EFFECTS OF TEMPERATURE AND BLENDING ON BIODIESEL DENSITY UTICAJ TEMPERATURE I SASTAVA NA GUSTINU BIODIZELA

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ABSTRACT

The physical properties of any fuel are of significant importance to determining its suitability for a particular engine. The prediction of various properties of biodiesel or biodiesel blends with gasoline is vital to the design of different diesel engines. Therefore, the purpose of this paper is to examine the characterization of biodiesel density according to the standard testing methods employed in the present study. On the basis of the experimental material research in the field of biofuels, the effect of gasoline addition to biofuel on the biofuel properties was studied. The density of biofuel was found to decrease linearly with an increase in the blending ratio. Based on the data obtained, $\rho = 0.8838 \text{ g/cm}^3$ for 100 % biodiesel is not fully acceptable according to the referenced standards, and thus cannot be used in the United States without blending. However, this value is still within the acceptable range for use in the EU.

Key words: biodegradable fuels, gasoline, density, EN 14214, ASTM D6751.

REZIME

Poslednjih godina postignut je značajan napredak u istraživanju biodizela, koji se, na kraju, pokazao kao dobra zamena za dizel, za razliku od drugih izvora. Prihvaćen je kao ekološko, alternativno gorivo i sada se koristi u mešavinama s klasičnim dizel gorivom u mnogim zemljama. Fizička svojstva bilo kojeg goriva su značajni faktori, koji pomažu da se odluči da li su ulja prikladna za motor ili ne. Predviđanje različitih svojstava biodizela ili mešavina biodizela sa benzinom je od vitalnog značaja za projektovanje različitih sistema dizel motora. Stoga se ovaj naučni rad bavi karakterisanjem gustine biogoriva prema sadašnjim standardnim metodama ispitivanja. Osnovu ovog rada čine eksperimentalna istraživanja materijala u oblasti biogoriva. Glavni cilj je da se proceni efekat dodavanja benzina u biogorivo. Napravljene su četiri smese, gde je u 100% biodizel dodavano 5%, 10%, 15% i 20% benzina. Primećeno je da se gustina linearno smanjuje s povećanjem procentualnog odnosa benzina. Na osnovu izmerenih podataka, gustina $\rho = 0,8838 \text{ g/cm}^3$ za 100% biodizel, nije u potpunosti prihvatljiva u svim navedenim standardima, i zbog toga se, bez mešanja, ne može koristiti u SAD. Međutim, još uvek je u prihvatljivim granicama za upotrebu u Evropi. Za opis rezultata je korišćena eksponencijalna zavisnost tipa Arrhenius, koja je bolje prilagođena fizičkoj interpretaciji.

Gljučne reči: biorazgradiva goriva, benzin, gustina, EN 14214, ASTM D6751.

INTRODUCTION

The mineral diesel is the prime liquid fuel used in different sectors such as transportation, power, agriculture, etc. The transport sector plays an important role in the economic development of a country and consumes more than 70 % of the total diesel consumption. An increasing number of vehicles are added to the existing fleet in the world annually, leading to a directly proportional increase in diesel consumption. The industrial and agricultural sectors also consume mineral diesel for generator sets and water pumps. Diesel engines are preferred, by both manufacturers and users, for their high reliability, energy efficiency, durability and low operational costs. However, mineral diesel resources are depleting, whereas the demand is increasing on a daily basis. This non-renewable fuel emits pollutants such as hydrocarbon (HC), carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM) and smoke (while burning). The vehicular pollution is a major source of air pollution, which is a prime cause of different respiratory diseases and global warming. The harmful effect of pollution is not only restricted to human beings, but it also affects other species. Moreover, the global vexing issues are also petroleum reserves and a constant increase in the price of fossil energy. The current use of fuels for transport is neither pure nor sustainable (Angelović et al., 2016).

