Characterization of the Viscosity of Soybean and Sunflower Biodiesel Relative to Temperature, Using Capillary Viscometers

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***Abstract*- In this article we compare the viscosity-temperature behaviour of two types of biodiesel. The biofuels investigated were produced from soybean and sunflower, both transesterified with methanol. Viscosity was measured with capillary viscometers from 20 ºC to 40 °C. Measurement uncertainty was calculated. The behaviour of the viscosity with temperature is analyzed considering the estimated uncertainty. Three mathematical models were applied to the experimental viscosity values of soybean and sunflower biodiesels as a function of temperature: a polynomial function of third degree, the Vogel equation, and the ASTM D341 equation. Results show that they all agree with the experimental data within 1% of relative deviation.**

Keywords- Soybean Biodiesel; Sunflower Biodiesel; Capillary Viscometer; Uncertainty of Measurement

I. INTRODUCTION

With the increase in price of the oil barrel, and with the increase of planet earth's pollution, governments of countries not self-sufficient in oil production started to encourage new alternative ways to generate energy. There are many studies directed towards electrical, solar and nuclear energies, as well as towards nanotechnology and biotechnology as new sources of energy.

Presently, the energy matrix of most industrialized countries in the world is oil based. However, most part of this kind of fuel available belongs to a small group of nations that, united, control its production and prices, leaving other countries dependent upon them.

Brazil has been adopting some measures in order to reduce its oil dependency in the last thirty years. Firstly, due to great investments, it has become self-sufficient regarding oil production in the first years of the 21st century. Furthermore, it has developed cars [1] fueled by hydrated alcohol, which, as an additional advantage, diminishes its carbon gas emissions in the atmosphere.

If on the one hand alcohol or gasoline fueled cars are a good solution for small vehicles, unfortunately diesel fueled machines fall short on this matter. Moreover, diesel oil is one of the "villains" in the Brazilian current energy matrix, since it is largely imported and is the most consumed fuel by automotive vehicles [2, 3] (Fig. 1).

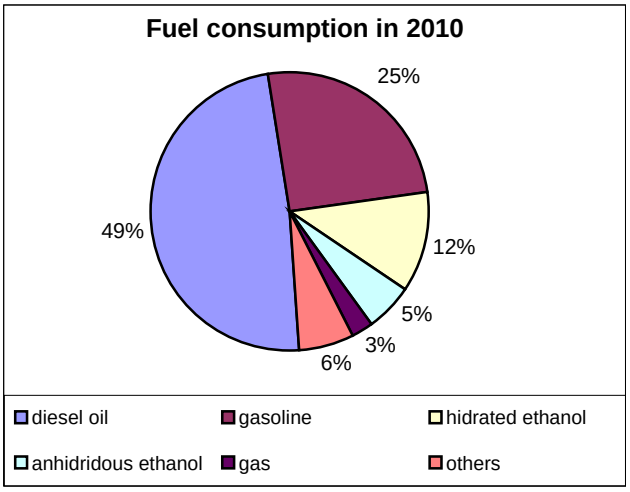


Fig. 1 Fuel consumption in Brazil, in 2010 – Picture based on the Energy Ministry

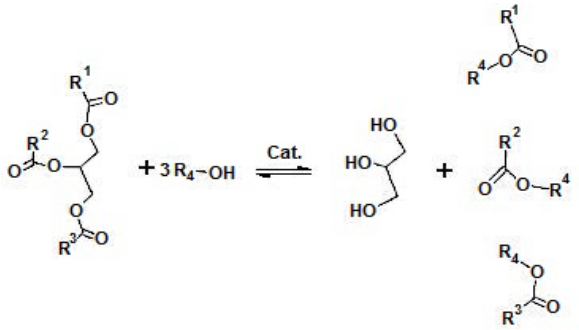
The need of importing diesel relies on a decision on Brazil's behalf of creating a larger quantity of refineries that processes more gasoline than diesel oil. Thus, even though Brazil informs its self-sufficiency in crude oil, it is not so regarding oil derivatives. Currently, Brazil produces an excess of gasoline, which is exported, whereas diesel oil is imported. Some ideas were then suggested which are being put into practice to reduce the problem of the country's fuel insufficiency. One of them is the production of biodiesel, with the objective of lowering fuel imports.

