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Technical note

The role of viscosity in the fluorescence behavior of the diesel/biodiesel blends

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ABSTRACT

Recently, the potentiality of fluorescence spectroscopy to be used in the quantification of biodiesel content in diesel/biodiesel blends (DBB) was demonstrated. However, the source of the fluorescence dependence of the DBB with biodiesel concentration remains unanswered. In the present paper, a close analysis of the optical properties of the DBB was performed over a wide composition range. The findings suggest that the alterations in the fluorescence intensity can be accounted for only after taking into account changes in viscosity as well as absorbance, in a model where the fluorophores were considered as molecular rotors.

1. Introduction

Biodiesel is a biodegradable fuel produced from renewable sources that can partly or completely replace petroleum-derived diesel fuel because its properties are quite similar to the ones of the diesel [1,2]. Consequently, the mandatory use of diesel and biodiesel blends (DBB) is growing around the world due to their environmental, economic, and social advantages [3,4]. In this worldwide scenario, to ensure compliance with legislation, it is necessary to either develop or improve methods able to determine the biodiesel content in the DBB. Of course, it is desirable that this determination be achieved via experimental methods that are easy to handle, provide rapid and accurate results, and have a low cost per sample analysis.

In a recent study, our research group proposed an alternative method based on the fluorescence spectroscopy to quantify the biodiesel content in DBB [5]. We showed that a linear increase in the fluorescence intensity of the blends occurs when the biodiesel content in the DBB increases from 0 to 10% (v/v). In consequence, this linear relationship can be used as a calibration curve to determine the biodiesel percentage [5]. This method has the advantage of working without a sample pre-preparation and can potentially be applied directly at the gas station by using a portable device. However, from a theoretical viewpoint, the origin of the fluorescence increase in these blends when raising the biodiesel concentration is not yet understood and deserves to be accounted for.

Here, to gain further insights into the fluorescence behavior of the DBB, a close analysis of the optical properties of these blends was performed by measuring and analyzing their UV–Vis absorption, molecular fluorescence, and viscosity data over a wide composition range.

2. Materials and methods

Biodiesel was obtained from the transesterification process of refined soybean oil, using a 6:1 M ratio of methanol/oil. The NaOH catalyst (0.4 wt.% with respect to oil weight) was dissolved in methanol and then added to the preheated soybean oil at 60 °C. The solution was stirred for 60 min and then placed in a separating funnel for 24 h. Two phases were observed, one containing mostly biodiesel and the other containing glycerol. After that, the biodiesel was rotary-evaporated under reduced pressure to eliminate excess methanol. Subsequently, the biodiesel was washed four times using tap water (30% v/v) at room temperature and intervals of 30 min. Finally, DBB samples were prepared by using a certified diesel provided by Petrobras (Petróleo Brasileiro S.A.). Henceforth, DBB

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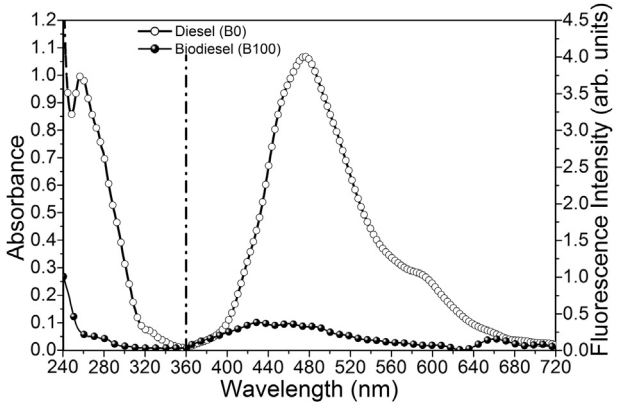

Fig. 1. Diesel and biodiesel absorbance between 240 and 360 nm; diesel and biodiesel fluorescence in the 360–720 nm region when excited at 260 nm.

are named BX, where *X* represents the volume percentage of biodiesel in the blend. This work was conducted on DBB samples with the composition varying from B0 to B100, in steps of 10%.

The UV absorption spectra were obtained in the 240–360 nm range using an absorption spectrophotometer (Cary 50, Varian). To prevent the saturation of the absorption signal in the UV region, the samples were diluted in n-hexane (1% v/v). All absorption measurements were performed at room temperature, using 1-cm path length quartz cells. Fluorescence emission spectra were obtained using a fluorescence spectrophotometer (Cary Eclipse, Varian). The system is based on Czerny–Turner monochromators, a R928 photomultiplier, and a Xenon pulsed lamp. UV light was used to excite the samples at 260 nm, while the fluorescence spectra were recorded in the spectral region between 360 and 720 nm. The "right-angle" geometry was used to collect the fluorescence spectra at room temperature, by using 1-cm path length quartz cells.

