FLOW BEHAVIOR OF DIESEL BLENDS WITH WASTE FISH OIL

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Abstract. *Oils obtained from non-fossil sources, such as animal and vegetable residue, may be employed as alternatives to burning petroleum fuels. The use of biofuels has the advantage of reducing emission of greenhouse gases in usual applications. This work presents the rheological characterization of a new alternative biofuel produced from waste fish oil (WFO), a residue of the aquaculture industry, which is obtained through a chemical silage process. The use of a byproduct also reduces the release of wastewater on the environment. Biofuels usually differ from petroleum based diesel regarding their flow behavior. Their greater viscosity is usually undesirable in injection systems of diesel engines, because it causes a great impact in spray formation and reduces combustion efficiency. Biofuels may be blended with regular diesel or warmed up in order to achieve acceptable properties. It is of great interest to have a characterization of the flow behavior of blends of various compositions and temperatures. In this work, the viscosity of diesel fuel and waste fish oil blends were studied against variations in temperature and composition. A rotational viscometer, namely Brookfield LV, was employed to perform rheological experiments. The study comprised tixotropy tests, flow curves and viscosity versus temperatures curves. From the flow curve, it was observed that the waste fish oil presented Newtonian time independent behavior. The viscosity against temperature behavior was quite well fitted employing the Andrade relation. A viscosity-temperature-composition mathematical relation was then introduced for WFO-diesel blends. Such result is fundamental in the design of heat and fuel injection systems for the use with such biofuel blends.*

Keywords*: biofuel-diesel blends; waste fish oil; viscosity measurement*

1. INTRODUCTION

According to Lin et al. (2010), fossil fuels accounted for 88% of global energy demand in 2009, with a share of 35% for oils. Also the IEO2009 – International Energy Outlook (2009), projects a use of 17 million m^3 of liquids per day in 2030. Biofuels, like ethanol or biodiesel are expected to supply almost 1 million m^3 per day in 2030. The major obstacle for widespread use of fats and oils as fuels and chemicals is the high cost of the finished products relative to petroleum (Graboski and McCormick, 1998).

Another important issue concerns "first-generation" biodiesel feedstocks. According to Lin et al. (2010), 75% is obtained from food-grade oils, threatening the economic viability of biodiesel industry, since the end cost depends on the price of the feedstock. One potential solution to this problem is employment of alternative feedstocks of varying type, quality, and cost. These feedstocks may include soapstocks, acid oils, tall oils, used cooking oils, and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae (Lin et al., 2010).

Among animal fats, stand out the ones originated from silage processing of fishing industry waste. Besides, of the total fishery production, about 50% by weight represent miscellaneous waste (viscera, fins, spine, head,...), for which the amount of oil varies from 40 to 65% (Arruda et al., 2007). Fish silage is defined as a liquid product produced from the whole fish or parts of it, to which acids, enzymes or lactic-acid-producing bacteria are added, with the liquefaction of the mass provoked by the action of enzymes from the fish (Arruda et al., 2009).

In order to replace diesel as fuel, the substitute must have similar properties, considering it will be used in the same equipments. The most important properties, according to Graboski and McCormick (1998), are related to combustion, like cetane number, flash point and heat of combustion. In a recent work, Cherng-Yuan Lin and Rong-Ji Li (2009) verified that biodiesel produced from crude fish oil shows higher cetane number, higher heating value and lower flash point than biodiesel made from waste cooking oil. Nevertheless, flow properties, as pour and cloud point, viscosity and surface tension play an important role in the viability of employing a particular fuel. These properties are also important for combustion quality due to its influence in spray formation. Considering flow properties, some studies in straight vegetable oils (SVO), animal fat, residues and its esthers have been performed to evaluate regular diesel replacement with biofuels.

