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Full Length Article

Assessing thermal and optical properties of biodiesel by thermal lens spectrometry: Theoretical and experimental aspects

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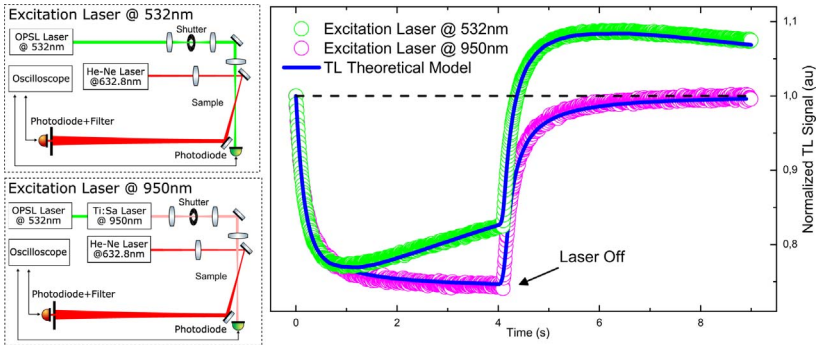
GRAPHICAL ABSTRACT



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ABSTRACT

Recent studies on laser induced thermal lens effect has made it possible to use this tool to investigate thermophysical and chemical properties of biofuels. During laser illumination, a number of light induced effects may take place in the excited volume of the sample. However, the complexity of information included in the thermal lens transients could lead to misinterpretation of the results. This work examines the theoretical and experimental aspects that must be considered when performing biodiesel analysis using thermal lens spectrometry. The induction of photochemical reaction and thermal diffusion processes is carefully accounted for by describing the localized optical path change due to the concentration gradient created within the sample. We characterize mechanical, chemical and photochemical properties of thermal degraded biodiesels, enabling quantitative access of mass diffusion coefficient, photobleaching cross-section, and thermal yield. Dynamic viscosity analysis corroborates the results obtained by thermal lens, describing the method as very sensitive to thermal stability discrimination of biodiesel.

1. Introduction

Biodiesel is an alternative sustainable source of energy to fossil fuel and its derivatives. Biodiesel is defined as a fuel compounded by monoalkyl esters of long-chain fatty acids that can be produced by the transesterification, blending, cracking, micro-emulsification, and pyrolysis of vegetable oils, animal fats or lipids provided from microalgae [1–4]. By transesterification method, biodiesel can be produced by any

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triglyceride feedstock that includes more than 300 oil-bearing crops as potential feedstock [5]. Due to the wide offer of feedstock, cost and simplicity, transesterification reaction of vegetable oils and animal fats with alcohols is the predominant method for large scale commercial production [2,5]. The reaction yield depends on the type of alcohol used, the amount of free fatty acids, and water present in the biodiesel feedstock [2,4].

Biodiesel is produced from a number of sources under different processes. The standardization of biodiesel is fundamental to make it a commercialized product for application as fuel for engines, for instance. The quality of biodiesel has been defined by standard specifications such as the ASTM D6751 and EN 14214 [3]. The quality control is characterized by specific properties such as calorific value, cetane number, mass density, viscosity, and oxidation stability, among others [3–6].

In order to develop a highly sensitive method for the characterization of biodiesel properties, recent studies have applied the thermal lens (TL) spectrometry to investigate thermal and optical properties of oil and diesel blends of biodiesel and the photo-stability of vegetable feedstock for biodiesel [7–13]. In the usual mode-mismatched TL configuration, a continuous wave (cw) Gaussian laser beam excites the sample and produces a localized thermal gradient. This heating induces an optical path variation in the excited volume acting as an optical lens. The optical path change is monitored by measuring the wavefront distortion caused by the optical element to a second cw probe Gaussian laser beam. The probe beam is detected in the far-field region [14,15] by measuring its on-axis intensity variation. In photo-sensitive materials, though, photo-induced chemical reactions may take place causing a decreasing of the optical absorption centers in the sample and, in some cases, a chemical induced concentration gradient can be produced [10,16–22]. In addition, thermo-diffusion or Soret effect – a thermally induced concentration gradient produced by the drift of disperse particles due a thermal gradient in a fluid mixture [23,24] – may also generate a thermally induced concentration gradient. Both photochemical and Soret effects create a time-dependent concentration of the absorbing species that affects the thermal lens signal [18].

The evolution of the theoretical description of the TL effect employed in the past decade used several different approaches to describe the time and spatial dependence of the optical absorption coefficient with the changes by photobleaching and/or mass diffusion within the excited volume of the sample [10,16–22]. These models and applications were capable of retrieving reasonable physical insights for simple and even complex mixtures using theories considering either photochemical reaction [16,17,20–22], mass diffusion or Soret effect [18], or a combination of both [10,18,19].

