High Pressure Viscosity Characterization of four Vegetable and Mineral Hydraulic Oils

Xavier Paredes[1], María J.P. Comuñas[1,*], Alfonso S. Pensado[1], Jean-Patrick Bazile[2], Christian Boned[2] and Josefa Fernández[1]

[1]Laboratorio de Propiedades Termofísicas, Departamento de Física Aplicada, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain.

[2]Laboratoire des Fluides Complexes et leurs Reservoirs (UMR-5150 with CNRS and TOTAL), Université de Pau et des Pays de l'Adour, BP 1155, F-64013 Pau Cedex, France.

*Corresponding author. Tel.: 34-881814046; fax: 34-981520676. Email: mariajp.comunas@usc.es

ABSTRACT

In the long term, environmental friendly oils from renewable sources seem to be the more realistic path to a sustainable future for the industry regarding the lubrication issue. Vegetable bases for lubricants have been studied in the last decade in order to analyze their potential industrial applicability. Their strengths and weaknesses are already known and thus, the next step is to study how the final mixture of vegetable base plus additives might perform in comparison to lubricants used in actual machinery. Here, we present the results obtained for the viscosity behavior of two hydraulic mineral oils and two vegetable oils formulated to substitute the mineral based ones. The measurements were taken at three temperatures: 313.15 K, 343.15 K and 363.15 K and at pressures up to 250 MPa using a high-pressure falling-body viscometer. To address the performance of these oils in the elastohydrodynamic lubrication regime, we also calculate the universal pressure-viscosity coefficient, α_{film}, and the temperature-viscosity coefficient, β.

1. Introduction

Liquid lubricants are used across all industrial sectors, and thus, at a global scale, advances in this field can have major economic and environmental impacts. Boyde (Boyde, 2002) investigated the issue, concluding that the primary objective should be improving the performance and energy efficiency delivered by new oil formulations, thus advocating for, essentially, a widespread use of synthetic basefluids together with better additives to attain longer life cycles for the machinery and extended periods of time between oil changes. Mineral (petroleum) based oils remain as the prominent actors on a global scale due to them being readily available and their lower cost. Some exceptions can be found in highly specialized applications that mainly use synthetic lubricants. Further, synthetic lubricants have been also slowly gaining terrain over mineral based lubricants in every sector when the specialists consider that the premium price paid for them is outweighed by their advantages, usually making them cheaper in the long run. However, environmental and availability concerns have shifted the interest of researchers and legislators towards vegetable based lubricants (van Dam et al., 2005), characterized by their biodegradability and by being obtained from renewable sources. Particularly in the European Union, the Ecolabel initiative regarding lubricants (2011), establishes certain criteria that should be met in order for a lubricant to be awarded this certification, among them, they should exceed a minimum amount of material from a renewable source and a minimum biodegradability, the absence or a maximum quantity of some toxic substances, among other requisites.

Vegetable bases present their own advantages like high viscosity index, high lubricity and low volatility among others, and disadvantages like their use in only reduced temperature range (high pour point and low thermal stability) or their mediocre viscosity range. Of course, these problems arise from their chemical structure. Vegetable oils obtained from crops are comprised of polyunsaturated fatty acids, mono-unsaturated fatty acids and saturated fatty acids in varying proportions depending on the plant of origin. It is this varying proportion of the different fatty acid compounds what confers each vegetable base with a higher or lower pour point, a better or worse lubricity and so on. For example, oils with a high level of oleic acid provide better oxidation stability although at the expense of poor cold flow properties. The oxidation stability being one of the main concerns, has been studied extensively (Erhan et al., 2006; Fox and Stachowiak, 2007). Over the years, various approaches have been taken to overcome these problems: chemical functionalization, genetic modification and mixing or additivation. Regarding chemical functionalization (Erhan et al., 2005), a more thermostable product can be obtained by means of alkylation, arylation, cyclization, hydrogenation, epoxidation (Campanella et al., 2010; Pan et al., 2011; Salih et al., 2011), and other reactions (Biswas et al., 2007) or the oil obtained from the plant can be used to produce a variety of polymers (Xia and Larock, 2010). Genetic modification corresponds to a direct modification of the DNA of the plant, giving birth to a new variety of the crop with a new desirable characteristic (Dietrich et al., 2005). The addition of antioxidants and pour point depressants can drastically improve the high and low temperature properties of a vegetable base (Schneider, 2006). Another way to enhance the properties of these bases is mixing them with other (usually synthetic) compatible bases with better oxidation and low temperature characteristics (Asadauskas and Erhan, 1999; Bantchev and Biresaw, 2012; Quinchia et al., 2012; Quinchia et al., 2011).

A fluid appropriate for its use in hydraulic applications should have low compressibility to transmit power efficiently and good lubricity and antiwear properties to avoid damages to the equipment. It should also have a high viscosity index and the adequate viscosity and pressure-viscosity coefficient to form the protective layer expected from a proper lubricant. A number of studies have been published that analyze the performance of vegetable derived oils in test rigs and field trials (Adamczewska and Wilson, 1997; Honary, 1996; Remmele and Widmann, 1999; Sivasankaran et al., 1988; Šraj et al., 2000; Vižintin et al., 2000) but, as far as we know, there are not many authors that investigate the film-forming capability of vegetable based lubricants, be it by direct measurement of the viscosity at high pressure (Mia et al., 2007), be it by way of interferometry, obtaining the pressure-viscosity coefficient from the measured film thickness and viscosity at atmospheric pressure at a given temperature (Biresaw and Bantchev, 2013). In this article, high pressure viscosity data are presented and used to address the viscosity behavior from 313.15 K to 363.15 K and up to 250 MPa, of four hydraulic fully formulated lubricants, two of them of mineral origin and the other two developed from high oleic sunflower oil to replace them. In this work we study how their viscosity changes with temperature and pressure. From these measurements the pressure-viscosity coefficient is obtained. With this information, it is possible to examine how the newly formulated vegetable oils fare against the in-use mineral oils in order to investigate how well they would perform as a biodegradable renewable alternative.

2. Material and methods

2.1. Materials

The four samples studied in this work are named following the nomenclature used in a previous article (Regueira et al., 2011), we name the mineral oils as MIN-H01 and MIN-H02, these two being aliquots of those in the previous paper, and the vegetable oils as BIO-H01 and BIO-H02, so that BIO-H01 would be the substitute for MIN-H01 and BIO-H02 for MIN-H02. MIN-H01 is a group I oil as per the classification of the American Petroleum Institute, whereas MIN-H02 is a base from group II with mainly viscosity improvers. MIN-H01 is actually used in the hydraulic circuits for direction, elevation and auxiliary services in small tractors. MIN-H02 is being used for blade orientation, rotor braking and nacelle rotation braking in wind turbines. BIO-H01 is a mixture of 83.5% high oleic sunflower oil (HOSO) and 13.5% ditridecyl adipate whereas BIO-H02 is a blend of the same HOSO at 73% and 24% of diisooctyl adipate. The concentration of the free fatty acids of HOSO has been determined by the company Verkol Lubricantes by using ISO660:2009 method obtaining a value of 0.03% expressed as oleic acid. Both BIO-H01 and BIO-H02 use the same additive package consisting of a pour point depressant, an anti-wear additive and a rust and oxidation inhibitor. They differ in the proportion of ester added to each of them to mainly adjust their viscosity. Information about tribological tests, biodegradability and toxicity, seal compatibility and other analyses like the pour point (– around 27ºC in both cases) for BIO-H01 and BIO-H02 have been already published by Mendoza et al. (Mendoza et al., 2011) where BIO-H01 corresponds to BIOGIR-06 and BIO-H02 to BIOGIR-04. These authors also determined, by using ASTM 2274, the acid number of both oils, being 0.78 mgKOH/g for BIO-H01 and 0.71mgKOH/g for BIO-H02.