Gopakumar et al. (2010) studied the properties of bio-oil produced from fast pyrolysis of pine wood and obtained a Newtonian behavior of the viscosity after a shear rate greater than 20 s^{-1} with a value higher than that of diesel fuel, but

lower than regular SVO. The viscosity decreased with temperature as expected, with a value at 30 ^{o}C 6-7 times greater than at 80 ^{o}C. Berrios et al. (2010) produced biodiesel from used frying oil and could not meet EN 14214 standards specification due to fatty acid methyl esther content and kinematic viscosity outside requirements. The kinematic viscosity upper limit is 5 $mm^2.s^{-1}$ at 40 ^{o}C and the values obtained varied from 5.13 to 5.64 $mm^2.s^{-1}$. The use of SVO is not recommended due to viscosity values much higher than diesel, although it can be lowered increasing its temperature and/or blending with diesel, according to Franco and Nguyen (2010). The study performed by these authors dealt with various straight vegetable oils, like canola, corn, olive, peanut, soybean and sunflower. The results showed that the least viscous oil (corn) is approximately 5 – 12 times more viscous than diesel when temperature is decreased from 80 to 20 ^{o}C. At 40 ^{o}C soybean oil viscosity is approximately 0.031 Pa.s, while diesel viscosity is approximately 0.0025 Pa.s. The measurements showed that the SVOs and its blends with diesel exhibit time-independent Newtonian flow behavior in the temperature range investigated (20 to 80 ^{o}C) and a simple and general model based on the Andrade viscosity mixing rule (Reid et al., 1977) was developed, which is applicable to predict blend viscosity at any temperature and composition from known transport properties of the individual pure components.

In this work, the viscosity of diesel fuel and waste fish oil blends is studied against variations in temperature and composition. A rotational viscometer, namely Brookfield LV, is employed to perform rheological experiments. The study comprises tixotropy tests, flow curves and viscosity versus temperatures curves. A viscosity-temperature-composition relationship is determined for these blends.

2. METHODOLOGY

The materials and methods employed in the present work are described in this section.

2.1. Waste fish oil production

The waste fish oil (WFO) was obtained through acid silage of filetage residues from Nile tilapia (Oreochromis niloticus), cultivated in the state of Rio Grande do Sul, Brazil. The residues (4kg) consisting of heads, spines, fins and viscera were ground and mixed to obtain a homogeneous mass. Subsequently, a 3% (v/v) mixture of propionic and formic acid in a 1:1 ratio and the antioxidant tocopherol (100 mg/kg) were added. The silage was kept at room temperature (24 ± 2 ºC) in plastic containers for 5 days at pH 4.0 and sequentially the material was centrifuged (3500 G for 30 minutes at 35 ºC), yielding 1500 mL of oily phase (WFO) and a solid phase.

The WFO was kept under refrigeration (4 ºC) in amber bottle for 07 days before the blends were prepared and the viscosity measurements were performed.

2.2. Blend preparation

In the present study, WFO-diesel blends were prepared using an analytical balance with precision of 0,1mg. Measured amounts of WFO and mineral diesel were blended in a 600 mL beaker under continuous stirring. The blends were mass based. The blends prepared were: WFO100 (100% WFO), WFO75 (75% WFO), WFO50 (50% WFO) and WFO25 (25% WFO). The notation D100 is employed herein to pure diesel.

2.3. Viscosity measurements

Before any viscosity measurement, each sample was heated in a thermal bath to a temperature of about 20 ^{o}C in order to melt any crystals that could have been formed during storage, under refrigeration.

The viscosity measurements were performed using a Brookfield LV DV-II Pro viscometer, using the Small Sample Adapter (SSA) and spindle SC4-18, as shown in Fig. 1, with diameter equal to 17.48 mm and side length equal to 31.72 mm (Brookfield, 2005). The SSA is a jacketed coaxial-cylinder accessory that can be coupled to the viscometer and is designed to give accurate results for small volume samples. When using the SC4-18 spindle, the sample size was about 7 cm^3.

The flow curve of pure WFO was obtained by measuring the sample viscosity keeping constant temperature of 45 ^{o}C and varying spindle rotation velocity from 9 to 89 RPM, which is equivalent to vary the shear rate from 11.88 to 117.48 reciprocal seconds. A tixotropy test was made using the up-down rate ramp methodology, described in Brookfield (2005). The sample was subjected to a low shear rate of 11.88 s^{-1}. Then, the shear rate was increased gradually to 117.48 s^{-1} , and after that gradually decreased back to 11.88 s^{-1}.

In the thermal behavior tests, the SSA was coupled to a thermal bath, which was used to heat the sample from about 30 ^{o}C until about 90 ^{o}C. The viscosity measurements were taken via software (Rheocalc®). The temperature interval between measurements was about 5 ^{o}C. Every test for the viscosity versus temperature curve was repeated three times, in order to check for the correctness of results and to provide statistically meaningful results.

