Measurement of biodiesel concentration in a diesel oil mixture

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Abstract

After the development and consolidation of automotive ethanol technology in the last thirty years, Brazil is starting the development of biodiesel technology pushed by the coming oil crisis. Since, the Brazilian biodiesel law sets the percentiles of biodiesel mixed in diesel oil 2% after 2008, and to 5% after 2013, the development of a method to measure such mixture percentiles becomes necessary. We present a method of measurement that covers the full range of mixtures (0–100%) of biodiesel in diesel oil using mid infrared spectroscopy. We show that the carbonyl (C=O) absorption peak, which is present only in biodiesel, presents power law proportionality with mixture percentile of 0.889 for peak area and 0.841 for peak height, respectively. Therefore it becomes possible to measure mixture percentiles of biodiesel in diesel oil, even at very low concentrations, allowing quality control and law enforcement.

Keywords: Biodiesel; Diesel oil; FTIR

1. Introduction

The first petroleum crisis, in the early seventies, started a search for alternative fuels, which in Brazil resulted in the development of ethanol technology for automotive applications [1]. Nowadays, this technology is mature and allowed the development of Flex fuel vehicles that run on gasoline, ethanol or on a mixture of both. In the first months of 2006, Flex fuel vehicles reached more than 70% of all sales in the Brazilian automotive market, of more than one hundred thousand vehicles a month [2]. The appeal of this technology is so convincing that even foreign carmakers are offering Flex fuel versions of their products [3] in the Brazilian market.

The growing geopolitical crisis, related to oil reserve control, and the global efforts to reduce green house effect gas emissions in the atmosphere, based on the Kyoto protocol, are the motivations to push biodiesel technology research in Brazil. The law 11,097, sanctioned January 13 of 2005, granted the biodiesel effort by turning mandatory the use of 5% biodiesel in diesel oil mixture by 2013, with an intermediate percentile of 2% to be used after 2008. As an ecological fuel, biodiesel seems to be the Flex option for diesel oil. Its very low or null percentile of sulfur [4] also ensures a reduction of acidic rains. Since, a major part of Brazilian cargo transport is based on diesel oil fueled trucks, biodiesel use will promote a considerable reduction in pollutant and green house gas emissions.

There will be a growing need for quality control in both manufacture and distribution networks, therefore a mixture percentile measurement method will be required.

In this work, we show an efficient method for biodiesel–diesel oil mixture percentile measurement over the full range (0–100%) that fulfills the needs of quality control and can be even used embarked for motor efficiency control. In the literature, similar methods are presented
as biodiesel production control tools using near infrared spectroscopy [5,6].

2. Experimental

The first effort of this work was the search for a parameter that could allow the measurement of biodiesel mixture percentile in diesel oil. Since, optical properties are widely used to characterize organic compounds, we aimed on infrared absorption (IR) for samples of both biodiesel and diesel oil. Initially the measurements were performed on pure samples, from 650 cm$^{-1}$ up to 4000 cm$^{-1}$ (15.4–2.5 μm), to determine the existence of useful differences. All absorbance measurements were performed with a Fourier Transform Infrared Spectrometer (Midac – Fuel Analyzer Model: Fox-F8001) that operates in the mid infrared. Diesel oil measurements were performed using type-D diesel oil, also known as “Metropolitan diesel oil”, in accordance with Brazilian legislation [7]. Measurements with biodiesel were performed using different raw material sources and types, all of them in accordance with Brazilian legislation [8].

For biodiesel–diesel oil mixture measurements we have used soybean ethyl ester biodiesel. Mixtures were performed by volume from 0% to 100% biodiesel in diesel oil. All measurements were performed on samples without pre-treatment, which are the conditions for future applications as quality control. Measurements of absorbance were performed using 32 scans in the range from 4000 cm$^{-1}$ to 600 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. The spectra were obtained without baseline corrections. Even the comparisons between different samples is performed using raw data.

3. Results and discussion

3.1. Pure sample spectra

After performing IR absorption measurements over both near infrared (NIR) and mid infrared ranges, we found the mid infrared range the more promising, since, in this range there are many unmatched peaks between biodiesel and diesel oil. Fig. 1 shows spectra for both pure type-D diesel oil and pure soybean ethyl ester biodiesel over the measured range.

Fig. 1 clearly shows evident differences of both spectra for wavenumbers smaller than 2000 cm$^{-1}$, which corresponds to mid infrared. Within this range two different sub-ranges were considered of most interest. The first from 1000 cm$^{-1}$ to 1300 cm$^{-1}$, where biodiesel presents many overlapping peaks, not present in diesel oil. The second goes from 1700 cm$^{-1}$ to 1800 cm$^{-1}$, where biodiesel presents a prominent peak, which corresponds to the carbonyl group (C=O) absorption, known as the carbonyl peak, typical of esters [9]. This absorption peak is connected to the stretching vibration of ester groups, and is known by its relatively constant position and freedom from interfering bands [9]. It also has been used in the study of ethyl biodiesel synthesis from vegetal oil [10]. We found no observable trace of this peak in the diesel oil spectra.