In the presence of thermal and concentration gradients, the complexity of information included in the TL transients could lead to misinterpretation of the results. Recently, in an all numerical approach, the role of individual contributions of photoreaction and mass diffusion in the thermal lens experiments was extensively explored [10,19]. This resulted in a powerful tool to better understand and discriminate the role of the photophysical processes in thermal lens of fluid. Considering the recent applications of thermal lens to study biodiesel, here we present a detailed theoretical discussion and experimental verification aspects that must be considered when performing thermal lens measurements in biodiesel. Photoreaction and mass diffusion properties are accessed by the rigorous theoretical description of the laser induced phenomena in the sample. As a result, quantitative results are obtained for the dependence of the optical absorption, concentration coefficients of refractive index, photo-reaction cross-section, and mass diffusion coefficient with the state of the thermal oxidation of the biodiesel.

2. Theory

In the thermal lens experiment, the optical absorption of the excitation beam causes a change in the thermal state of the sample. The refractive index varies in the excited volume of the sample and induces an optical path change that acts as an optical lens to the probe beam. The on-axis intensity variation of the probe beam, at the far-field detector, is given by [14]

$$\frac{I(t)}{I(0)} = \left| \int_0^\infty \exp[-(1+iV)g - i\Phi(g,t)]dg \right|^2, \quad (1)$$

where $I(0)$ is the initial intensity (for $t = 0$), V is a geometric parameter from the experimental setup [14], $g = (r/\omega_{1P})^2$, ω_{1P} is the probe beam radius at the sample, and $\Phi(g,t)$ is the phase-shift induced to the wavefront of the probe beam by the optical path change. Assuming that the excitation laser beam causes photochemical reaction or Soret effect, even in very low optical absorptive liquids, the phase-shift induced to the probe beam can be described by [18]

$$\Phi(g,t) = \theta_T T(r,t) + \theta_C C_R(r,t). \quad (2)$$

Here $T(r,t)$ and $C_R(r,t)$ are the temperature and reagent concentration distributions over time. As described in previous work [25], the ratio between saturated and unsaturated species changes as a result of the biodiesel degradation. In order to account for the degree of degradation, we consider the biodiesel as a pseudo-binary mixture, with $C_R(r,t)$ describing the time evolution of saturated and unsaturated species concentration. $\theta_T = (2\pi L/\lambda_p)(\partial n/\partial T)$, $\theta_C = (2\pi L/\lambda_p)(\partial n/\partial C)$, $\partial n/\partial T$, and $\partial n/\partial C$ are the temperature and concentration coefficients of refractive index variation for the probe beam wavelength (λ_P) and L is the thickness of the sample.

Under laser-induced photochemical reaction, the temperature and concentration distributions (ratio between saturated and unsaturated species) in the absence of Soret effect and convection can be described by the solutions of [19]

$$\frac{\partial}{\partial t}T(r,t) - D_{th}\nabla^2 T(r,t) = \theta_{th}[(1-\epsilon)C_R(r,t) + \epsilon] \times e^{-2r^2/\omega_{0e}^2}[1-H(t-\xi)], \quad (3)$$

and

$$\frac{\partial}{\partial t}C_R(r,t) - D_m\nabla^2 C_R(r,t) = -\theta_R C_R(r,t)e^{-2r^2/\omega_{0e}^2} \times [1-H(t-\xi)], \quad (4)$$

where $\theta_{th} = 2P_e\beta\varphi/\rho c\pi\omega_{0e}^2$ and $\theta_R = 2P_e\sigma/\pi\omega_{0e}^2 h\nu$. β is the optical absorption coefficient at $t = 0$,ρ is the mass density, c is the specific heat, D_{th} and D_m are the thermal diffusion and mass diffusion coefficients. P_e, ω_{0e} and ν are the absorbed power, the excitation beam radius at the samples position, and the optical frequency of the excitation laser, respectively. σ is the photo-reaction cross-section, h is the Planck constant, ϵ is the optical absorptivity of the reactants (ϵ_R) and the products (ϵ_P) ratio, that participate in the photochemical reaction. φ is the fraction of the absorbed energy available for conversion to heat. $H(1-t)$ is the Heaviside Theta function, which accounts for the laser-on ($t < \xi$) and laser-off ($t > \xi$) excitation regimes. The Soret effect is a concentration gradient induced by the thermal gradient, and does not depend on the excitation wavelength. The absence of this effect will be experimentally demonstrated by performing the TL experiments in different excitation wavelengths.

As described in previous works [10,19], the solutions of the equations presented here are obtained numerically employing the "NDSolve" input in the Mathematica software, using the internal method "MethodOfLines", under the boundary conditions: $T(r_0,t) = 0$, $\partial T(r_0,t)/\partial r = 0$, $C_R(r_0,t) = 1$ and $\partial C_R(r_0,t)/\partial r = 0$, in which $r_0 \gg \omega_{1P}$. By this method, Eq. (1) can be used to fit the experimental TL transients, providing quantitative information on the parameters θ_T, θ_C, θ_{th}, θ_R, ϵ, D_{th}, and D_m.

3. Material and methods

The biodiesel tested in this work was a commercial sample provided by BSBIOS Renewable Energy Company. The biodiesel was derived