

Article

Effect of Sunflower, Almond, and Rapeseed Oils as Additives on Thermal Properties of a Machinery Oil

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Abstract: Vegetable oils are considered to be eco-friendly and to offer good lubricant properties; however, their low thermo-oxidative stability makes their use as a lubricant base challenging. In this research, sunflower, almond, and rapeseed vegetable oils were added in volumes of 5, 10, 15, and 20% to a machinery oil, and the thermal properties of the resulting fluids were studied. Sunflower, almond, and rapeseed oils were chosen considering their fatty acid composition and the tocopherol content. During this investigation, thermal diffusivity was measured by using the thermal wave resonance cavity technique, while thermal effusivity was determined by the inverse photopyroelectric method, and the obtained values ranged from 4.63 to $5.75 \text{ W s}^{1/2} \text{ m}^{-2} \text{ K}^{-1} \times 10^2$. The thermal conductivity was calculated by obtaining a complete thermal characterization. The results showed a linear relationship between the percentage of vegetable oil and the thermal diffusivity. It was also noted that the thermal properties of diffusivity and effusivity could be tuned when using almond, sunflower, and rapeseed oils in the appropriate percentages. Hence, the influence of vegetable oils on the thermal properties of lubricating oil were closely related to the number of fatty acids.

Keywords: photothermal techniques; biofuels; renewable resources

1. Introduction

Since scientists have become aware of how harmful and irreparable carbon footprints can be, as well as the fact that about half of the lubricating oil used in an engine is released into the environment through engine exhaust vapors, leaks, and spills, many researchers have started to make use of technological advances such as renewable resources, biofuels, and synthetic oils obtained from vegetable sources to reduce the damage of carbon footprints. This is important because previous investigations into fossil substitution with vegetable oils show that they are more than 95% biodegradable, eco-friendly, less toxic, and have a low volatile effect on the environment [1,2]. Economically, edible and non-edible vegetable oils can be easily produced by local farmers, making them an important economic driver. In contrast to what has previously been stated, the extraction of fossil oils is costly, and the oils take a long time to obtain [3,4].

Since lubricants work as an antifriction interface in an engine, with viscosity being their main characteristic, the parameters to be considered when selecting a lubricant should include its chemical stability, corrosivity, environmental effects, and availability, as well

as its thermal behavior. Thus, it is necessary to take an engine's thermal behavior into consideration. Furthermore, it is important to keep in mind that an oil's thermal diffusivity must be related to its heat penetration, while thermal effusivity must be related to its superficial heat interchange. It is important to note that friction will produce interfacial heat, making its dissipation necessary; therefore, thermal effusivity is a crucial thermal parameter to take into consideration [5].

Due to the fact that vegetable oils have been used in lubrication applications [2], as well as cutting fluids [4] and biofuels [6], they have been tested for their ability to modify viscosity and thermal properties when used as additives for fossil oils [7–9]. Modifications to various vegetable oils' thermal properties have been reported as a function of temperature [10,11] when adding nanoparticles [12], as biofuel bases [13], and when modifying tribological and thermal properties [7,14,15]. Hence, the influence of a vegetable oil as an additive in a lubricant oil has been reported to be successful. Additionally, lower emissions of NO_x (25–62%) and SO_x (61–88%) have been reported after adding colza oils [16].

Since tocopherol, a lipid-soluble substance, has the capability to reduce free radicals and has antioxidant properties, it has become an important subject of investigation [3,17]. Samples have been chosen considering the fatty acid composition and the high tocopherol content which can be found in rapeseed, sunflower, and almond oils, at 18–51, 1–59, and 1–44 mg per 100 g, respectively [17,18].

As is well known, the sunflower (*Helianthus annuus*) seed is used as a raw material for oil extraction. In order to do so, the oil is extracted by pressing the seeds or by leaching using solvents [19]. Since the primary use of sunflower oil is as edible oil, it is one of the four most important oils in the world. Furthermore, this oil is made up of polyunsaturated fatty acids, among which linoleic, linolenic, and oleic compounds stand out and are an abundant source of tocopherol [20]. Furthermore, sunflower oil has gained attention because of its capacity to be used as biodiesel through transesterification [21].

