The influence of temperature on the rheology of biodiesel and on the biodiesel-glycerin-ethanol blend

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ABSTRACT. After transesterification reaction, biodiesel and glycerin (the resulting co-product), coupled to reaction excesses and impurities, make up two distinct phases that must be separated. The use of ethanol as a transesterificating agent impairs the above-mentioned separation due to the greater affinity of ethyl esters (biodiesel from ethanol) to glycerin. Current research provides an analysis of the influence of temperature on the rheology of biodiesel and the bio-diesel-glycerin-ethanol blend. Rheology behavior is highly important not merely in issues involving, for instance, discharging and pumping, but also as a factor that should be evaluated within the process of separation of the biodiesel-glycerin phases by decantation and centrifugation.

Keywords: biofuel, phase separation, rheology.

Influência da temperatura na reologia do biodiesel e da mistura biodiesel–glicerina–etanol

RESUMO. Após a reação, o biodiesel e a glicerina (subproduto formado), juntamente com excessos reacionais e impurezas, constituem duas fases distintas que precisam ser separadas. O emprego de etanol como agente transesterificante dificulta esta separação, pela maior afinidade dos ésteres etílicos (biodiesel) à glicerina. Dentro deste contexto, neste trabalho, é feito um estudo da influência da temperatura na reologia do biodiesel e da mistura biodiesel-glicerina-etanol, tendo em vista a importância deste comportamento reológico não só em problemas que envolvem, por exemplo, o seu escoamento/bombeamento, mas, também, sua importância, como um fator a ser avaliado no processo de separação das fases biodiesel-glicerina por decantação e centrifugação.

Palavras-chave: biocombustível, separação de fases, reologia.

Introduction

Biodiesel is currently highlighted in Brazilian energy scenario due to its economical, social and environmental benefits and to the country's great production potentiality.

Biodiesel, a natural substitute of the oil-derived diesel, may be employed pure or mixed to diesel in diesel-cycle engines. Diesel which is commercialized in Brazil contains 5% biodiesel (ANP, 2009).

The conventional process of biodiesel production occurs through the transesterification reaction by homogenous basic catalysis. The sub-products biodiesel and glycerin, after reaction, imbued by reaction and impurity excesses, become two distinct phases that must be separated, as a rule, by decantation. However, conversely to methanol, ethanol as a transesterificating agent impairs separation due to the great affinity of ethylic esters (biodiesel) with glycerin (GERPEN et al., 2004).

Current research is an analysis of the influence of temperature on biodiesel rheology and on the biodiesel-glycerin-ethanol mixture. Besides its

relevance to discharging and pumping, rheological behavior is a factor that should be evaluated in the separation process of the biodiesel-glycerin phases by decantation and centrifugation.

Rheological behavior is the mechanical behavior of materials within the deformation process by tension fields. Rheological characteristics are highly important in phenomena related to mass transference which occurs in industrial processes and are indispensable in the processes' optimization, control and calculation (REID et al., 1977).

A liquid's discharge characteristics are defined by its resistance to discharging which may be calculated by a capillary discharge speed or by the resistance to discharging when the fluid is sheared between two surfaces (CONCEIÇÃO et al., 2005).

Newton defined a fluid's viscosity as the resistance to the sliding of its molecules by internal friction (REID et al., 1977). The higher the internal friction of a fluid, the greater is its viscosity. According to Newton's model, the force required by a unit of area ($F\ A^{-1}$) to maintain a difference of

velocity between two parallel plates ($\frac{dv}{dx}$) is directly proportional to the gradient of velocity through the liquid, as Equation 1 shows. The coefficient of proportionality is equal to viscosity (μ). Force per unit of area is the tension of shearing (τ) and the gradient of velocity is the shearing rate (γ) – Equation 2 - (BARNES et al., 1989).

$$\tau = \frac{F}{A} = \mu \frac{dv}{dx} \qquad (1)$$

where:
    τ: shearing tension;
    F: shearing force;
    A: shearing area;
    μ: viscosity;
    $\frac{dv}{dx}$: gradient of velocity in direction x.

$$\mu = \frac{\tau}{\gamma} \qquad (2)$$

where:
    γ: shearing rate (or deformation rate).

The viscosity of a fluid is equal to the ratio between the tension and the deformation rate applied to the fluid. In the case of Newtonian fluids, ratio is a constant and viscosity does not depend on the deformation rate. Viscosity in non-Newtonian fluids depends on the applied shearing rate. Non-Newtonian fluids may be classified in pseudo-plastic (viscosity decreases with the increase in shearing rate), dilating (viscosity increases according to shearing rate), plastic (an initial tension, also known as yield stress, is required so that movement of particles may occur) and time-dependent (thixotropic and rheopectic fluids). Figure 1 shows the rheological behavior of the main types of fluid.

