Environment & Technology ISSN: 2711 4422
Vol. 2 No. 1 Enero-Junio, 2021: 64-79
URL: https://revistaet.environmenttechnologyfoundation.org/
DOI: https://doi.org/10.56205/ret.2-1.4

Similitud de las propiedades físicas del biodiesel y de un fluido hidráulico para tractor

Similitude of physical properties of biodiesel and a tractor hydraulic fluid

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Resumen

Se discute el uso potencial del biodiesel puro como fluido de transmisión de energía mecánica, como una mezcla equivolumétrica de dos marcas del bioproducto hechos en Costa Rica. Este fluido neotérico fue comparado *vis à vis* con un fluido hidráulico usado para equipo de alta demanda hidráulica. Las propiedades físicas consideradas fueron el coeficiente térmico de expansión cúbica, la compresibilidad isotérmica, la entalpía de vaporización, la capacidad calórica y la conductividad térmica. La mezcla de biodiesel mostró mejores o iguales propiedades que el producto comercial.

Palabras clave: Ésteres grasos, líquido hidráulico, expansión térmica, compresibilidad isotérmica, conductividad térmica

Abstract

The potential use of neat biodiesel as fluid for transmission of mechanical energy is discussed for an equi-volumetric mixture of two biodiesel samples made in Costa Rica. This neoteric fluid was compared *vis à vis* a commercial petroleum-derived fluid for heavy-duty equipment. The physical properties considered were thermal coefficient of cubic expansion, isothermal compressibility, vaporisation enthalpy, heat capacity, and thermal heat conductivity. Biodiesel showed equal or better properties than the petroleum-derived product.

Keywords: Fatty esters, hydraulic liquid, thermal expansion, isothermal compressibility, thermal conductivity.

Recibido: *09/05/2021*
Revisado: *28/06/2021*
Aprobado: *23/08/2021*

Introduction

The use of vegetable oils as hydraulic fluids and lubricants has been considered in the last few years [Regueira, T., *et al.*, 2011, Paredes, *et al.*,2014]. Waynick and Peebles [2017] filed a patent application on the formulation of hydraulic fluids and lubricants that incorporated biodiesel, amongst other petroleum-derived base components.

The kind of materials collectively known as biodiesel are mixtures of methyl fatty esters, obtained by transesterification of vegetable oils or animal fats with methanol.

Most investigations on this topic are devoted to its use as substituent of petroleum-derived diesel fuel. The analysis and technical assessment on the subject mainly have to do with economic, political, and industrial aspects [Mittelbach 2004, Pahl 2005].

As indicated above, the main uses of biodiesel are as fuel for transportation (land, maritime and air), farm equipment, electricity generation, and industrial and space heating. Modern injection devices for thermal equipment require a minimum lubricity capacity of fuels, to avoid excessive wear of the moving parts of fuel pumps and injectors.

Biodiesel has particularly good lubricating properties [Mittelbach 2004], and therefore lubricity in general as potential application is the result of its relatively high viscosity index and low isothermal compressibility, $\kappa_T = -1/V\,(\partial V/\partial p)_T$ [Castellón-Elizondo, *et al.* 2006, Encinar *et al.* 2020].

Consider molecular layers of lubricants under mechanical stress. This type of long-chain molecules must not get *squeezed out* from the space between sliding surfaces. The layers must sustain the bidimensionality of the force field developed during sliding.

Alvarado-Montero *et al.* [2018] have reported the statistically-significant absence of any molecular structural effect on some physical properties of six biodiesels studied in our laboratory from different biochemical origins, such as the thermal coefficient of cubic expansion, $\alpha = 1/V\,(\partial V/\partial T)_p$, the isothermal compressibility, the enthalpy of vaporisation, and the Hildebrand solubility parameter [Hildebrand and Scott, 1964]. For example, the average value of κ_T found for these fatty esters was $(8{,}2 \pm 0{,}7) \times 10^{-10}$ Pa^{-1}. This figure checks well with the corresponding values observed for machine lubrication oils in the range 6×10^{-10} Pa^{-1} – 8×10^{-10} Pa^{-1}) [Štěpina & Veselý 1992].