The new lubricants based on high oleic sunflower oil (83% of oleic acid) had to comply with the Ecolabel standard for lubricants (2011) considered compatible with the environment. That means some limitations as to the components that can be added to the base to keep the final mixture environmentally friendly, a minimum concentration of vegetable base oil and the technical requirements that the formulated oil has to pass depending on the industrial application. For example, in the present case (hydraulic fluids), the final product must have at least a 50% of carbon content derived from renewable raw materials and at least the technical performance criteria as laid down in the current standard ISO 15380.

2.2. Methods

Viscosity η_0 at atmospheric pressure was measured with a rotational automated viscometer Anton Paar Stabinger SVM3000. It is based on a modified Couette principle with a rapidly rotating outer tube and an inner measuring bob that rotates at a slower velocity. The viscosity uncertainty is lower than 1% (Paredes et al., 2009). This equipment has a built-in function to determine the viscosity index according to ASTM D2270 standard. Viscosities at high pressure were measured using a falling body viscometer, VisLPT2 that can operate at pressures up to 280 MPa. This viscometer is similar to the one previously used by Boned and co-workers (Daugé et al., 2001), and the VisLPT1 equipment at our laboratory (Gaciño et al., 2012). The main differences with VisLPT1 lie in the method for pressurizing the sample, which, in this case, is achieved through a pneumatic pump; and the use of two coils instead of four to detect the passing of the falling body, also, as the liquids under study are not particularly hydrophilic, we use a funnel to fill the system. Fig. 1 shows a schematic of this apparatus. The measuring principle is based on the determination of the time (Δt) that a solid takes to travel a fixed distance through a fluid, under conditions of terminal velocity and laminar flow, which is linked to its viscosity (η). The reader will find detailed discussion concerning our device in a previous article (Gaciño et al., 2012). This imposes an upper limit to the Reynolds number that needs to be checked for every fluid. The way to determine it has been already fully explained in a previous article (Gaciño et al., 2012). For all four liquids studied in this work the Reynolds number falls well behind that limit under our measurement conditions. We have also used the same calibration procedure than in our previous work (Gaciño et al., 2012) and so, the estimated experimental uncertainty for the dynamic viscosity with this particular set-up is of 5%.

In order to verify the calibration procedure, we measured the falling times for squalane at the same temperatures and pressures. The density values needed to determine the viscosity of this fluid were taken from a correlation published by Ciotta et al. (Ciotta et al., 2009). Our viscosity data for squalane were correlated as a function of the pressure (p) and the temperature (T) with the following modified Vogel–Fulcher–Tammann equation proposed by Comuñas et al. (Comuñas et al., 2001):

$$\eta(p,T)=A\left(\frac{p+E}{p_{ref}+E}\right)^{D}\exp\left(\frac{B}{T-C}\right) \tag{1}$$

where

$$E=E_0+E_1T+E_2T^2 \tag{2}$$

The parameters A, B and C have been determined in a preliminary fit of the viscosity as a function of the temperature at the reference pressure in this case p_{ref} = 0.1 MPa. Coefficients D, E_0, E_1 and E_2 have been fitted to the viscosity measurements for pressures higher than 0.1 MPa. The average absolute deviation (AAD) of the correlation to our experimental data is of 1.0%. From this fit, we calculated the viscosity at the pressures and temperatures given in the literature references of squalane (Bair, 2006; Bair et al., 2002; Ciotta et al., 2009; Harris, 2009, 2011; Hata and Tamoto, 2010; Kumagai et al., 2006; Kuss and Golly, 1972; Pensado et al., 2006; Tomida et al., 2007) and within the range of applicability of our data. The relative deviations obtained are plotted in Fig. 2 where it can be seen that the majority of the data show relative deviations lower than 4%.

3. Results and discussion

In Table 1 we present the viscosity data at atmospheric pressure for BIO-H01 and BIO-H02, those for MIN-H01 and MIN-H02 can be found in a previous publication (Regueira et al., 2011). As it can be seen in Fig. 3, the lubricants with the vegetable base show a gentler dependence with temperature than the corresponding mineral based ones. Thus the viscosity variation with temperature is higher for MIN-H01 than for BIO-H01 and for MIN-H02 than for BIO-H02. Although at low temperatures the viscosity of the new lubricants is lower to its counterpart, as temperature rises, the situation is inverted. This is due to the high viscosity index of the vegetable oils, BIO-H01 (198) and BIO-H02 (205), compared with mineral lubricants MIN-H01 (144) and MIN-H02 (138).

We measured the falling times that the sinker takes to fall through the four lubricant samples (MIN-H01, MIN-H0, BIO-H01 and BIO-H02) at three temperatures: 313.15 K, 343.15 K and 363.15 K and pressures up to 250 MPa. To determine the viscosity we need to know the density of the four oils at the same temperatures and pressures that our viscosity measurements are taken. The density of the four liquids has been previously determined at our laboratory (Regueira et al., 2008; Regueira et al., 2011) with an Anton Paar HPM vibrating tube densimeter up to 60MPa and from 278.15 to 353.15 K for BIO-H01 and BIO-H02, and from 298.15 to 373.15 K for MIN-H01 and MIN-H02. Regueira et al. (Regueira et al., 2008; Regueira et al., 2011) have correlated these density values using a Tamman-Tait equation against temperature and pressure with standard deviations lower than $7 \cdot 10^{-5}$ $g \cdot cm^{-3}$. This is the equation we use to obtain density at the same temperatures and pressures that our viscosity measurements are taken. Using those correlations means we have to extrapolate some of the density data from 60 MPa to 250 MPa but this fact leads to an error significantly small compared with the overall viscosity uncertainty estimated for the apparatus. In Table 2, we show the viscosity obtained at different pressures. It can be seen that no data is shown at low pressures and some temperatures, as the falling time measured at those points was considered too short. We present in Fig. 4 the viscosity versus pressure at the 343.15 K isotherm for the four fluids. Like what happened with the temperature dependence at atmospheric pressure, the mineral oils present a steeper dependence with pressure than the vegetable oils to the point that even the less viscous of the mineral lubricants reaches viscosity values superior to the most viscous of the vegetable based ones. This behavior also occurs at the other two temperatures measured. The dependence of the viscosity with pressure is then MIN-H01 > MIN-H02 > BIO-H01 > BIO-H02.

