frac{1}{\mu} = \mathbf{A} + \frac{\mathbf{B}}{\mathbf{I}} \tag{7}$$

where μ is the dynamic viscosity (cp), I is the refractive index and A,B are constants specific to each component. The majority of the correlations described above depends of constants and vary with the percentage of blends and biodiesel type.

Density

The density of biodiesel has been investigated by many researchers. Alptekin and Canakci [15] investigated the density of various blends of biodiesel blends such as soybean oil, sunflower oil, canola oil, waste palm oil, corn oil, and cottonseed. They proposed a 1st degree empirical equation which relates the density of fuel with the percentage of a biodiesel used (eq.8).

$$\mathbf{D} = \mathbf{A}\mathbf{x} + \mathbf{B} \tag{8}$$

where D is density (g/cm³), x is the biodiesel fraction, and A, B are constants that vary with the biodiesel type. There are a number of methods for estimating biodiesel viscosity [24, 25] such as:

The Modified Rackett Equation:

$$\rho = \frac{\rho_{\rm R}}{(0.29056 - 0.08775\omega)^{\Phi}}$$
(9)

where ρ_{R} is the reference density given in tables and φ is a fugacity coefficient.

$$\phi = (1 - \mathbf{T}_{\mathbf{r}})^{\frac{2}{7}} - (1 - \mathbf{T}_{\mathbf{r}}^{\mathbf{R}})^{\frac{2}{7}}$$
(10)

The Hankinson-Brobst-Thomson Equation:

$$\frac{M}{\rho V_{\rm c}} = V_{\rm R}^{(0)} [1 - \omega V_{\rm R}^{(6)}]$$
(11)

where $V_R^{(0)}$ and $V_R^{(\delta)}$ are expressed as:

$$\begin{split} V_R^{(0)} &= \mathbf{1} + \mathbf{a}(\mathbf{1} - \mathbf{T}_r)^{\frac{1}{3}} + \mathbf{b}(\mathbf{1} - \mathbf{T}_r)^{\frac{2}{3}} + \mathbf{c}(\mathbf{1} - \mathbf{T}_r) + \mathbf{d}(\mathbf{1} - \mathbf{T}_r)^{\frac{4}{3}} \\ & (0.25 < \mathbf{T}_r < \mathbf{0.95}) \end{split}$$

$$V_{R}^{(\delta)} = \frac{[e + fT_{r} + gT_{r}^{2} + hT_{r}^{3}]}{T_{r} - 1.0001}$$
$$(0.25 < T_{r} < 1)$$

where a, b, c, d, e, f, g, f are constants.

Experimental part

Materials and methods

Commercial unrefined vegetable oil from sunflower was purchased from the local market (Aliment Ulei SRL). All chemicals used in the production and transesterification process were purchased from Laborex S.R.L. Romania. Ultra low sulfur diesel obtained from a local producer was used in the experiments.

Transesterification process

The method applied was the conversion of sunflower oil in biodiesel by a basic transesterification process in the presence of an alcohol (methanol) and a catalyst (sodium hydroxide) and analyzed biochemically in biochemistry laboratory of Chemistry Department of University of Craiova [6, 9, 26, 27].

Because the acid value of vegetable oil was under 1mgKOH/g, it was not needed to perform any pretreatment. The parameter used for transesterification reaction was selected as follows: 60°C reaction temperature, 60 min reaction time, 6:1 alcohol/oil molar ratio and 1.25% catalyst concentration. The experiments were carried out in a laboratory scale apparatus equipped with a thermometer, magnetic stirrer heater and spiral reflux condenser. Before the reaction NaOH was dissolved in methanol separately and then added in the preheated sunflower oil. After the process was complete the lower phase (glycerol) was separated while upper phase (biodiesel) is subjected to a wash with distilled water to remove the excess methanol and catalyst. Biodiesel is heated to remove excess alcohol and water.

Density and viscosity measurements

Density measurements are performed at 30°C, 40°C and 50°C using a pycnometer in accordance with ISO 4787 standard [28]. The pycnometer is a Gay-Lussac type. For a guarantee of reliable results because biodiesel is affected by the exposure to oxygen and light which can modify his density the flask was covered during experiments with silicon foil. For the determination of the viscosity the test is relatively simple and follows a basic procedure. The biodiesel is placed into a calibrated glass viscosity tube and is submerged in a warm bath at 30 $^\circ$ C - 50 $^\circ$ C. Then the fluid is suced up a portion of the tube to the highest line on the right side of the tube seen. Once the biodiesel's meniscus touches this line a timer is started and continues until the oil's meniscus touches the lower line. The time intervals are then converted into seconds and multiplied by a constant that is specific for the glass viscosity tube used. This number is then the kinematic viscosity of the fluid [28]

For the experimental data to be acceptable, the tests were carried twice with the condition the first and second measurements should be within an accuracy of $0.02 \text{ mm}^2/\text{s}$. If this condition is satisfied the average of the two tests was taken in consideration.

Biodiesel blends

The biodiesel of sunflower oil was blended by a volume basis with ultra low sulfur diesel at a percentage of 10, 20, 30...100%. The notation BX represents a blend that contains



Fig. 1 Variations of density vs. biodiesel fraction for different temperatures

Variations of kinematic viscosity vs. biodiesel fraction for different temperatures

X% v/v biodiesel. In total (including diesel) 11 samples were used for the density and viscosity measurements.

Results and discussions

Effect of biodiesel fraction and temperature on density

Density can be defined as the mass per unit volume. The density of biodiesel blends was measured at various temperatures (30, 40 and 50°C). The density of the blend increases with the increase in biodiesel content. The correlation between density and biodiesel blend function of temperature can be expressed by an empirical second degree equation as is shown in Fig.1. The density of biodiesel varies with the purity and fatty acid composition [29].

