Fiber optic sensor for methanol quantification in biodiesel

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ABSTRACT

In this work a refractometric sensor for assessment of methanol presence in biodiesel is reported. The transducer relies on the interference between the forward and back propagating modes of a single long period grating, written close to an end-face mirror optical fiber. The sensing method is thermally assisted in order to overcome the drawback caused by the high refractive index (close to the fiber cladding index) of methanol-biodiesel blends at low temperatures. Sensor showed a combined standard uncertainty of 0.6 % v/v of methanol in biodiesel for a confidence level of 68.27%, within the methanol concentration ranging from 0 to 25 % v/v.

Keywords: Optical fiber refractometric sensor, methanol content in biodiesel, biodiesel analysis.

1. INTRODUCTION

Biodiesel consists of alquil esters and it is produced by transesterification reaction, which occurs by the alcoholysis (with methanol or ethanol) of vegetable oils, animal fats or waste oils in the presence of a catalyst. Biodiesel has similar physical properties of diesel and can be considered as an alternative fuel, once it is obtained from renewable, biodegradable and non-toxic resources. For such reasons, it has been the focus of study and great attention in recent decades [1, 2]. The preference for the biodiesel synthesis using methanol is associated with budget factors, once methanol is more accessible in the actual production process. In the case of methanolysis the oil solubility in methanol is minor and the mass transfer reaction is limited, but due the fact that methanol presents a shorter molecular chain and higher polarity, the separation process of the ester and glycerin is easier. On the other hand, ethanol has a larger chain, which makes the glycerin miscible in ester and is a drawback in the phase separation process [3]. Besides, the production of methyl ester occurs in a shorter period of time and with higher efficiency under the same reaction conditions [4]. The product of the transesterification reaction is a mixture of biodiesel, glycerides, glycerol, residual catalyst and alcohol. The residuals, contaminants and the glycerol must be removed from biodiesel to ensure the quality of the product. For that sake, it is necessary to control important parameters, which must follow standards based on the American (ASTM D6751) and European (EN – 14214) specifications. Methanol is responsible for metal corrosion, mainly aluminum corrosion, as well as for the decreasing of the fuel flash point. It is also responsible for cetane number (indicator of ignition quality) [5]. The low fuel quality increases the fuel consumption, results in heating and acceleration of the motor engine, also causing emission of particulate matter and toxic gases [5]. Methodologies commonly used in the analysis of fuels are expensive and time consuming, requiring specialized laboratories. Techniques usually used for biodiesel analysis, as liquid and gas chromatography, high performance liquid chromatography and nuclear magnetic resonance spectroscopy [6], require the separation of biodiesel components. This procedure results in time delay compromising all the fuel production process. The excess of methanol is typically removed from biodiesel by extraction and distillation [7]. The maximum amount of methanol that can be present in biodiesel is about 0.2% mass/mass (test method EN – 14110) or 0.2% volume (test method D93 by ASTM standard) [8]. From the mentioned reasons, there is an increasing interest on the development of new sensing technologies able to provide information about the product conformity. Optical fiber sensors, when applied as refractive index transducers, show unique properties that allow its use as concentration sensor [9,10]. In the past few years, refractometric optical fiber sensors based on long period gratings (LPG) have been proposed for real-time monitoring of liquid mixtures [11]. Particularly in the analysis of fuels and biofuels, optical fiber sensors have been emerged as a promising tool and over the years several works have been presented in this area. LPG based devices have been used as refractometric sensors to measure the concentration of ethanol in blends ethanol – gasoline [12] and to determine concentrations of biodiesel in blends biodiesel and biodiesel-diesel-oil [13].

In this work, is evaluated the performance of an optical fiber grating refractometric sensor in the analysis of biodiesel regarding the presence of remaining alcohol. Results showed the sensor capability to determine small concentrations of methanol, making the sensor a promising device to the assessment of biodiesel quality.