Since, biodiesel can be obtained from many different seeds or plants, and in either ethyl or methyl types, we performed spectra measurements for different sets of each type. Fig. 2 shows the ethyl ester biodiesel mid infrared absorption spectra for a series of different raw materials were a quite perfect overlap was observed over the full range. The differences are smaller than the line thickness used in the plots.

The same procedure was performed for methyl ester biodiesel obtained from different sets of raw materials. As in the previous case all the spectra overlap over the full range, as shown in Fig. 3.

Finally, we have compared soybean synthesized ethyl and methyl ester biodiesel spectra, as shown in Fig. 4. Again, we noticed a difference in the region from 1000 cm$^{-1}$ to 1300 cm$^{-1}$ and an unimportant shift in the carbonyl absorption peak. Such stability despite raw material and process changes makes this absorption peak a...
strong candidate for biodiesel–diesel oil mixture measurements.

3.2. Mixed sample spectra

The mixed samples were prepared by mixing different volumes of pure soybean ethyl ether biodiesel in pure diesel oil. The choice for soybean was done based on the actual focus of the Brazilian biodiesel program. The mixture percentile was varied from 0% to 10% in steps of 1%, and from 10% to 100% in steps of 10%. Thus, the whole mixture range was characterized, with emphasis in the low percentiles, which are within the range required by Brazilian legislation. Fig. 5 presents the spectra evolution over the full range of mixture, with the intent to emphasize the peak evolution, and therefore the individual spectrum identification is not relevant.

Fig. 6 shows a three dimensional evolution of the carbonyl peak with mixture percentile. It is important to notice that the peak is observable even at very low mixture percentiles.

The carbonyl peak evolution quantification was performed over the range from 1700 cm\(^{-1}\) to 1800 cm\(^{-1}\) using OriginLab-Origin 7 software. Parameters were obtained by fitting Lorentzian curves to the peaks after subtracting the baseline. We found that both peak area and peak height present a slight non-linearity when plotted against mixture percentile. The proportionality was obtained performing a linear fit over a log–log plot of the data, shown in Fig. 7, that indicated the existence of power law proportionality of 0.889 and 0.841 with the mixture percentile for peak area and peak height, respectively. The equation obtained for peak area can be written as

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\text{Peak area} = 0.373 \times (\text{Vol\%})^{0.889},
\]

where Vol\% is the volumetric concentration of biodiesel. For peak area the fitting correlation factor \((R)\) is 0.9995 and the standard deviation 0.017 indicating a rather good
quality. Most of data (94.7%) is within 5% deviation from the fitted function. For peak height the equation is

$$\text{Peak height} = 0.0199 \times (\text{Vol})^{0.841}.$$  \hspace{1cm} (2)

For peak height the fitting correlation factor is 0.9993 and the standard deviation is 0.0197, which is also good for the applications intended. Although peak height present bigger deviation still most of the data (84.2%) is within 5% deviation from fitted function.

We also observed a uniform, but very small peak position displacement toward small wavenumbers with concentration increase, reaching 0.2% over the full mixture range. The FWHM (Full-Width Half-Maximum) of the peak showed a linear increase from 11.9 cm\(^{-1}\) to 15.4 cm\(^{-1}\) over the same range.

### 4. Conclusions

We have performed near and mid infrared absorbance measurements of diesel oil and biodiesel, from different processes and sources. The spectra obtained indicated two different ranges of interest, where peaks of biodiesel and diesel oil do not overlap. Measurements performed with different biodiesel raw materials and manufacture processes pointed to the carbonyl (C=O) absorption peak as the choice for measurements of biodiesel–diesel oil mixture. Mixture percentile measurements were performed from pure diesel oil (0% biodiesel) up to pure biodiesel (100% biodiesel), in steps of 1%, from 0% to 10% biodiesel, and in steps of 10%, from 10% to 100% biodiesel. The carbonyl peak evolution presented power law proportionality with mixture percentile of 0.889 and 0.841 for peak area and peak height, respectively, allowing direct measurement of mixture percentile over full range of possible mixtures of biodiesel in diesel oil. This result is very important, since, it proposes a simple way to perform quality control and continuous monitoring of mixture percentiles in the field or in the laboratory. Since, this subject is law regulated, the existence of a control method to allow law enforcement is of fundamental importance. A confirmation for the method validity was found in two patents regarding the measurement of gasoline–alcohol mixtures using absorption peaks in near infrared spectra [11,12].

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