An almond (*Prunus dulcis*) is a shelled seed found in a tree, and its oil is a widely used product for everyday use. However, only when the almond oil is submitted to transesterification can it be used for biodiesel [22]. The best-known method to extract its oil is by dry-pressing it.

Additionally, rapeseed (*Brassica napus*) is a bright yellow flowering plant. Its oil extraction is carried out by employing three different methods: cold pressing, hot pressing, and extraction with hexane. One of the uses of this oil can be as a lubricant due to its biodegradable characteristics, but it can only be turned into biodiesel through transesterification [23,24].

Finally, the use of vegetable oil as a lubricant has been limited because of its low thermo-oxidative stability. Even though its thermo-oxidative stability can be improved by using chemical additives or even by using herbal extracts [25,26], the chemical compositions of vegetable oils vary according to the weather, harvest region, and processing method. For these reasons, it is not recommended to use pure oils when lubricating an engine [8]. On the other hand, the most important change in thermal properties occurs when the blending of vegetable and mineral oils takes place in concentrations lower than 20% [7,8]. Lastly, the effect of adding different vegetable oils with high tocopherol contents and different fatty acid compositions over a mineral-based oil is studied in this research, in which vegetable oils with a concentration within a 5% to 20% range are used as additives mixed with fossil oils.

2. Materials and Methods

2.1. Samples

Vegetable oil samples were obtained from a local supplier (F. Paris[®], Merck, Mexico City, Mexico) with 99% purity. It must be pointed out that the physicochemical properties of vegetable oils are affected by agro-climatic growing conditions. Therefore, some variations could be found among the sample types [27].

Motor oil (MO) for high-speed machines SAE15W40 (Mexicana de Lubricantes®, Mexico City, Mexico) [28] and pure vegetable oils from almond (AO), sunflower (SO), or rapeseed (RO) were used during this research. Blends were prepared by using MO as a base lubricant and various percentages (5%, 10%, 15%, and 20% mass-volume) of vegetable oil as an additive, with the percentages of additives selected according to previous studies [7,8]. An automatic stirrer was used for 30 min to ensure homogeneous mixtures; all measurements were made at a room temperature of 23 °C.

2.2. Thermal Effusivity

As a good alternative for obtaining the thermal parameters of different substances, photothermal techniques (PT) have been used to obtain properties such as thermal effusivity (e), diffusivity (α), conductivity (κ), and specific heat (c). In the case of bio-oils, previous knowledge of thermal performance allows the prediction of specific conditions. Thus, the thermal parameters of a wide variety of samples could be obtained by using the photopyroelectric (PPE) technique, which is commonly used for thermal characterization as it uses a frequency-modulated light and a pyroelectric sensor as a thermal wave detector [7,8].

When using PPE techniques, it is possible to obtain the effusivity and thermal diffusivity of liquid samples through reliable and straightforward configurations of techniques such as those known as the inverse photopyroelectric technique (IPPE) and thermal wave resonance cavity (TWRC). Therefore, different samples can be studied by using these configurations in liquids such as oils or mixtures [7,8,29].

As seen in Figure 1, the inverse photopyroelectric configuration (IPPE) was used to obtain the thermal effusivity of the sample. This technique is based on the incident radiation measured directly on the surface of a pyroelectric (PE) sensor, in which the light is modulated by the internal oscillator of a lock-in amplifier. The IPPE signal can be obtained as a function of the light modulation frequency (f), which can be varied in a specific range. When the frequencies are such that the sample is considered to be thermally thick ($l_s > \mu_s$) and the PE sensor is optically opaque, the IPPE signal is expressed as shown in Equation (1) [8,29]. It is also important to know that the experimental setup was always temperature controlled.