Avoidance of fugitive emissions and zero leakage are crucial for the effective control of performance of hydraulic circuits. Meeting of environmental requirements is also an important aspect of the issue. Biodiesel is a biodegradable material. Lutz *et al.* [2006] studied the kinetics of the microbial degradation of palm biodiesel by a wild-type aerobic bacterial population at 20 ± 2 °C obtained from common open environments (Superbugs®). The biodegradation experiments showed that the initial rate of oxygen uptake for palm biodiesel was similar to the quantities observed in biodegradation experiments of aqueous solutions of a group of carbohydrates and amino-acids, with concentrations of 1,0 $mmol/dm^3$. Pieces made of elastomeric materials are susceptible to chemical attack by organic liquids. Lutz and Mata-Segreda [2008] measured the rate of absorption of biodiesel and petrodiesel by synthetic-rubber gaskets and found that biodiesel absorption takes place around 10% more slowly than the fossil analogue. This estimation may be in some error, since the authors assumed that either liquid did not dissolve the polymer, or unnoticed detachment of small superficial particles [Shahin Akhlaghi *et al.*, 2015]. The solid matrix showed a degree of biodiesel absorption of 97% by mass and 189% for the petroleum derivative. The observation led to the conclusion that worries for use of biodiesel as fuel, solvent, lubricant, or transfer fluid can be considered of lesser concern about negative externalities, relative to petroleum-derived materials.

This work compares physical properties of an equal-volume mixture of two commercial biodiesel samples as neoteric fluid for the transfer of mechanical energy *vs. Castrol Universal Tractor Fluid®* used for heavy-duty equipment.

Methodology

Materials. Biodiesel samples were obtained from Biodiesel H&M, S. A. (Santa Clara, Costa Rica) and Energías Biodegradables, S. A. (Ochomogo, Costa Rica). *Castrol Universal Tractor Fluid®* was obtained from the garage of Transportation Services Department of the University of Costa Rica.

Laboratory measurements. The thermal coefficient of cubic expansion of the liquids studied, $\alpha = 1/V\,(\partial V/\partial T)_p$, was determined by measuring the effect of temperature on density by using a pycnometer and analytical balance. The linear relation observed between *ln* ($mass_{liquid}$) *vs.* temperature allowed the calculation of α as the negative of the slope of such a line, as discussed in any standard textbook of experimental physical chemistry [Shoemaker & Garland, 1968]. Other properties were assessed by numerical analysis (*vide infra*).

The thermal conductivity determination was obtained from the Newton's cooling kinetics, as described by Rodríguez-Acevedo *et al.* (2018).

Results and discussion

The analysis of findings is described as follows.

Thermal expansion (α). The transfer of mechanical energy *via* a working fluid is not 100% efficient. Part of the mechanical work done on the fluid system is transformed into an increase in its internal energy and a flux of heat towards the surroundings. The increase in internal energy has an expanding effect on the working fluid. This effect needs also to be considered in terms of the structural integrity of the hydraulic system, due to deleterious effects on couplings, hoses, gaskets, and other pieces of equipment.

It is desirable that transmission fluids have low α. The value reported by Alvarado-Montero *et al*. [2018] for different biodiesel types was $(8{,}5 \pm 0{,}4) \times 10^{-4}\ K^{-1}$. The average value found for the biodiesel mixture in this study was $\alpha = (7{,}7 \pm 0{,}2) \times 10^{-4}\ K^{-1}$. Thus, one may use the mean value $\alpha = (8{,}4 \pm 0{,}5) \times 10^{-4}\ K^{-1}$ for the bioproduct. Prestone® brake fluid showed $\alpha = (8{,}56 \pm 0{,}03) \times 10^{-4}\ K^{-1}$, and Adarga® household lubricant $\alpha = (7{,}21 \pm 0{,}09) \times 10^{-4}\ K^{-1}$. The find for the biodiesel mixture checks well with the data for these materials chosen for comparison.

