The use of thermal lens spectroscopy to assess oil–biodiesel blends

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HIGHLIGHTS

▶ Thermal lens and mass diffusion effects to assess oil–biodiesel blends.
▶ Thermal and mass diffusivities give significant information on oil–biodiesel blends.
▶ Thermal lens spectroscopy can be used to certify the quality of biodiesel.

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ABSTRACT

Thermal lens (TL) spectroscopy in a dual-beam configuration was applied in a study on biodiesel and oil–biodiesel blends. The goal of this work was to evaluate the behavior of the thermal and mass diffusivities that arose when oil was added to biodiesel and to verify the capability of the method to identify small concentrations of triacylglycerol in biofuel. When transitioning from pure biodiesel to a blend consisting of 98% biodiesel and 2% soybean oil, the thermal diffusivity decreased 15% and the mass diffusivity increased 59%, which indicated that both parameters can provide significant information about the presence of oil in biodiesel. Therefore, TL spectroscopy can be a useful method for certifying the quality of biodiesel and biodiesel blends.

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1. Introduction

It is well known that biodiesel is an alternative fuel that is economically competitive, environmentally healthy and easily available. As such, biodiesel constitutes a viable alternative to traditional fuel, particularly for compression-ignition engines, because, in addition to being a renewable energy source, it can be used directly in existing fuel engines [1]. Currently, the modern diesel engine can operate with 5–10% biodiesel having been added into the total volume of diesel without any efficiency loss [2].

Biodiesel can be produced from a variety of raw materials. Production generally occurs through a transesterification process in which a vegetable oil or animal fat reacts with methyl or ethyl alcohol. This reaction occurs in the presence of a catalyst, which is generally basic, and primarily forms biodiesel (ester) and glycerol [3,4]. Following the reaction, small amounts of triacylglycerol can remain in the final biodiesel product. In addition, traces of

glycerol, residual alcohol and the catalyst can remain, and these substances contaminate the final product; therefore, detecting these traces is critical in biodiesel quality control. Contaminants or impurities can cause serious operational problems when biodiesel is used because they may easily clog an engine's filter. Because of this problem, it is extremely important to monitor the steps involved in biodiesel production to recognize and fix any possible problems that may have been created during the trasesterification procedure. To do so, a rigorous system of quality control is necessary to achieve commercial success in the production of biodiesel [5]. Thus, it is important to search for methods that are able either to standardize and certify biodiesel or to indicate the presence of impurities [6].

A methodology used to study biodiesel and its blends that has been explored only to a very limited extent is thermal lens (TL) spectroscopy, which can characterize the thermo-optical properties of different types of materials [7]. TL spectroscopy is a high-sensitivity optical technique that has been applied in the study of samples with a small optical absorption, and it is attractive because it is neither destructive nor invasive and could possibly be used at gas stations to directly analyze the quality of oils and biofuels. Castro et al. were the first to use the TL method for different biodiesel samples. They concluded that, because of the simplicity

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of the method, it can be applied both in the study of the physico-chemical properties of biodiesel and for certification purposes [8]. Subsequently, Lima et al. used a single-beam TL configuration to indicate the presence of impurities, such as antioxidants, residual catalysts and alcohol, in biodiesel [9]. More recently, the same TL experimental setup was used to characterize biodiesel and diesel and to distinguish biodiesel–diesel blends [10].

In the present work, a dual-beam TL experimental configuration was used to characterize soybean oil, biodiesel and soybean oil–biodiesel blends. To obtain the oil–biodiesel blends, soybean oil was added to biodiesel in a quantity no smaller than 1% and no larger than 5% of the total volume of the biodiesel, which would, therefore, be anywhere from 99% to 95% biodiesel. In the context of this work, soybean oil (triacylglycerol) was regarded as an impurity (i.e., a contaminant) in the biofuel (ester), and our aim was to verify the capability of the TL method to identify small concentrations of this type of impurity in biodiesel.

2. Materials and method

The samples of refined soybean oil (SO) and biodiesel (B) were acquired through local commerce in Brazil. The soybean oil–biodiesel (SOB) blends were prepared in the laboratory according to the concentrations indicated in Table 1.

The SO, B and SOB samples were analyzed using a time-resolved TL technique in a dual-beam mode-mismatched configuration. Fig. 1 shows a schematic diagram of the TL experimental setup that was used in the measurements. This method was based on the TL effect, which is created when laser radiation with a Gaussian intensity distribution profile (an excitation laser) focuses on a material and a fraction of absorbed energy produces a radial temperature change $\Delta T(r)$ [11,12]. This variation in the temperature causes a change in the refractive index of the material in the heated region, and this change is proportional to $\Delta T(r)$. When a wave front from another laser (a probe laser) crosses the heated region, it under-

Table 1
The concentrations of biodiesel (B), soybean oil (SO) and soybean oil–biodiesel (SOB) blends that were studied in this work.