At present, more than 80 % of the energy demand is catered for by fossil fuels (Atabani et al., 2013a). The greenhouse gases

emitted by motor vehicles may be attenuated using alternative drives or alternative fuels (Kosiba et al., 2016). Therefore, a number of studies have been conducted to find alternatives to fossil fuels which meet the eco-friendly criteria. Biodiesel is considered to be a notable option for at least complementing conventional fuels (Aransiola et al., 2014). The quality of biodiesel is regulated by standards and the two most utilized are ASTM D6751 in the United States and EN 14214 in the European Union. Many countries encourage the development and use of biodiesel. Biodiesel blends, such as B5, are approved by ASTM for safe operation in any compression-ignition engine designed to be operated on diesel vehicles including electrical generators, trucks, tractors and boats.

A number of researchers have studied the physical and chemical properties of biodiesel and biodiesel blends either experimentally or theoretically. The properties of biodiesel vary consequently due to their diverse fatty acid composition, which evidently affects the engine performance. Therefore, it is important to characterize biodiesels according to the present standard testing methods (Atabani et al., 2013b).

Most of the researchers reported the biodiesel (BD) – gasoline (G) blend impact on the gasoline compressed ignition (GCI) engine performance and emission (Putrasari and Lim, 2018; Putrasari and Lim, 2017a; Putrasari and Lim, 2017b; Adams et al., 2013) or the common rail diesel engine (Chen et al., 2017). These studies argue that BD – G blends have better low temperature fluidity and vaporization values than biodiesel

itself. The gasoline addition to biodiesel reduces smoke and ultrafine particle emissions (UFP), whereas the NO_x emissions increase slightly. However, a detailed study on the physicochemical properties of such blends has not been published yet. There is a limited body of information on the specification of biodiesel – gasoline blends. This paper is dealing with one of the physical properties of BD – G blends, namely density, which is important to propellants. Fuel density is related to its molecular mass and generally increases with the increasing molecular mass. Dinkov et al. (2009) report that an increase in density occurs mainly due to the formation of both acidic and polymer products in untreated biodiesel/diesel blends. However, the reported increase was more rapid in the later stages of oxidation. This increase can be attributed to the enhanced molecular interaction of degraded biodiesel due to the formation of peroxides (Pattamaprom et al., 2012).

The density of biofuels is only specified in EN 14214 with a range of 0.860–0.900 g/cm³. Density is an important liquid feature required for converting the volume and mass units and calculating the kinematic viscosity. The density of any substance is its mass per unit volume.

Temperature is a parameter that greatly affects the properties of any material, density included. As temperature is a measure of the kinetic energy of molecules, an increase in temperature, provided it does not occur in the phase change, leads to an increase in the volume of the body and a decrease in the density. Temperature-induced density changes can be mathematically described using the exponential equation of the Arrhenius type. However, at certain temperature intervals, the density dependence on temperature can also be described as a linear dependence. Božiková and Hlaváč (2013) conducted a study on the rheological properties of rapeseed oil. The authors reported that the dependence between temperature and density showed an exponentially decreasing trend, which was described using the modified Arrhenius equation.

Density is an important fuel property which affects the engine performance as change in density affects the mass of the fuel injected. The fuel injection system of an engine measures the fuel by volume. Any change in the fuel density will directly influence the engine output (Acharya et al., 2017).

MATERIAL AND METHOD

Selected biodiesel and biodiesel blends

Commercial gasoline (G) and rapeseed methyl ester biodiesel (BD), as well as four gasoline - biodiesel blends (95 % BD + 5 % G, 90 % BD + 10 % G, 85 % BD + 15 % G and 80 % BD + 20 % G) were used in this study. The chemical composition of the rapeseed methyl ester derived biodiesel contain the following five components: methyl palmitate (C₁₇H₃₄O₂), methyl stearate (C₁₉H₃₈O₂, C18:0), methyl oleate (C₁₉H₃₆O₂, C18:1), methyl linoleate (C₁₉H₃₄O₂, C18:2) and methyl linolenate (C₁₉H₃₂O₂, C18:3) (Herbinet et al., 2010). The concentrations of gasoline in the blends were set at 5, 10, 15 and 20 % by volume. The gasoline-biodiesel blends were prepared by mixing/shaking for about 3–5 min to produce homogeneous blends. This homogenization process was repeated prior to every measurement.

