BIODIESEL DENSITY CHARACTERIZATION USING A PYCNOMETER

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Abstract: This study shows an alternative method to digital density meters to characterize biodiesel density. The possibility of using a pycnometer for biodiesel density measurements was hereby investigated considering biodiesel instability when in contact with air. The choice of method of pycnometer was due to its small measurement uncertainty compared with the requirements of existing regulation in Brazil and ASTM and ISO standards, that consider approved the biodiesel fuel within a range between 850 kg/m³ and 900 kg/m³ at a temperature of 20 ºC. The biofuel is isolated from the atmosphere by covering the pycnometer flask with a plastic foil during the density measurement. Results obtained from samples measured by digital density meters and by this alternative method are compared at several temperatures. The highest difference occurs for 40 ºC being of the order of a few tenths of g/cm³, which shows significant variation considering the values obtained by national metrology institutes. However, it is still compatible with the Brazilian official specification for biodiesel commercial operations.

1. INTRODUCTION

Brazil is one of the world's greatest biofuel producers. The Brazilian alcohol is mainly ethanol which is derived from sugar cane [1] and biodiesel is produced from vegetable oil and from animal fat [2].

In addition Brazil is in a very singular position compared with the other countries regarding the production and consumption of biofuels. Approximately 80 % of the Brazilian automobiles produced in 2009 are fueled with biofuels [3]. Moreover Brazil is the second largest producer of this kind of fuel, being the first position occupied by the USA [4]. A great variety of biodiesels can also be produced in Brazil [5]. By law enforcement [6], 5 % of biodiesel is added to the consumed diesel oil in order to reduce the importation of diesel oil in approximately 10 % of the total production [7].

For commercial reasons, it is important to characterize biodiesel properties in order to ensure that they can be mixed to diesel oil without damaging combustion motors. It is a well-known fact that density values vary when biofuels are in contact with ambient air due to its chemical instability when exposed to oxygen [8]. In this respect, this work is concerned with biodiesel density characterization and its traceability.

Biodiesel requirements established by official standards [9-10] are much less restrictive than metrological standards. The Brazilian resolution [11] states that commercial biodiesel should have a density value between 0.85 g/cm³ and 0.90 g/cm³ at 20 ºC. From a metrological point of view, this is a very broad range as density values can be determined with a precision of the order of microgram per cubic centimeter.

Fluids Laboratory at the Mechanics Division of Inmetro (Laflu) is responsible in Brazil for the traceability of four quantities: volume, surface tension, viscosity and density. Taking into account the range considered in the resolution mentioned above, this study performed at Laflu is intended to compare density values from biodiesel samples taken from the same production lot measured with a digital density meter and with a gay-lussac pycnometer. The measurements were carried out simultaneously in order to observe how significant the difference is in the results obtained by both methods.

Table 1 shows the best uncertainty estimates for density measurements obtained in Brazil at present.

Table 1 *Best expanded uncertainties of measurement obtained by Fluids Laboratory at Inmetro.*

Density	**Fluid**	**U (g/cm³)**
Hydrostatic weighing system	water	0.000 020
	n-dodecane	0.000 016
	ethanol	0.000 027
Pycnometer	ethanol and biodiesel	0.000 08

2. EXPERIMETAL SETUP

Two biodiesel samples from the same production lot were used for measurements with a density meter model DMA 4500 at 20 ºC, 25 ºC, 30 ºC, 35 ºC and 40 ºC. The measuring procedures followed are described elsewhere [12]. These measurements are rapidly accomplished when compared to those obtained when using a pycnometer. In order to ensure repeatability, two measurements for each sample were taken at each temperature. The measuring procedure for biodiesel samples using a pycnometer will be described below.

2.1 Pycnometer

The pycnometer used to measure density of biofuels is of gay-lussac type as depicted in figure 1.