$$\theta(\omega) = \frac{(1 - e^{\sigma_p l_p})(1 + b) + (e^{-\sigma_p l_p} - 1)(1 - b)}{(g - 1)e^{-\sigma_p l_p}(1 - b) + (1 + g)e^{\sigma_p l_p}(1 + b)} \tag{1}$$

where $\omega = 2\pi f$, $\sigma_j = (1 + i)/\mu_j$, with the thermal diffusion length defined as $\mu_j = (\alpha_j/(\pi f))^{1/2}$, where α_j and l_j are the thermal diffusivity and thickness of the j -th element in the PE cell, respectively; f is the light modulation frequency, and $b = e_s/e_p$, $g = e_g/e_p$ with e_s , e_g and e_p are the thermal effusivities of the sample, gas (air), and PE sensor, respectively.

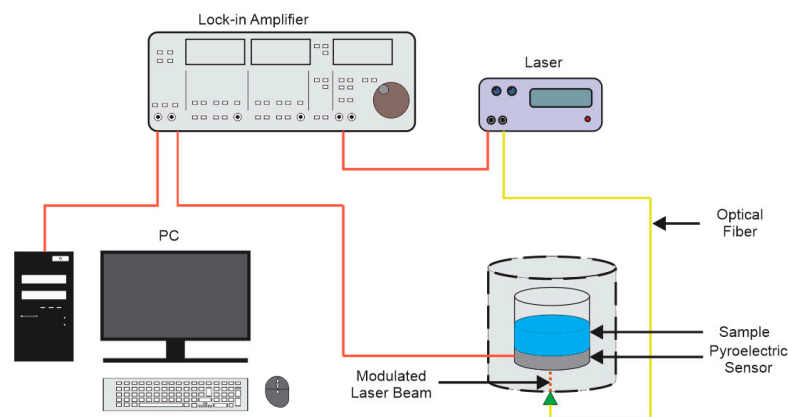


Figure 1. IPPE technique: experimental setup.

Pyroelectric signals obtained from experimentation with air, the analyzed sample, and a specific frequency range were used to calculate the thermal effusivity by using Equation (1). Therefore, the experimental data and Equation (1) were used to calculate the thermal effusivity values [8,29].

2.3. Thermal Diffusivity

In the analysis of thermal diffusivity by the thermal wave resonator cavity (TWRC), in which the sample is enclosed in a chamber formed by a copper foil and a pyroelectric temperature sensor, the chamber should be of variable length so that the thickness of the sample (l_s) can be modified. In this technique, thermal waves are generated at the sample surface opposite to the pyroelectric source, and a lock-in amplifier is used to modulate the laser beam frequency to obtain the pyroelectric signal (Figure 2). The generated thermal waves travel through the sample with the same modulation frequency (f) as the incident beam. The oscillation temperature caused by the thermal waves is measured with a pyroelectric sensor (PE) as a function of the thickness of the sample l_s . For a thermally thick PE detector ($l_p \gg \mu_p$), and a thermally thick sample ($l_s > \mu_s$), the output voltage can be indicated by Equation (2) [7,29]:

$$V = A \left(\frac{\eta_s \alpha_p}{k_p (1 + b) \omega} \right) \exp[-a_s l_s] \exp \left\{ -i \left[\frac{\pi}{2} + a_s l_s \right] \right\} \quad (2)$$

where A is an instrumental factor, η_s is the non-radioactive conversion efficiency for the absorbent sample, and k_p is the thermal conductivity of the pyroelectric sensor. When the light modulation frequency is fixed, only exponential terms are length-dependent; the other terms can be considered constant and grouped into a second constant (B). Therefore, the output voltage can be expressed as

$$V = B \exp[-a_s l_s] \exp \left\{ -i \left[\frac{\pi}{2} + a_s l_s \right] \right\} \quad (3)$$

