



Full Length Article

Determination of the biodiesel content in diesel/biodiesel blends by using the near-near-infrared thermal lens spectroscopy

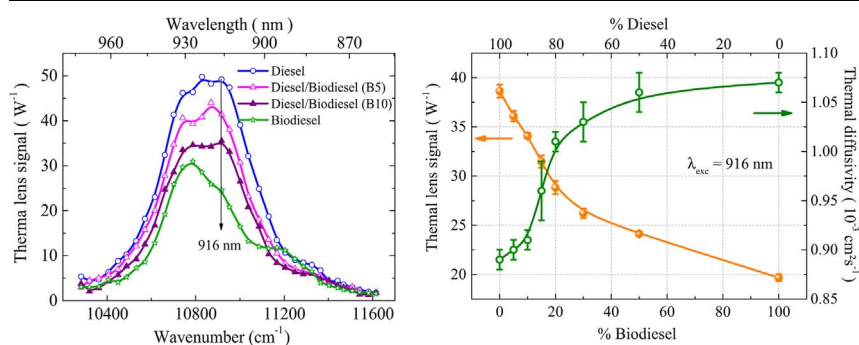


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GRAPHICAL ABSTRACT



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ABSTRACT

A dual-beam mode-mismatched configuration of the Thermal Lens (TL) technique was applied to characterize biodiesel, diesel and diesel/biodiesel blends. The excitation was performed using a tunable laser in the near-near infrared region in order to assess overtones and combination bands of the vibration modes. The thermo-optical properties of the fuels were also determined. The results showed that the biodiesel contents in diesel/biodiesel blends can be monitored with this technique, by excitation the third overtone of the C–H (4ν(C–H)) bond stretching vibration at 916 nm. Both the amplitude of the photothermal signal and thermal diffusivity are important parameters to quantify the biodiesel content in diesel/biodiesel blends.

1. Introduction

The use of alternative fuels is growing on the world in the last few years. The biodiesel produced from vegetal or animal fats have being the main substitute for petroleum-derived diesel fuel due to some factors, such as high combustion efficiency, lower sulfur content, excellent lubricity and high cetane number [1,2]. In addition, its economic and environmental advantages can be highlighted [1–3]. Since biodiesel is

completely miscible in diesel fuel and have similar properties, the use of diesel/biodiesel blends in different proportions is increasing, mainly in Brazil. Currently, the National Energy Policy Council has approved the addition of 8% (v/v) of biodiesel in diesel oil for commercial use [4]. In this context, it becomes necessary to develop or improve methods able to provide fast and efficient results on the biodiesel content in diesel/biodiesel blends, in order to control the quality of the commercialized product.

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A variety of analytical techniques have been developed for the quantification of biodiesel content in diesel/biodiesel blends [5–8], among them, spectroscopic methods involving absorption [9–11] and fluorescence [12]. Infrared (IR) spectroscopy is a reliable and non-destructive analytical technique appropriate for these applications. However, in the NIR spectral range (780–2500 nm) the absorptions of the overtones and combination bands of biofuels are broad, with low absorption coefficients, becoming hardly selective. In addition, differences among samples may cause very subtle spectral differences that are difficult to distinguish without a statistical interpretation [13]. Thus, chemometric methods need to be applied to extract information from NIR spectra obtained with transmittance technique, in order to determine some quality parameters in biodiesel and diesel/biodiesel blends [11].

The Thermal Lens (TL) spectrometry is a time-resolved photo-thermal technique that has been applied in the characterization of oil, biodiesel, biodiesel/oil and diesel/biodiesel blends [14–17]. Castro et al. were the first to use TL in the study of physico-chemical properties of biodiesel and certification purposes [18]. As an ultra-sensitivity technique, TL enable the study of samples with very small optical absorptions ($< 10^{-8} \text{ cm}^{-1}$ in liquids) [19–23]. It is also attractive because it is neither destructive nor invasive, so it could be used at gas stations to monitor the quality of oils and biofuels. Besides, the thermo-optical properties can be directly determined, without the requirement of any statistical analysis. In 1976, Long et al. [19], firstly demonstrated the application of TL as a spectroscopic technique, using a tunable dye laser in the visible range (637–575 nm). Swofford et al. obtained the absorption spectra of benzene, naphthalene and anthracene corresponding to the fifth overtone of the C–H stretching vibrations, with absorptions coefficients as small as 10^{-6} cm^{-1} [20]. More recently, the absorption of overtones and combination bands of sulfentrazone pesticide in the near-near infrared (N-NIR) region were evaluated by the TL spectroscopy, using a Ti^{3+} :Sapphire laser [21]. In this paper, a marker for the pesticide in methanol was identified, enabling the determination of very low concentrations ($\sim 2 \text{ ng}/\mu\text{L}$).

The goal of this work is to apply the TL technique, in both spectroscopic and spectrometric forms, in biodiesel, diesel and diesel/biodiesel blends in order to obtain their absorption spectra and thermo-optical properties. The dual-beam mode-mismatched TL configuration was set with excitation in the N-NIR region (860–980 nm). The absorptions bands were assigned to vibrations of overtones and combination bands of C–H stretching bonds. This electromagnetic region is interesting comparable to the visible one, due to be absence of laser-induced of photochemical reactions or Soret effect (mass diffusion) that can affect the TL signal [22].

