J Fluoresc (2011) 21:1027–1031
DOI 10.1007/s10895-010-0815-x

SHORT COMMUNICATION

# Determination of the Biodiesel Content in Diesel/Biodiesel Blends: A Method Based on Fluorescence Spectroscopy

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Received: 27 June 2010 / Accepted: 29 December 2010 / Published online: 8 January 2011


**Abstract** Blends of biodiesel and diesel are being used increasingly worldwide because of environmental, economic, and social considerations. Several countries use biodiesel blends with different blending limits. Therefore, it is necessary to develop or improve methods to quantify the biodiesel level in a diesel/biodiesel blend, to ensure compliance with legislation. The optical technique based on the absorption of light in the mid-infrared has been successful for this application. However, this method presents some challenges that must be overcome. In this paper, we propose a novel method, based on fluorescence spectroscopy, to determine the biodiesel content in the diesel/biodiesel blend, which allows *in loco* measurements by using portable systems. The results showed that this method is both practical and more sensitive than the standard optical method.

**Keywords** Fluorescence spectroscopy · Biodiesel · Diesel · Blend

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## Introduction

Biodiesel is a biodegradable fuel derived from renewable sources such as vegetable oils and animal fats. This fuel can partly or completely replace petroleum-derived diesel because its properties are quite similar to those of diesel fuel. Consequently, blends of biodiesel and diesel have been used worldwide because of their environmental, economic, and social advantages. Several countries including Brazil, Japan, the United States, and most European countries have adopted biodiesel blends, but with different blending limits. To illustrate, Brazil mandated the use of 5% biodiesel by volume in the diesel/biodiesel blend (DBB) [1]. To ensure compliance with legislation, it is necessary to develop or improve methods to quantify the biodiesel content in DBB. Additionally, it is desirable that the biodiesel percentage in the blend be determined by methods that are easy to use, have a low cost per sample analysis, and provide rapid and accurate results.

Fourier transform mid-infrared (FT-IR) spectroscopy has been successfully used for quantification of biodiesel in DBB [2, 3]. The Brazilian Association of Technical Standards (ABNT) regulated, by means of the NBR 15568 standard, the experimental conditions for determination of biodiesel content, in the range between 0.5% (v/v) and 30.0% (v/v), in diesel oil by FT-IR spectroscopy. This quantification is based on the infrared absorption of around 1746 $cm^{-1}$ assigned to the molecular vibration of C=O bonds in biodiesel molecules. This vibration was chosen for monitoring because petroleum-derived diesel does not contain C=O bonds in its structure.

Despite the good results obtained by FT-IR spectroscopy, some challenges must be overcome, such as the possibility of obtaining misleading results due to the presence of contaminants containing C=O bonds, and the difficulty of

applying this method directly at gas stations. A variety of analytical techniques have been developed for quantifying biodiesel content in DBB [4]. Methods based on radiocarbon analysis [5], ester number [6], saponification number [7], near-infrared spectroscopy [4, 8, 9], ultraviolet absorption spectroscopy [10], liquid and gas chromatography [11–13], and nuclear magnetic resonance spectroscopy [4] have been reported. Despite the several proposed methods, the development of alternative methods that combine low cost, fast and accurate results, and portability is still the object of research. Portability is desirable to allow fuel measurements directly at the point of sale instead of in the laboratory, reducing cost and analysis time.

Methods based on fluorescence spectroscopy appear promising because they might meet all these requirements. Fluorescence spectroscopy has been used in the characterization of different materials, and allows *in loco* measurements by means of portable systems that are already commercially available.

In this study, we present a method based on fluorescence spectroscopy for use in determining the biodiesel content in DBB. UV-Vis absorption and FT-IR measurements of biodiesel, diesel, and DBB were also carried out to support the development of the method. We also assessed the accuracy of the fluorescence spectroscopy method compared to the technique based on FT-IR spectroscopy.

## Material and Methods

Biodiesel was obtained from the transesterification process of refined soybean oil, using a 6:1 molar 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 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, the DBB, hereafter called BX, where X represents the volume percentage of biodiesel in the blend, was prepared. The diesel used in this study was obtained from Petrobras (Petróleo Brasileiro S.A.).

The UV absorption spectra in the 240–340 nm range were obtained using an absorption spectrophotometer (Cary 50, Varian). The samples were diluted in dichloromethane (DCM) in order to prevent the saturation of the absorption signal in the UV-Vis region. Each 10-ml sample of DBB was diluted in 50 ml DCM. All measurements were performed at room temperature.