Biodiesel is one of the most attractive immediate solutions to diminish, or at least stagnate, diesel oil imports. While electrical motors and those moved by wind, solar and other kinds of energy do not provide immediate results as good as oil, biodiesel will have leverage, as its use does not require a radical change in diesel motors so they can still work with good efficiency.

In January 2008, a Brazilian law (Law 11097/2005) [4] established a mandatory addition of 2% of biodiesel to petrodiesel. From July 2008 to the first half of 2009, the percentage of B100 compulsorily added to mineral diesel was 3%, rising to 4% on July 1st. This percentage was held constant until the end of the year 2009 [2]. Since January

2010, this addition has increased to 5%, representing at the end of 2010 a volume of biodiesel equivalent to 5.8% of diesel oil production. In 2010, the main raw material used for biodiesel production was soybean oil (82.2%), followed by bovine tallow (13.0%) [3].

On the other hand, Brazil has a great possibility of producing several different types of biodiesel. The idea of using biodiesel in motors stems from the assumption that this fluid's characteristics are much similar to those of diesel oil. This happens because, in the process of transesterification of the oil from an oilseed or from animal fat, the carbon chain is broken down (Fig. 2) [5, 6] and is reduced to a number of carbon atoms similar to that of the carbon chains present in diesel oil.



Triglycerides Alcohol Glycerol Methyl esthers (biodiesel)

Fig. 2 Biodiesel transesterification process

Thus, it is possible to infer that these new fuels' behavior in relation to its properties as substitutes of diesel oil in a motor is similar to that of diesel oil.

Biodiesel can be produced through a methylic or ethylic route, depending on the alcohol, which, in the presence of a catalyzer, enables a reaction starting from triglycerides that will produce biodiesel and glycerin.

Fluids Laboratory (Laflu) of the Mechanical Metrology Division (Dimec) from Instituto Nacional de Metrologia, Qualidade e Tecnologia (Inmetro) is responsible for the traceability of the measurements of kinematic viscosity in Brazil.

The ANP's decree [7] that specifies the parameter of diesel oil viscosity informs that its kinematic viscosity must be analyzed at 40 ºC, and must be in the range from 2.5 mm²/s to 5.5 mm²/s. Regarding biodiesel, a resolution from the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) states that this oil must be marketed with a kinematic viscosity, at a temperature of 40 ºC, in the range from 3.0 mm²/s to 6.0 mm²/s, and must be clean and speck free [8].

To study the behavior of viscosity with temperature [9], as well as the behavior of biodiesel obtained from different sources, including the large number of vegetable oils and animal fats, it is an important step to optimize the use of biodiesel as a petrodiesel substitute. In this study, we show the viscosity behavior of these methyl esters between 20 °C and 40 °C.

II. Experimental Procedure

A. Viscosity Study

Viscosity was measured following the procedures established in ISO 3105 [10] and in ASTM D 445 [11].

A capillary viscometer is an instrument which properly measures Newtonian fluid's kinematic viscosities, and, according to its application, many types and models can be used. In this work, an Ubbelohde glass capillary viscometer was used [10]. Size Number 1 of this viscometer was chosen, for it is capable of measuring kinematic viscosities from 2.0 mm²/s to 10.0 mm²/s.

The temperature values selected for the assays were 20 ºC, 25 ºC, 30 ºC and 40 ºC.

The thermostatic baths used were Lauda D-40 (as hot source), with a Tamsom TLC-15 (as cold source), controlled with one over a thousand ºC precision thermometers.

The viscosity was evaluated by measuring the flow time of the fluid with a chronometer, calibrated at the Observatório Nacional of Brazil.

Fig. 3 shows a schematic diagram of the Ubbelohde viscometer used during the measurements.