Determination of α for *Castrol universal tractor fluid*® gave the result $(7{,}1 \pm 0{,}6) \times 10^{-4}\ K^{-1}$, and **figure 1** shows the raw experimental data from 4 runs.

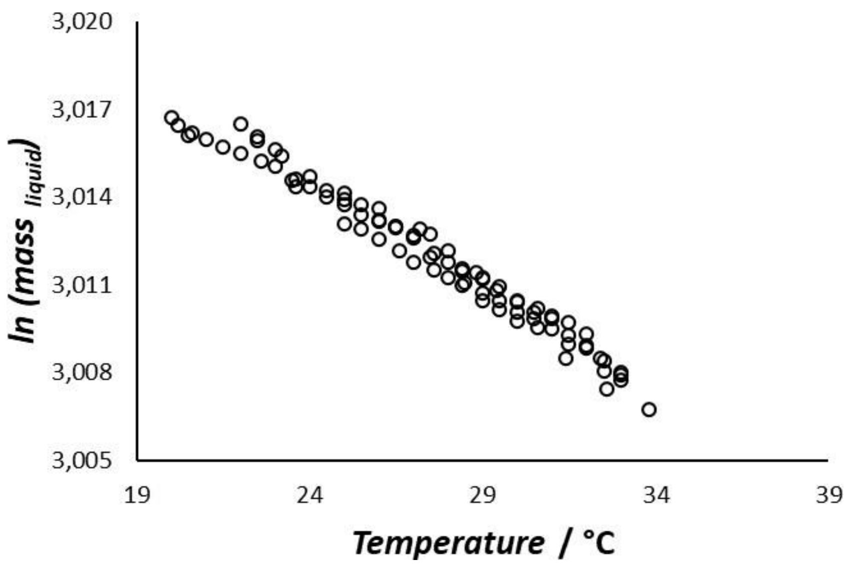

Figure 1. Determination of the thermal coefficient of cubic expansion of *Castrol Universal Tractor Fluid*® under ambient pressure. Source: own elaboration.

The thermal expansivity of the heavy-duty liquid is about 20% more adequate than for the neoteric fluid ($p < 0{,}01$). Despite of the difference, the observation indicates that biodiesel may be considered satisfactory from the thermal viewpoint.

Enthalpy of vaporisation ($\Delta_{vap}H$). This thermodynamic parameter is pertinent to this study because it gives an indirect notion about liquid volatility. Besides an assessment of risk of fire or explosion, one has to consider the probability of generation of bubbles by boiling inside the hydraulic lines. The calculation of $\Delta_{vap}H$ was done from the α value, according to the model of *liquids as soft-solids* of Castellón-Elizondo *et al.* [2006]:

$$a = \frac{7\, C_p}{72\beta\, \Delta_{vap}H} \qquad \textbf{(1)}$$

Where C_p is the specific heat of the material, and β is the molecular packing parameter. The magnitude of the two parameters for long-chain hydrocarbon materials such as the *Castrol* petroleum-derived material produce Eq. (2) [Lezcano-González & Mata-Segreda, 2011]:

$$a = \frac{\mathbf{0,154}}{\Delta_{vap}\boldsymbol{H}} \qquad \textbf{(2)}$$

and the resulting value of $\Delta_{vap}H$ for the *Castrol*® product is (2,2 ± 0,2) × 10^2 kJ/kg. This value is smaller than the equivalently reported value (3,5 ± 0,2) × 10^2 kJ/kg for biodiesel by Alvarado-Montero *et al.* (2018) and the present study. The greater intermolecular forces between the more polar biodiesel molecules explains the observation, thus resulting in a positive characteristic of the biologically-derived neoteric fluid, that is, a lower degree of volatility relative to the petroleum-derived material.