In order to interpolate the value of the viscosity at temperatures and pressures not directly measured with our equipment, but within the range considered in this study and also to obtain the derived properties of the viscosity for these liquids, it is necessary to fit the obtained results to an equation that accurately follows the measured experimental points. After testing a number of expressions, we have decided to employ five different equations which will allow us to also find out the variations one might encounter on the derived properties owing to distinct dependencies. The first one is the same equation used to check the calibration of the viscometer, Eq. 1, that involves seven parameters and represents the variation of the viscosity with pressure mainly through p and a second degree polynomial in T. The second one, also a modified VFT equation, has eight parameters and employs a third degree polynomial in pressure to correlate the data:

$$\eta = A\exp\left(a_1\Delta p + a_2\Delta p^2 + \frac{B + b_1\Delta p + b_2\Delta p^2 + b_3\Delta p^3}{[T - C]} \right) \tag{3}$$

where $\Delta p = p - p_{\mathrm{ref}}$, with the reference pressure, $p_{\mathrm{ref}} = 0.1$ MPa. Parameters A, B and C are those used in Eq. 1. Eq. 3 corresponds to a small modification of a relation employed recently by Harris (Harris, 2009) (through the use of Δp rather than p). Ducoulombier et al. (Ducoulombier et al., 1986) and Paredes et al. (Paredes et al., 2012b) have used very similar equations in the past. Coefficients a and b_i have been fitted to the viscosity measurements for pressures higher than 0.1 MPa. The third one is a revised Yasutomi (Yasutomi et al., 1984) correlation recently published by Bair et al. (Bair et al., 2013) that relies in the following expressions:

$$\eta = \eta_g \, exp\left[\frac{-2.303 C_1 \left(T - T_g\right) F}{C_2 + \left(T - T_g\right) F}\right] \tag{4}$$

where T_g is the glass transition temperature which varies with the pressure p as

$$T_g = T_g^0 + A_1 \ln\left(1 + A_2 p\right) \tag{5}$$

and the function F is given by

$$F = \left(1 + f_1 p\right)^{f_2} \tag{6}$$

In Eq. 6 lies the improvement over the original model. This new function for the relative thermal expansivity of the free volume avoids a non-physical behavior encountered with the previous expression, achieving a more reliable representation of the viscosity. Eq. 6 has been proposed for pressures higher than those investigated in this work, although Bair et al. have observed that it represents better than the original Yasutomi equation the viscosity, even at low pressures. As expected, other parameter values will be obtained if a wide pressure range is considered in the fitting procedure. This is also the case of equations 1 and 3.

Finally, the fourth and fifth equations used in this work come from the so-called viscosity scaling. It has been already shown for a fair amount of liquids (Lopez et al., 2011; Pensado et al., 2008), that it can be established a relation of the kind $\eta(T,v) = f(Tv^{\gamma}) = f(T/\rho^{\gamma})$ where $v=1/\rho$ is the specific volume. The value of γ reflects the strength of the interactions occurring in the liquid and the lower the value, the greater the interacting forces. We correlated the viscosity data of the four liquids as a function of temperature (T) and density (ρ) through the expression:

$$\eta(T,\rho) = A_S \, exp\left(\frac{B_S \, \rho^{\gamma}}{T}\right)^{\phi} \tag{7}$$

where $A_{S,}$ B_S, γ and ϕ are adjustable parameters, which can be obtained from viscosity data at different temperatures and densities.

Several authors have proposed to use the reduced viscosity (η^*) (Fragiadakis and Roland, 2011) or the residual reduced viscosity (Galliero et al., 2011). In this article we have used:

$$\eta^* = \rho^{-2/3} m^{1/6} \left(k_B T\right)^{-1/2} \eta \tag{8}$$

where m is the molecular mass and k_B the Boltzmann constant. As we do not know the molecular mass for these liquids, we can leave out the constant quantities altogether:

$$\frac{\eta^*}{m^{1/6} k_B{}^{-1/2}} = \rho^{-2/3} T^{-1/2} \eta = A_S{}^* exp\left(\frac{B_S{}^* \rho^{\gamma^*}}{T}\right)^{\phi^*} \tag{9}$$

In this manner, when the viscosity is plotted against the quantity ρ^γ/T all the points fall into a master curve for each liquid as it can be seen in Fig. 5. $A_S{}^*$, $B_S{}^*$, γ^* and ϕ^* are fitting coefficients.

The parameters and relative deviations obtained for these five equations are presented in Table 3. Among the selected models, the one that overall better correlates the experimental data is the modified VFT equation with a third degree polynomial in pressure (Eq. 3). From Table 3, we can see that the γ values range from 4.1 to 4.8 and the γ^* from 3.5 to 4.2 for the four oils studied in this work. This reduced scaling coefficients γ^* are slightly lower than the γ values because as the viscosity decreases when the temperature increases, the product $\eta T^{-1/2}$ decreases more rapidly, so the effect of temperature on the reduced viscosities is stronger than on the actual viscosities. The factor $\rho^{-2/3}$ does not affect the γ^* values to any significant degree (Fragiadakis and Roland, 2011; Lopez et al., 2011). The vegetable oils exhibit a lower γ (and γ^*) than the mineral oils, probably owing to the dipole-dipole interactions present in the former.

The γ values obtained are similar to those found previously for other viscous fluids. Harris (Harris, 2009) obtained a value of 4.16 for squalane, 3.69 for 2-ethylhexylbenzoate, 3.65 for di(2-ethylhexyl) phthalate and 3.96 for disodecylphthalate. Paredes et al. (Paredes et al., 2012a; Paredes et al., 2010) have found values around 4.1 for di(2-ethylhexyl)sebacate and two poly(propylene glycol) dimethyl ethers, respectively. Roland et al. (Roland et al., 2006) proposed a value of 3.2 for dibutylphthalate. Fandiño et al. (Fandiño et al., 2007) obtained values of γ from (3.1 to 5.4) for pentaerythritol esters.

We have also determined the pressure-viscosity (α) and the temperature-viscosity (β) coefficients. The expressions for these coefficients are essentially derivatives of the viscosity:

$$\alpha = \left(\frac{\partial \ln \eta}{\partial p}\right)_T = \frac{1}{\eta}\left(\frac{\partial \eta}{\partial p}\right)_T \tag{10}$$

$$\beta = -\frac{1}{\eta}\left(\frac{\partial \eta}{\partial T}\right)_p \tag{11}$$

In this manner, one must resort to a model that allows for this kind of calculation, since the experimental measurements are too spaced to enable a numerical determination of the derivative. Having three different correlations, it is possible to compare the results yielded by each one of them. In Table 4 and Fig. 6, some of the values obtained for α are presented. In general, it can be observed that at the same temperature α is lower for the formulated vegetable oils than the corresponding mineral oils, regardless of the equation used to calculate them. Fig. 6a has been made with the results obtained from Eq. 1 still, if it had been made with any other of the equations, the gap between mineral and vegetable oils would have been approximately the same. Notable discrepancies can also be seen, that can go up to 25%, when comparing among the different results retrieved for the same liquid but with different equations. The general trend showed in Fig. 6b for MIN-H01 also occurs for the rest of the liquids, with the scaling equations displaying a smooth slope when compared to the Comuñas et al. (Eq. 1) and Yasutomi models (Eq. 4). Thus, the final outcome is highly dependent on the model. Mia et al. (Mia et al., 2007) have also estimated the pressure-viscosity coefficient for several vegetable oils by using the Barus equation finding values around 8.10 for olive oil at 313.15 K.

The determination of the temperature-viscosity coefficient from Eq. 11 however, does not yield quite the same trends. A gap exists between mineral and vegetable based oils as can be seen through Table 5 and Fig. 7a, and there can be notable differences for the same liquid at the same temperature among the values obtained from the five equations as showed in Fig. 7b. The relative positions of the curves given by the values obtained with Eqs. 1 and 4, from 313.15 to 363.15 K, are swapped, being the turning temperature around 343.15 K.

