



Full Length Article

Thermal Lens Temperature Scanning technique for evaluation of oxidative stability and time of transesterification during biodiesel synthesis



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ABSTRACT

In this work, laser-induced Thermal Lens Temperature Scanning technique (TL-TS) is applied to evaluate oxidative stability and time of transesterification during biodiesel synthesis. Samples collected at different time intervals during the transesterification process of sunflower (SF) and soybean (SB) oils were submitted to fast oxidation through temperature scanning (between 22 and 190 °C), and simultaneously measured with the TL-TS technique. Temperature dependence of Thermal Lens effect amplitude showed the occurrence of oxidation, with the onset (T_{onset}) changing with the transesterification stages from 149 to 169 °C for sunflower and from 120 to 142 °C for soybean samples. The characteristic evolution of T_{onset} with reaction duration was estimated to be ~7 min for sunflower and ~10 min for soybean samples. The thermal diffusivity values were shown to be sensitive to rapid changes at transition temperatures, which could be related to molecular ruptures. Additional measurements were performed with DSC, TG and FTIR, to validate the information obtained by the TL-TS technique. In conclusion, the results showed the TL-TS technique as a promising tool for oxidative stability evaluation and determination of both chosen working temperature and minimal time interval for the solution to reach an optimized transesterification stage, thus contributing for reduction of costs, quality control and consequently for certification of biodiesel fuels.

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1. Introduction

Biodiesel is non-flammable, nonexplosive, biodegradable, non-toxic and free from sulphur and aromatic compounds. Biodiesel also produces fewer harmful emissions compared to petroleum diesel fuel [1,2] which makes it a good alternative to substitute petroleum diesel [3]. However, long-term storage has been a problem because the unavoidable presence of residual unsaturated fatty acid esters makes biodiesel susceptible to oxidation or autoxidation [4,5].

Usually, biodiesel has esters of oleic, linolein or linolenic acids and the trend of increasing stability follows the sequence of concentrations as linolenic < linoleic < oleic [6]. These esters undergo autoxidation at different rates depending upon the number and

positions of the double bonds. As a consequence, occurs formation of peroxides and hydroperoxides and a series of by-products with shorter-chain compounds of low molecular weight such as acids, esters, aldehydes, ketones, lactones, etc. [7–9]. Oxidation stability is, thus, a parameter that describes the degradation tendency of biodiesel and therefore it is of great importance in the context of possible problems in engine performance. Another important aspect is knowledge of the minimal time interval for the reaction to reach the optimal transesterification stage, since it plays an important role in the reduction of the cost of biodiesel production [10,11].

Thermal Lens technique (TL) is a high sensitivity method and it is attractive because of its remote characteristic that allows quantitative measurements to be performed without physical contact between the sample and the detector. This feature has been explored for studies submitting the tested samples to temperature scanning [12–14], external electrical fields [15], different crys-

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talline orientations [16] and composition changes [17–19]. The possibility of construction of low-cost compact setups suggests the TL method for use at gas stations to directly analyze the quality of oils and biofuels. Castro et al. [19] used the TL method to study different biodiesel samples, and recommended the method for certification purposes. Subsequently, Lima et al. used the TL method to detect the presence of impurities in biodiesel, such as antioxidants, residual catalysts and alcohol [20]. The method was also used to distinguish biodiesel from diesel blends [21].

In this work, the Thermal Lens method in the Temperature Scanning mode [12–14], here defined as (TL-TS), is applied for evaluation of oxidative stability and time of transesterification during biodiesel synthesis. The experiments were performed in samples obtained at different time intervals during the transesterification process of soybean (SB) and sunflower (SF) oils. These oils were selected because they have been used on a large scale for biodiesel production in Brazil.

2. Material and methods

2.1. Sample preparation

The main goal in this study was to evaluate samples collected during the biodiesel synthesis in order to monitor different stages of the transesterification process. The samples were produced using SF and SB oils, which were purchased in the local market. The choice of the concentration and the working temperature for solution are known to be important to maximize the conversion of oils into esters. For the present study, we used the optimized condition obtained by Gandolfi [22], with the initial solution containing (ethylic) alcohol/oil molar ratio of 9:1, (KOH) catalyst concentration of 1% and reaction temperature at 40 °C. Here, when the temperature of the solution reached 40 °C, small portions were withdrawn at different times, obtaining samples for several stages of the transesterification process [23]. The first sample was collected 1 min after the solution reached 40 °C, and the last one after 180 min. Next, they received 0.1 mol/L of HCl solution, and then were shaken, cooled down for reaction halting, centrifuged and put in desiccators to constant weight. They were insert in small flasks and stored in a refrigerator for 24 h, when the measurements were started.