Fluorescence emission spectra were obtained using a bench fluorescence spectrophotometer (Cary Eclipse, Varian). The bench system is based on Czerny-Turner monochromators, a R928 photomultiplier, and a Xenon pulsed lamp. Fluorescence measurements were also performed using a portable spectrofluorimeter (MM Optics) that consists of a laser operating at 405 nm, a monochromator, a Y-type optical fiber, and a portable computer. UV light at 260 nm (405 nm) was used to excite the fluorophores present in the samples, and the fluorescence was collected using the bench spectrophotometer (portable system). All fluorescence spectra were recorded using 1-cm path length quartz cells.

Mid-infrared absorption measurements were carried out using a spectrophotometer (Nexus 670, Thermo Nicolet) combined with an attenuated total reflectance (ATR) accessory. The spectrophotometer was purged with dry air in order to eliminate water vapor during the experiment. For each sample, 64 scans were made, and spectra were obtained between 4,000 and 400 $cm^{-1}$ with a 2-$cm^{-1}$ resolution.

## Results and Discussion

The UV absorption of diesel (B0) and biodiesel (B100) was measured to determine the best excitation wavelength to be used in the fluorescence measurements. Figure 1 shows the absorption spectra of the B0 and B100 samples between 240 and 340 nm. From this result, it can be seen that B0 has a higher absorbance in the UV region than does B100, principally due to the aromatic compounds present in B0, which exhibit a well-defined absorption band around 260 nm [10]. Absorption measurements of the DBB (B1 to B10) were also made, and the data, shown in Fig. 2, revealed a linear decrease of absorbance at 260 nm as a function of biodiesel content, as reported in Ref. [10]. An

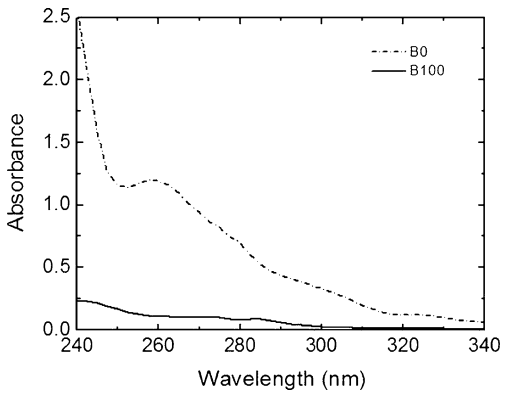


**Fig. 1** UV absorption spectra of the diesel (B0) and biodiesel (B100) diluted in dichloromethane

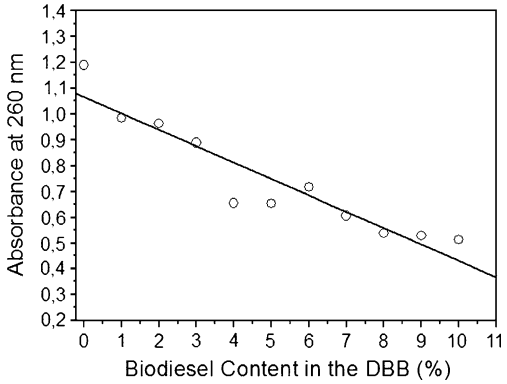


**Fig. 2** Absorbance at 260 nm as a function of biodiesel content in the DBB

angular coefficient (β) of −0.063 and a correlation coefficient ($R^2$) of 0.8682 were obtained by fitting the experimental data.

Figure 3 shows the fluorescence spectra of B0 and B100 when excited at 260 nm. B0 shows two fluorescence bands centered on 475 and 585 nm, and B100 shows two bands with fluorescence peaks at 470 and 660 nm. However, the fluorescence intensity at 470 nm from B0 is about five times higher than that from B100. In order to evaluate the fluorescence behavior of DBB, the emission spectra were obtained, and the area under each spectrum in the 280–800 nm range was calculated. The data indicated an increase in the emission intensity of the blends when the biodiesel content in the DBB increases, and this fluorescence enhancement is linearly dependent on the biodiesel content. Additionally, the similar emission profile shape of B0 was observed for the DBB (B1 to B10) samples. The $\delta$ parameter ($\delta = [(A - A_o)/A_o].100\%$, where $A_o$ and $A$ are the area of spectrum of the B0 and DBB curves, respectively) was determined for each sample. This parameter indicates the relative change of the fluorescence intensity of the blend with respect to the fluorescence of