The plastic viscosity, η, of the samples was determined in a Brookfield digital rheometer model LVDV-III through the Bingham math model available in the Rheocalc V2.5 software. A thermostatic bath was used to ensure a temperature of 25.0 ± 0.5 °C. Measurements were made using the coaxial-cylinder geometry with a cylinder of external diameter of 100 mm (reference Spindle SC4-18).

3. Results and discussion

Fig. 1 shows both the absorption and fluorescence spectra of the diesel (B0) and biodiesel (B100) samples. As pointed out in the previous section, the UV absorption was measured between 240 and 360 nm, while the fluorescence signal was collected in the 360–720 nm range with a 260 nm excitation light. In particular, B0 shows two fluorescence bands centered at 475 and 585 nm, and B100 shows two bands with fluorescence peaks at around 440 and 660 nm. Of great significance for this work is the observation that B0 presents a higher absorbance and fluorescence than B100, a result ascribed to the aromatic compounds present in B0, which exhibit a well-defined absorption band at around 260 nm [6]. The origin of the fluorescence in B100 may be attributed to remaining fluorophores from vegetable oil used in the biodiesel production, such as tocopherols and chlorophyll, since biodiesel has an emission spectral profile similar to the one observed in the oil feedstock [7]. Nevertheless, the contribution of the mono- and polyunsaturated fatty acid methyl esters to the fluorescence may not be ruled out [7,8].

For the reason given below, we will focus our attention on analyzing the optical properties of those DBB ranging from B10 to B90. Absorbance (at 260 nm) and fluorescence (at 475 nm)

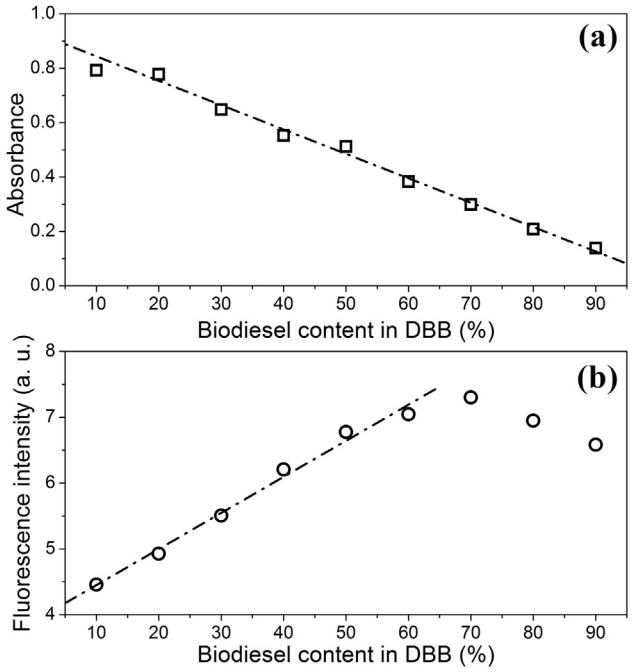

Fig. 2. Absorbance at 260 nm (a) and fluorescence at 475 nm (b) as a function of the biodiesel content in diesel/biodiesel blend.

magnitudes of the blends upon biodiesel content variation are shown in Fig. 2. The results reveal that, in the one hand, DBB absorbance presents a linear decrease with biodiesel content (Fig. 2a); the fitting giving a linear correlation coefficient (R^2) of 0.9932. On the other hand, regardless (i) the above monotonous decrease of absorption and (ii) the fact that the fluorescence intensity of B100 is lower than B0 (refer to Fig. 1), Fig. 2b rather shows a linear increase of the DBB fluorescence intensity within B10–B60 composition range, reaching a maximum value for B70, after which the emission decreases. Before proceeding with discussion of these results, the following comments should be made. The fluorescence data presented in the current study were all collected from non-diluted samples with the expectation that fluorescence spectroscopy could be used to quantify the biodiesel content in DBB without any previous sample preparation. Nevertheless, we should point out that fluorescence measurements performed on diluted samples (data not shown here) also revealed similar DBB fluorescence comportment when the biodiesel content is altered.

As the DBB fluorescence behavior cannot be totally attributed to the absorption changes, we looked for further insights into this issue by evaluating whether the fluorescence increase (in the B0–B70 composition range) might be associated with changes in the viscosity of the blends. The results are presented in Fig. 3, and show a linear increase of the DBB viscosity upon variation of the biodiesel content, with a high linear correlation coefficient (R^2) of 0.9922. This result is predictable as biodiesel is well known to be more viscous than diesel, because the former is slightly more polar due to the presence of oxygen in the structure. As a consequence, the increase in the viscosity may lead to an increase of the fluorescence quantum yield, Φ_F, due to the potential dependence of fluorescence with respect to the viscosity of the medium in which the fluorophores are immersed [9]. In the following, aiming to evaluate whether the observed fluorescence behavior can be explained by considering both the absorption and viscosity changes in the blend, the relationship between Φ_F and the emission spectra as well as the viscosity dependence of Φ_F will be presented and discussed.