Renewable Energy 63 (2014) 507–510

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Technical note

Development of an algorithm for correction of specific gravity of biodiesel

David M. Fernandes*, Douglas Q. Santos, Daniela F. Vieira, Rodrigo A.A. Munoz

Institute of Chemistry, Federal University of Uberlandia, Av. João Naves de Ávila, 2121, Bloco 1D, 38400-902 Uberlândia, MG, Brazil

ARTICLE INFO

Article history:
Received 18 September 2012
Accepted 25 September 2013
Available online

Keywords:
Specific gravity
Algorithm
Cottonseed oil biodiesel

ABSTRACT

This communication reports the development of an algorithm for correction of specific gravity of biodiesels. The specific gravity of cottonseed oil biodiesels (for example) was measured at different temperatures and the algorithm was proposed for correction of this parameter depending on temperature, which highly influences loading and discharging of biodiesel. The obtained algorithm differs from that reported in EN 14214 and suggests that individual algorithms should be obtained for biodiesels produced from different oil sources.

1. Introduction

Increasing concerns have caused an intensified search for alternative sources of energy. These concerns include feedstock availability as related to the security of the supply, use of domestic energy sources, price volatility, continuing depletion of the reserves of non-renewable petroleum and greenhouse gas emissions [1].

Accordingly, the esters from vegetable oils (biodiesel) have attracted a great deal of interest as substitutes for petrodiesel to reduce dependence of petroleum and provide a fuel with more benign environmental properties. From a chemical point of view, biodiesel is referred as mono-alkyl esters of long-chain-fatty acids obtained from renewable lipid sources (vegetable oils, recycled cooking oils or animal fats) by the trans-esterification process [2].

Biodiesel is an attractive and eco-friendly alternative to petrodiesel due to its biodegradable, renewable, and non-toxic characteristics. In addition, biodiesel contributes to improved lubricity, higher flash point, similar viscosity, and reduction in most exhaust emissions when compared to conventional diesel fuel [3–5]. The use of biodiesel can reduce the emission of unburned hydrocarbon (HC) particles, sulfur dioxide (SO_2) and carbon monoxide (CO), but at the cost of an increase in nitrogen oxide (NOx) [6,7].

The measurement of thermal properties of biodiesel such as flash point, kinematic viscosity and specific gravity reveals important information about the biofuel quality and limited values for these parameters are established by Brazilian, European and US control agencies. The specific gravity is a property related to the structure of molecules which compose biodiesel and its value increases proportionally with the length of carbon chain and inversely with the number of double bonds. Accordingly, biodiesel has a higher specific gravity than mineral diesel fuel and this fact has to be considered when estimating the amount of mass injected into the common-rail direct-injection system [8].

The specific gravity of biodiesel changes in function of the temperature and therefore the volume of biodiesel loaded and/or unloaded varies in function of temperature. The Brazilian and European norms establish the measurement of specific gravity at 20 °C and 15 °C, respectively, and then the estimation of fuel volume for loading and unloading procedures is based on different temperature values. The EN14214 (European norm) provides an equation for correction of the volume at 15 °C. Additionally, the loading and unloading procedures may take place at different temperatures, and consequently the initial volume may vary significantly from the final one. Due to the difficulty of keeping a constant temperature for loading and unloading, the best solution for this drawback is the development and application of a mathematical algorithm that can correct the difference in volume resulting from the different densities. This algorithm is of capital importance in the calculation of sales of biodiesel in the industries and/or base load.

* Corresponding author. Tel.: +55(34)32394143; fax: +55(34)32394208.
E-mail addresses: davidmaikel@icte.uftm.edu.br, davidmaikel@hotmail.com (D.M. Fernandes).

0960-1481/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.renene.2013.09.037

Table 1
Physio-chemical properties of the methyl (FAME) and ethyl (FAEE) cottonseed biodiesels.[a]

Property (units)	Mean (FAME)	Mean (FAEE)	EN 14214 limits	EN 14214 method
Flash point (°C)	170 ± 2	168 ± 2	Min. 120	EN ISO 3679
Viscosity ($mm^2\ s^{-1}$ at 40 °C)	4.45 ± 0	4.51 ± 0	3.5–5.0	EN ISO 3104
Specific gravity ($kg\ m^{-3}$, at 20 °C)	882 ± 1	887 ± 1	850.0–900.0	ASTM 4052
Acid value (mg of KOH g^{-1})	0.17 ± 0.02	0.16 ± 0.01	Max. 0.5	EN 14104
Free glycerol (% w/w)	0.008 ± 0.001	0.009 ± 0.001	Max. 0.01	EN 14105, EN 14106
Total glycerol (% w/w)	0.21 ± 0.01	0.18 ± 0.02	Max. 0.25	EN 14105, EN 14106
Oxidation stability (h, at 110 °C)	4.9 ± 0,8	4.8 ± 0.6	Min. 6	EN 14112
Peroxide value (meq kg^{-1})	11 ± 0.3	12.9 ± 0.4	–	[a]
Moisture (ppm)	248 ± 0.6	372 ± 2	500	EN ISO 12937

[a] Physico-chemical properties of the methyl (FAME) and ethyl (FAEE) cottonseed biodiesel showed in Table 1 in accordance with Ref. [9].