Fig. 1 *Gay-lussac pycnometer with biodiesel.*

Firstly, the volume of the pycnometer is determined by filling it with water as the density of water is already known at several temperatures [13-14]. Pycnometers differ by their nominal volumes [15], such as 25 mL, 50 mL, 100 mL and so on. When using a pycnometer the density of the liquid ρ_L in g/cm³ is determined by the following expression:

Where:

$$\rho_L = \frac{(M_C - M_S)\cdot(\rho_b - \rho_a)}{V\cdot(1+\alpha\cdot(T_L - T_r))\cdot\rho_b} + \rho_a + \gamma(T_L - T_r) + \delta_{repet} \qquad (1);$$

M_C is the total mass (pycnometer mass + liquid mass), in g;

M_S is the dry mass (pycnometer mass), in g;

V is the corrected pycnometer volume, in cm³;

α is the volume expansion coefficient, of the pycnometer in ºC^{-1};

T_L is the temperature of the liquid during the measurement, in ºC;

T_r is the reference temperature, in ºC;

ρ_a is the air density, in g / cm³;

ρ_b is the density of the weight used to calibrate the balance, in g / cm³;

γ is the density gradient of the liquid with respect to the temperature, in g / (cm³ ºC);

δ_{repet} is the contribution due to the repeatability of the measurements.

The evaluation of the density values of biofuels requires a few extra precautions in order to guarantee reliable results. It is a well-known fact that biodiesel is susceptible to chemical modifications when exposed to oxygen and/or light [16] which in turn lead to density changes. Here we describe a simple and effective way to accomplish the characterization avoiding a significant density value alteration. Pycnometers are open glass containers as shown in figure 1. We have performed the biofuel density measurements with such appliances by covering the flask during the assay with a PVC or silicon foil as shown in figure 2.

Fig. 2 *The gay-lussac pycnometer is covered by a PVC foil when biodiesel density is to be determined.*

After filling the pycnometer with biodiesel and covering it with the PVC foil, the assembly is then placed in a thermostatic bath until it reaches the selected temperature for density measurement. The time interval required for thermal equilibrium is of approximately one hour. This as was verified by previously placing a pt-100 thermometer inside the pycnometer with a biodiesel sample at two different levels, after which the sample was discarded. Care should be taken to assure that the flask is thoroughly filled at such temperature.

Figure 3 shows how the temperature gradient is evaluated in this case. Thermometers are positioned around the pycnometer as the flask is sealed by the PVC foil. This does not need to be done when stable fluids are being measured. Instead, a thermometer pt-100 is placed in the pycnometer for stable fluids. This procedure is also required because pt-thermometers could not be properly cleaned after biofuel immersion.

Fig. 3 *Covered gay-lussac pycnometer with biodiesel in the thermostatic bath where temperature gradient is measured with a pt-100 thermometer.*

When retrieving the pycnometer from the bath, the flask is sealed with its lid .The temperature drift inside the pycnometer is of 0.2 ^{o}C when it is removed from the bath. Then, acetone is sprayed on the pycnometer. The volume of the fluid is slightly reduced which can be noticed by looking at the pycnometer capillary. Figure 4 and figure 5 show those sequential steps.

Fig. 4 *Gay-lussac pycnometer filled with biodiesel being dried out faster with the aid of acetone.*

Fig. 5 *Biodiesel volume reduction can be observed by looking at the pycnometer capillary.*

The pycnometer is then dried and weighed as depicted in figure 6. This procedure is repeated at least seven times.

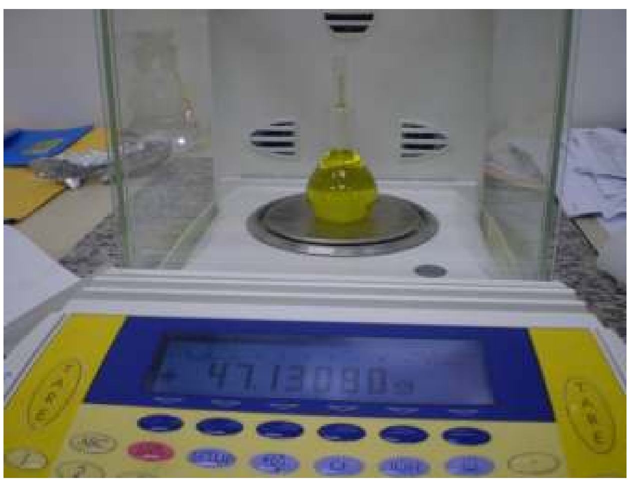

Fig. 6 *The mass of the pycnometer filled with biodiesel is being determined.*

3. ON THE POSSIBILITY OF USING BEEF TALLOW BIODIESEL FOR QUALITY CONTROL

It is a well-known fact that biodiesel physical properties are determined by the chemical structure of its components. The extent of the fatty esters chains, the amount of unsaturated bonds and the number of branched chains are the main features that characterize biodiesel properties [17].