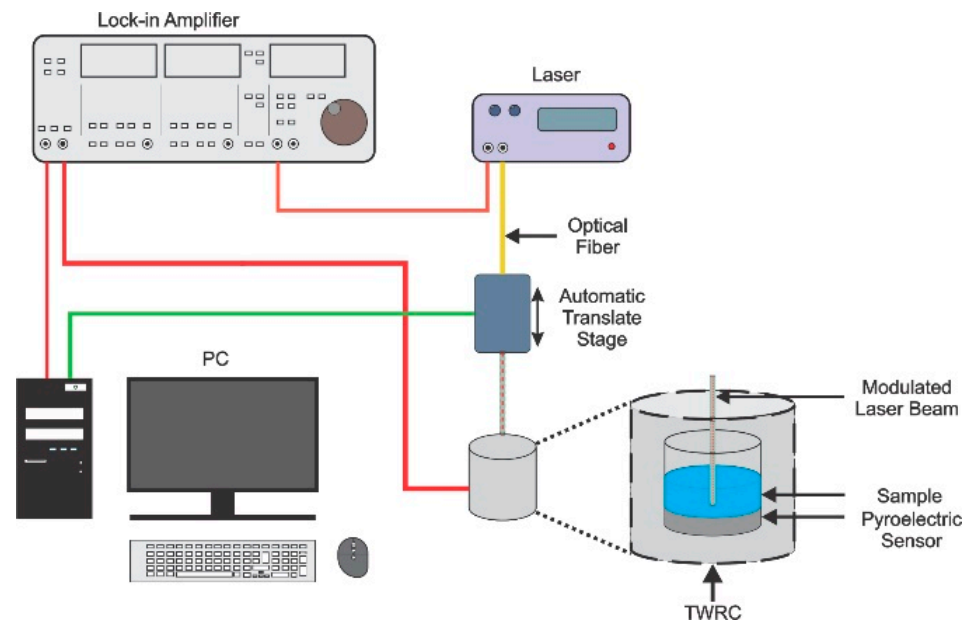


Figure 2. Scheme of the experimental setup of the TWRC.

In Equation (3), the pyroelectric signal only depends on the thermal diffusion coefficient $a_s = 1/\mu_s$, μ_s is a thermal diffusivity function, and l_s is the thickness of the sample; therefore, thermal diffusivity is calculated from the logarithm's slope of the photopyroelectric signal (PPE) phase as a function of l_s [8,29].

3. Results

Figure 3 shows the experimental pyroelectric signal amplitude for the AO/MO mixture, in which the symbols represent experimental points and the solid lines correspond to the best fitting of Equation (1) to the data. Equation (1) was also fitted to RO/MO and SO/MO signals to obtain the corresponding thermal effusivity.

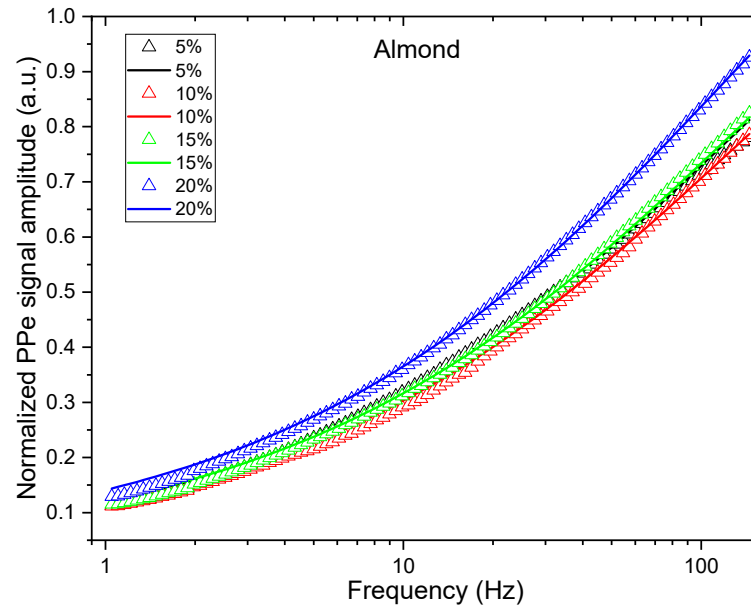


Figure 3. Experimental IPPE signal amplitude with AO/MO mixtures as the sample; triangles represent the experimental points, and solid lines are the best fitting of Equation (1) to the experimental points.