The objective of this work is to determine a mathematical algorithm to correct the specific gravity of biodiesel. The algorithm was applied for the correction of the specific gravity of methyl and ethyl biodiesels from cottonseed oil as a proof of concept. In Brazil cottonseed oil is the second largest source of vegetable oil used for biodiesel production and cottonseeds are a secondary product from cotton production worldwide. For this reason, cottonseed oil biodiesel was selected in this communication.

2. Experimental

2.1. Samples

Diesel oil was donated from Petrobras S.A. (Paulinia, Brazil). Biodiesel from cottonseed oil was produced by trans-esterification of the oil with methanol and ethanol under reflux conditions in accordance with a previous work [9]. The cottonseed oil donated by Cargill® (Uberlandia, Brazil).

2.2. Instruments

The specific gravity (μ) was determined using a Kyoto DA-500 equipment, in accordance with ASTM D-4052, in the temperature range of 10–50 °C at intervals of 5 °C. The calibration was performed with water with a default expanded uncertainty of ± 0.01 kg m^{-3} in order to ensure reliable measurements.

3. Results and discussion

Table 1 presents the physio-chemical properties of the methylic (FAME) and ethylic (FAEE) biodiesels obtained from cottonseed oil. The physio-chemical properties of biodiesels met the minimum or maximum limits of the EN 14214 except the values of oxidation stability that can be corrected by addition of synthetic antioxidants [10].

The specific gravity values of diesel oil, FAME and FAEE (obtained from cottonseed oil) were measured at different temperatures and are listed in Table 2.

According to EN14214, the linear regression of μ versus T provides a mathematical algorithm (slope of the curve) that corrects the specific gravity of biodiesels. The value indicated by EN14214 is 0.723 kg m^{-3} °C^{-1} for all biodiesels (independently from the oil source), which is the mean correction factor of seven samples. Eq. (1) is recommended by EN 14214 to calculate the specific gravity of biodiesel at 15 °C. It is not mentioned in EN 14214 if this equation can be applied in tropical countries such as Brazil, in which the national regulation establishes the measurement of specific gravity at 20 °C.

Table 2
Specific gravity measurements as a function of temperature for methyl (FAME) and ethyl (FAEE) biodiesels and for diesel oil.

T/°C	FAME (kg m^{-3})	FAEE (kg m^{-3})	Diesel oil (kg m^{-3})
10	890.0	884.2	862.1
15	886.4	880.6	858.6
20	882.7	876.9	855.1
25	879.0	873.2	851.6
30	875.4	865.9	848.0
35	871.7	865.9	844.5
40	868.1	862.3	840.9
45	864.5	858.7	837.4
50	860.9	855.0	833.8

$$\mu(15\ ^\circ\mathrm{C}) = \mu_{\mathrm{measured}} - 0.723 \times (15 - T) \quad (1)$$

Using data from Table 2 for FAME and FAEE produced from cottonseed oil and for diesel oil, plots μ versus T were obtained, resulting in linear curves. The slope values were found to be 0.7287, 0.7300, and 0.7089 kg m^{-3} °C^{-1} for FAME, FAEE, and diesel oil, respectively. A simple analysis shows that these slope values are slightly different from the value indicated by EN 14214. However, a deeper analysis of the μ versus T plots reveals that the obtaining of a linear regression is not adequate because the plots of residual distribution display parabolic behavior (not shown), which indicates heteroscedasticity of the method. The presence of heteroscedasticity invalidates statistical tests of significance that stipulate that the modeling errors are uncorrelated and normally distributed and that their variances do not vary with the modeled effects. Therefore, a polynomial regression of second degree was plotted by correlating μ with T obtaining a mathematical algorithm for FAME, FAEE and diesel oil (Eqs. (2)–(4)), respectively:

$$\mu T = \mu_{\mathrm{measured}} - 0.7422 \times (T - T_{\mathrm{measured}}) + 0.0002 \times (T - T_{\mathrm{measured}})^2 \quad (2)$$

$$\mu T = \mu_{\mathrm{measured}} - 0.7414 \times (T - T_{\mathrm{measured}}) + 0.0002 \times (T - T_{\mathrm{measured}})^2 \quad (3)$$

$$\mu T = \mu_{\mathrm{measured}} - 0.6986 \times (T - T_{\mathrm{measured}}) - 0.002 \times (T - T_{\mathrm{measured}})^2 \quad (4)$$

Using Eqs. (2)–(4), it is possible to accurately correct a specific gravity value of FAME, FAEE and diesel oil at a measured

Table 3
Polynomial regression data for methyl (FAME) and ethyl (FAEE) biodiesels and for diesel oil.

Sample	Confidence interval of regression data[a]		R^2	$F_{calculated}$	$F_{tabulated}$	p-Value
	1° Order	2° Order				
FAME	±0.0112	±0.0002	99.99%	3.69×10^5	5.59	5.55×10^{-16}
FAEE	±0.0152	±0.0002	99.99%	2.01×10^5	5.59	3.33×10^{-15}
Diesel oil	±0.0001	0	99.99%	2.89×10^9	5.59	0

[a] Regression data from Eqs. (2)–(4).