Biodiesel ml (%)	Soybean oil ml (%)	Definition
5 (100)	0 (0)	B
4.95 (99)	0.05 (1)	SOB_1
4.90 (98)	0.10 (2)	SOB_2
4.85 (97)	0.15 (3)	SOB_3
4.80 (96)	0.20 (4)	SOB_4
4.75 (95)	0.25 (5)	SOB_5
0 (0)	5 (100)	SO
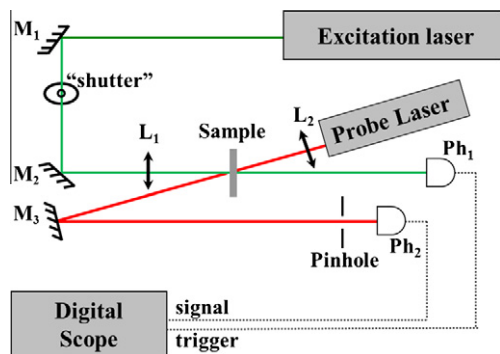
Fig. 1. The dual-beam TL experimental configuration: the items labeled L are lenses, the items labeled M are mirrors, and the items labeled Ph are the photodetectors.

goes a phase variation, which results in either divergence or convergence of the beam, depending on the nature of the material. By controlling this beam profile in the far field (Ph_2 in Fig. 1), some thermal–optical properties of transparent materials, such as thermal diffusivity, can be studied.

In the configuration that was used, the sample was inserted in a quartz cuvette with a thickness of 1 mm, which was then placed in the minimum position of the beam waist of an Argon laser that was tuned at $\lambda_{ex} = 514.5$ nm (the excitation laser), and the TL effect was probed by a HeNe laser at 632.8 nm (the probe laser). The intensity $I(t)$ of the probe laser in the far field was monitored as a function of time. The theoretical model developed by Shen et al. [11] was used to fit the TL experimental data; this model is expressed by the following equation: which is expressed by:

$$I(t) = I(0)\left\{1 - \frac{\theta}{2}\arctan\left[\frac{2mV}{\left[(1+2m)^2 + V^2\right]\left(\frac{t_c}{2t}\right) + 1 + 2m + V^2}\right]\right\}^2.$$
(1)

In the above equation, $I(0)$ is the signal intensity when either t or θ is zero; $t_c = w_{oe}^2/4D_{Th}$ is the characteristic time constant of the TL effect's formation; w_{oe} (m) is the beam's radius in the sample position; D_{Th} (m²/s) is the thermal diffusivity; $V = Z_1/Z_c$, with Z_1 (m) being the distance between the minimum beam waist and the sample position; $Z_c = \pi w_{op}^2/\lambda_p$, with w_{op} (m) being the minimum beam radius and λ_p (nm) is the probe beam's wavelength; and $m = (w_{1p}/w_{oe})^2$, with w_{1p} (m) being the probe beam's radius in the sample position. To gain a better understanding of the geometric beam's position around the sample, please see Fig. 2, which shows an outline of the experimental setup and lists the default parameters: in our setup, $w_{oe} = (45.9 \pm 0.9)$ μm, $w_{op} = (151 \pm 3)$ μm, $Z_1 = (0.205 \pm 0.005)$ m, and $Z_c = (0.113 \pm 0.005)$ m. The distance between the sample and the detector (Z_2) was approximately 4 m, which means that $Z_2 \gg Z_c$ and this is the condition that implies $V = Z_1/Z_c$.

According to the TL theoretical model, θ is proportional to the induced phase difference in the probe laser after it passes by the heated area of the sample, and the equation for θ is as follows [11,12]:

$$\theta = -\frac{PAL}{K\lambda_p}\varphi\frac{dn}{dT}$$
(2)

in which P (W) is the incident power, A (m⁻¹) is the absorption coefficient at the excitation wavelength λ_e (nm), L (m) is the cuvette thickness, K (W/Km) is the thermal conductivity, dn/dT (K⁻¹) is the refractive index temperature coefficient and φ is the fraction of the absorbed energy that is converted into heat.

3. Results and discussion

3.1. Soybean oil and biodiesel

Fig. 3 shows the characteristic TL transients for both refined soybean oil (SO) and biodiesel (B) over a short time interval (a) and a long time interval (b). The SO and B samples were excited at 514.5 nm and had incident powers of 15 and 2 mW, respectively. Because B has a larger TL effect than SO in the excitation wavelength that was used, the measurements could not be developed using the same excitation power. Thus, the powers were chosen so that the amplitudes of the TL signals were approximately 10%, which is within the limit proposed by the theoretical model of the TL (i.e., $\theta < 20\%$), and so the visual comparison was easier. For a short time interval, the experimental data are in very good agreement with the theoretical model of the TL, which is described by Eq. (1). Based on the fit, both θ and t_c could be determined. The values of t_c were (5.0 ± 0.1) and (4.0 ± 0.1) ms for the SO and B