Several instruments are available to measure viscosity and rheology based on the principle of rotational or tubular functioning. Rotational equipments may function with stationary (constant angular velocity) or dynamic (oscillatory) shearing. The equipments basically consist of two concentric cylinders on which a shearing rate in the fluid is applied and thus the shearing tension is assessed. The opposite may also occur. As a rule one cylinder turns around its own axis whereas the other is fixed. Shearing rate (γ) is related to the variation of angular velocity according to radius (r). Shearing tension (σ) is related to torque (G), or rather, to the force per area required to trigger shearing in the fluid (KLEIN et al., 1995).
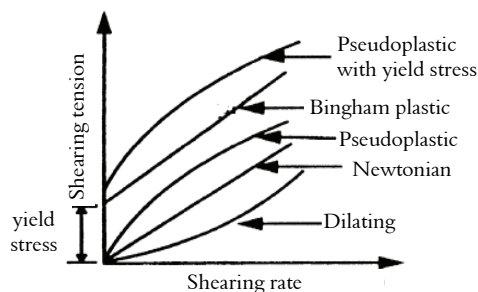

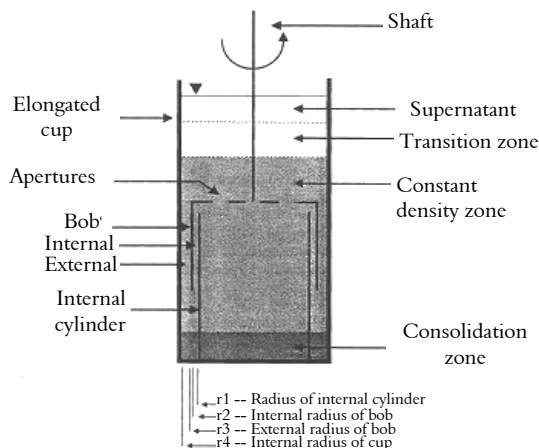**Figure 1.** Rheologic behavior of the main types of fluids (KAWATRA; BAKSHI, 1996).

Figure 2. Cup and bob fixture for rheological measures of suspensions, developed by Klein et al. (1995).

Material and methods

Preparation of samples

Two types of samples were analyzed in the experiments: pure biodiesel (B-100) and a synthesized sample, called E-3, with biodiesel, glycerin and ethanol, which corresponds to the product of the transesterification reaction. Bi-distilled glycerin and P.A. analytic-degree ethanol were also used, besides biodiesel.

Biodiesel was provided by the firm BIOLIX - Indústria e Comércio de Combustíveis Vegetais Ltda., Rolândia, Paraná State, Brazil, obtained from forage turnip oil.

E-3 composition was obtained from the stoichiometry of the transesterification reaction in which the quantity of ethanol was a reference to the use of 100% of the excess (3 mols). When the stoichiometry equation of the transesterification reaction (below) is taken into account, the blend E-3 comprised the following mass proportion: 100:10:15 of biodiesel, glycerin and ethanol respectively, obtained from the stoichiometric equation:

$$C_{57}H_{104}O_6 + 3C_2H_5OH \rightarrow 3C_{20}H_{38}O_2 + C_3H_8O_3$$
  Oil   ethanol   biodiesel   glycerin
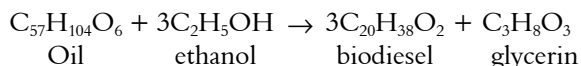
Materials

The following materials were used to determine the rheological behavior of the samples:
- Rheometer Brookfield (rotation cylinder);
- Computer linked to Rheometer;
- Thermostatic bath;
- Sample B-100 (100% biodiesel);
- Sample E-3.

Viscosity was measured in a Rotational Brookfield Rheometer LV-DV III, at a temperature range between 25 and 75ºC, at intervals of 10ºC. Computer registered data on viscosity, deformation rate and shearing tension at the temperature of the operation and thus establish the samples' rheological behavior and the relationship of viscosity to the temperature of the samples.

The specific mass of biodiesel B-100 was measured at 40ºC with an Anton-Paar densimeter 4500 to calculate the kinematic viscosity.

Results and discussion

Rheological experiments included samples B-100 and E-3. Whereas sample B-100 was analyzed to evaluate the rheological behavior of biodiesel, sample E-3 evaluated the variation of the sample's viscosity with the temperature and thus the possibility of the temperature as an influential variable in the separation process of the biodiesel-glycerin phases by decantation or centrifugation.