3.3 Specific heat. This thermodynamic property gives the amount of energy required to heat up a material by one degree [Çengel & Boles, 2015]. This value was calculated for the *Castrol* hydrocarbon by way of Eq. (3) (Cameron, 1966):

$$\boldsymbol{C_p} = \frac{\mathbf{1}}{\sqrt{\boldsymbol{specific\ gravity}}} \times (\mathbf{0,403} + \mathbf{0,00081}\,\boldsymbol{T})\,\frac{\boldsymbol{cal}}{\boldsymbol{g\ °C}} \qquad \textbf{(3)}$$

The value C_p = 1,88 kJ K^{-1} kg^{-1} results for T = 25 °C and specific gravity = 0,882 [MSD for *Castrol tractor fluid*®, 2019]. An identical value of C_p = 1,89 kJ K^{-1} kg^{-1} is obtained for the neoteric mixture (specific gravity = 0,88).

Thermal conductivity. The increase in internal energy accumulated by the working fluid during its performance must be removed by flow of heat to the surrounding environment. Thus, it is necessary to determine the thermal conductivity of the *Castrol* product, in order to compare the property with that of the biodiesel mixture.

Rodríguez-Acevedo *et al.* [2018] set a semiempirical model that correlates the thermal conductivity of liquids (λ) with their Newton's cooling rate constant k_N as follows: $J = k_N \times \rho \times C_p$, where ρ is the liquid density. The experimental quantity J allows the correlation of k_N with λ with an acceptable degree of certainty ($p < 0,01$), described by the calibration equation:

$$J = 1,5 + 2,2\,\lambda \qquad (4)$$

Figure 2 shows the raw data for the kinetic runs measured for the petroleum-derived product.

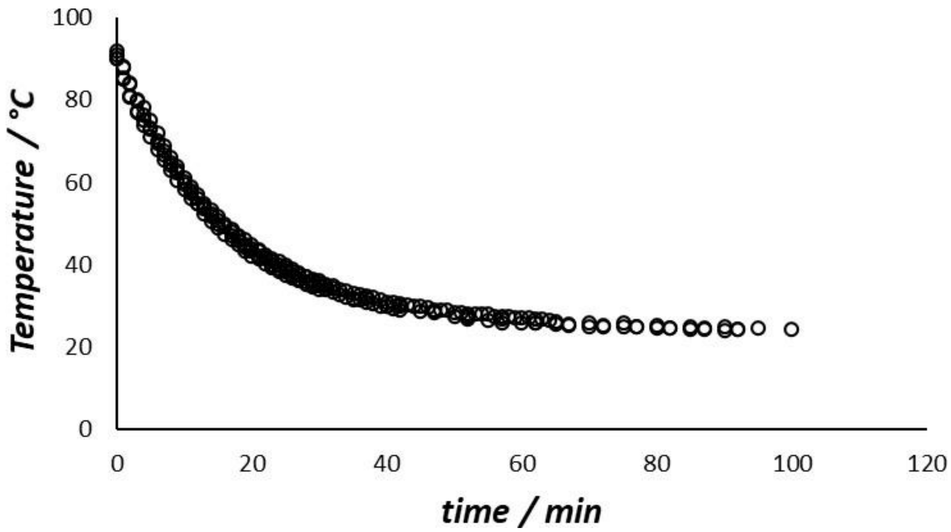

Figure 2. Determination of Newton's cooling rate constant for *Castrol Universal Tractor Fluid*®. *Source: own elaboration.*

The time-temperature data pairs were fitted to an exponential-decay equation, according to Newton's cooling law [Maruyama & Moriya, 2021]:

$$-dT/dt = k_N\,(T - T_{final}) \qquad (5)$$

$$T\,/\,°C = T_{final} + (T_{initial} - T_{final})\,\exp(-k_N\,t) \qquad (6)$$

The average k_N value resulted from four runs for the petroleum-derived product was $(1{,}07 \pm 0{,}07) \times 10^{-2}$ s^{-1}. By using C_p = 1,88 kJ K^{-1} kg^{-1} and ρ = 882 kg m^{-3}, one obtains J = 1,77 kW K^{-1} m^{-3}, which finally gives λ = 0,12 kW K^{-1} m^{-1}. This value checks well with λ = 0,13 kW K^{-1} m^{-1} calculated from Eq. (7) (Cameron, 1966):

$$\lambda = \frac{0,000276}{specific\ gravity}\left(1 - 0,0005 \times \frac{T}{3}\right)\frac{cal}{s\ cm^2\ °C\ cm^{-1}} \quad \textbf{(7)}$$