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2. MATERIAL AND METHODS

Binary samples of methanol-biodiesel used in this work were prepared by mixing soybean biodiesel (97% of ester content) and methanol (99.9%) in different proportions. Samples were named MX, where X stands for the methanol content in the blend. Two 25 mL graduated burettes (0.1 mL resolution) were used to prepare 20 mL of each sample, from M0 to M20 in steps of 10 mL. Five samples with small concentration of methanol (M1, M2, M3, M4 and M5) were also prepared by using 10 mL graduated pipettes (0.1 mL resolution). An Abbe refractometer (Atago, DR-A1, resolution of 0.5×10^{-4}) was employed to measure samples refractive indices at 20 °C and at 40 °C. Temperature was controlled with the help of a calibration thermostatic bath (Lauda - Ecoline Staredition E200, resolution of 0.01°C). Measurements were also carried out with a cascaded long period grating refractometric sensor (CLPG). The experimental procedure adopted consists of the complete immersion of the CLPG (LPG plus cavity) into the MX samples. To keep the sample temperature constant, test tubes that contain the binary samples were immersed into the calibration thermostatic bath. As the refractive index of pure biodiesel is close to the refractive index of the optical fiber cladding at 20°C, samples were heated and kept at 40 °C during the experiments. Due to the biodiesel negative thermo-optic coefficient, the temperature increase reduces the samples refractive index, enabling the visualization of the CLPG interference fringes when the grating is immersed in these samples[13, 14]. CLPG sensor employed in the experiments was produced by coating with a silver layer one of the tips of the fiber that contains the LPG, resulting in a device with a round-trip cavity 8 cm long. LPG was engraved in photosensitive Nufern-GF1 fiber by using a KrF laser at 248 nm and the point-to-point technique. The CLPG works as an in-fiber Michelson interferometer, the fiber cladding and core along the cavity length being the interferometer arms. A superluminescent LED (*Superlum*, *Pilot-2*) and an optical spectrum analyser (OSA - *Anritsu, MS9710B*) with ± 5 pm of wavelength stability and 0.1 nm resolution were used to obtain the CLPG spectra. For each sample were taken 30 successive measurements under repeatability conditions. After the analysis of each MX sample and before inserting the device in another sample, CLPG sensor was cleaned by immersing the device in isopropanol, ketone and isopropanol again. This procedure was adopted in order to remove droplets of the sample measured before and possible residues. CLPG refractometric sensor metrological characteristics were calculated and expressed in terms of the volumetric percentage of methanol into biodiesel (% v/v) [12, 15].

3. RESULTS AND DISCUSSION

Figure 1 shows MX samples refractive indices measured with the Abbe refractometer. It is observed that the higher the methanol content in methanol-biodiesel blend, the lower the sample refractive index. Despite the visible decrease in the samples refractive indices with the increase of the temperature from 20 °C to 40 °C, consequence of the biodiesel and methanol negative thermo-optic coefficients [13], error bars prevent an accurate determination of the refractive index and also cause misinterpretation of the results obtained at these two different temperatures. This behavior is more significant for samples from M0 to M5 which present smaller content of methanol.

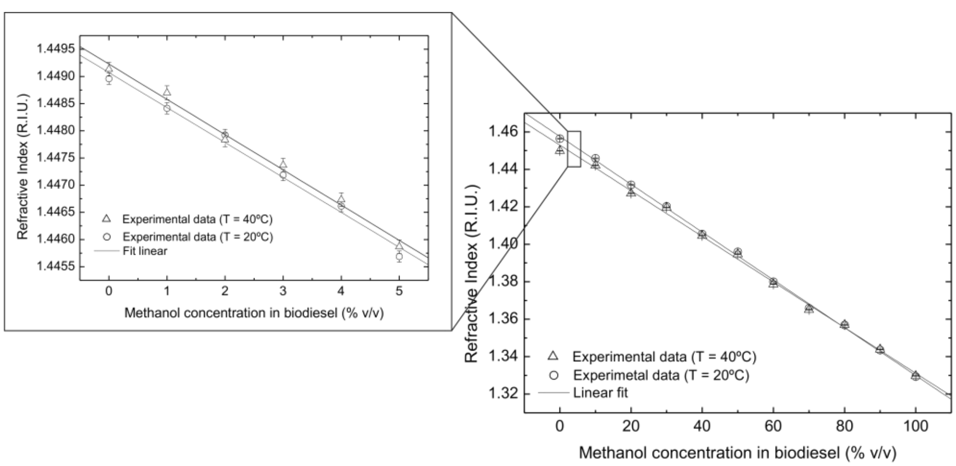

Figure 1. Refractive indices of biodiesel-methanol samples measured with the Abbe refractometer at 20.0 °C and 40.0 °C.