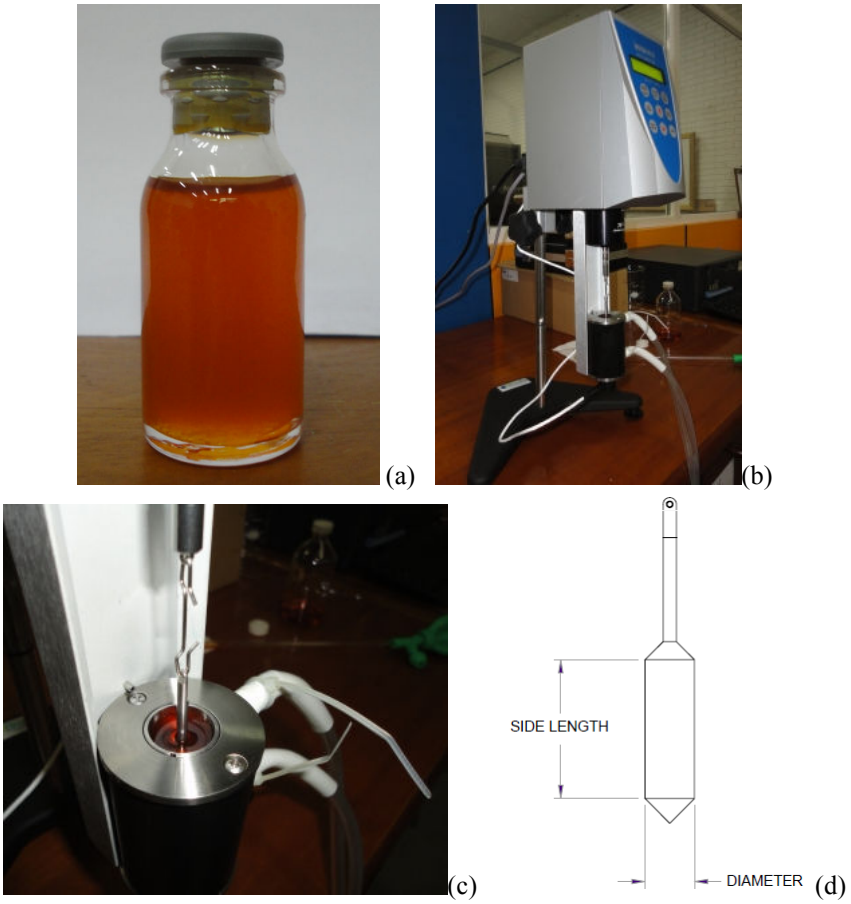

Figure 1: (a) Waste fish oil sample. (b) Viscometer and Small Sample Adapter during a test. (c) Detail of experimental apparatus during a test. (d) Spindle SC4-18, schematic view.

2.4. Data analysis

The classical correlation employed to predict the behavior of viscosity under variations of temperature for Newtonian fluids is the Andrade equation (Reid et al., 1977):

$$\mu = A \cdot e^{\left(\frac{E}{R \cdot T}\right)} \tag{1}$$

where μ is the dynamic viscosity, T is the absolute temperature, A is a constant, E is an activation energy for viscous flow (following Barnes, 2000, a measure of the height of a potential energy barrier associated with the force needed to produce elemental quantum steps in the movement of molecules) and R is the universal gas constant ($R = 8.314472 \cdot 10^{3}$ kJ/(mol K).

In order to fit experimental data employing Eq. (1), the data was algebraically manipulated, so that the coefficients A and E could be obtained by a linear fit of $\ln(\mu)$ versus $1/T$. The linear correlation coefficient, R^2, was determined for each data fit. Also, the mean relative error (MRE) was calculated by comparing experimental data with results predicted by Eq. (1) using the coefficients A and E obtained by the linear fit of $\ln(\mu)$ versus $1/T$ via the following relation:

$$MRE(\%) = \frac{\sum\left[\frac{\left(\mu_{calc} - \mu_{\exp}\right)}{\mu_{\exp}}\right]}{N} * 100 \tag{2}$$

Finally, an analysis of how the coefficients A and E varied with WFO mass concentration in each blend was performed, with the purpose of obtaining $A(w)$ and $E(w)$ functions.

All data analysis was performed using Microsoft Excel software.

3. RESULTS AND DISCUSSION

In this section the results obtained are presented and discussed.

