

# METROLOGICAL APPROACH IN THE CHARACTERIZATION OF VISCOSITY OF CORN BIODIESEL RELATIVE TO TEMPERATURE, USING CAPILLARY VISCOMETERS

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**Abstract:** in this article we study the behavior of biodiesel viscosity from corn biodiesel, transesterified with methanol, in relation to temperature. These quantities were measured with capillary viscometers, from 20 °C to 40 °C. Measurement uncertainty was calculated. The behavior of viscosity with temperature is analyzed considering the estimated uncertainty.

**Keywords:** corn biodiesel, capillary viscometer, uncertainty of measurement

## 1. INTRODUCTION

With the increasing oil prices and environmental concerns about the Earth's pollution by the GHG, governments are looking for alternative ways to generate energy. Brazil is leading this process which involves two main aspects: reducing the dependence on fossil fuel to help building an environmentally cleaner world and to promote a more effective social inclusion with the upcoming economic opportunities in a new and growing field. Despite the self-sufficiency of Brazil in crude oil production, the refined products show some peculiarities. Gasoline, for instance, due to the amount of bioethanol in the blend – 25% of bioethanol - for domestic consumption, has a large volume being exported. On the other hand, diesel due to the transport matrix is being imported to fulfill the strong growing need in Brazil. The volume of diesel imported in 2006 was around 10% of consumption.

In January 2008, a Brazilian law (Law 11097/2005) [1] established a mandatory addition of 2% of biodiesel to petrodiesel. From July 2008 the mandatory addition changed

to 3%, representing a volume of, biodiesel equivalent to 1,6% of the market.

Brazil has a great possibility of producing several different types of biodiesel. In addition to the transesterified vegetable oils being studied here, there are still various types of biodiesel that can be produced from animal fats.

The fuel performance in an engine is dependent on many variables characterized as quality parameters presented as Fuel Standards. Among these variables, the density and the viscosity play important roles.

To study the behavior of the viscosity with the temperature, 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 corn oil as well as the behavior of this methyl ester between 20 °C and 40 °C.

The viscosity of a liquid is its internal resistance to flow [2]. The capillary viscometers used in this study belong to the Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (Inmetro) [3], and are national standards [4]. In the chain of traceability, the viscometers are calibrated starting from the viscosity of water.

## 2. EXPERIMENTAL PROCEDURE

The motivation for this study relies on the following facts: 1) viscosity behavior as a function of temperature that characterizes biodiesel obtained from corn biodiesel, considering the estimated measurement uncertainty, is not completely known yet; 2) viscosity curve as a function of temperature of mixtures of biodiesel from corn oil with

diesel, considering the estimated measurement uncertainty, has not been done so far; 3) the obtained data would be very useful in commercial transactions (for instance, in custody transfer).

It is worth to emphasize that all the required metrological treatment (instrument calibration and uncertainty calculations) in this research is being undertaken by Inmetro [4]. In this way, the reliability of results obtained can be worldwide confirmed.

### 3. VISCOSITY STUDY

Viscosity was measured also at Inmetro following the procedures established at ISO 3105 [5] and at ASTM-D 445 [6]. An Ubbelohde capillary viscometer number 1 (range from 1,2 mm<sup>2</sup>/s to 10,0 mm<sup>2</sup>/s) was used. The temperature values selected for the essays were 20 °C, 25 °C, 30 °C and 40 °C. 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 °C precision thermometers. As the constant of the viscometer was previously determined at Inmetro when the instrument was calibrated, the viscosity was evaluated by measuring the time with a chronometer calibrated at the National Observatory of Brazil.

Figure 1 shows an Ubbelohde viscometer used during the measurements.

### 4. OIL MEASUREMENTS

The procedures adopted [6] for oil measurements are described as follows. The fluid sample is poured into a clean beaker and the presence of air bubbles is checked. If bubbles are noticed, the beaker is covered up, protected against light, and placed on a spot free from vibration until the bubbles disappear.