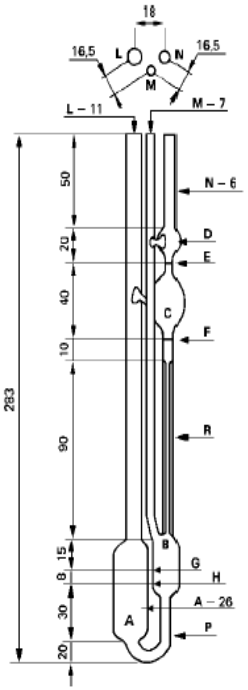


Fig. 3 Schematic diagram of the Ubbelohde viscometer used during the measurements Letters and numbers designate quantities indicated in [7].

B. Sample Preparation

Samples were prepared using oil extracted from soybean and sunflower. Both oils were then transesterified with methanol. The transesterification process was undertaken according to Lobo, Ferreira and Da Cruz [6].

C. Oil Measurements

Calibration of this instrument was carried out by starting from the viscosity of water [12] and following the

procedures in the standard ISO 3105 [10]. The nominal value of viscosity must be taken into account when picking out the adequate viscometer.

At least 30 minutes is required for thermal equilibrium. Vacuum was applied to drain the fluid through bulb C, until approximately 1 cm above timing mark E. The vacuum apparatus was then withdrawn from the viscometer. Liquid flow in the instrument then started by gravity. The flow time of the sample was measured observing its meniscus from timing mark E to timing mark F. These marks are shown in detail in Fig. 4. The capillary through which the fluids flow allows a maximum viscosity accuracy of 0.1%.

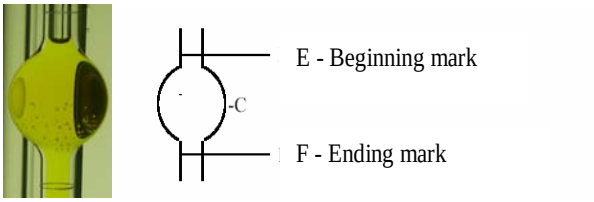


Fig. 4 Time measurement bulb with timing marks E and F

The thermostatic bath was characterized based on the standard DKD-R 5-7 [13] for each of the measurement temperatures and at three different heights. A PT100 thermometer is immersed at heights A0, B0 and C0 (the distance from the top of the bath to the liquid line is X0, from the top of the bath to A0 is X1, from A0 to B0 is X2 and from B0 to C0 is X3) to determine bath stability at these heights. The gradient is determined placing a PT100 thermometer in B0 while another moves in clockwise circles at positions A1, A2, A3 and A4, B1, B2, B3 and B4 and C1, C2, C3 and C4, respectively, as shown in Fig. 5.

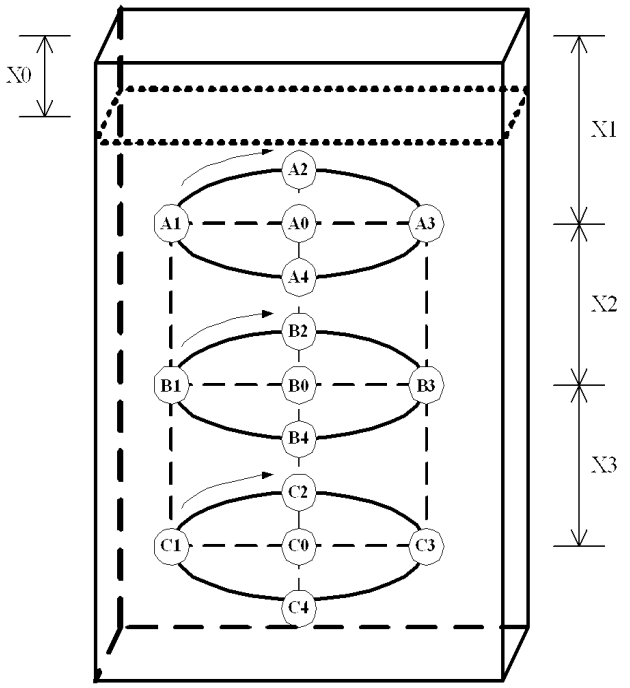


Fig. 5 Thermostatic bath characterisation

The viscometers were thoroughly cleaned after the measurements with a volatile petroleum spirit.

