Sensing biodiesel and biodiesel-petrodiesel blends

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ABSTRACT

This work describes two approaches for refractometric sensors based on cascaded long period gratings for evaluating substances with refractive indices equal to or higher than the fiber cladding at room temperature. The devices are experimented on the assessment of fuel quality regarding the presence of remaining vegetable oil in biodiesel, as well as to determine the concentration of biodiesel in the biodiesel-petrodiesel blends.

Keywords: Optical fiber sensor, cascaded long period grating, long period grating, fuel quality

1. INTRODUCTION

Nowadays, non-renewable fossil fuels still are the most important energy source in most countries. However, the economy world-wide scenario and the negative environmental effects contributed to the search for new energy sources. Biofuels emerge as a possible solution to reduce part of these problems, and among them ethanol and biodiesel present as viable options[1]. Although the use of vegetable oil as fuel for diesel engines dates back to Rudolf Diesel's time more than a hundred years ago[2], the use of biodiesel as alternative energy source experienced an increase due to the recent shortage of fossil fuel resources[3]. In order to assure a good acceptance by the market, the fuel characteristics must be in accordance with standards for properties and quality. Several countries and regions around the world present biodiesel standards, most of them based on ASTM D 6751 (USA) and EN 14212 (Europe). Fuel quality includes determination of contaminants and other minor components of biodiesel by means of chromatography and spectroscopy, as well as the analysis of physical and chemical properties[4,5,6]. These techniques are time demanding and require adequate equipments, making difficult field applications. Sensor systems based on fiber optic devices are suitable for field applications, showing characteristics as portability, low response time and compatibility with in-line real time measurements. A few works using refractometric optical fiber sensor to evaluate fuels have already been reported on the literature. The first refractometric optical fiber grating sensor for analysis of biodiesel quality was presented in 2007[7]. Although refractive index is not a characteristic specified in the biodiesel standards, it can be related to the density, dynamic viscosity or other standardized property. A surface plasmon resonance (SPR) fiber sensor[8] for refractive index measurement of alcohols was also demonstrated. In other work, a fiber sensor based on long period grating (LPG) was employed in the hydrocarbon detection[9]. A fiber Bragg grating (FBG) etched transducer was also employed resulting in a highly sensitive alcohol sensor, but at the expense of fiber strength[10]. An LPG fiber sensor was proposed, resulting in a device able to identify gasoline samples as conform or non-conform to the standards[11]. However, the sensors based on fiber gratings showed not to work properly to analyze substances with refractive indices equal to or above the fiber cladding refractive index[12,13]. In this work, different sensor configurations employing cascaded long period gratings (CLPG) are experimented as concentration transducers in the analysis of fuel samples with refractive index equal to or higher than the fiber cladding at room temperature.

2. MATERIAL AND METHODS

LPGs were engraved in photosensitive Nufern-GF1 optical fiber by point-to-point technique using a KrF laser at 248 nm. The CLPGs were obtained by coating the fiber tip with a silver layer, resulting in a round-trip cavity 8 cm in length for CLPG1 and 12 cm in length for CLPG2. These devices work as in-fiber Michelson interferometers, with the cladding and the core along the cavity length constituting the interferometer arms. The cladding refractive index of fiber was estimated as (1.4558 ± 0.0025) at 589.3 nm by fitting the theoretical response of a single LPG to the external refractive

index at (20.0 ± 0.5) °C. The fuel samples used, Table 1, were mixtures of biodiesel and its vegetable oil source (OX blend, where X is the volumetric concentration of oil in the mixture) and mixtures of biodiesel and petrodiesel (BX blend, where X is the volumetric concentration of biodiesel in the mixture). Refractive indices of samples were determined with an Abbe refractometer (Bausch & Lomb, 589.3 nm wavelength, 0.0001 of resolution).

Table 1. Refractive index of the samples at (20.0 ± 0.5) °C measured with an Abbe refractometer.