We have also evaluated the reciprocal asymptotic isoviscous pressure α^* from Blok (Blok, 1963) and the universal pressure-viscosity coefficient α_{film} defined by Bair (Bair et al., 2006), results are shown in Table 5. These coefficients can be used to estimate the lubricant dependent factor of the film thickness it may provide in the elastohydrodynamic regime. The equation for α_{film} is

$$\alpha_{film} = \frac{1-\exp(-3)}{p_{iv}\left(3/\alpha *\right)} \tag{12}$$

being p_{iv} the isoviscous pressure given by

$$p_{iv}(p) = \int_0^p \frac{\eta(p'=0)dp'}{\eta(p')} \tag{13}$$

and α^* the reciprocal asymptotic isoviscous pressure

$$\alpha^* = \frac{1}{p_{iv}(\infty)} = \left[\int_0^\infty \frac{\eta(p=0)dp}{\eta(p)}\right]^{-1} \tag{14}$$

What can be seen from Table 6 is that mineral oils display a higher pressure-viscosity coefficient than the vegetable oils, in line with the more pronounced dependence of the viscosity with pressure for the mineral oils. Regarding the different values obtained upon using the other equations, the biggest deviation in α_{film} (at about 13%) appears in MIN-H01 between the value obtained with the Yasutomi model and the thermodynamic scaling at 313.15 K. Halving the maximum difference encountered for Blok's definition of α. The bulk of the disparities in the values determined through the various models is actually built up within the measurement range, i.e. it is not so much an extrapolation artifact as it is a consequence of the different results of the diverse functional forms used in the measurement interval. Making calculations, most of the final value of α^* for example (around 85 to 98% of the values of the integral Eq. 14), comes from the integration up to 250 MPa which is our measurement range. This probably means that one could reduce these differences measuring at more pressures within the range considered, thus making less important the correlation used as whatever it is, it should follow more closely the actual viscosity-pressure curve of the lubricant. However, falling body viscosity measurements tend to be lengthy and the more pressure points measured the longer it takes to carry them out. We must mention here that for temperatures higher than those studied in this work a pressure of 250 MPa is insufficient for the integral in equation 14 to converge. The values obtained for the formulated vegetable oils studied in this work are just slightly higher than those presented by Bantchev and Biresaw for a pure high oleic sunflower oil (Bantchev and Biresaw, 2012), determined by means of film-thickness measurements, or through Barus or Bair pressure-viscosity coefficients. The existing expressions for the central thickness of a lubricant film under EHL can be expressed with the functional form:

$$h_{cent} = k\eta_0^a\alpha^b \tag{15}$$

Where k is a constant dependent on the surface geometry, the applied load, the elastic parameters of the contact elements and the entrainment speed, η_0 is the viscosity of the lubricant at atmospheric pressure, α is a pressure-viscosity coefficient and a and b are values that usually range between 0.4 and 0.8 with $a > b$. Written like this, it becomes clear that maintaining the load and entrainment speed in the same machine, lubricants with different viscous properties will generate films with different thicknesses and that changes in viscosity will have a greater impact than an equal change in the pressure-viscosity coefficient. To showcase the different response in film thickness of the liquids studied in this work, we have selected 0.69 for coefficient a and 0.56 for b, which correspond to an equation from AGMA (American Gear Manufacturers Association) based on a mathematical estimation (Errichello, 2004). It should be noted though, that the superscripts for η_0 and α vary ever so slightly depending on the author or the geometry. We should warn the readers that the film lubricant formulas have not been fully validated. More information regarding this matter can be found in the literature articles from Bair and his colleagues (Bair, 2012, 2014; Bair et al., 2009; Kumar et al., 2010), who using EHL simulation try to reconcile film-thickness formulas, like eq. 15, by choosing an appropriate definition of the pressure viscosity coefficient, α, which should be determined from viscosity measurements in an appropriate pressure range. To accomplish this task accurate film-thickness measurements are needed.

We have chosen the universal pressure-viscosity coefficient α_{film} definition as α in eq.15, because it is adequate in the case of liquids with exponential viscosity pressure behavior, like the mineral and vegetable oils (Kumar et al., 2010; Liu et al., 2006). The results obtained using $\eta_0^{0.69}\alpha_{film}^{0.56}$ for the four oils are plotted in Fig. 8. As it can be seen the film thickness provided by newly formulated oils is lower to that of their counterparts in the range considered. Although as expected, when approaching the upper values of the temperature interval considered here, their values draw nearer owing to the higher viscosity index of the vegetable oils. At these high temperatures, the difference in the thickness attained by each pair of fluids (one mineral and its vegetable substitute) can be almost entirely attributed to the notable gap in their respective α_{film} values, with the mineral oils showing values 32 % to 50 % higher than their formulated replacements. This is because the viscosities at atmospheric pressure (Regueira et al., 2008; Regueira et al., 2011) for each pair of lubricants get closer to each other as temperature raises to a point where they are swapped at around 310 K for BIO-H02/MIN-H02 and 340 K for BIO-H01/MIN-H01. At even higher temperatures than those studied here, we would expect the film thickness from the new oils to be larger than that provided by the mineral lubricants but for the applications they are intended, 363 K seems to be more than a fair upper limit for the temperature.

Different authors (Errichello, 2004; Perry et al., 2006; Spikes, 1990) have shown that fluids with higher pressure-viscosity coefficients provide better protection at extreme pressures, as long as the fluids being compared have about the same viscosity. However, in order to minimize wear, not only the lubricant layer has to be thick enough to prevent contact between asperities, but the pressure peaks should be not too high so as to avoid sub-surface stress resulting in the apparition of pitting (Cardoso et al., 2009; Hoglund, 1999; Larsson et al., 2001). Better efficiency also requires lower friction. Lubricants with low pressure-viscosity coefficients are preferable to decrease friction, sub-surface stress and pressure peaks (Hoglund, 1999; Larsson et al., 2001).

From Eq. 14, the film thickness is proportional to the viscosity at atmospheric pressure, thus a more viscous lubricant will generate a thicker layer but at the same time more internal friction. These problems are all well known within the tribology community. There is just no perfect lubricant and one can only hope to choose the best one for a given application. This election has to take into account the material of the lubricated parts, if it is resistant against friction or pressure peaks, or if it has a good smooth finish for example. The general agreement indicates that it is better to have a thicker film than risking boundary lubrication although that might mean less efficiency, but only a little less efficiency so the protective layer cannot be too thick. What seems to be clear is that regardless of the use of the lubricant, it is desirable that the product $\eta_0^{0.69}\cdot\alpha_{film}^{0.56}$ (or the almost identical $\eta_0^{0.69}\cdot\alpha^{*0.56}$) would change as little as possible within operating temperature. That requisite is better accomplished in this study by the vegetable based oils as it can be seen in Fig. 8, thanks mainly to their high viscosity index. Regarding the possibility of the thickness of the film not being sufficient in order to protect the moving parts, friction and fatigue tests (Mendoza et al., 2011) made by other partners in the research project indicate that the protection provided by the new formulated oils is satisfactory. This suggests that the mineral oils in use might be generating a film thicker than necessary and thus diminishing the efficiency of the machinery. That is particularly interesting for hydraulic systems because moving less viscous liquids through the pipes requires less energy. Finally, in order to compare the quantity $\eta_0^{0.69}\cdot\alpha_{film}^{0.56}$ when possible, it should be performed between values determined with the same equation. The greatest difference in the product $\eta_0^{0.69}\cdot\alpha_{film}^{0.56}$ between two correlations for a given liquid occurs for MIN-H01 at 313.15 K obtaining a deviation of 7% between Eq. 4 and Eq. 7. This could be particularly important when differences are especially narrow but, the deciding factor about what lubricant to choose would probably rest upon other factors like oxidative stability, low temperature properties and so on depending on the application.