Afterwards, a standard viscometer with a previously known constant is selected. Calibration of this quantity was done by starting from the viscosity of water [7] and following the procedures in the ISO 3105 [5]. The nominal value of viscosity must be taken into account when picking out the adequate viscometer.

Because of the high temperature sensitivity, small variations of the temperature of the thermostatic bath (in the order of one hundredth of °C) affect the time registered by the chronometer, which in turn influences the viscosity value of the analyzed liquid. The viscometer is immersed in a thermostatic bath until equilibrium temperature is reached. at least 30 minutes is required for thermal equilibrium. it is important to highlight once again that the bath temperature must be very stable. at Inmetro (responsible of the brazilian national viscometer standards) the temperature at which viscosity is measured does not change more than 0.005 °C.

Considering the schematic picture in figure 1, vacuum was applied to drain the fluid thru c, until around 1 cm up e mark. The vacuum apparatus was then withdrawn from the viscometer. The flow time of the samples was then measured (flow occurs by gravity) by a calibrated chronometer between marks e (beginning mark) and f (ending mark). These marks are shown in detail in Fig. 2.

The capillary through which the fluids flow allow an accuracy equal or less than 0.1 %.

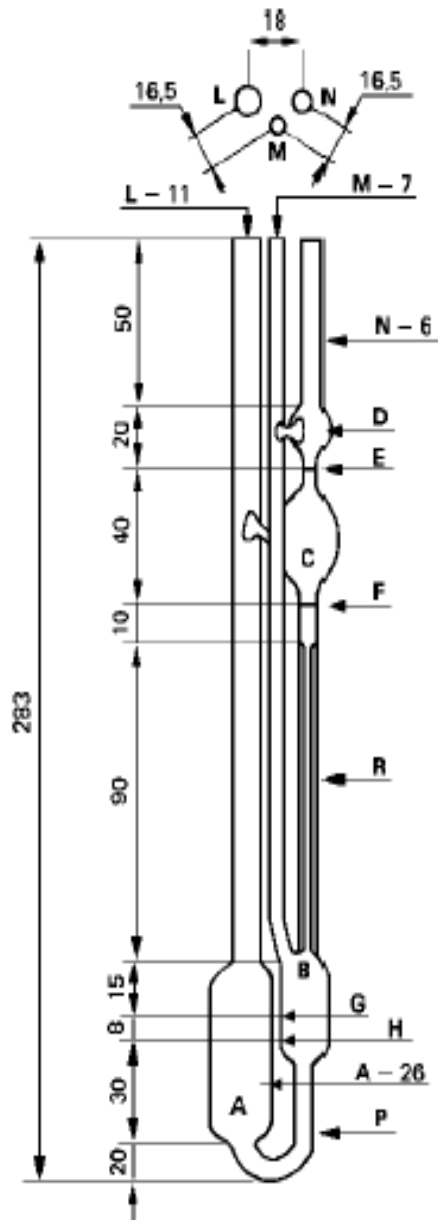


Fig. 1. Ubbelohde Viscometer

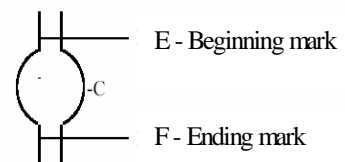


Fig 2. Measurement bulb

Flow time of samples and bath temperature during the measurements were evaluated at least five times for each reference temperature, i.e., at 20 °C, 25 °C, 30 °C and 40 °C.

The viscometers were thoroughly cleaned after the measurements.