It is well known that CLPG spectrum shows an interference fringe pattern strongly dependent on the surrounding medium refractive index [13]. Spectral shifts can be observed as consequence of external medium refractive index changes and are related to changes in both, the LPG phase-matching condition and phase shift between the interferometer arms. At surroundings media with refractive indices above the cladding one, the CLPG spectrum consists of a broad resonance band resulting from the Fresnel reflection at the interface cladding-external medium [14]. This can be observed in Figure 2 for the CLPG immersed in samples with small content of methanol (M0, M3, M5) and therefore, samples that present higher refractive indices, close to the biodiesel one. As a consequence, when samples with lower concentrations of methanol are analyzed at room temperature, 20 °C, the interference fringes disappear. Obviously, the use of this kind of device at temperatures close to the room temperature is not advisable to determine small contents of methanol in biodiesel.

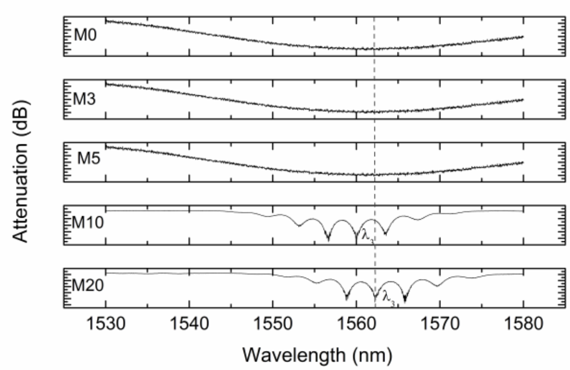

Figure 2. Transmission spectra of CLPG immersed in MX samples at 20 ºC.

In order to solve this drawback, MX samples were analyzed with the CLPG sensor at 40 °C. This temperature increase is enough to decrease the refractive index of the samples allowing the CLPG fringes to appear even for samples with small concentrations of methanol [13]. The CLPG sensor response and sensitivity curves are shown in Figure 3.

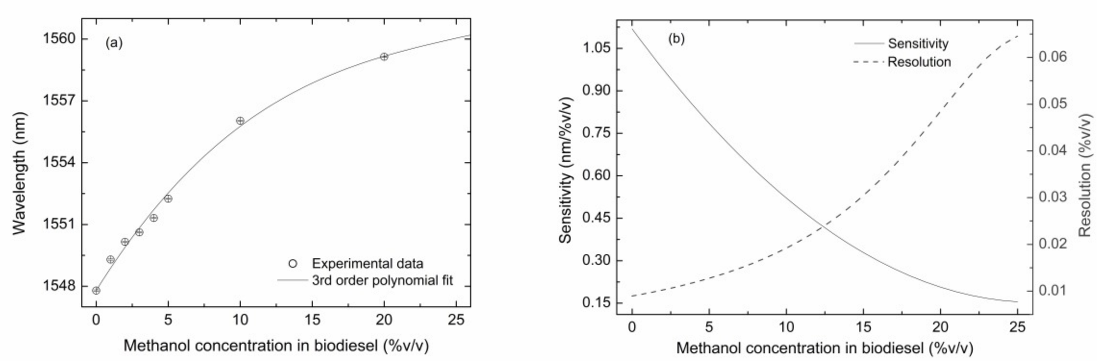

Figure 3. (a) Response curve of CLPG immersed in MX samples at 40.0 ºC, (b) Sensitivity (solid line) and resolution curves (dashed line).

Graph of figure 3a shows the response curve of the sensor fitted by a third-order polynomial to the experimental data with a correlation coefficient of 0.99839. The sensitivity of the sensor was calculated from the numerical derivative of the function adjusted to the experimental points, and the sensor resolution was obtained by dividing the wavelength stability of the OSA by the sensitivity. It can be seen from Figure 3b, that the lower the concentration of methanol in biodiesel the higher the sensor sensitivity. This is an important feature for a sensor which is intended to determine small concentrations of residual methanol. The sensor repeatability, resolution, concentration uncertainty associated to the sample preparation and conformity were combined to provide the combined standard uncertainty of 0.6% v/v for a confidence level of 68.27% [15].

4. CONCLUSION

In this work, the metrological performance of a CLPG based refractometric optical sensor applied on the determination of methanol content in biodiesel was evaluated. An important improvement on the sensor performance was observed when it is used in the analysis of biodiesel samples with small concentrations of methanol (< 5% v/v). This fact suggests that this kind of sensor can potentially be applied at the biofuel production plant to monitor the transesterification reaction. Useful information about the efficiency of the process could be provided by the sensor at real-time.

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