4. Conclusions

The viscous behavior of four lubricants has been analyzed for pressures up to 250 MPa between 313.15 K and 363.15 K. The viscosity values obtained were correlated with five different equations and used to obtain coefficients that characterize the behavior of those oils with temperature and pressure. By comparing the values of the coefficients obtained from the diverse equations, it becomes apparent that great care must be taken when evaluating coefficients dependent upon derivatives of the functions used to fit viscosity data, as considerable variations can occur. If α^* or α_{film} are to be evaluated, the differences in the values obtained reduce considerably but, when possible, comparisons should be made with estimates coming from the same equation. Looking at the scaling relations, the oils with vegetable bases show stronger interactions than their mineral counterparts. That is probably due to the presence of dipolar interactions in the esters of the triglycerides. The results presented for the film thickness evaluation show that the vegetable based oils provide a thinner protective layer than the mineral based ones. If too thin, this would lead to increased friction and wear due to metal – metal contact however, tribology essays and data of actual usage indicate that this is not the case. Looking at the behavior of the four liquids, it can be safely said that the oils with a vegetable base should offer better energy efficiency due to the thinner protective layer they grant specially at low temperatures. The advances made so far in the field of lubricants obtained from renewable, readily available materials are encouraging. Although as of now, they are mainly used in niche applications, the research and development efforts put into them have started showing good results in different, more ample applications. By addressing and correcting their drawbacks, not only more environmentally friendly lubricants can be attained from an ecological point of view (precedence and biodegradability) but also from a performance point of view (extended cycle of life of the machinery).

Acknowledgements

This work was carried out within the framework of the strategic and singular project “Biolubricants based on vegetable oils and their synthetic derivatives”, funded by Spanish Science and Innovation Ministry and the EU FEDER program (PSE- 320100-2006-1, PSE-420000-2008-4). We are very grateful to Verkol Lubricantes company for their excellent advice and for providing us the samples of the products, as well as the free acid concentration of vegetable oils. Authors acknowledge Dr. Antoine Baylaucq for his guidance with the experimental technique.

List of symbols

a_i	parameters of modified VFT equation (eq. 3)
A	coefficient of modified VFT equation (eq. 1)
A_i	coefficient of modified VFT equation (eq. 4)
A_S	coefficient of the scaling equation (eq. 7)
A_S^*	parameter of scaling equation for reduced viscosity (eq. 9)
α	local pressure-viscosity coefficient
α^*	reciprocal asymptotic isoviscous pressure coefficient
α_{film}	universal pressure-viscosity coefficient
b_i	parameter of modified VFT equation (eq. 3)
B	coefficient of modified VFT equation (eq. 1)
B_S	coefficient of the scaling equation (eq. 7)
B_S^*	parameter of scaling equation for reduced viscosity (eq. 9)
β	temperature-viscosity coefficient
C	coefficient of modified VFT equation (eq. 1)
C_i	coefficients of Yasutomi equation (eq. 4)
D	parameter of modified VFT equation (eq. 1)
E_i	parameters of modified VFT equation (eq. 2)
η	dynamic viscosity
η_0	dynamic viscosity at atmospheric pressure
η_g	parameter of Yasutomi equation (eq. 4)
η^*	reduced dynamic viscosity
f_i	parameter of modified VFT equation (eq. 3)
γ	scaling parameter (eq. 7)
γ^*	scaling parameter for reduced viscosity (eq. 9)

ϕ	parameter in equation 7
ϕ^*	parameter of scaling equation for reduced viscosity (eq. 9)
k	parameter depending on surface geometry
$\mathrm{k_B}$	Boltzman constant
h_{cent}	central film thickness
m	molecular mass
p	pressure
$p_{iv}(p)$	isoviscous pressure
$p_{iv}(\infty)$	asymptotic isoviscous pressure
p_{ref}	reference pressure
ρ	density
T	temperature
$\mathrm{T_g}$	glass transition temperature
T_g^0	parameter of Yasutomi equation (eq. 4)

References

Commission decision, 2011. On establishing the ecological criteria for the award of the EU Ecolabel to lubricants. Official Journal of the European Union L 169/28, 2011/2381/EU.

Adamczewska, J.Z., Wilson, D., 1997. Development of ecologically responsive lubricants. Journal of Synthetic Lubrication 14, 129-142.

Asadauskas, S., Erhan, S.Z., 1999. Depression of pour points of vegetable oils by blending with diluents used for biodegradable lubricants. Journal of the American Oil Chemists' Society 76, 313-316.

Bair, S., 2006. Reference liquids for quantitative elastohydrodynamics: Selection and rheological characterization. Trib. Lett. 22, 197-206.

Bair, S., 2012. A critical assessment of the role of viscometers in quantitative elastohydrodynamics. STLE Tribol. Trans. 55, 394–399.

Bair, S., 2014. Comments on ‘‘pressure–viscosity coefficient of vegetable oils’’ by biresaw and bantchev. Trib. Lett., DOI 10.1007/s11249-11013-10219-11246.

Bair, S., Fernandez, J., Khonsari, M.M., Krupka, I., Qureshi, F., Vergne, P., Wang, Q.J., 2009. An argument for a change in elastohydrodynamic lubrication philosophy Proc. Inst. Mech. Eng. Part. J. J. Eng. Tribol. 223,, I–II.

Bair, S., Liu, Y., Wang, Q.J., 2006. The pressure-viscosity coefficient for newtonian ehl film thickness with general piezoviscous response. Journal of Tribology 128, 624-631.

Bair, S., Mary, C., Bouscharain, N., Vergne, P., 2013. An improved yasutomi correlation for viscosity at high pressure. Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology 227, 1056-1060.

Bair, S., McCabe, C., Cummings, P.T., 2002. Calculation of viscous ehl traction for squalane using molecular simulation and rheometry. Tribology Letters 13, 251-254.

Bantchev, G.B., Biresaw, G., 2012. Film-forming properties of blends of high-oleic sunflower oil with polyalkyl glycol. Journal of the American Oil Chemists' Society 89, 2227-2235.

Biresaw, G., Bantchev, G.B., 2013. Pressure viscosity coefficient of vegetable oils. Tribology Letters 49, 501-512.

Biswas, A., Sharma, B.K., Willet, J.L., Vermillion, K., Erhan, S.Z., Cheng, H.N., 2007. Novel modified soybean oil containing hydrazino-ester: Synthesis and characterization. Green Chemistry 9, 85-89.

Blok, H., 1963. Inverse problems in hydrodynamic lubrication and design directives for lubricated flexible surfaces, in: Muster, D., Sternlicht, B. (Eds.), Proceedings of international symposium on lubrication and wear. Berkeley, Calif., McCutchan Pub. Corp, Houston, Texas, USA, pp. 7-79.

Boyde, S., 2002. Green lubricants. Environmental benefits and impacts of lubrication. Green Chemistry 4, 293-307.

Campanella, A., Rustoy, E., Baldessari, A., Baltanás, M.A., 2010. Lubricants from chemically modified vegetable oils. Bioresource Technology 101, 245-254.

Cardoso, N.F.R., Martins, R.C., Seabra, J.H.O., Igartua, A., Rodríguez, J.C., Luther, R., 2009. Micropitting performance of nitrided steel gears lubricated with mineral and ester oils. Tribology International 42, 77-87.

Ciotta, F., Maitland, G., Smietana, M., Trusler, J.P.M., Vesovic, V., 2009. Viscosity and density of carbon dioxide + 2,6,10,15,19,23-hexamethyltetracosane (squalane). Journal of Chemical & Engineering Data 54, 2436-2443.