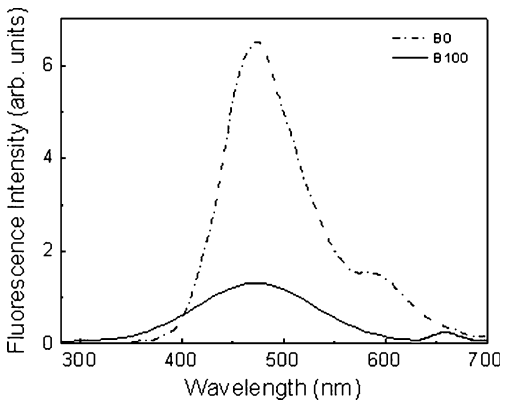


**Fig. 3** Fluorescence spectra of diesel (B0) and biodiesel (B100) under excitation at 260 nm

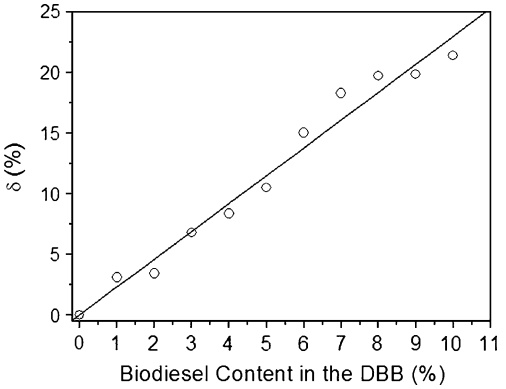


**Fig. 4** δ as a function of biodiesel content in the DBB for excitation at 260 nm. The δ indicates the percentage variation of the area under the curve of the fluorescence signal, calculated in the region between 280 nm and 800 nm

the diesel. Figure 4 shows that the $\delta$ value increases linearly with the increase in the biodiesel concentration. The theoretical fit of the data shown in Fig. 4 (solid line) led to a coefficient of correlation ($R^2$) of 0.9872 and an angular coefficient ($\beta$) of 2.30. These data show that the addition of 10% (v/v) biodiesel to the blend yielded a 22% increase in fluorescence intensity.

In order to assess the applicability of the fluorescence method by using it directly in the gas station, a portable commercial fluorescence system with excitation at 405 nm was also used to characterize the DBB samples. This excitation wavelength was chosen because a GaN-based diode laser with enough power (~50 mW) to excite the DBB samples is easy to find commercially. In this case, only one emission band around 497 nm was observed in the diesel and DBB (data not shown). Nevertheless, a linear dependence of the fluorescence intensity on the biodiesel content was also observed, as can be seen in Fig. 5 by the $\delta$ parameter versus

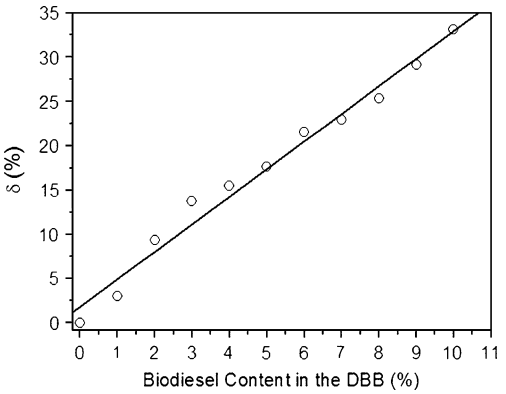


**Fig. 5** δ as a function of biodiesel content in the DBB for excitation at 405 nm. The δ indicates the percentage variation of the area under the curve of the fluorescence signal, calculated in the region between 415 nm and 800 nm

the biodiesel content in the blend. From the linear fit, the values obtained for $R^2$ and $\beta$ were 0.9903 and 3.11, respectively. This result shows that in the biodiesel concentration range studied here, the increase in the fluorescence intensity was 33%.

Although the discussion above has taken into account the area under the fluorescence spectra, a linear behavior was also obtained when the analysis was based on the fluorescence peaks. The fluorescence enhancement might be associated with the change in viscosity of the blend as the biodiesel content increases. It is well known that physical properties (e.g., viscosity and optical density) and chemical composition (e.g., concentration of fluorophores and quenching species) play an important role in the emission intensity and spectral profile. For instance, the fluorescence emission of heavy oils is generally broader, weaker, and has shorter lifetimes than that observed in lighter oils [14–16]. In addition to the different chemical structure of biodiesel from that of diesel fuel, biodiesel is more viscous than diesel because it is slightly more polar due to the presence of oxygen in the structure. Consequently, the viscosity of the blends increases when the biodiesel content rises, as reported by Kulkarni and co-workers [17]. An increase in the viscosity of the blend leads to a reduction in the collision frequency of the molecules, improving the probability that molecules in the excited state will return to the ground state via the radiative process and thus enhancing the fluorescence intensity of the blend.