2.2. Characterization

2.2.1. Thermal Lens spectroscopy

The experimental setup used for the Thermal Lens technique was described elsewhere [14]. Excitation was performed with an Ar⁺ laser, Coherent Innova 90 Plus, tuned at 514.5 nm and the probe was a He-Ne laser, JDS Uniphase, at 632.8 nm. These wavelengths were selected far from the UV region of the spectrum in order to avoid laser induced photo degradation of the samples. The oscilloscope was a Hewlett-Packard, model 54615B of 500 MHz. Both photodiodes present linear behavior to the variation of light intensity and the response times are on the order of few microseconds. The samples were placed in a 2 mm optical path quartz cuvette; next, they were inserted in an oven containing a pinhole allowing the passage of the two laser beams. Temperature scanning was performed with a Lake Shore 340 temperature controller. The lenses were mounted on a XY moving plate to allow perfect alignment of the two beams. Laser incidence on the sample was controlled by a Melles Griot light shutter.

The experiment was performed in the following way: first, the probe beam was aligned by using mirrors that drive it to have its center pass through a pinhole positioned in front of the detector; after that, the mirrors drove the excitation beam to the central part

of the probe beam at the sample position, inducing the Thermal Lens effect. As a consequence, an intensity change in the detector was obtained. The transient of the TL signal lasted around 200 ms and was recorded by the digital oscilloscope. The data were transferred to a personal computer for subsequent analysis. The device comprising the furnace and the cuvette with the sample were heated under a rate of 1 °C/min, ranging from 20 to about 190 °C. Each consecutive excitation beam shot was performed at 10 s-intervals, resulting in six transients per °C of the scanning temperature.

The analytical expression to fit the transients provides the values of two parameters, θ and t_c . The first is related to the induced phase difference in the probe beam wave front after its passing through the Thermal Lens effect formed in the sample, while t_c reveals the thermal diffusivity (D) of the material under investigation [12–16]. For experiments as a function of temperature, θ and t_c are temperature dependent, given by (1):

$$\frac{\theta(T)}{P_e L_0} = - \frac{A_e(T)}{\rho(T)c_p(T)D(T)} \left(\frac{dn(T)}{dT} \right) \frac{1}{\rho \lambda_p} \quad (1)$$

and

$$t_c(T) = \frac{\omega_e^2}{D(T)} \quad (2)$$

here P_e is the excitation beam power, L_0 the sample thickness, A_e the optical absorption coefficient at the excitation beam wavelength, ρ the mass density, c_p the specific heat, dn/dT the temperature coefficient of refractive index and λ_p , the probe beam wavelength. By performing the measurements with the sample positioned in the heating unit, the temperature dependence of the parameters can be measured. In other words, $\theta(T)$ and $D(T)$ can be obtained by plotting the respective fitting parameters against the temperature of the measurements. Further details of this procedure can be found elsewhere [12].

Thermal diffusivity of non-crystalline materials, in first approximation [12], can be described by the Debye model, which can be calculated by considering only lattice phonons contributing for thermal conductivity, $k = \frac{1}{3} C v_s m$. Here, volume heat capacity is $C = c' / Vol$. Thermal diffusivity is defined as $D = \frac{k}{\rho c}$, in which specific heat is $c = c' / mass$. By using the relation for k and D , it follows that thermal diffusivity (D) is dependent on sound speed (v_s) and phonon mean free path (m) and may be written as [12] Eq. (3):

$$D = \frac{1}{3} v_s m \quad (3)$$

In this way, one can say that thermal diffusivity is sensitive to changes in the microstructure of solids or liquids, which is printed in the values of the mean free path and the average speed of sound. It is known from kinetic theory that heat conduction predicts thermal conductivity dependent on defects and crystallinity of the medium. Furthermore, thermal diffusivity reflects how quickly a material reacts to a change in temperature, which also reflects changes in its microstructure. Then, in a dynamic experiment dependent on temperature, as in this work, it may also reflect the oxidation process.

2.2.2. Differential scanning Calorimetry (DSC) and Differential thermal analysis (DTA)

The samples were analyzed in a Netzsch, STA 409 PG/4/G Luxx Model. The samples were submitted to a heating rate of 10 °C/min. Measurements were performed in atmosphere of pure nitrogen (100% N₂) and synthetic air (80% N₂ and 20% O₂).

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