Biodiesel chemical characteristics, however, can be changed by its contact with the atmosphere through degradation processes. Oxidative stability of biodiesel has been the subject of considerable research. It is an important issue mainly when one considers extended biodiesel storage. Generally, factors such as presence of air, elevated temperatures or presence of metals facilitate oxidation. Notwithstanding, the influence of compound structure of the fatty esters, especially unsaturation, is even greater. The reason for autoxidation is the presence of double bonds in the chains of many fatty compounds. The autoxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds. Polyunsaturated fatty acids such as linoleic acid and linolenic acid are more susceptible to autoxidation than saturated ones. Most biodiesel oils have polyunsaturated fatty acids in their composition. As a result of autoxidation, the compounds formed will eventually deteriorate the fuel [16].

On the other hand, beef tallow biodiesel is mainly formed with saturated and monounsaturated fatty esters [17]. This represents an advantage over other types of biodiesel fuels produced from vegetable origin which are predominantly formed by polyunsaturated fatty acids [18]. The smaller content of polyunsaturated fatty esters present in beef tallow biodiesel should confer more stability towards oxidation effects. Thus if one considers a biodiesel fuel with a higher polyunsaturated fatty ester content, like for instance the one originated from soy bean [19], in addition to water absorption effects which contribute to density variation, there would be the alterations due to oxidative degradation. As it is, we can assume that the density values will change more rapidly as the fuel is in contact with air when compared to a biodiesel produced with saturated fatty acids.

4. RESULTS

The results obtained with the pycnometer and with the digital density meter are displayed below (Tables 2 and 3). The traceability for the density meter was provided by the hydrostatic weighing method.

5. DISCUSSION

Two measuring methods are compared in this work to evaluate biodiesel density: using a density meter and a pycnometer. It should be noted that both methods investigated provide density values with respect to temperature which agree up to the third decimal place. Discrepancies can only be seen at higher temperatures and on the fourth decimal place. It is evident that the pycnometer density values at temperatures 30 °C, 35 °C and 40 °C are higher than the ones obtained with the digital density meter. Although the pycnometer was sealed throughout the measurements, it is possible that the PVC foil was not enough to completely avoid water absorption, which would account for the higher density values obtained.

It is important to note, however, that even though results obtained by the two different methods differ, they still remain within the range admitted by Brazilian standards [9-10]. For instance, taking into account the measurements at 40 ºC, results by the two methods presented in this work differ even when computing the expanded uncertainties. This is evidenced in Figure 7. At 40 ºC, the density meter yields (0.85041 ± 0.00007) g/cm³ whereas the pycnometer yields (0.85077 ± 0.00019) g/cm³. If one considers only two decimal places, as is required by the Brazilian standards, the two values will then agree.

As a disadvantage, measuring density with a pycnometer increases the estimated uncertainty of measurement when compared with results obtained by a hydrostatic weighing system, which is another method of determining density.

Table 2 *Results obtained with the pycnometer.*

Reference Temperature ºC	Calculated Liquid Density g/cm³	Expanded Uncertainty g/cm³	Combined Uncertainty g/cm³	Coverage Factor *k*	Degrees of Freedom ν_{eff}
20.00	0.864 93	0.000 18	0.000 0872	2.00	$6{,}71 \times 10^6$
25.00	0.861 47	0.000 20	0.000 0956	2.00	1230
30.00	0.857 88	0.000 18	0.000 0902	2.00	13702
35.00	0.854 40	0.000 19	0.000 0947	2.00	1687
40.00	0.850 77	0.000 19	0.000 0919	2.00	3424

Table 3 *Results obtained with the digital density meter [12].*

Reference Temperature ºC	Calculated Liquid Density g/cm³	Expanded Uncertainty g/cm³
20.00	0.864 96	0.000 07
25.00	0.861 35	0.000 07
30.00	0.857 70	0.000 07
35.00	0.854 05	0.000 07
40.00	0.850 41	0.000 07