Methods and the measuring equipment

Densimeter Mettler Toledo DM40 was used for density measurements. It is a modern, compact device designed for different purposes such as the quality control or research and development purposes. Densimeter Mettler Toledo DM40 was used in the Laboratory of Raw Materials and Foodstuffs Physical Properties at the AgroBioTech Research Center SUA in Nitra, Slovakia.

The DM40 density measurement (Fig.1) is based on the electromagnetically induced oscillation of the U-shaped glass tube (Mettler Toledo, 2010).

Fig. 1 The principle of the DM40 density measurement (Mettler Toledo, 2010)

Each glass tube vibrates on its own frequency. Frequency is a function of the total mass and changes when the tube is filled with gas or liquid. As the tube mass increases, the frequency decreases and the period of oscillation T will be longer. This can be expressed as follows:

$$T = 2\pi \sqrt{\frac{\rho V_c + m_c}{K}} \quad (\text{s}) \quad (1)$$

where ρ – the density of the sample in the measuring cell (g/cm³), V_c – the sample volume (cm³), m_c – the mass of the measuring cell (g) and K – the constant of the measuring cell (g/s²).

The density value of the measured sample is calculated as follows:

$$\rho = \frac{K}{4\pi^2 V_c} T^2 - \frac{m_c}{V_c} \quad (2)$$

All the samples were measured in the temperature range from 15 °C to 90 °C. The measured sample was pressed into the measuring tube and the density was read off for each measured temperature until the measurement stabilized. On the basis of the values measured, the graphical dependences (Fig. 2) of fuel density on temperature were designed for each individual sample.

The density dependence can be mathematically described using the linear and exponential regression equations with a high coefficient of determination. Due to the physical interpretation of the results obtained, it is better to use the exponential regression equation. This is the Arrhenius type equation used for describing the dependence of some physical properties of biological materials on temperature.

$$\eta = \eta_0 e^{\frac{E_A}{RT}} \quad (3)$$

where η – the dynamic viscosity (Pa·s), η_0 – the reference value of dynamic viscosity (Pa·s), E_A – the activation energy (J/mol), R – the gas constant (J/(K·mol)) and T – the absolute temperature (K).

The exponential regression equation is of the following form:

$$\rho = Ae^{-Bt} \quad (4)$$

where A and B are the coefficients of the regression equation.

The linear regression equation can be written in the following form:

$$\rho = -Cx + D \quad (5)$$

where C and D are the coefficients of the regression equation.

RESULTS AND DISCUSSION

Density itself can serve as a quick quality control tool for different samples. The density of diesel oil is relevant because it provides a parallel to the ignition quality (the delay between the injection and combustion of the fuel) and the specific energy required per unit mass. The density of RME is related to the molecular structure of its molecules, increasing as the length of the carbon chain of the alkyl ester increases, and decreasing as the number of unsaturations present in the molecule increases (Pelegrini et al., 2017).

It has been observed that the density decreases linearly with an increase in the blending ratio due to an increase in the volumetric percentage of gasoline in biodiesel-gasoline blends as the density of gasoline is lower than that of biodiesel. Hlaváč (2017) argued that the density of the measured oil samples decreases with increasing temperature. In some parts of the graphical dependence, the decrease was almost linear. Upon comparing the values obtained with the values specified by the manufacturer, small differences were found, which can be accounted for by measurement uncertainties, aging, and sample storing.

Fig. 2 Dependence of biofuel density on temperature

Table 1 shows the exponential regression equations and the coefficients of determination R^2 . As can be seen from the dependencies obtained for all the samples, the development is well characterized by the curve presented. The determination coefficients for all the samples are very high, which also

confirms a strong exponentially decreasing dependence. Kumbar et al. (2013) compared the linear and exponential models and found that both measured coefficients were very high. They also reported that there were no significant differences between the linear and exponential mathematical models from the mathematical perspective. We selected an exponential model for the graphical dependence (Fig.2) based on Csillag (2017), who performed a similar comparison. The author found that the exponential dependence of the Arrhenius type is better suited to physical interpretation. The accuracy of the density measurement was 0.0001 g/cm³.