Sample	Refractive index	Sample	Refractive index
B0 (100 % petrodiesel)	1.4701 ± 0.0005	O0 (100 % biodiesel from sunflower oil)	1.4563 ± 0.0004
B10 (biodiesel 10 % x 90 % petrodiesel)	1.4691 ± 0.0008	O20 (biodiesel 80 % x 20 % oil)	1.4601 ± 0.0001
B20(biodiesel 20 % x 80 % petrodiesel)	1.4671 ± 0.0007	O40 (biodiesel 60 % x 40 % oil)	1.4634 ± 0.0001
B40(biodiesel 40 % x 60 % petrodiesel)	1.4639 ± 0.0003	O60 (biodiesel 40 % x 60 % oil)	1.4665 ± 0.0001
B60(biodiesel 60 % x 40 % petrodiesel)	1.4612 ± 0.0004	O80 (biodiesel 20 % x 80 % oil)	1.4687 ± 0.0001
B80 (biodiesel 80 % x 20 % petrodiesel)	1.4582 ± 0.0003	O100 (100 % sunflower oil)	1.4738 ± 0.0002
B100 (100 % biodiesel from canola oil)	1.4563± 0.0005		

CLPG2 responses were determined by immersing 2.5 mm of the cavity in the samples at (20.0 ± 0.5) °C. CLPG1 responses were determined by the total (LPG plus cavity) immersion in the samples at (90.0 ± 0.5) °C. A superluminescent LED (MRV Communications, central wavelength at 1547.1 nm, 55 nm FWHM bandwidth) and an optical spectrum analyzer (OSA, Anritsu-MS9710B, ± 5 pm of wavelength stability, ± 0.02 dB of intensity resolution) were employed to interrogate the gratings.

3. RESULTS AND DISCUSSION

The CLPG spectrum shows an interference fringe pattern strongly dependent on the surrounding medium refractive index. Two factors are responsible by the spectral shifts observed as consequence of external medium refractive index changes: the changes in the LPG phase-matching condition and phase shift between the interferometer arms. As the phase-shift depends on the cladding and core effective refractive indices, fringe shifts are observed when the surrounding medium changes. However, this behavior modifies strongly for surroundings media with refractive indices equal to above the cladding refractive index. In the first case the coupling is not verified, while in the second case the coupling is very weak and LPG resonance bands appear with lower intensity at longer wavelengths resulting from the Fresnel reflection at the interface cladding-external medium[12,13]. Nevertheless, the coupling intensity is not sufficient to allow the CLPG fringe pattern formation. A partial immersion of the CLPG cavity in the substances can overcome these drawbacks. The Fresnel reflection in the cavity portion kept in air supplies the intensity necessary to provide a proper visibility of the interference fringes. In this situation, changes in the intensity and fringes visibility are the main observed effect in the spectral pattern when the device is immersed in different samples with refractive indices higher than the cladding one. Generally, the total immersion of the CLPG (LPG and cavity) in the sample can supply an efficient refractometric measurement only if the sample refractive index is lower than the cladding one. Biodiesel and petrodiesel present refractive indices above the cladding at room temperature, but these indices can be reduced if the sample is heated up to a proper temperature. Therefore, CLPG can be used as a refractometric sensor for substances with refractive indices higher than the cladding at room temperature choosing the cavity length immersed in the substances, or properly heating the sample.

3.1 Biodiesel-petrodiesel blend analysis

A portion of CLPG2 cavity with length of 2.5 mm (which corresponds to a round-trip 5.0 mm long) was immersed in different BX blend samples obtained by the mixture of canola biodiesel and petrodiesel (see Table 1). Figure 1a shows spectra at (20.0 ± 0.5) °C obtained with 4 different samples. Spectral changes are evaluated at 1553.7 nm by the difference in intensity between the crest (indicated by the dashed line) and the nearest (higher wavelength) trough. Figure 1b shows experimental data points and a calibration curve corresponding to a 3rd degree polynomial fit. Figure 1c shows the sensitivity and resolution dependence with the biodiesel concentration in biodiesel-petrodiesel blend. CLPG2 sensitivity curve results from the numerical derivative of the function adjusted to the experimental points and sensor resolution is obtained dividing the OSA intensity resolution ± 0.02 dB by the sensitivity. For lower biodiesel