3.1. Flow curve and tixotropy test for WFO

In order to identify the flow behavior of WFO subjected to pure shear flow, a flow curve test was performed, in which the shear rate was varied between 11.88 and 117.48 reciprocal seconds. The shear rate ramp was sequentially performed in two directions, increasing and then decreasing it, so that tixotropy effects could be noticed. The test was conducted in a fixed temperature of 40.25 ^{o}C (± 0.15 ^{o}C). The viscosity remained constant with a value around 33.38 mPa.s (± 0.39 mPa.s), in which the variations were mainly due to temperature oscillations and could not be correlated to time advance or shear rate increase or decrease. Thus, no tixotropy or shear-thinning behaviors were detected. As the pure diesel also presents Newtonian behavior, it was inferred that all blends present Newtonian behavior.

3.2. Thermal flow behavior of blends

Figure 2 shows the viscosity versus temperature behavior for the WFO-diesel blends which were studied. The experimental data points are plotted over the curves which represent results predicted using the coefficients A and E obtained via data fit. It is possible to observe that the WFO100 has greater viscosity than pure diesel. For lower temperatures (around 30 ^{o}C), this relation is about eleven times. As the temperature increases, the viscosity of WFO100 experiments a steeper decay when comparing to D100 and so, for higher temperatures (80 ^{o}C) the WFO100 viscosity is less than six times greater than D100. The intermediate blends presented intermediate behavior.

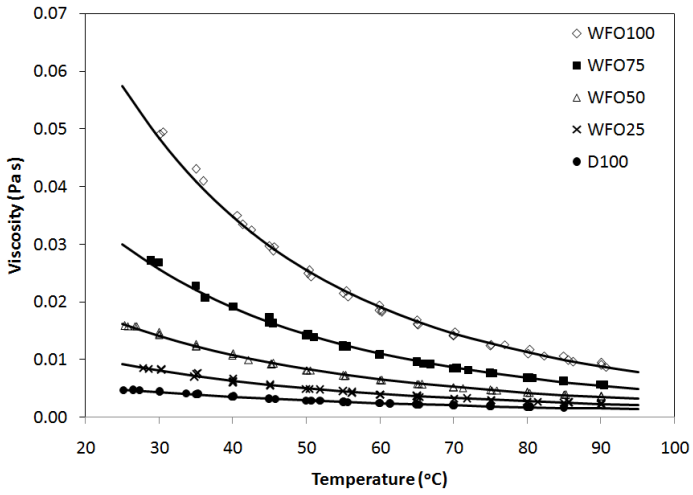

Figure 2: Viscosity of various blends plotted against temperature.

Viscosity versus temperature run tests were performed three times, and the $\ln(\mu)$ versus $1/T$ curves were fitted considering all data points, giving values of E and A in Eq. (1) for each blend. These values are listed in Table 1.

Table 1. Coefficients A and E in Eq. (1) obtained by data fitting for the various blends.

Blend	A (μPa.s)	E (kJ/mol)	R^2	MRE (%)
WFO100	1.658	25.911	0.9964	2.51
WFO75	2.194	23.613	0.9982	1.67
WFO50	3.113	21.213	0.9981	1.70
WFO25	4.417	18.940	0.9953	2.01
D100	7.283	16.118	0.9969	1.54

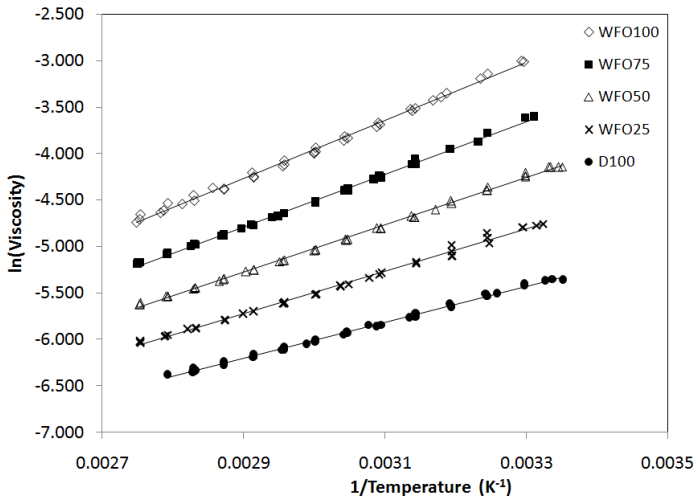

Figure 3: Logarithm of viscosity plotted against reciprocal of temperature and the tendency curves used to fit data.