III. VISCOSITY EQUATIONS – EXPERIMENTAL DETERMINATION

Equations 1 and 2 shown below are used to determine the viscosity of a liquid.

$$v = f(C_1, t) = C_1 \times \left(t - \frac{0.00166 \times \sqrt{V^3}}{C_2 \times L \times \sqrt{C_2 d}} \times \frac{1}{t^2} \right) \tag{1}$$

$$C_1 = C_2 \times \left\{ 1 + \left[\alpha \times (T_r - Temp) \times \left(\frac{\cos \phi_1}{\cos \phi_2} \right) \times \left(\frac{g_1}{g_2} \right) \times \left(1 + \frac{2}{g_1 h} \right) \times \left(\frac{1}{r_u} - \frac{1}{r_l} \right) \times \left(\frac{\sigma_1}{\rho_1} - \frac{\sigma_2}{\rho_2} \right) \right] \right\} \tag{2}$$

Where:

v is the kinematic viscosity (mm²/s);

t is the flowing time (s);

C_1 is the corrected constant of the calibrated viscometer (mm²/s²);

C_2 is the constant of the calibrated viscometer (mm²/s²);

V is the volume of the flowed liquid (mm³);

L is the lenth of the capillary (mm);

d is the capillary diameter (mm);

g_1 is the acceleration of gravity at the measurement place (m/s²);

g_2 is the acceleration of gravity at the calibration place (m/s²);

h is the hydrostatic pressure height (m);

r_u is the inner radius of the upper tube (m);

r_l is the inner radius of the lower tube (m);

σ_1 is the surface tension of the measured oil (N/m), in this study measured with a Krüss K100MK2 tensiometer;

σ_2 is the surface tension of the oil used in the calibration (N/m), in this study measured with a Krüss K100MK2 tensiometer;

ρ_1 is the density of the measured oil (kg/m³), in this study measured with an Anton Paar DMA 4500 digital density meter;

ρ_2 is the density of the oil used in the calibration (kg/m³), in this study measured with an Anton Paar DMA 4500 digital density meter;

ϕ_1 is the verticality angle in the measurement (close to zero);

ϕ_2 is the verticality angle in the calibration (close to zero);

$Temp$ is the measurement temperature (°C);

T_r is the reference temperature of the viscometer (°C);

α is the glass volumetric thermal expansion coefficient ($^oC^{-1}$).

Note: In this study, g_1 and g_2 are considered equal as the measurement and instrument calibration took place at the location. In practice, the difference between the quantities r_u and r_l is negligible.

IV. VISCOSITY RESULTS

Experimental results and the estimated expanded uncertainty of viscosity measurement are shown in Table I and Fig. 4, with a 95.45% confidence and a coverage factor of k=2. For each reference temperature, five measurements were performed. The presented value is the average of them. The measurements for petrodiesel oil have also been included for comparison [5, 7].

TABLE I MEASUREMENTS AND THEIR UNCERTAINTIES FROM SOYBEAN AND SUNFLOWER BIODIESEL AND DIESEL OIL

	Sunflower Biodiesel		Soybean Biodiesel		Diesel Oil	
Temperature (ºC)	Value (mm^2/s)	Expanded Uncertainty (mm^2/s)	Value (mm^2/s)	Expanded Uncertainty (mm^2/s)	Value (mm^2/s)	Value (mm^2/s)
20	7.3816	0.0082	6.6547	0.0074	5.0867	0.0057
25	6.4785	0.0073	5.8670	0.0065	4.4671	0.0050
30	5.7590	0.0064	5.2137	0.0058	3.9586	0.0044
40	4.5835	0.0051	4.2084	0.0047	3.1691	0.0038

V. MATHEMATICAL MODELS

From these results, fitting functions were applied to the data. Three mathematical models were analyzed for the viscosity values of soybean and sunflower biodiesels as a function of temperature.