Equation (3) was used to obtain thermal diffusivity values for the studied vegetable–motor oil mixtures. The obtained thermal diffusivity values as concentration functions are presented in Figure 4. In the range of interest (5% to 20%), SO/MO and AO/MO mixtures decreased linearly, while the thermal diffusivity of RO/MO increased. Table 1 shows linear coefficients for sunflower, almond, and rapeseed mixtures. It can be observed that the linear adjustment was more approximate in the values found for almond and rapeseed oils. Although the measurement errors were low, the linear fitting of the sunflower mixture had a low R^2 value, indicating a non-linear behavior.

Table 1. The linear coefficient for thermal diffusivity behavior for the studied samples.

Sample	Slope $\times 10^{-10}$	Intercept $\times 10^{-8}$	R^2
Sunflower	−1.08	7.25	0.32
Almond	−4.54	8.02	0.93
Rapeseed	3	7.12	1

In Table 2, the obtained values of thermal diffusivity and effusivity for the studied mixtures are shown; also, the values for the pure oils are presented. Thermal conductivity values were calculated by using the relationship $\kappa = e\sqrt{\alpha}$. The presented error for thermal conductivity was calculated by error propagation by using the uncertainty values from experimental measurements. It can be seen that the obtained uncertainty values were lower than 2%.

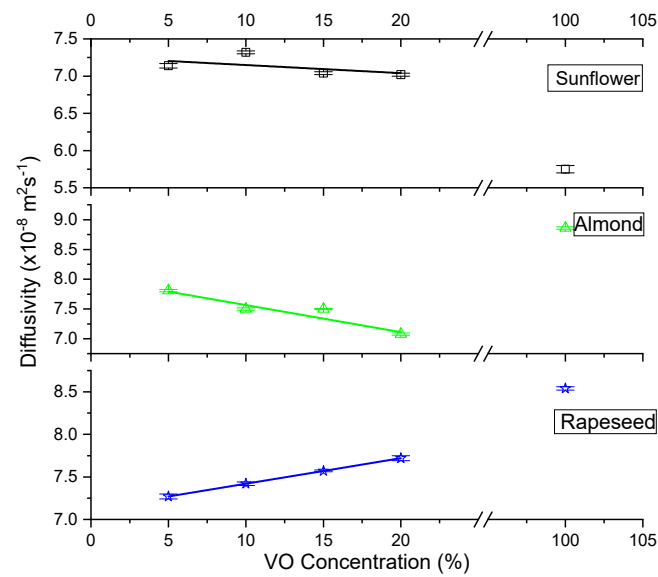


Figure 4. Thermal diffusivity values for sunflower (squares), almond (triangles), and rapeseed (stars); solid lines represent linear fitting in the 5% to 20% range for the corresponding samples.

Table 2. Obtained values for thermal effusivity and thermal diffusivity.

Vegetable Oil to Motor Oil	Vegetable Oil to Motor Oil		Effusivity ($W \cdot s^{1/2}/m^2 \cdot K$) $\times 10^2$	Diffusivity (m^2/s) $\times 10^{-8}$	Conductivity (Calculated) ($m \cdot s^{-1} \cdot K^{-1}$) $\times 10^{-1}$
	VO%	MO%			
Motor Oil	-	100	4.80 ± 0.04	8.88 ± 0.04	1.43 ± 0.01
	5	95	5.20 ± 0.04	7.14 ± 0.01	1.39 ± 0.01
	10	90	4.63 ± 0.01	7.32 ± 0.02	1.25 ± 0.01
	15	85	4.77 ± 0.02	7.04 ± 0.02	1.26 ± 0.01
	20	80	4.81 ± 0.02	7.02 ± 0.02	1.27 ± 0.01
Sunflower	100	-	5.75 ± 0.07	5.75 ± 0.05	1.38 ± 0.02
	5	95	5.04 ± 0.08	7.81 ± 0.02	1.41 ± 0.02
	10	90	5.05 ± 0.08	7.50 ± 0.02	1.38 ± 0.02
	15	85	5.00 ± 0.09	7.50 ± 0.01	1.37 ± 0.02
	20	80	4.86 ± 0.09	7.08 ± 0.02	1.29 ± 0.02
Almonds	100	-	5.72 ± 0.03	8.86 ± 0.02	1.70 ± 0.02
	5	95	4.93 ± 0.10	7.27 ± 0.03	1.33 ± 0.02
	10	90	4.95 ± 0.07	7.42 ± 0.02	1.35 ± 0.02
	15	85	4.92 ± 0.09	7.57 ± 0.01	1.35 ± 0.02
	20	80	4.55 ± 0.02	7.72 ± 0.03	1.26 ± 0.01
Rapeseed	100	-	5.58 ± 0.03	8.54 ± 0.02	1.63 ± 0.01