The low values of MRE show that Eq. (1) fits quite well the experimental data.

The dependence of the coefficients A and E with WFO mass concentration was also studied. Figure 4 shows a plot of these coefficients against the WFO mass fraction w ($0 \leq w \leq 1$) in the blend.

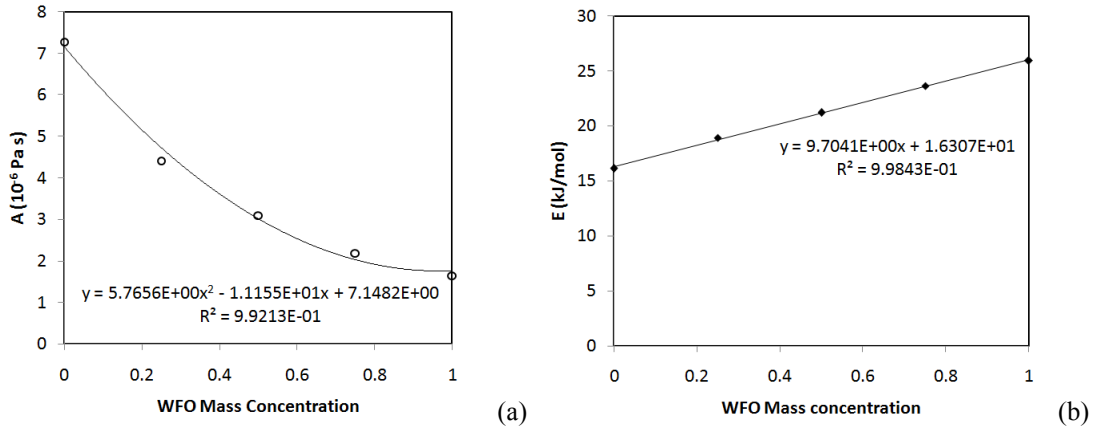

Figure 4: Data fitting of coefficients (a) A and (b) E versus WFO mass concentration.

The curve fits resulted in the following correlations for the coefficients A and E given a WFO concentration in a WFO-Diesel blend:

$$E\ [\text{kJ/mol}] = 9.7041\ w + 16.307 \tag{3}$$

$$A\ [10^{-6}\ \text{Pa s}] = 5.7656\ w^2 - 11.155\ w + 7.1482 \tag{4}$$

So, a unique correlation may be introduced in order to give the viscosity-temperature-concentration relation for WFO-diesel fuel blends:

$$\mu\ [10^{-6}\ \text{Pa s}] = (5.7656\ w^2 - 11.155\ w + 7.1482)\ *\ \exp[(9.7041\ w + 16.307)/(RT)] \tag{5}$$

where R is the universal gas constant ($R = 8.314472 \cdot 10^{-3}$ kJ/(mol K)) and T is the absolute temperature.

Although the viscosity of WFO decreased with temperature, its value at 80 °C, for example, is much higher than pure diesel. In order to meet the viscosity upper limit of 5 $\text{mm}^2\ \text{s}^{-1}$, as specified by EN 14214 standard, Eq. (5) can be used varying WFO concentration to determine the correct blend for a specific temperature. At a temperature of 80 °C, a blend of approximately 55% of WFO and 45% of pure diesel would meet the viscosity limit, while to a temperature of 40 °C less than 10% of WFO would be possible to use with diesel to keep the fuel inside the limits.

4. CONCLUSIONS

Rheological properties of waste fish oil (WFO), a non edible oil, and its blends with diesel fuel were studied as functions of shear rate and temperature. In the flow curve test, the WFO presented time independent Newtonian behavior. Viscosity against temperature data, obtained in thermal flow behavior tests, were well fitted by the Andrade equation (Reid et al., 1977). Furthermore the same Andrade equation was used to develop an empirical correlation for the blend viscosity as function of temperature and mass concentration of WFO.

It was possible to observe that pure WFO did not reach diesel viscosity at 40 ^{o}C even when heated up to 85 ^{o}C. The use of heated WFO-diesel blends might be a good choice in view that lower viscosities are achieved, and also because the current production of WFO is not very large. Although there is a limit for fuel viscosity, performance and durability studies must be made to check engine behavior in terms of power, consumption and emissions with high viscosity fuels to see if it is possible to operate the engine with straight biofuels.

5. ACKNOWLEDGEMENTS

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