λ values for biodiesel obtained in our laboratory cluster around 0,3 kW K^{-1} m^{-1} (Zúñiga-Campos, 2018). This shows that biodiesel has a better performance as coolant than the *Castrol*® product (0,3 kW K^{-1} m^{-1} *vs*. 0,12 kW K^{-1} m^{-1}).

Isothermal compressibility. Compressibility is one of the key characteristics that must be considered, when a material is considered as fluid for transfer of mechanical energy. A low κ_T value assures fast mechanical response time, high pressure transmission velocity and low power loss [Regueira *et al*., 2011], and also low heat generation upon compression. Other consequences from low κ_T are good lubricity, high viscosity index and adequate viscosity and pressure-viscosity coefficient to make the protective layer between sliding surfaces [Paredes, *et al*., 2014].

The soft-solid model for liquids [Castellón-Elizondo *et al.*, 2006] allows the estimation of κ_T from α for nonpolar or moderately polar liquid substances:

$$\kappa_T \cong \frac{\alpha\, T}{\Delta_{vap} U / V_m} \quad \textbf{(8)}$$

The value of the molar volume of the multicomponent hydrocarbon tractor fluid was not available. Therefore, κ_T had to be evaluated by other means. The technical information found in SAE Technical Paper Series *Physical and Chemical Properties of a Typical Automatic Transmission Fluid* [Kemp & Linden, 2018] allows the estimation of the bulk modulus ($1/\kappa_T$) for *Castrol universal tractor fluid*®, by interpolation of data shown graphically, such that $\kappa_T = 7,7 \times 10^{-10}$ Pa^{-1} at ~300 K. This result indicates that biodiesel is only 6% more compressible than the petroleum-derived product. ($8,2 \times 10^{-10}$ Pa^{-1} *vs*. $7,7 \times 10^{-10}$ Pa^{-1}), property that is compatible with its proposed use as hydraulic transmission fluid for equipment used for low hydraulic tasks.

Volume changes of liquids is the composite result of simultaneous thermal expansion and isothermal compression. Eq. (9) explains the situation:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \quad \textbf{(9)}$$

$$dV/V = a\ dT - \kappa_T\ dp \quad \textbf{(10)}$$

Integration of Eq. (10) gives surfaces $V/V_o = f(T, p)$. The results are shown in **figure 3** and **figure 4**, from the initial values 25 °C and 0,1 MPa up to 60 °C and 70 MPa.

