Thermal characterization of castor oil as additive in lubricant oil using photothermal techniques

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Over the last years extensively research has been carried out on full or partial substitution of supplies resources coming from renewable resources on traditionally non-renewable, in the case of the automobile sector there are progresses in bio-combustibles (biofuel) and synthetic oils coming from vegetable sources. There are strong efforts to find oil additives which can improve oils features in automobile industry, by adding vegetables oils to commercial lubricant oils, is expected to improve oil thermal stability. In the present research, different ratios of castor oil (ricinus comunis)-motor oil blends were obtained and their thermal properties were characterized by using the so-called Back and Front Photopyroelectric (BPPE/FPPE) techniques. Several oil-additives concentrations were measured and thermal diffusivities and effusivities as well as densities are reported, getting full thermal characterization for every concentration.

Introduction

The awareness of pollution, scarce of fossil fuels and the environmental footprint, are rising and they are subject of important research around the world, regarding fuels there is an important concern about the development of ecological friendly combustibles and two main research lines have been developed, the first one is the introduction of the so-called biodiesel, and the second one is the improvement of the existing fuels [1-5].

Regarding fuels, vegetable oils had appeared as the option of choice, not only as biodiesel source but also as additives in the fossil fuels. Among different varieties of seeds, available as biodiesel source and additive [1,3,4,6-10], Castor oil (ricinus comunis) is well known as renewable source of chemical industry [11-13] as well as biodiesel starting material [14-16]. Additionally, results from rheological behaviour of castor oil biodiesel suggest that pure castor oil increase viscosity when is used as oil additive and its chemical structure had been already studied [17], even though there is scarce information about its thermal behaviour of this oil as lubricant when it is used as oil additive.

As a way to give more insight about thermal properties of castor oil –synthetic oil blends SAE40W, which is a highly refined mineral oil, the present work deals with the thermal characterization of those mixes, using two well-known photopyroelectric methods: BPPE and FPPE techniques [18-20].

Experimental details

Photopyroelectric techniques are non-destructive methods used in thermal and optical characterization of many materials including liquid samples these techniques are characterized by using information carried on thermal waves generated over the pyroelectric detector as well as sample under study. BPPE is used to analyze thermal diffusivity of liquids and, it is based on the variation of the sample thickness by means of a setup showed in Figure 1.

In this experimental setup, the sample is enclosed in a chamber of variable length which is formed by a metal foil (Cu 100 μm thick) and PZT (500 μm thick) pyroelectric temperature sensor. A laser diode beam, impinges on the surface of the metallic foil, which acts as light absorber as well as thermal wave generator, laser beam is modulated by the internal oscillator of a lock-in amplifier, this arrange is known as thermal wave resonator cavity (TWRC).

Absorbed light at the metal foil induces thermal waves at sample metal interface those thermal waves travel through the sample and, have the same modulation frequency that the incident beam (f). The temperature oscillations at $x = l$ can be measured using the pyroelectric (PE) sensor as a function of the sample thickness l_s. For a thermally thin copper foil ($a_{cu}l_{cu} \ll 1$), thermally thick sample ($a_s l_s \gg 1$) and, thermally thick PE detector ($a_p l_p \gg 1$) (where $a_j = \sqrt{(\pi f/\alpha_j)}$) is the thermal diffusion coefficient, l_j and α_j are the thickness and the thermal diffusivity of the *j-th* element in the PE cell), the output voltage can be expressed as [21, 22]:

$$V = A\left(\frac{\eta_s a_p}{\kappa_p(1+b_{sp})\omega_0}\right) exp[-a_s l_s] exp\left\{-i\left[\frac{\pi}{2}+a_s l_s\right]\right\} \quad (1)$$

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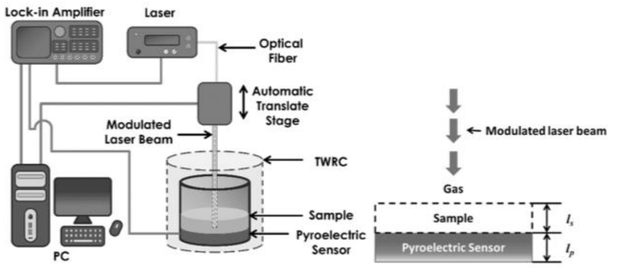

Figure 1. Left: BPPE experimental setup, right: PE-sample arrange detail.