Comuñas, M.J.P., Baylaucq, A., Boned, C., Fernández, J., 2001. High-pressure measurements of the viscosity and density of two polyethers and two dialkyl carbonates at high pressures. International Journal of Thermophysics 22, 749-768.

Daugé, P., Baylaucq, A., Marlin, L., Boned, C., 2001. Development of an isobaric transfer viscometer operating up to 140 mpa. Application to a methane + decane system. Journal of Chemical & Engineering Data 46, 823-830.

Dietrich, C., Schmidt, M., Cahoon, E., 2005. Biotechnological enhancement of soybean oil for lubricant applications, Synthetics, mineral oils, and bio-based lubricants. CRC Press.

Ducoulombier, D., Zhou, H., Boned, C., Peyrelasse, J., Saint-Guirons, H., Xans, P., 1986. Pressure (1-1000 bars) and temperature (20-100ºC) dependence of the viscosity of liquid hydrocarbons. J. Phys. Chem. 90, 1692-1700.

Erhan, S., Adhvaryu, A., Sharma, B., 2005. Chemically functionalized vegetable oils, Synthetics, mineral oils, and bio-based lubricants. CRC Press.

Erhan, S.Z., Sharma, B.K., Perez, J.M., 2006. Oxidation and low temperature stability of vegetable oil-based lubricants. Industrial Crops and Products 24, 292-299.

Errichello, R., 2004. Selecting oils with high pressure-viscosity coefficients increase bearing life by more than four times. Machinery Lubrication, 200403.

Fandiño, O., Comuñas, M.J.P., Lugo, L., López, E.R., Fernández, J., 2007. Density measurements under pressure for mixtures of pentaerythritol ester lubricants. Analysis of a density−viscosity relationship. Journal of Chemical & Engineering Data 52, 1429-1436.

Fox, N.J., Stachowiak, G.W., 2007. Vegetable oil-based lubricants—a review of oxidation. Tribology International 40, 1035-1046.

Fragiadakis, D., Roland, C.M., 2011. On the density scaling of liquid dynamics. The Journal of Chemical Physics 134, 044504.

Gaciño, F.M., Paredes, X., Comuñas, M.J.P., Fernández, J., 2012. Effect of the pressure on the viscosities of ionic liquids: Experimental values for 1-ethyl-3-methylimidazolium ethylsulfate and two bis(trifluoromethyl-sulfonyl)imide salts. The Journal of Chemical Thermodynamics 54, 302-309.

Galliero, G., Boned, C., Fernandez, J., 2011. Scaling of the viscosity of the lennard-jones chain fluid model, argon, and some normal alkanes. The Journal of Chemical Physics 134, 064505-064508.

Harris, K.R., 2009. Temperature and pressure dependence of the viscosities of 2-ethylhexyl benzoate, bis(2-ethylhexyl) phthalate, 2,6,10,15,19,23-hexamethyltetracosane (squalane), and diisodecyl phthalate. J. Chem. Eng. Data 54, 2729-2738.

Harris, K.R., 2011. Personal communication.

Hata, H., Tamoto, Y., 2010. High-pressure viscosity measurements for various lubricants, and prediction of atmospheric pressure-viscosity coefficient from the easily measurable properties of lubricant (part 2). Journal of Japanese Society of Tribologist 55, 647-658.

Hoglund, E., 1999. Influence of lubricant properties on elastohydrodynamic lubrication. Wear 232, 176-184.

Honary, L.A.T., 1996. An investigation of the use of soybean oil in hydraulic systems. Bioresource Technology 56, 41-47.

Kumagai, A., Tomida, D., Yokoyama, C., 2006. Measurements of the liquid viscosities of mixtures of n-butane, n-hexane, and n-octane with squalane to 30 mpa. Int J. Thermophys. 27, 376-393.

Kumar, P., Bair, S., Krupka, I., Hartl, M., 2010. Newtonian quantitative elastohydrodynamic film thickness with linear piezoviscosity. Trib. Int. 43, 2159-2165.

Kuss, E., Golly, H., 1972. Das viskositats-druckverhalten von gas-flussigkeitslsungen. Berichte der Bunsen-Gesellschaft 76, 131-138.

Larsson, R., Kassfeldt, E., Byheden, Å., Norrby, T., 2001. Base fluid parameters for elastohydrodynamic lubrication and friction calculations and their influence on lubrication capability. Journal of Synthetic Lubrication 18, 183-198.

Liu, Y., Wang, Q.J., Wang, W., Hu, Y., Zhu, D., Krupka, I., Hartl, M., 2006. Ehl simulation using the free-volume viscosity model. Tribol. Letters 23, 27-37.

Lopez, E.R., Pensado, A.S., Comunas, M.J.P., Padua, A.A.H., Fernandez, J., Harris, K.R., 2011. Density scaling of the transport properties of molecular and ionic liquids. The Journal of Chemical Physics 134, 144507/144501-144507/144511.

Mendoza, G., Igartua, A., Fernandez-Diaz, B., Urquiola, F., Vivanco, S., Arguizoniz, R., 2011. Vegetable oils as hydraulic fluids for agricultural applications. Grasas y Aceites 62, 29-38.

Mia, S., Hayashi, S., Ohno, N., 2007. High pressure tribological behavior of vegetable oils as lubricant, International Conference on Mechanical Engineering, Dhaka, Bangladesh, pp. 29-31.

Pan, X., Sengupta, P., Webster, D.C., 2011. Novel biobased epoxy compounds: Epoxidized sucrose esters of fatty acids. Green Chemistry 13, 965-975.

Paredes, X., Fandiño, O., Comuñas, M.J.P., Pensado, A.S., Fernández, J., 2009. Study of the effects of pressure on the viscosity and density of diisodecyl phthalate. The Journal of Chemical Thermodynamics 41, 1007-1015.

Paredes, X., Fandiño, O., Pensado, A.S., Comuñas, M.J.P., Fernández, J., 2012a. Experimental density and viscosity measurements of di(2ethylhexyl)sebacate at high pressure. The Journal of Chemical Thermodynamics 44, 38-43.

Paredes, X., Fandiño, O., Pensado, A.S., Comuñas, M.J.P., Fernández, J., 2012b. Pressure–viscosity coefficients for polyalkylene glycol oils and other ester or ionic lubricants. Tribology Letters 45, 89-100.

Paredes, X., Pensado, A.S., Comuñas, M.a.J.P., Fernández, J., 2010. How pressure affects the dynamic viscosities of two poly(propylene glycol) dimethyl ether lubricants. Journal of Chemical & Engineering Data 55, 4088-4094.

Pensado, A.S., Comuñas, M.J.P., Lugo, L., Fernández, J., 2006. High-pressure characterization of dynamic viscosity and derived properties for squalane and two pentaerythritol ester lubricants: Pentaerythritol tetra-2-ethylhexanoate and pentaerythritol tetranonanoate. Industrial & Engineering Chemistry Research 45, 2394-2404.

Pensado, A.S., Pádua, A.A.H., Comuñas, M.J.P., Fernández, J., 2008. Relationship between viscosity coefficients and volumetric properties using a scaling concept for molecular and ionic liquids. Journal of Physical Chemistry B 112, 5563-5574.

Perry, R., Quinn, C., Traver, F., Murthy, K., 2006. Silicones, in: Rudnick, L.R. (Ed.), Synthetics, mineral oils, and bio-based lubricants. CRC Press, Boca Ratón, pp. 201-215.