The first mathematical model representing the behavior of soybean (3) and sunflower biodiesels (4), with respect to temperature is a polynomial fit of third degree. The parameters of the fitting function to the above experimental data were determined through the least square method. Results are as follows.

$$\nu = -0.00003397 \times T^3 + 0.00052355 \times T^2 - 0.34133833 \times T + 11.65900000 \quad (3)$$

$$\nu = -0.00009577 \times T^3 + 0.01085450 \times T^2 - 0.52302833 \times T + 14.266550000 \quad (4)$$

where:

T is the measurement temperature (ºC);

ν is the kinematic viscosity (mm^2/s).

Another model considered in this work is the Vogel equation [14, 15]. This equation can also be used to represent the behavior of soybean (5) and sunflower biodiesels (6) with respect to temperature, in order to determine the parameters for the Vogel equation. The viscosity experimental results for 20 °C, 25 °C and 40 °C were used and the obtained system of equations was solved. Results are presented below.

$$\nu = 0.1566 \times e^{(538.5269)/(T+123.6363)} \quad (5)$$

$$\nu = 0.0195 \times e^{(1360.3490)/(T+209.1532)} \quad (6)$$

Another reported viscosity-temperature function is the ASTM D341 equation [16]. This equation also represents adequately the behavior of soybean (7) and sunflower biodiesels (8) as a function of temperature. The calculation of the parameters for this equation was based on the experimental viscosity results for 20 °C and 40 °C, where the corresponding system of equations was solved. Results for both types of biodiesel are shown below.

$$\nu = \left(e^{e^{(20.1852(-3.4317 \times \ln(273.15+T)))}}\right) - 0.7 \quad (7)$$

$$\nu = \left(e^{e^{(20.3092(-3.4454 \times \ln(273.15+T)))}}\right) - 0.7 \quad (8)$$

VI. CONCLUSIONS

The Brazilian fuel resolution for diesel [7] states that viscosity values of fuel for adequate engine functioning should be between 2.0 mm^2/s and 5.0 mm^2/s at 40 ºC. It can be observed from the results presented that biodiesel oils [17] produced both from sunflower and soybean can be used as fuel addition because they meet the requirements determined by the Brazilian government.

Table II shows experimental results and the corresponding theoretical viscosity values as calculated from the mathematical models described in the previous section. For the percent relative deviations, the experimental results were considered the correct values. The experimental data fits within less than 1% of the standard deviation of the three mathematical models presented in the temperature range investigated. The third degree polynomial fit, however, was the best fitting function due to the mathematical approach used. In this case, the relative deviation remained under 1.0%.

In a metrological approach, depending on the experimental setup for the assays (thermostatic baths, thermometers and environmental conditions), temperature changes cannot be neglected however small they are. As a

consequence of such variations, a small change of the viscometer constant will follow. Strict temperature control is also important to improve the estimated uncertainty of measurement.