where A is an instrumental factor, η_s is the nonradiative conversion efficiency for the absorbing sample, κ_p is the thermal conductivity of the pyroelectric sensor, $b_{sp} = e_s/e_p$, with e_j the thermal effusivity of the *j-th* element in the PE cell and ω_0 the angular frequency of the laser beam ($\omega_0 = 2\pi f$). When the light modulation frequency is fixed, the constant A and all the terms before the first exponential in Equation 1 remains constant and can be joined in a second constant (B), therefore the output voltage can be reduced as:

$$V = B\,exp[-a_s l_s]exp\left\{-i\left[\frac{\pi}{2} + a_s l_s\right]\right\} \qquad (2).$$

From Equation 2 is possible to see that the measured voltage over the PE depends only on the sample thermal diffusivity (α_s) and thickness. By performing a sample thickness scan, it is possible to get the sample thermal diffusivity from the slope of the logarithm of the photopyroelectric (PPE) signal amplitude as function of l_s or from the slope of the linear PPE signal phase as a function of l_s.

The light modulation frequency used in the present study was chosen at 0.5 Hz, in order to guarantee that sample and pyroelectric sensor were thermally thick; the light source was a diode laser beam, 40 mW power, at 785 nm wavelength.

Thermal effusivity of oil blends were obtained by using the so-called Front Photopyroelectric Technique (FPPE),the experimental setup of this technique is shown in Figure 2, in this configuration the sample is placed on an intimate thermal contact with the PE detector and on the opposite site a modulated laser beam is applied, under the assumption that the sample is thermally thick, i.e. sample thermal diffusion length, $\mu_s = \left(\frac{\alpha_s}{\pi f}\right)^{1/2}$,is shorter than sample thickness, then PE signal can be expressed as [19, 23]:

$$h(\omega) = C\left[\frac{(1-e^{\sigma_p l_p})(1+b)+(e^{-\sigma_p l_p}-1)(1-b)}{(g-1)e^{-\sigma_p l_p}(1-b)+(1+g)e^{\sigma_p l_p}(1+b)}\right] \qquad (3)$$

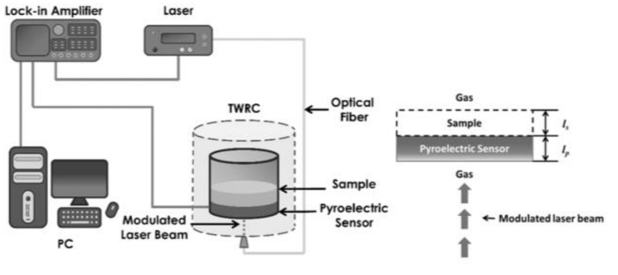

Figure 2. Left: FPPE technique setup, right PE-sample detail

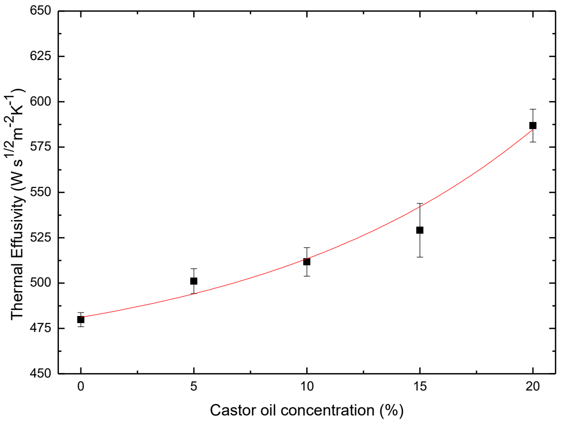

Figure 3. SAE 40W-castor oil blends thermal effusivity behavior as function of castor oil, solid line is a fit of thermal effusivity with an exponential function.

where C is a fitting parameter depending on every pyroelectric sensor, σ_p is the PE complex thermal diffusion coefficient $\sigma_p = (1+i)/\mu_p$, where: $i=(-1)^{1/2}$ and $\mu_p = (\alpha_p/(\pi f))^{1/2}$, with α_p the PE sensor thermal diffusivity, l_p is the PE thickness, $b = e_s/e_p$, $g = e_g/e_p$, with e_s, e_g and e_p, thermal effusivities for sample, air and pyroelectric sensor respectively, using Equation 3 and suitable frequency scan, sample thermal effusivity can be extracted by fitting the theoretical expression to the experimental data. All measurements were performed at room temperature.

Results and discussion

Thermal effusivity as function of castor oil concentration was obtained using the IPPE setup, PE thermal properties were determined a priori by using reference samples with well-known thermal properties. For castor oil- SAE40W oil blends in the 0 to 20 % range castor oil content, thermal effusivity behavior is showed in Figure 3, black squares represent the obtained experimental values, with the respectively confidence interval (± 15 $Ws^{1/2}m^{-2}k^{-1}$), the solid curve is a fit with an exponential function, representing the exponential like behavior of the thermal effusivity as function of castor oil concentration. As expected thermal effusivity increases its value when castor oil content increases, due to castor oil thermal effusivity is about 60% higher than base oil [24].

