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Thermal expansion coefficient and algebraic models to correct values of specific mass as a function of temperature for corn biodiesel

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HIGHLIGHTS

- Thermal coefficient of biodiesel has different magnitude of diesel.
- Algorithm specific mass of biodiesel differs from that presented by the standard EN 14214.
- The differences in the algorithms impact directly the billing of the plants.

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ABSTRACT

Values of thermal expansion coefficients (b) were experimentally determined for three samples: a mineral diesel and two biodiesels constituted by either fatty acid ethyl esters (FAEE) or fatty acid methyl esters (FAME), from transesterification reactions using raw corn oil and ethyl or methyl alcohol. Values of b were found to be 8.36 (±0.06) 10^{-4} °C^{-1}, 8.43 (±0.09) × 10^{-4} °C^{-1} and 8.39 (±0.03) × 10^{-4} °C^{-1}, respectively, within 95% of statistical confidence. The thermal expansion coefficients for biodiesels from corn are higher than that for the mineral diesel. The expansion coefficient is also a key parameter in modeling fuel injection system of internal combustion engines. Comparing the two sets of data, for fossil diesel and biodiesel provides essential information to support the design and optimization of more efficient engines. A higher value for the cubic expansion coefficient implies that less specific mass of fuel is injected at higher temperatures, which can cause a loss in engine power. This is a fundamental parameter, reinforcing further the interest to establish an algebraic model to estimate the specific mass for a biofuel as a function of temperature, which is thought to be significantly different from that more commonly used for the fossil diesel. Polynomial models for such a correction were determined in this work; resulting rates for diesel and for corn oil biodiesels, based on either fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), were respectively −0.7089 kg m^{-3} T^{-1}, −0.7323 kg m^{-3} T^{-1} and −0.7313 kg m^{-3} T^{-1}. From the linear correlation between these data and those from standard EN 14214, values for the sensitivity (slope term) are seemingly small, or roughly 0.723, but are high enough to cause relatively large impacts, in financial terms, for cases involving considerably big volumes of biodiesel, in commercial transactions.

1. Introduction

Environmental problems linked to the use of fossil fuels and the high costs of petrol have stimulated research into new alternative energy sources [1–4]. In this regard, biodiesel fuel obtained from the transesterification of oils and fats basing on acid, basic or enzymatic catalysts is of particular interest [5–8]. The main advantage of biodiesel compared to diesel is to reduce the carbon dioxide emission, considering the life cycle of CO_2 and its good lubricity and biodegradability [9]. Being a product which can be obtained from various raw materials, there is a need to establish quality standards for biodiesel.

The quality of biodiesel can vary according to the molecular structures of the esters which, in turn, are dependent on the constituents or contaminants of the raw material, the production process and the storage system. Thus, the quality of a biodiesel will determine not only the quality of emissions from burning but also the performance, engine operation and safety during storage and transport [10–13].

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One promising area of research in terms of characterizing these bio-materials involves the determination of their thermal properties. These properties reveal important information on the physico-chemical behavior of the material and can supplement the traditional methodologies for the characterization of biodiesel [14–16].

The physico-chemical properties, such as flash point, melting point, viscosity and specific mass, influence the quality of a biodiesel. Some material properties vary considerably with increasing temperature, while others remain unchanged [17,18]. The thermal expansion coefficient is a fundamental physical property that may be of considerable importance in applications related to mechanical structure and material design [19,20]. The thermal expansion coefficient (β), also known as coefficient of volume expansion or volume expansivity, indicates the variation in the volume (V) with changes in temperature (T) while the pressure (P) remains constant, and is defined as:

$$\beta = \left(\frac{1}{V}\right) \times \frac{\partial V}{\partial T} \quad (1)$$

The specific mass of biodiesel is directly related to the structure of its molecules. Higher the carbon chain length and degree of unsaturation of the chain, the higher the specific mass, because they are positively correlated properties [13]. Biodiesel has a higher specific mass than mineral diesel and this is the physico-chemical property which most influences the amount of mass injected into the common-rail direct injection system [21].

With the inclusion of biodiesel in Brazil's energy matrix it is necessary to obtain a mathematical algorithm for the correction of the specific mass [22].

In Brazil, the measurement of the fuel volume is based on the reference volume at 20.0 °C (reference temperature). However, as loading and unloading at industrial level are done at ambient temperatures, it is necessary to convert the volume at a given temperature to the reference temperature. Thus, using a mathematical algorithm may be a determining procedure to establish real transaction prices for biodiesel in industries and/or at any loading bases [23]. The European standard EN 14214 provides an equation for this conversion; however, biodiesel in Europe is mostly obtained from raw materials that are different from those used in Brazil and are mainly obtained with methyl alcohol.