## 5. VISCOSITY EQUATIONS

The equations to determinate the viscosity of a liquid are shown below. Viscosity is a function of the viscometer constant and of the liquid flow time, in seconds, from the top line to the bottom line of the measurement bulb (fig.2). For this study, the energy correction is considered very small, but not negligible, in spite of efflux time being higher than 200 s and below 1000s. Literature [8] indicates that it can be considered neglectible but, as it is a metrologic study, it is being considered.

$$v = f(K_1, t) \quad [1]$$

$$v = K_1 \times \left( t - \left[ \frac{0,00166 \sqrt{V^3}}{K_2 \cdot L \cdot \sqrt{K_2 d}} \times \frac{1}{t^2} \right] \right) \quad [2]$$

$$K_1 = K_2 [1 + \alpha(T_0 - T)] \times \left[ \frac{\cos \varphi_1}{\cos \varphi_2} \right] \times \left[ \frac{g_1}{g_2} \right] \times \left[ 1 + \frac{2}{g_1 h} \times \left( \frac{1}{r_u} - \frac{1}{r_l} \right) \times \left( \frac{\sigma_1}{\rho_1} - \frac{\sigma_2}{\rho_2} \right) \right] \quad [3]$$

where:

$v$  = kinematic viscosity (mm<sup>2</sup>/s);

$t$  = flowing time(s);

$K_1$  = corrected constant of the calibrated viscometer (mm<sup>2</sup>/s<sup>2</sup>);

$K_2$  = constant of the calibrated viscometer (mm<sup>2</sup>/s<sup>2</sup>);

$V$  = volume of the flowed liquid (mm<sup>3</sup>);

$L$  = length of the capillary (mm);

$d$  = capillary diameter (mm);

$g_1$  = acceleration of gravity at the measurement place (m/s<sup>2</sup>);

$g_2$  = acceleration of gravity at the calibration place (m/s<sup>2</sup>);

$h$  = hydrostatic pressure height (from E mark until B mark, according to Fig.1) (m);

$r_u$  = the inner radius of the upper tube (m);

$r_l$  = the inner radius of the lower tube (m);

$\sigma_1$  = surface tension of the measured oil (N/m);

$\sigma_2$  = surface tension of the oil used in the calibration (N/m);

$\rho_1$  = density of the measured oil (kg/m<sup>3</sup>);

$\rho_2$  = density of the oil used in the calibration (kg/m<sup>3</sup>);

$\varphi_1$  = verticality angle in the measurement (close to zero);

$\varphi_2$  = verticality angle in the calibration (close to zero);

$T$  = measurement temperature (°C);

$T_0$  = reference temperature of the viscometer (°C);

$\alpha$  = glass volumetric thermal expansion coefficient (1/°C);

## 6. VISCOSITY RESULTS

An Ubbelohde viscometer, size 1 (with a range between 1.2 mm<sup>2</sup>/s to 10 mm<sup>2</sup>/s) was used to measure the corn biodiesel. The measurements were performed at 4 different temperatures (20° C, 25° C, 30 ° C and 40° C). Results and the estimated expanded uncertainty of measurement, with 95.45 % and coverage factor of  $k=2$ .

From these results, were elaborated a characteristic curve from corn biodiesel.

The best fitting function representing the behavior of corn biodiesel (transesterified with methanol) is a polynomial fit of third degree, as follows.

$$v = -0,00004x^3 + 0,00638x^2 - 0,42333x + 14,06850 \quad [4]$$

Where:

$x$  = measurement temperature (°C);

$v$  = kinematic viscosity (mm<sup>2</sup>/s).

In most studies, the best fitting function reported is the Arrhenius ansatz or the Vogel-Fulcher-Tammann equation. [9]. This equation could be used too.

Table 1 shows the measurements and their uncertainties. For each temperature, five measurements were performed. The value is the average of then.

Table 1: Measurements and their uncertainties from corn biodiesel and diesel oil.

Temperature (° C)	Corn biodiesel		Diesel Oil	
	Value (mm <sup>2</sup> /s)	Expanded Uncertainty (mm <sup>2</sup> /s)	Value (mm <sup>2</sup> /s)	Expanded Uncertainty (mm <sup>2</sup> /s)
20	7,8381	0,0087	5,0868	0,0057
25	6,8560	0,0076	4,4673	0,0050
30	6,0449	0,0067	3,9589	0,0045
40	4,8173	0,0054	3,1694	0,0037

It is interesting to note (see Table 2) that the viscosity difference between the biodiesel oil and the diesel oil decreases when temperature is increased.