Figure 4 shows the sample thermal diffusivities obtained by BPPE setup, using the sample thermal diffusivity as fitting parameter in Equation 2, confidence interval for each value was calculated by means of least squares method with a value of ± 3 x10^{-9} m^2s^{-1}. As it can be seen between 10% and 15% of castor oil content, the SAE 40W thermal diffusivity values decreased from 8.9 m^2s^{-1}, value close to the sesame oil or grape seed oil [25, 26], to 8.2 m^2s^{-1} this is a reduction of around 8% of the initial value.

Since the thermal diffusivity ($\alpha_s = \kappa_s/(\rho_s c_s)$) is inversely proportional to the sample density (ρ_s) and specific heat (c_s), then if ρ_s or c_s increases more than thermal conductivity (κ_s) in the oil blends, as a function of the castor oil concentration, then the thermal diffusivity will tend to decrease. In this

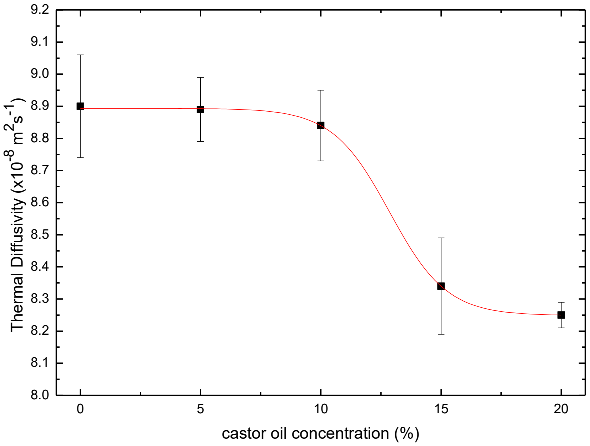

Figure 4. SAE 40W-castor oil blends thermal diffusivity behavior as function of castor oil, solid line is a fit of the thermal diffusivity with a sigmoidal function.

research it was also measured the density of the oil blends and these results are reported at the final of this section, then it will be possible to justify the behavior of the thermal diffusivity in the oil blends.

By using the relation $\kappa = e\sqrt{\alpha}$ thermal conductivity was calculated from thermal diffusivity and effusivity measured, when compared thermal conductivities castor oil presents higher thermal conductivity (0.18 Wm^{-1}K^{-1}) than SAE 40W (0.159 Wm^{-1}K^{-1}) [26, 27] then, it is expected an increment in thermal conductivity when castor oil percentage rises.

It was also measured the densities of the castor oil blends as a function of their concentration which are showed in Figure 5. Densities were measure using a pycnometer method at room temperature results show that castor oil blends present linear increment when castor oil content increase.

Conclusions

Depending on castor oil percentage, thermal effusivity increases as Figure 3 shows, this can be due to pure castor oil thermal effusivity is higher than pure oil.

Blend densities increases as castor oil content increase; SAE 40W density is similar that Sperm whale and castor oil presents higher value [28-30], therefore it is expected and increase in density as function of castor oil content.

Castor oil content provokes that thermal diffusivity diminishes as sigmoidal function, this could be due to the increment in the oil blend densities, by using the relationship $\kappa = e\sqrt{\alpha}$ thermal conductivity was obtained, from calculated values it is possible to see an increment in thermal conductivity as castor oil content rises, as expected due to castor oil thermal conductivity is higher compared with SAE 40W thermal conductivity, then it is possible to increase thermal conductivity by means of adding the adequate content of castor oil.

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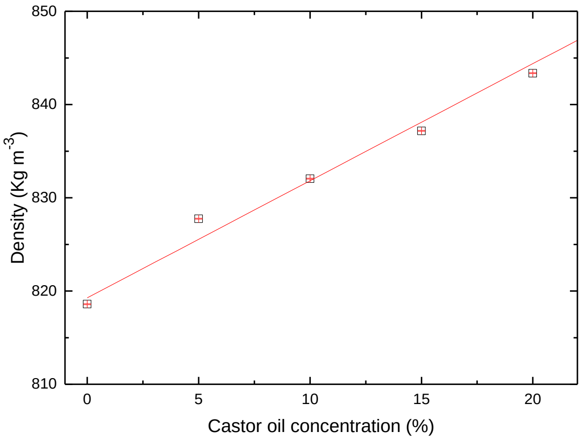

Figure 5. SAE 40W-castor oil blends density.

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