FT-IR measurements were also carried out to probe the structural change in the blends with the addition of biodiesel. Figure 6 shows the typical FT-IR spectra of the B0 and B100. The absorption band around 1746 $cm^{-1}$

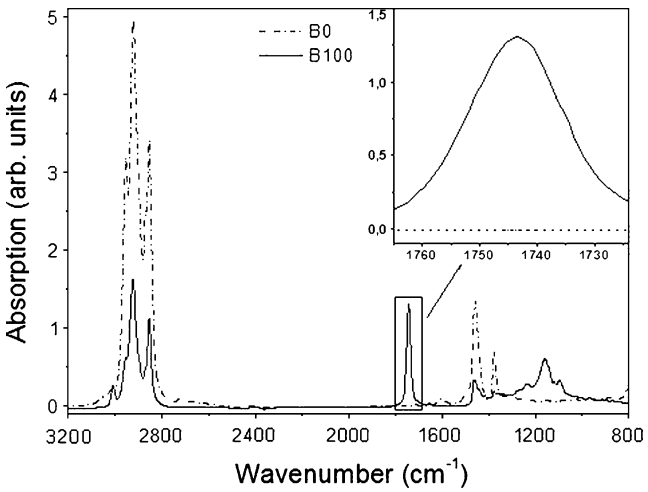


**Fig. 6** Absorption spectra of diesel (B0) and biodiesel (B100) in the mid-infrared range. The inset shows the absorption dependence of the vibration peak of C=O around 1746 $cm^{-1}$

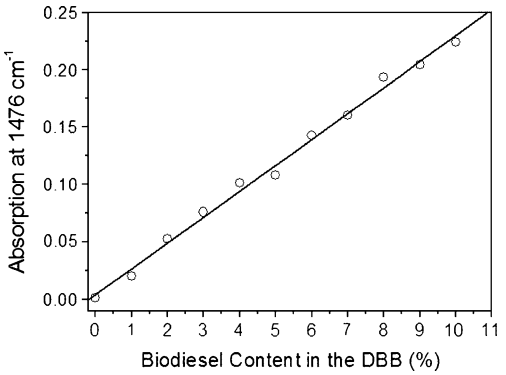


**Fig. 7** Absorption intensity at 1746 $cm^{-1}$ as a function of biodiesel content in the DBB

assigned to the C=O vibration, shown in the inset in Fig. 6, might be used to determine the percentage of biodiesel in a blend. A linear increase of the absorption at 1746 $cm^{-1}$ of the DBB is displayed in Fig. 7. The solid line is a theoretical fit of the data. The angular coefficient ($\beta$) and coefficient of determination ($R^2$) associated with the fit are 0.023 and 0.9969, respectively. The results indicate that the blends used in this study were properly prepared.

In a comparative analysis, it can be noted that the increase of the fluorescence signal obtained under 405 nm laser excitation as a function of the percentage of biodiesel content in the DBB was about 135 times more intense than that obtained by the FT-IR signal, indicating that fluorescence spectroscopy can be much more sensitive to detect the biodiesel content in the DBB in the concentration range from 0 to 10%. Moreover, in terms of application, a laser fluorescence device operating in the visible region is easier and cheaper to construct than the FT-IR device, because FT-IR requires expensive optical components to operate in the middle infrared region.

## Conclusions

In summary, both bench and portable fluorescence systems are able to determine the biodiesel percentage in the blends as well as the methods based on FT-IR and UV absorption spectroscopy. However, the fluorescence method has the advantage of being portable, allowing tests to be conducted at gas stations. In addition, this technique allows biodiesel quantification without prior sample preparation. The results also showed that the fluorescence method was more sensitive than the FT-IR technique in the process of determining the percentage of biodiesel in the DBB (B1 to B10). Although the present study demonstrated the applicability of the fluorescence method to the process of quantifying the biodiesel content in the DBB, further

investigations are necessary to verify if the method will work with biodiesel produced from different raw materials and will be independent of the diesel fuel used.

**Acknowledgments** We are grateful for financial support from CNPq, CAPES, and FUNDECT. This work was performed under the auspices of the National Institute of Science and Technology of Photonics and the National Institute of Science and Technology of Optics and Photonics.

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