Quinchia, L.A., Delgado, M.A., Franco, J.M., Spikes, H.A., Gallegos, C., 2012. Low-temperature flow behaviour of vegetable oil-based lubricants. Industrial Crops and Products 37, 383-388.

Quinchia, L.A., Delgado, M.A., Valencia, C., Franco, J.M., Gallegos, C., 2011. Natural and synthetic antioxidant additives for improving the performance of new biolubricant formulations. Journal of Agricultural and Food Chemistry, 12917-12924.

Regueira, T., Lugo, L., Comuñas, M.J.P., Fernández, J., 2008. Experimental density and viscosity data of some vegetable oils, ECTP 2008, Pau, France.

Regueira, T., Lugo, L., Fandiño, O., López, E.R., Fernández, J., 2011. Compressibilities and viscosities of reference and vegetable oils for their use as hydraulic fluids and lubricants. Green Chemistry 13, 1293-1302.

Remmele, E., Widmann, B., 1999. Suitability and environmental compatibility of rapeseed oil based hydraulic fluids for agricultural machinery. Journal of Synthetic Lubrication 16, 129-145.

Roland, C.M., Bair, S., Casalini, R., 2006. Thermodynamic scaling of the viscosity of van der waals, h-bonded, and ionic liquids. J. Chem. Phys. 125, 124508/124501-124508/124508.

Salih, N., Salimon, J., Yousif, E., 2011. The physicochemical and tribological properties of oleic acid based triester biolubricants. Industrial Crops and Products 34, 1089-1096.

Schneider, M.P., 2006. Plant-oil-based lubricants and hydraulic fluids. Journal of the Science of Food and Agriculture 86, 1769-1780.

Sivasankaran, G.A., Bisht, R.P.S., Jain, V.K., Gupta, M., Sethuramiah, A., Bhatia, V.K., 1988. Jojoba-oil-based two-stroke gasoline engine lubricant. Tribology International 21, 327-333.

Spikes, H.A., 1990. A thermodynamic approach to viscosity. Tribology Transactions 33, 140 - 148.

Šraj, R., Vižintin, J., Svoljšak, M., Feldin, M., 2000. Rapidly biodegradable hydraulic fluids on the basis of rapeseed oil. Lubrication Engineering 56, 34–39.

Tomida, D., Kumagai, A., Yokoyama, C., 2007. Viscosity measurements and correlation of the squalane + CO_2 mixture. Int. J. Thermophys. 28, 133-145.

van Dam, J.E.G., de Klerk-Engels, B., Struik, P.C., Rabbinge, R., 2005. Securing renewable resource supplies for changing market demands in a bio-based economy. Industrial Crops and Products 21, 129-144.

Vižintin, J., Arnšek, A., Ploj, T., 2000. Lubricating properties of rapeseed oils compared to mineral oils under a high load oscillating movement. Journal of Synthetic Lubrication 17, 201-217.

Xia, Y., Larock, R.C., 2010. Vegetable oil-based polymeric materials: Synthesis, properties, and applications. Green Chemistry 12, 1893-1909.

Yasutomi, S., Bair, S., Winer, W.O., 1984. An application of a free volume model to lubricant rheology i—dependence of viscosity on temperature and pressure. Journal of Tribology 106, 291-302.

Table 1.

Experimental dynamic viscosities at atmospheric pressure, η/mPa s, for BIO-H01 and BIO-H02.

T / K	**BIO-H01**	**BIO-H02**	**T / K**	**BIO-H01**	**BIO-H02**
278.15	199.7	134.3	328.15	22.43	17.11
283.15	149.0	101.9	333.15	19.29	14.86
288.15	113.6	78.80	338.15	16.74	13.00
293.15	88.08	62.05	343.15	14.63	11.46
298.15	69.56	49.64	348.15	12.88	10.17
303.15	55.80	40.32	353.15	11.42	9.08
308.15	45.38	33.20	358.15	10.18	8.16
313.15	37.41	27.67	363.15	9.13	7.37
318.15	31.21	23.33	368.15	8.23	6.68
323.15	26.33	19.89	373.15	7.45	6.09

Table 2.

Experimental values of the dynamic viscosity at different pressures, η/mPa·s, for the hydraulic fluids under study.

	T / K					
	MIN-H01			**BIO-H01**		
p / MPa	**313.15**	**343.15**	**363.15**	**313.15**	**343.15**	**363.15**
10	45.4	[a]	[a]	38.6	[a]	[a]
25	69.7	22.6	[a]	52.0	19.8	[a]
50	123	36.7	18.9	78.9	28.7	17.2
75	199	55.2	27.7	113	39.5	23.2
100	306	79.7	38.7	156	52.5	30.1
125	457	112	52.1	209	68.1	38.0
150	671	154	68.4	277	86.9	47.1
175	974	210	87.7	363	110	57.4
200	1401	284	110	470	137	69.1
225	2004	380	134	606	170	82.1
250	2855	505	157	777	209	96.5
	MIN-H02			**BIO-H02**		
p / MPa	**313.15**	**343.15**	**363.15**	**313.15**	**343.15**	**363.15**
10	36.8	[a]	[a]	38.7	[a]	[a]
25	47.0	15.5	[a]	44.0	16.3	[a]
50	72.1	23.0	13.1	58.0	22.0	13.6
75	110	33.5	18.5	78.4	29.2	17.9
100	167	48.0	25.6	106	38.4	23.0
125	251	67.8	34.5	143	49.9	28.9
150	372	94.3	45.6	191	63.9	35.7
175	544	130	58.9	252	81.0	43.1
200	790	177	74.5	329	101	51.0
225	1138	239	92.3	427	126	59.0
250	1631	320	112	552	155	67.0

[a] The falling time measured at these conditions was too short.

Table 3.

Parameters and relative deviations of the equations considered.

	MIN-H01	**BIO-H01**	**MIN-H02**	**BIO-H02**
	Eq. 1			
$A\cdot 10^{3}$ / mPa·s	72.5	111.0	72.3	117.4
B / K	937.24	908.98	858.89	852.65
C / K	165.65	156.98	167.32	157.07
E_0 / MPa	2313.1	821.87	1794.9	1639.1
E_1 / MPa·K^{-1}	-14.307	-4.7447	-10.984	-9.7986
$E_2\cdot 10^{3}$/ MPa·K^{-2}	24.43	9.456	20.02	17.30
D	5.5747	4.4685	6.9732	4.4163
AAD / %	2.8	1.8	2.6	2.3
	Eq. 3			
$a_1\cdot 10^{3}$ / MPa^{-1}	5.0000	7.2415	7.6224	6.8320
$a_2\cdot 10^{6}$ / MPa^{-2}	-29.802	-24.934	-36.632	-24.949
b_1/ MPa^{-1}· K	2.7385	1.4419	1.9699	1.3714
$b_2\cdot 10^{3}$/ MPa^{-2}· K	-1.8882	-0.1491	1.1053	0.2746
$b_3\cdot 10^{6}$ / MPa^{-3}· K	9.4352	5.3344	6.2653	5.4393
AAD / %	2.1	1.2	1.6	1.6
	Eq. 4			
η_g/ mPa·s	10^{15}	10^{15}	10^{15}	10^{15}
T_{g0} / K	190.22	187.72	172.43	175.21
$A_1\cdot 10^{7}$ / K	1.75	21.1	1.98	1.38
$A_2\cdot 10^{-9}$ / MPa^{-1}	4.49	0.42	4.87	2.17
$f_1\cdot 10^{3}$ / MPa^{-1}	12.8	6.90	10.6	7.18
f_2	-0.3377	-0.5414	-0.3318	-0.4479
C_1	16.136	15.807	16.495	16.015
C_2 / K	25.278	22.153	30.289	25.107
AAD / %	3.1	2.1	2.8	2.7
Bias / %	-0.1	0.1	-0.3	0.0
	Eq. 7			
A_S / mPa·s	0.6148	0.5453	0.4929	0.6437
B_S / K·$\rho^{-\gamma}$·cm$^{3\gamma}$·	1588.0	1368.6	1757.9	1278.4
Γ	4.5895	4.0819	4.8510	4.4026
Φ	1.5373	1.3823	1.4597	1.3835
AAD / %	5.4	3.3	3.3	3.3
	Eq. 9			
$A_S^{*}\cdot 10^{4}$ / mPa·s	35.7	30.6	28.9	34.1
B_S^{*} / K·$\rho^{-\gamma}$·cm$^{3\gamma\cdot}$	1369.0	1183.9	1474.6	1114.6
γ^{*}	4.0048	3.4806	4.1967	3.6858
φ^{*}	1.6919	1.5447	1.6248	1.5533
AAD / %	4.7	2.6	2.8	2.8