Table 1. Density exponential regression equations and determination coefficients

Sample	Exponential regression equation	Coefficient of determination R^2
100BD	$y = 0.8965e^{-9E-04x}$	0.9992
95BD:5G	$y = 0.8912e^{-9E-04x}$	0.9980
90BD:10G	$y = 0.8854e^{-9E-04x}$	0.9981
85BD:15G	$y = 0.8798e^{-9E-04x}$	0.9979
80BD:20G	$y = 0.8748e^{-9E-04x}$	0.9988

Figure 3 shows a comparison between the density values of the blends, biodiesel and the standards applied to fuel mixtures. The ASTM D6751 limits of 0.880 g/cm³ and the EN 14214 standards limit the range of density between 0.860 g/cm³ and 0.900 g/cm³. Based on these data, $\rho = 0.8838$ g/cm³ for RME is not fully acceptable according to all the referenced standards, and thus cannot be used in United States without blending. This value is still within the acceptable range for use in the EU. Blends 95 % BD 5 % G, 90 % BD 10 % G, 85 % BD 15 % G, 80 % BD 20 % G meet the cited standards.

Fig. 3 Measured biofuel density at 15 °C compared to the EN 14214 and ASTM D6751 standards

On the basis of the results obtained, it can be seen that 100 % BD at 15 °C has a density of 0.8838 g/cm³. A slightly lower value of 0.882 g/cm³ was reported by Baczewski and Szczawinski (2011) and 0.8823 g/cm³ by Putrasari and Lim (2017a, 2017b, 2018). Chen et al. (2017) reported a density value of 0.87 g/cm³ for 100 % BD, which is also a little bit lower than our value. In the same article they state a density of 0.85 g/cm³ for 90 % BD 10 % G blend, which is noticeably lower than 0.8714 g/cm³ obtained in this study. Finally, they report a value of 0.84 g/cm³ for 83 % BD 17 % G blend. Such a blend was not examined in the present study, but the values were between our 0.8655 g/cm³ for 85 % BD 15 % G and 0.8612 g/cm³ for 80 % BD 20 % G. The results obtained in this study are significantly higher than those of the authors mentioned above, probably due to the initial value of biodiesel density. However, Atabani et al. (2013a) measured fuel density at 40 °C and obtained a result of 0.8660 g/cm³, which is basically consistent with our results (0.8662 g/cm³) at the same temperature.

The density values at 15 °C of all the samples were within the acceptable range (0.860-0.900 g/cm³) prescribed by the

standards. However, the consumption of fuel is higher when the density is lower.

CONCLUSION

The physical properties of biomaterials, including biodiesel, are of crucial importance to many technological processes, especially their quality control (Božiková and Hlaváč, 2014). Accordingly, this study highlighted the physicochemical properties of various biodiesel–gasoline blends. A detailed description of physicochemical properties entails the knowledge and understanding of the effect of combustion and storage on the material parameters.

We emphasize that temperature and thermal history have an important impact on the material microstructure, and hence exert a significant effect on the properties of biodiesel. As temperature increased, the density of the samples under consideration decreased. During measurements, a great dependence was found between the density of biofuel and temperature. The results obtained indicate that gasoline could effectively lower the density of biofuel.

It was also found that a majority of the measured biodiesel densities meet the standards specified by EN14214 and ASTM D 6751. Of all the parameters examined, temperature and blending affect the density of biofuel blends the most.

In future, we plan to study the engine performance and emission characteristics of biodiesel–gasoline blends at different blending ratios to obtain the optimal engine performance and emission characteristics. It would also be interesting to measure the density and viscosity of biodiesel at low temperatures in order to examine the biodiesel behaviour at negative temperatures.

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