The main objectives of this study were to determine the thermal expansion coefficient from experimental data on the specific mass as a function of temperature and to determine the mathematical algorithm for a more precise correction of the specific mass of fatty acid ethyl esters (FAEE) and fatty acid methyl esters (FAME) obtained from corn, if compared with mineral diesel.

2. Experimental

The fatty acid ethyl esters (FAEE) and fatty acid methyl esters (FAME) analyzed in this study were obtained by the alkaline transesterification route, using refined corn oil as the raw material, applying the following process conditions: rotation 100 rpm, temperature 55 °C, alcohol:oil molar ratio 11:1, potassium hydroxide catalyst concentration 1.1 wt%, and reaction time 60 min. After the alkaline transesterification reaction, the system resulted in two phases with impure biodiesel being formed at the top and glycerine at the bottom. The biodiesel was removed from the mixture, adjusted the pH to near 7 and then washed 3 times with water at 80 °C. A high temperature of the wash water was necessary to solubilize and remove impurities. The methods used to analyze the biodiesel were: acidity ASTM D-664, humidity ASTM D-6304, viscosity ASTM D-445 e D-446, oxidative stability EN 14112, flash point ASTM D-93 [24]. The specific mass was determined on a Kyoto density/specific mass meter (model DA-500), according to ASTM D-4052, within the temperature range of 10–50 °C at intervals of 5 °C. The calibration was performed with water, in order to ensure the reliability of the metrological experiments. Typical uncertainty is ±0.01 kg m^{-3}. Using simple linear regression of $\ln(\mu_0/\mu)$ versus $(T - T_0)$, T_0 and μ_0 are respectively the initial specific mass and initial temperature and μ and T are final specific mass and final temperature, it was possible to calculate the slope of the line which is numerically equal to the thermal expansion coefficient of the biodiesel. Also, using linear regression, μ versus T, it was possible to determine the mathematical algorithms for the correction of the specific mass of ethyl (FAEE) and methyl (FAME) biodiesels obtained from corn.

3. Results and discussion

The Table 1 presents the physico-chemical properties of the fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE) obtained by alkaline transesterification. Results are found to be within the limits recommended by ANP and ASTM [23,25] and the methyl and ethyl biodiesels have only slight differences in their properties.

The Table 2 gives the measured values for the specific mass as a function of temperature for the fatty acid methyl esters and fatty acid ethyl esters obtained from corn, FAME and FAEE, respectively. These values are close to those obtained by Aparicio et al. [26] who reported that the specific mass for methyl esters of refined sunflower oil was 887.76 kg m^{-3} and for diesel oil was 830.20 kg m^{-3} at 15 °C; the value for the methyl esters of unrefined sunflower oil was 886.22 kg m^{-3}. These values are slightly different to those obtained in this study because this parameter is dependent on the raw material employed.

On integrating both sides of Eq. (1), replacing the volume variable for specific mass and carrying out adjustment by linear regression, we obtain Fig. 1 from the data in Table 2, and the thermal expansion coefficients for each biodiesel and the diesel fuel were determined.

The coefficient of thermal expansion is numerically equal to the slope of the straight line. Values within 95% confidence were found to be 8.36 (±0.06) × 10^{-4} °C^{-1}, 8.43 (±0.09) × 10^{-4} °C^{-1} and 8.39 (±0.03) × 10^{-4} °C^{-1} for diesel, ethyl biodiesel and methyl biodiesel, respectively. The percentages of explained variance for this model were 99.99%, 99.98% and 99.99%, respectively indicating a good correlation of the linear model with the experimental data, $F_{calculated}$ being larger than $F_{tabulated}$ in all cases, as shown in Table 3, demonstrating that the regression was statistically significant at the 95% level of confidence. The thermal expansion coefficient is a fundamental parameter in the modeling of a fuel injection system. Comparing the data for biodiesel and diesel fuel will provide the information necessary to adapt engines in the future.

To explore the possibilities of using biodiesel, a knowledge of their thermo-physical properties as a function of temperature is required [27]. The experimental specific mass data associated with the temperature, together with certain concepts of thermodynamics, was used to predict the thermal expansion coefficients of the diesel fuel and the fatty acid ethyl esters (FAEE) and fatty acid methyl esters (FAME) obtained from corn. A higher coefficient of cubic expansion implies a lower specific mass when there is an increase in temperature, which causes a greater loss of engine power as a result of the heating of the fuel [18]. The thermal expansion study allows the change in the volume with temperature to be determined. The thermal expansion coefficients for the fatty acid ethyl esters (FAEE) and fatty acid methyl esters (FAME) were 8.43 × 10^{-4} °C^{-1} and 8.39 × 10^{-4} °C^{-1}, respectively. For a temperature increase of 10.0 °C, the increase in the biodiesel volume is