Table 2. Difference of Viscosity Between Oils per Temperature.

Temperature (° C)	Corn oil – diesel oil (mm <sup>2</sup> /s)
20	2,7513
25	2,3887
30	2,0860
40	1,6479

## 7. CONCLUSIONS

Considering viscosity, the study shows that corn biodiesel (transesterified with methanol) can be used as fuel immediately after their fabrication as a replacement for diesel oil. Nevertheless, there is still the need to study their behavior with respect to homogeneity and stability.

The curve that better represents the viscosity of the studied biodiesel is the polynomial of third degree within the investigated temperature range, and the studied biodiesel present newtonian fluid characteristic in the investigated range.

In future studies, the temperature range must be expanded to confirm the decreasing tendency of the biodiesel oil in comparison to diesel oil., and other biodiesel results will be shown.

In a metrological approach, depending on the experimental setup for the essays (thermostatic baths, thermometers and environmental conditions), the temperature change cannot be neglected however small they are. It is important to improve the estimated measurement uncertainty. As a result, there is a small change of the constant.

With regard to viscosity values, the type of biodiesel studied in the present work are in agreement with national and international laws[10][11].

## 8. ACKNOWLEDGMENTS

We thank our colleague Claudia Santos Cardoso de Castro, from mass laboratory at Inmetro, for the important contributions to this work.

## 9. REFERENCES

- [1] "LAW N° 11.097, 01-13-2005, Brazilian Federative Republic" D.O de 14.01.2005, seção 1, p. 52, v. 142, n. 10. - LEI N° 11.097, DE 13 DE JANEIRO DE 2005. República Federativa do Brasil.
- [2] J. F. Swindells, J. R. Coe, Jr., and T. B. Godfrey. *Absolute Viscosity of Water at 20 °C*. Journal of Research of the National Bureau of Standards, Vol. 48, No. 1, January 1952, Research Paper 2279.
- [3] C. Patrick Maggi, David Trowbridge, M Thomas Zubler - CCM.V-K2 Comparison Draft B rev VI December 15, 2008.

- [4] [http://kcdb.bipm.org/AppendixC/M/BR/M\\_BR.pdf](http://kcdb.bipm.org/AppendixC/M/BR/M_BR.pdf)
- [5] ISO 3105:1994 - Glass Capillary Viscometers Specification and Operating Instructions.
- [6] ASTM Designation:D446-93. Standard Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers.
- [7] ISO 3666:1998: Viscosity of Water.
- [8] Dabir S. Viswanath, Tushar K. Ghosh, Dasika H. L. Prasad, Nidamarty V.K.Dutt and Kalipatnapu Y. Rani. *Viscosity of Liquids. Theory, Estimation, Experiment, and Data*. Springer, 2007.
- [9] M.R. Cannon, R.E.Manning and J.D.Bell - *Viscosity Measurement: The Kinetic Energy Correction and a New Viscometer* – Analytical Chemistry, Vol.32, N ° 3, ACS Publications, March, 1960.
- [10] "Resolution N °7, 03-19-2008, Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP)." Available at [http://nxt.anp.gov.br/NXT/gateway.dll/leg/resolucoes\\_anp/2008/mar%C3%A7o/ranp%207%20-%202008.xml](http://nxt.anp.gov.br/NXT/gateway.dll/leg/resolucoes_anp/2008/mar%C3%A7o/ranp%207%20-%202008.xml), accessed: 01/15/2009. Agência Nacional de Petróleo, Gás Natural e Biocombustíveis, Resolução ANP n° 7, de 19.03.2008 – DOU 20-3-2008.
- [11] ASTM D 6751 - 08 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.

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