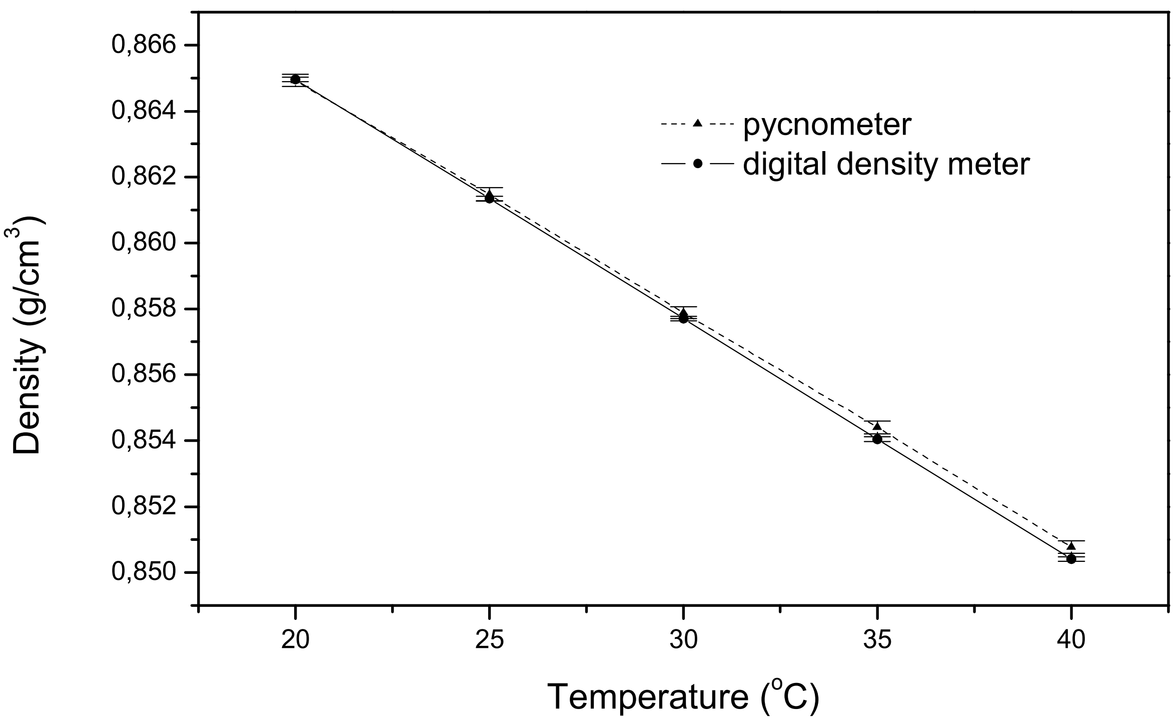

Fig. 7 *Biodiesel density values measured with a pycnometer (squares) and with a digital density meter (circles) at Laboratório de Fluidos - Inmetro. The solid lines are only a guide to the eye.*

6. CONCLUSION

The increase in density values shown through the measurements obtained with a pycnometer as compared with a digital density meter, although significant for high resolution density determinations, is negligible for the purposes of biofuel applications, since the governmental regulations are not very demanding when compared to measuring density at the state of art.

One should consider, however, that biodiesel regardless of its source may be hygroscopic. Thus, its density value tends to increase with time. Notwithstanding, this study shows that the increment in density is of the order of a tenth of milligram per cubic centimeter if the appropriated precautions are taken during the measurements. Despite this increment, density values are still in the range established by official norms [9-10].

Digital density meters can be traceable by hydrostatic weighing systems or by means of certified reference materials. For those who are not equipped with such system, the pycnometer is a reasonable alternative to provide traceability for biodiesel density measurements provided that reference fluids, such as water or n-dodecane, are used accordingly. It should be emphasized that biodiesel is not fit to be a reference fluid in open systems as the pycnometer.

As one more advantage of using pycnometers, they are much less expensive than digital density meters.

A cheaper method to determine the density of biodiesel is proposed and is confronted with the Brazilian official regulation and international ASTM and ISO standards. The idea is that the official requirements determine the density within the range between 0.85 and 0.90 g/cm^3. We show that using the pycnometer and beef tallow biodiesel, an unstable fluid, one can still obtain density values which are in conformity with the official requirements. We show that in spite of the biodiesel instability, changes in density values appear at the fourth decimal place when the official standard states only two decimal places. In this context, biodiesel could be also used as an important tool as a quality control material [20] of the certificate of the results issued by the laboratories. This can be done because there are several types of reference material [21].

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