Table 4.

Pressure-viscosity coefficient obtained with the five different correlations for the fluids studied in this work at 343.15 K.

	MIN-H01					**BIO-H01**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
p/MPa	α / GPa^{-1}									
0.1	19.85	20.42	21.92	17.62	18.36	14.54	14.98	14.86	14.28	14.60
100	14.64	13.94	13.81	13.21	14.44	10.97	10.70	10.81	10.83	10.81
250	10.50	10.17	10.85	10.78	12.14	8.02	7.49	7.93	8.75	8.56
	MIN-H02					**BIO-H02**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
p/MPa	α / GPa^{-1}									
0.1	18.18	18.82	19.76	18.50	18.60	14.08	14.20	14.17	13.84	14.22
100	14.42	13.83	13.62	13.96	13.61	10.68	9.14	10.31	10.45	10.52
250	11.01	10.33	11.26	11.46	10.92	7.84	7.95	7.86	8.44	8.37

Table 5.

Temperature viscosity coefficient obtained with the five different correlations for the fluids studied in this work at 343.15 K.

	MIN-H01					**BIO-H01**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
p/MPa	$10^3\beta$ / K^{-1}									
0.1	29.75	29.75	29.59	30.92	30.35	26.22	26.23	25.58	27.30	26.78
100	42.57	38.13	38.98	38.96	38.55	32.45	30.49	31.38	32.00	31.60
250	52.76	52.40	50.22	49.89	49.69	37.61	38.76	37.13	38.42	38.21
	MIN-H02					**BIO-H02**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
p/MPa	$10^3\beta$ / K^{-1}									
0.1	27.78	27.78	28.49	28.72	28.12	24.62	24.63	24.86	25.55	24.67
100	38.14	34.71	36.71	36.76	36.33	31.68	28.82	30.43	30.62	29.94
250	47.56	49.10	47.38	47.29	47.03	37.57	37.47	36.62	37.39	36.99

Table 6.

α^* and α_{film} of the four lubricants at the measured temperatures.

	MIN-H01					**BIO-H01**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
T / K	α^* / GPa^{-1}									
313.15	19.99	20.04	20.55	18.62	18.84	13.22	13.63	13.53	13.20	13.32
343.15	16.31	16.34	16.45	15.64	15.75	11.36	11.58	11.33	11.44	11.47
363.15	13.49	14.35	14.42	14.01	14.07	10.12	10.41	10.19	10.43	10.42
	MIN-H02					**BIO-H02**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
T / K	α^* / GPa^{-1}									
313.15	18.73	18.64	19.01	18.06	18.34	12.86	13.35	13.00	12.56	12.74
343.15	15.57	15.56	15.62	15.23	15.37	10.98	11.36	10.83	10.85	10.95
363.15	13.38	13.81	13.88	13.65	13.73	9.54	10.22	9.71	9.94	10.00
	MIN-H01					**BIO-H01**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
T / K	α_{film} / GPa^{-1}									
313.15	21.08	20.77	21.51	19.01	19.30	14.15	14.11	14.42	13.70	13.87
343.15	17.19	17.21	17.36	16.05	16.22	12.14	12.20	12.11	11.95	12.04
363.15	14.21	15.32	15.29	14.41	14.54	10.79	11.15	10.91	10.94	10.99
	MIN-H02					**BIO-H02**				
	Eq. 1	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**	**Eq. 1**	**Eq. 3**	**Eq. 4**	**Eq. 7**	**Eq. 9**
T / K	α_{film} / GPa^{-1}									
313.15	19.51	19.11	19.69	18.48	18.82	13.77	13.63	13.70	13.02	13.27
343.15	16.22	16.26	16.27	15.66	15.86	11.73	11.77	11.48	11.32	11.50
363.15	13.93	14.71	14.52	14.07	14.22	10.17	10.72	10.32	10.41	10.55

Figure Captions

Fig. 1. Schematic diagram of VisLPT1 apparatus: V_1, V_2, V_3 and VP_1 and VP_2 are high pressure valves.

Fig. 2. Deviations between the correlation obtained with our viscosity data and other values published in the literature: ■ Kuss and Golly (Kuss and Golly, 1972); ▲ Bair et al. (Bair et al., 2002); ○ Pensado et al. (Pensado et al., 2006); ♦ Bair (Bair, 2006); × Kumagai et al. (Kumagai et al., 2006); △ Tomida et al. (Tomida et al., 2007); ● Ciotta et al. (Ciotta et al., 2009); □ Harris (Harris, 2009), ✳Hata and Tamoto (Hata and Tamoto, 2010) and + Harris (Harris, 2011). (--) uncertainty of VisLPT2

Fig. 3. Viscosity at atmospheric pressure for ▲ MIN-H01 (Regueira et al., 2011), ● BIO-H01, ♦ MIN-H02 (Regueira et al., 2011) and □ BIO-H02

Fig. 4. Dynamic viscosity versus pressure at 343.15 K: ▲ MIN-H01, ● BIO-H01, ♦ MIN-H02 and □ BIO-H02. The lines correspond to the fitting of Eq. 1.

Fig. 5. Reduced viscosity scaling for ▲ MIN-H01, ● BIO-H01, ♦ MIN-H02 and □ BIO-H02. The lines correspond to the fitting.

Fig. 6. (a) Pressure- Viscosity coefficient at 313.15 K determined from Eq. 1 for: for ▲ MIN-H01, ● BIO-H01, ♦ MIN-H02 and □ BIO-H02. (b) Pressure- Viscosity coefficient determined for MIN-H01 at 313.15 K from: ▲ Eq. 1, ♦ Eq. 3, ■ Eq. 4, ● Eq. 7 and × Eq. 9.

Fig. 7. (a) Temperature-Viscosity coefficient at 313.15 K determined from Eq. 1 for: ▲ MIN-H01, ● BIO-H01, ♦ MIN-H02 and □ BIO-H02. (b) Temperature - Viscosity coefficient determined for MIN-H01 from for: ▲ Eq. 1, ♦ Eq. 3, ■ Eq. 4, ● Eq. 7 and × Eq. 9.

Fig. 8. Lubricant-dependent film thickness response in temperature for α_{film} obtained from Eq. 1: ▲ MIN-H01, ● BIO-H01, ♦ MIN-H02 and □ BIO-H02. Lines showed as visual guides.