2. Materials and methods

The samples of methyl biodiesel (B100), S-10 and S-500 diesel types (B0) used in this research are commercially available in Brazil. The diesel/biodiesel blends were prepared by us according to the concentrations indicated in Table 1. The Brazilian National Agency of

Table 1
Concentrations of biodiesel (B100), diesel oil (B0) and diesel/biodiesel blends used in the study. Two sets of samples were prepared with both S-10 and S-500 diesel types.

Biodiesel mL (%)	Diesel mL (%)	Diesel/Biodiesel Blends
0 (0)	20 (100)	B0 (diesel)
1 (5)	19 (95)	B5
2 (10)	18 (90)	B10
3 (15)	17 (85)	B15
4 (20)	16 (80)	B20
6 (30)	14 (70)	B30
10 (50)	10 (50)	B50
20 (100)	0 (0)	B100 (biodiesel)

Petroleum, Natural Gas and Biofuels [24] has the following classification: types A (without biodiesel) and B (diesel/biodiesel blends). Both diesel types can be S-10 or S-500, according to the sulfur content in the fuel, 10 or 500 mg/kg, respectively.

The mid-infrared (MIR) absorption spectra, in the range from 4000 to 400 cm^{-1} , were obtained with a Fourier transform infrared (FTIR) spectrophotometer Nexus 670 from Thermo Nicolet, coupled to an attenuated total reflectance accessory (ATR – Nexus Smart ARK). The spectrophotometer was purged with dry air to remove any water vapor and the detector was cooled with liquid Nitrogen. The measurements were performed using 0.5 cm^{-1} of resolution and 16 scans.

Absorption measurements in the NIR spectral region (780–2500 nm) were performed using transmittance spectrometer (NIRQUEST by Ocean Optics), with a tungsten lamp and an of 300 μm diameter optical fiber (TP300-VIS-NIR). The absorption spectra were collected with 500 ms integration time and average of 5 spectra per collection.

The TL experimental setup in the dual-beam mode-mismatched configuration is shown in Fig. 1. In this configuration, the sample was inserted in a quartz cuvette with $L = 1 \text{ mm}$ thickness, placed in the position of minimum waist (w_{oe}) of the excitation beam, a Ti^{3+} :Sapphire laser pumped by a 532 nm semiconductor. The TL effect was probed by a 632.8 nm HeNe laser, which passes through the sample almost collinear through the excitation beam. Both beams are nearly TEM_{00} Gaussian.

In the TL experiment the excitation induces a refractive index profile which results in a lens like effect. In most liquids, dn/dT is negative, so sample behaves like a divergent lens. The theoretical model for the mode-mismatched TL experiment was developed by Shen et al. [25]. According to this model, the on-axis transient intensity of the probe beam, $I(t)$, can be expressed by:

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

in which $I(0)$ is the intensity when $t = 0$ or $\theta = 0$, m and V are intrinsic geometric parameters from the probe and excitation lasers (see Ref. [26] for details). In Eq. (1) $t_c = w_{oe}^2/4D$ is the TL characteristic time constant; w_{oe} (cm) is the waist of the excitation beam in the sample position and D ($\text{cm}^2 \text{ s}^{-1}$) is the thermal diffusivity. The amplitude of the TL signal is proportional to the parameter θ , which is approximately to the probe beam thermally induced phase difference and is given by [25,26]:

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

in which P (W) is the excitation power, A (cm^{-1}) is the absorption coefficient at the excitation wavelength, λ_p (cm) is the probe wavelength, L (cm) is the cuvette thickness, dn/dT (K^{-1}) is the thermo-optical coefficient at the probe beam wavelength and $K = \rho CD$ is the thermal conductivity ($\text{Wcm}^{-1}\text{K}^{-1}$), ρ (gcm^{-3}) is the volumetric density of the sample and C ($\text{Jg}^{-1}\text{K}^{-1}$) is the specific heat. With these definitions it is possible to rewrite Eq. (2) as:

$$\theta = -\frac{PAL}{\lambda_p D} \left(\frac{dn}{dQ} \right) \quad (3)$$

with $\frac{dn}{dQ} = \frac{1}{\rho C} \frac{dn}{dT}$ defines how the refractive index changes with the heat deposited per unit volume in the sample.

Fig. 2 presents a typical normalized TL transient signal, $I(t)/I(0)$, obtained for the S-10 diesel with $P = 4 \text{ mW}$ and $\lambda_{exc} = 916 \text{ nm}$. The experimental data were fitted with Eq. (1) from which two parameters were determined: $t_c = (40 \pm 2) \text{ ms}$ and $\theta = (0.151 \pm 0.003) \text{ rad}$. From t_c and $w_{oe} = 119 \mu\text{m}$, the thermal diffusivity $D_{B0(S-10)} = (0.89 \pm 0.01) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ was calculated. The value $dn/dQ = -2.45 \times 10^{-4} \text{ cm}^3 \text{ J}^{-1}$ was obtained using the following

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