The performance characteristics of a diesel engine are influenced by density which affects the mass of fuel injected into the combustion chamber and thus, the airfuel ratio. The change of biodiesel blend density will influence engine output power due to a different mass of fuel injected [30].

Effect of biodiesel fraction and temperature on viscosity As in shown in figure 2 the kinematic viscosity increases with the increase of biodiesel content for all blends and studied temperatures. The sunflower oil density is higher as compared with diesel fuel. The experimental data were correlated with empirical logarithmic equations. These models can be used further in the investigations of fuel supply systems (fuel filter, fuel pipe, fuel pump, and injectors) and design as well as the prediction of combustion characteristics and air-fuel mixing phenomena. Due to the high viscosity of biodiesel blends the fuel tends to form larger droplets which can cause poor fuel atomization, increases in engine deposits and ware of fuel pump elements and injectors.

Conclusions

In this study two models have been developed for predicting the density and kinematic viscosity of sunflower oil blends at different volume fractions and temperatures. The variations of density with the temperature are better represented by a second degree equation, compared to the other models given in the literature. An empirical logarithmic equation was proposed for the variation of density function of blend and temperature which is close to other logarithmic equations proposed by various researchers. Density and viscosity are important properties of biodiesel that affects the engine performance. The developments of mathematical models that accurately describe these properties function of temperature are of great interest for the elaboration of combustion models and the design of injection systems.

References

1.LAPUERTA, M., OCTAVIO ARMAS, O., BALLESTEROS, R., FERNANDEZ, J., Fuel, **84**, (6), 2005, p.773.

2. KNOTHE, G., STEIDLEY, K. R., Fuel, 86, 2007, p. 2560.

3. LAPUERTA, M., ARMAS, O., HERREROS, M., Prog. Energy. Combust. Sci., **34**, 2008, p.198.

4. DUMITRU, M. G., NAGI, M., BUCULEI, M. E., PICIOREA, G. D.,

HITICAS, I. D., STANCIU, T., Bulg. J. Agric. Sci., 19(6), 2013, p.1445.

5. BITA, M. G., GRECU, D. R., TUTUNEA, D., POPESCU, A., BICA, M., J. Environ. Prot. Ecol., **13**(2A), 2012, p. 1061.

6. DUMITRU (BITA), M. G., GRECU, R., TUTUNEA, D., POPESCU, A., BICA, M., Rev. Chim. (Bucharest), **61**, no.9, 2010, p. 882.

7. BENJUMEA, P., AGUDELO, J., AGUDELO, A., Fuel, **87**, 2008, p. 2069. 8. TATE, R., WATTS, K. C., ALLEN, C. A., WILKIE K. I., Fuel, **85**(7e8), 2006, p. 1004.

9. DUMITRU, M. G., TUTUNEA, D., Rev. Chim. (Bucharest), **68**, no.11, 2017, p. 2676.

10. DEMIRBAS, A., Fuel, 87, 2008, p. 1743.

- 11. BARABAS, I., TODORUT, I. A., Energy Fuels, 25, 2011, p. 5767.
- 12. KANAVELI, I., P., ATZEMI, M., LOIS, E., Fuel, 199, 2017, p. 248.
- 13. TATE, M., GARPEN, J., J. Am. Oil. Chem. Soc., 77(2), 2000, p. 115.

14. EJIM, C. E., FLECK, B. A., AMIRFAZLI, A., Fuel, 86, 2007, p. 1534.

15. ALPTEKIN, E., CANAKCI, M., Renew. Energy, 33, 2008, p. 2623.

16. FAHD, M. E. A., LEE, P. S., CHOU, S. K., WENMING, Y., YAP, C., Renew. Energy **68**, 2014, p. 282.

17. ERYILMAZ, T., YESILYURT, M. K., YUMAK, H., ARSLAN, M., SAHIN,

S., Int. J. Automot. Technol., **3**(2), 2014, p. 79.

18. ANDRADE, E. N. da C., Nature, **25**, 1930, p. 309.

19. LIEW, K.Y., SENG, C. E., OH, L. L., J. Am. Oil. Chem. Soc., **69**(2), 1992, p. 155.

20. MAKHIJA, R. C., STAIRS, R. A., Can. J. Chem., 48, 1970, p. 1214.

21. TAT, M., GERPEN, J., J. Am. Oil. Chem. Soc., 76(12), 1999, p. 1511e3.

22. KRISNANGKURA, K., YIMSUWAN, T., PAIRINTRA, R., Fuel, **85**(1), 2006, p.107e13.

23. RIAZI, M. R., AL-OTAIBI, G. N., Fuel, 80(1), 2001, p. 27e32.

24. REID, R.C., PRAUSAITZ, J. M., POLING, J. M., Properties of Gases and Liquids, 4th ed., McGraw Hill, N. Y, 1987.

25. ZHAO, H. L., WANG, F. K., CHEN, S. K., Chemical Industry Press, N.Y, 2006.

26. BITA, M.G., PREDA, M., Riv. Ital. Sostanze Gr., 80(6), 2004, p. 377.

27. DUMITRU, M. G., Rev. Chim. (Bucharest) 67, no.6, 2016, p. 1127.

28. DUMITRU, M. G., NICA BADEA, D., TUTUNEA D., Rev. Chim. (Bucharest), **68**, no.12, 2017, p. 2771.

29. TATE, M., GARPEN, J., J. Am. Oil. Chem. Soc., 77(2), 2000, p. 115e9.

30. TUTUNEA, D., AUO-FMTE ., XI (XXI), 2012/1, p 145.

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