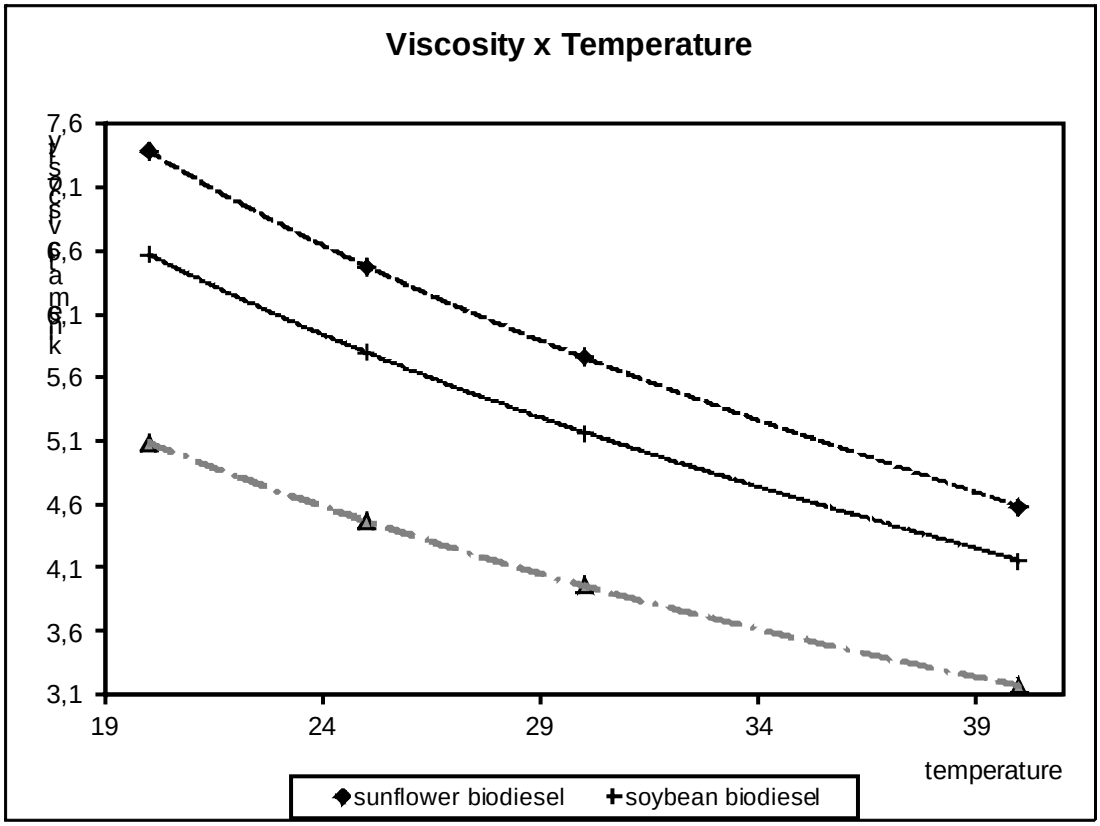


Fig. 4 Kinematic viscosity values from soybean, sunflower biodiesel and diesel oil as a function of temperature and their respective uncertainties

In Table III, other diesel properties are shown in order to compare biodiesel and traditional diesel efficiencies in an engine.

Results shown in Table III demonstrate that density of vegetal oil biodiesels is 3.0 to 3.5 % higher than that of traditional diesel. The difference can be seen in the second decimal place, which is significant from the engine functioning point of view. If this fuel with a higher density is used in a fuel supply system of a diesel engine, for a specific load condition, a greater fuel mass would be injected in it, since engine injection systems perform dosage control by volume. In this case, it is expected that engine biofuel consumption would be higher.

If the injected volume analysis is undertaken from the heating value point of view, the power of traditional diesel is in the order of 2.6% higher than that of soybean diesel. Again it would be expected that consumption of biodiesel would be higher.

It should be noted, however, that the above considerations refer to an engine which has been optimized and approved for diesel. Furthermore, cetane number and combustion behavior characteristics have not been taken into account under such conditions. For this reason, the engine should be submitted to several dynamometer tests in order to reach a definite conclusion. Such tests would be of great importance to optimize the use of alternative fuels, mainly to evaluate emission of pollutant products.

ACKNOWLEDGMENTS

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TABLE II EXPERIMENTAL VISCOSITY VALUES AND THE RELATIVE DEVIATIONS FROM MATHEMATICAL MODELS APPLIED TO THE EXPERIMENTAL DATA, FOR SUNFLOWER BIODIESEL

T (ºC)	Polinomial P (mm²/s)	ASTM D341 (mm²/s)	Vogel ν (mm²/s)	Experimental (mm²/s)	Error P (%)	Error W-U (%)	Error V (%)
20.0	7.3816	7.3816	7.3816	7.3816	0.000	0.000	0.000
25.0	6.4784	6.4801	6.5028	6.4785	0.001	0.002	0.374
30.0	5.7589	5.7336	5.7590	5.7590	0.002	0.442	0.000
40.0	4.5833	4.5835	4.5835	4.5835	0.005	0.000	0.000

TABLE III OTHER FUEL PROPERTIES INVESTIGATED

Property	Diesel	Soybean Biodiesel	Sunflower Biodiesel
Density g/cm^3 (20 °C)	0.85519	0.88230	0.88654
Higher heating value (kJ/kg)	42800	41685	41330 [18]
Diesel difference	-	-0.02715	-0.03139
Diesel difference (%)	-	-3.1748816	-3,540731383
Diesel difference	-	1115	1470
Diesel difference (%)	-	2.61	3.43

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