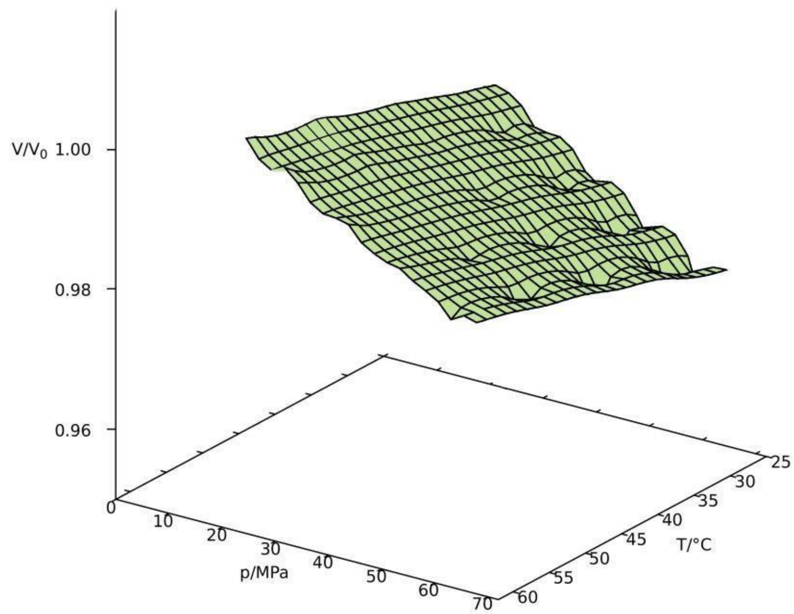

Figure 3. Simultaneous effect of pressure and temperature on the equal-volume biodiesel mixture. Source: own elaboration.

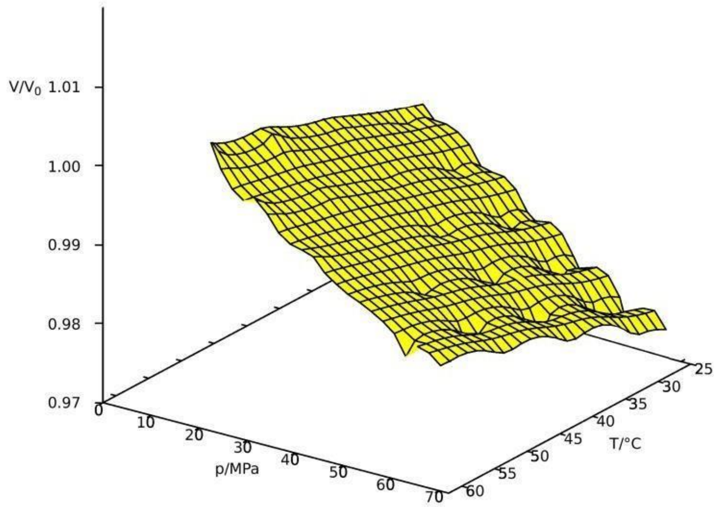

Figure 4. Simultaneous effect of pressure and temperature on *Castrol Universal Tractor Fluid*®. Source: own elaboration.

The independent variables in the plots were chosen according to the maximum pressures generated in different instruments such as hydraulic steering (~ 21 MPa), hydraulic lifts (~ 22 MPa), hydraulic jacks (25 MPa – 42 MPa), or hydraulic pistons (70 MPa). The data were estimated from different catalogue booklets.

The overall thermomechanical effect is similar for both liquids. One obtains a net compression of 2,3 % for the biodiesel mixture and 2,5 % for the petroleum-derived material. The compressive mechanical effect predominates over the thermal expanding effect.

A more formal analysis for this result comes from the calculation of the so-called *thermal pressure coefficient*:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{a}{\kappa_T} \qquad \textbf{(11)}$$

The resulting values are 1,0 ± 0,1 MPa K^{-1} for the biodiesel mixture and 0,90 ± 0,09 MPa K^{-1} for the petroleum-derived product.

The macroscopic interpretation of $(\partial p/\partial T)_V$ is simply the rate of variation of pressure caused by temperature at fixed liquid volume. One encounters its molecular significance from the *thermodynamic state equation* [Berry, Rice & Ross, 2000]:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad \textbf{(12)}$$

Where U is the internal energy of the system.

The so-called internal pressure, $(\partial U/\partial V)_T$, gives an estimate of the magnitude of cohesive forces of liquids [Abdulagatov, *et al.*, 2018, Ivanov & Abrosimov, 2005], since it quantifies the amount of energy needed to obtain a unitary isothermal expansion. Cohesion generates a pressure within the liquid that is found to fall in the range 10^2 MPa – 10^3 MPa. Internal pressure is sensitive to applied external pressure. As a liquid is compressed, its molecules are positioned closer to each other, and the internal pressure increases up to a point, where it becomes negative. This is interpreted as the predominance of repulsive forces at extremely high pressures. On the other hand, internal pressure decreases with temperature. The molecular interpretation is that an increase in temperature is associated with an increase in the degrees of freedom of molecules, which can bring about a decrease of the attractive interactions if these are directional, such as hydrogen bonds or dipole-dipole interactions, because they restrict the motion of molecules in the supra-structural packing of the fluid. Thus, the stronger attractive dipole forces amongst biodiesel molecules explain its potential for use as hydraulic fluid.