The thermal diffusivity of RO/MO mixtures increased linearly as the concentration increased, similar to the Jathopha mixtures already reported in the literature [7]. However, SO/MO and AO/MO thermal diffusivity values decreased when the vegetable oil concentration increased; a similar behavior was found in castor oil [27]. The increase in the thermal diffusivity of RO/MO mixture could be related to the difference in the relationship of monounsaturated/polyunsaturated fatty acids, as Table 3 shows. In sunflower and almond oils, the content of monounsaturated fatty acids was lower than the content of polyunsaturated fatty acids. Furthermore, the linear relationship between thermal diffusivity and mixture concentrations has already been established [30], and the calculated values for thermal conductivity were within the range for vegetable oils reported in the literature [8,31–33].

Table 3. Fatty acids content and density for the studied samples.

Sample	Fatty Acids (%)		Density $\times 10^2$ (gr·cm ⁻³)	Reference
	Oleic	Linoleic		
Sunflower	15	62	9.16	[34]
Almond	34	46	9.21	[35]
Rapeseed	61	21	9.14	[34]

Previous studies have shown that absolute thermal conductivity variations lower than 10% can result in smaller wear scars [7]; therefore, the addition of sunflower (5%), almond (5%, 10%, and 15%) and rapeseed (5%, 10%, 15%) can result in wear scar reduction without disrupting the thermal stability of the hydrocarbons.

4. Discussion and Conclusions

Photothermal techniques provide enough precision to measure thermal properties with errors lower than 2%; this precision makes it possible to obtain the variation of thermal properties when vegetable oils are added to motor oil.

Vegetable oils as additives in motor oil can modify thermal diffusivity values for the obtained mixtures; this can be useful depending on the application. During this research, different vegetable oils percentages in the range of 5% to 20% were used; the carboxyl groups in the bio lubricant offered improved lubricity compared to commercial grade SAE15W40 lubricant and potential next-generation lubricants.

It was concluded that the thermal properties of machinery oil can be changed by adding an appropriate percentage of vegetable oil; sunflower and almond oils can raise the thermal diffusivity, while rapeseed oil lowers the thermal diffusivity. Furthermore, the viscosity coefficient is closely related with the thermal properties, because the modification of thermal properties implies a modification of lubricant properties. Photothermal techniques provide an alternative method for indirectly determining the lubricant properties of oils. This alternative method has the advantage of avoiding the use of mechanical parts, which are susceptible to failing.

The influence of vegetable oils on the thermal properties of lubricating oil is closely related to the number of fatty acids. Rapeseed oil raises the thermal conductivity in the same manner as jatropha oil; in both cases, the increase in thermal diffusivity can help in cooling applications. On the other hand, almond and sunflower oils lead to a reduction of thermal diffusivity, like castor oil. The content of vegetable oils is a crucial factor in tuning the thermal parameters of lubricant oils, which are generally used as gear oils, automatic transmission fluids, power steering fluids, and hydraulic fluids.

Future research into tribology is proposed to establish a possible wear scar reduction. Other options could be to explore viscosity and thermal properties as a function of temperature in future investigations.

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