Figure 3 shows that rheograms, τ versus γ, constructed for pure biodiesel (B-100) and for E-3, demonstrated that qualitatively, within the temperature bands studied, the fluids behaved as Newtonian, since both had a linear relationship between shearing tension (τ) and shearing rate (γ).
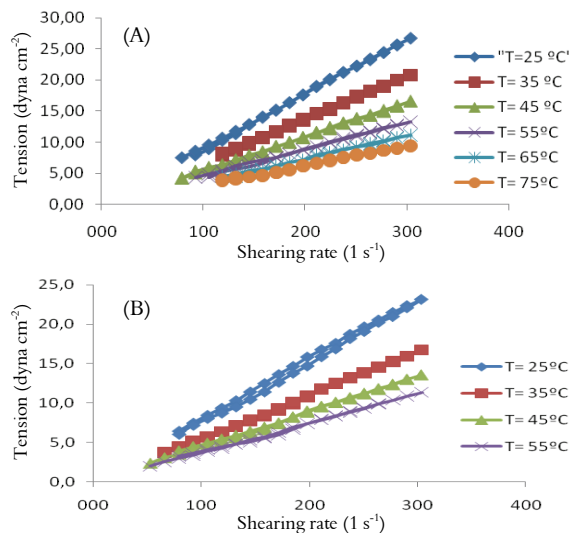

Figure 3. Rheological behavior (flux curves) of B-100 (A) and E-3 (B).

Viscosity rate was thus constant with shearing rate variations. These rates were determined by calculating the mean rate of absolute viscosity for each temperature to the shearing tensions (or deformation rate) applied to the sample. Table 1 shows the results with their respective standard deviations.

A possible source of error with regard to results of sample E-3 is the possibility of glycerin at the bottom of the cylinder, due to its greater density.

Table 1. Absolute viscosity of samples B-100 and E-3.

Temperature (ºC)	Mean viscosity (cP) ± standard deviation	
	Sample B-100	Sample E-3
25	8.86 ± 0.18	7.69 ± 0.25
35	6.84 ± 0.08	5.47 ± 0.10
45	5.41± 0.11	4.46 ± 0.15
55	4.43 ± 0.12	3.71 ± 0.12
65	3.66 ± 0.08	-
75	3.11 ± 0.09	-

Absolute viscosity of B-100 and E-3 varied reciprocally to temperature, following a polynomial non-linear dependence, as Figure 5 shows.

Table 2 shows the empirical correlation of viscosity with regard to temperature for each sample.
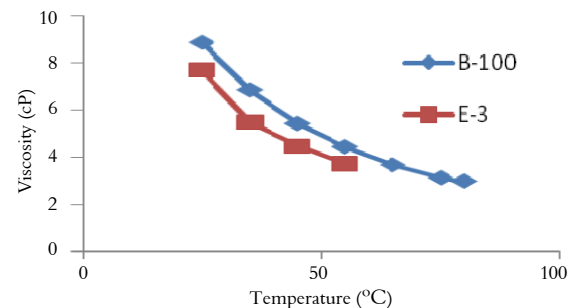

Figure 5. Effect of temperature on absolute viscosity.

Table 2. Empirical correlation of viscosity with regard to temperature of B100 and E-3.

Sample	Empirical correlation	Coefficient – R^2
B-100	$\mu = 0.001T^2 - 0.283T + 14.79$	0.998
E-3	$\mu = 0.003T^2 - 0.422T + 15.91$	0.995

Specific mass (ρ) of sample B-100 was calculated at 40ºC. Kinematic viscosity (ν) was obtained from the conceptual relationship shown in Equation 3 and absolute viscosity was obtained from the polynomial empirical correlation in Table 2 for B-100. Table 3 shows the determined rates.

$$\nu = \frac{\mu}{\rho} \tag{3}$$

Table 3. Specific mass and kinematic viscosity of B-100.

Physical characteristics (40ºC)	B-100	Allowed limits – ANP
ρ (kg m^{-3})	$875 \pm 5 \times 10^{-4}$	850 – 900
v (cSt)	$5.79 \pm 5 \times 10^{-4}$	3.0 – 6.0

Determined rates comply with allowed rates by ANP legislation for biodiesel.

Conclusion

Results show that biodiesel under analysis had a Newtonian behavior since all graphs indicate that viscosity remained constant at all temperatures, regardless of applied shearing rate, and that a linear relationship was extant between shearing tension and rate.

The blend E-3 produced similar results as those by sample B-100, or rather, a Newtonian behavior with slightly lower viscosity rates. However, difference in viscosity rates at 25 and 55ºC indicate that temperature is a factor that must be evaluated in the separation process of the biodiesel-glycerin phases by decantation or centrifugation.

Acknowledgements

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