It is therefore interesting having found a balancing effect on the molecular cohesion between the more polar biodiesel material with average chain length of 17-19 atoms [$(\partial U/\partial V))_T$ = (3,0 ± 0,3) MPa] and the case of nonpolar 40 carbon-atom petroleum-derived products [$(\partial U/\partial V)_T$ = (2,7 ± 0,3) MPa].

Economic and environmental aspects. Countries that do not produce/process petroleum have to face the economic (and sometimes political) instabilities derived by the oscillating price of this *commodity*. It is therefore important to promote the development of new materials and technologies independent from fossil sources.

The incorporation of biodiesel as neoteric material for use beyond fuel should be considered as relevant, not only for petroleum non-producing countries but also for those that have this non-renewable asset.

Vegetable oils and animal fats are renewable feedstocks, and the derivatives from their oleochemistry display greater intermolecular forces than hydrocarbons, an advantage that brings about better properties such as high viscosity index, high lubricity, and lower volatility, as indicated in this account based on primary experimental data such as thermal expansivity and heat-transfer properties.

At the time of working on this project, the price of nationally produced biodiesel was only 13 % the price of *Castrol Universal Tractor Fluid*®, in the local market. If biodiesel were in definite use as hydraulic fuel its real cost would obviously be higher because the need to incorporate additional additives, such as antioxidant agents. Nevertheless, the final figures are expected to be clearly advantageous for the neoteric biomaterial.

There are positive externalities bound to neoteric uses of renewables such as vegetable or animal lipids and their derivatives. Perhaps the most important is their biodegradable nature. As it was mentioned at the beginning of this account, the biodegradable action of wild-type microorganisms on biodiesel is comparable to simple biochemicals such as amino-acids or carbohydrates [Lutz *et al.*, 2006].

Biochemicals such as biodiesel can also be included in circular-economy loops, mainly those cases where the product is made from used cooking oils. But this is another task that must be taken in a future research project.

Conclusions

- The α value of the biodiesel mixture studied is similar to the values of the *benchmark* materials indicated: “pure” biodiesels, brake fluid or household lubricant.
- The heavy-duty hydraulic tractor fluid has an α value similar to the neoteric mixture studied.

- The enthalpy of vaporisation of biodiesel is higher than the value found for the petroleum-derived material. This implies lower volatility of the neoteric biomaterial.
- The specific heat of biodiesel and of the heavy-duty hydraulic fluid are similar.
- The thermal conductivity of the neoteric mixture is twice as large as the value determined for the petro-product. This makes biodiesel to perform better as coolant.
- The isothermal compressibilities of both petro and bioproducts are similar. Thus, the combined thermo-mechanic characteristics of these fluids show no significant differences.
- An interesting balance was found between the effect of polarity and molecular size on the degree of molecular cohesion between the more polar biodiesel material with average chain length of 17-19 atoms and the nonpolar 40 carbon-atom petroleum-derived products.
- Another advantage from the use of the neoteric mixture and by extension of “pure” biodiesels in general, over the petroleum-derived hydraulic material, is clear from their renewable nature and biodegradability.
- The overall finding is that fatty esters possess a true potential as fluids for transfer of mechanical energy.

Acknowledgement

The authors thank Biodiesel H&M, S. A. and Energías Biodegradables, S. A. for providing samples of their biodiesel products. JAM-B wishes to thank the academic guidance of Prof. Andre Tabash in the process of writing a thesis document submitted to the Latin University of Costa Rica School of Electromechanical Engineering as partial fulfilment of the requirements for graduation as electromechanical engineer.

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