concentrations (from 0 % to ~10 %) the sensor performance is poor and the resolution is ~9.4 % v/v. However, for concentrations higher than 90 % it presents resolution as better as 0.8 % v/v. As tampering with consists in increasing the biodiesel amount in the BX blend above the legal concentration, the device resolution for higher concentrations of biodiesel allows its use for the sake of analysis.
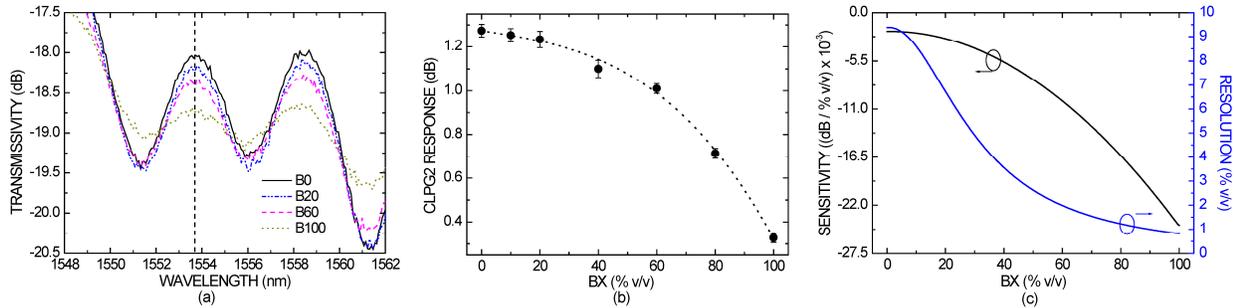
Figure 1. CLPG2 with a cavity length of 2.5 mm immersed in BX samples at (20.0 ± 0.5) ºC: (a) transmission spectra, (b) crest to trough intensity data points and the 3rd order polynomial fit, (c) sensitivity and resolution curves.

3.2 Biodiesel-oil blend analysis

Mixtures of sunflower biodiesel and sunflower oil were analyzed with the CLPG1 (LPG plus the cavity) immersed in samples at (90.0 ± 0.5) °C, resulting in spectra showed in Figure 2a. Samples were produced with different proportions of oil and biodiesel (Table 1). At room temperature, all the samples have refractive indices higher than the fiber cladding (see Table 1) and the interference pattern was not observed in the CLPG spectra. However, as the thermo-optic coefficients of samples are negative, their refractive indices decrease while the samples are heated, exceeding the fiber cladding refractive index for a specific temperature. CLPG fringes shift to lower wavelengths as the sample refractive index increases at (90.0 ± 0.5) °C. The CLPG response to the samples, obtained by the wavelength shifts of dip 2, is showed in Figure 2b.
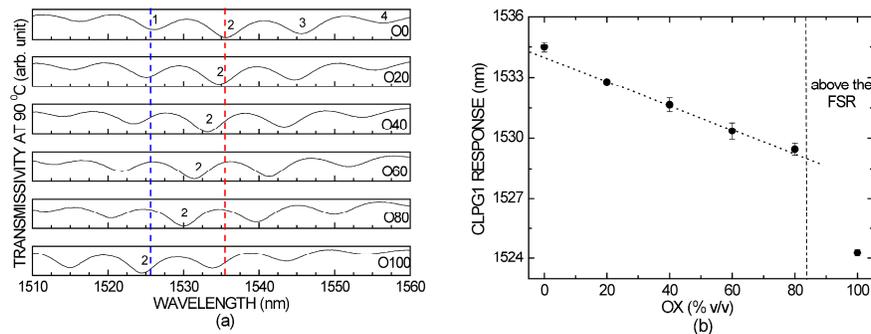
Figure 2. (a) Transmission spectra of CLPG1 immersed in OX samples at (90.0 ± 0.5) ºC; (b) Wavelength position of CLPG1 dip 2. Dotted line is a linear fit to the experimental data.

An approximately linear behavior is observed in the CLPG response for oil proportions in the samples between 0 and 80 % v/v. For oil proportions higher than 80 % v/v, the sample refractive index becomes close to the cladding index and, consequently, there is an abrupt increase in the CLPG sensitivity[11]. Consequently, the free spectral range (FSR) for the sensor operation corresponds to oil concentrations in the samples ranging from 0 to 80 % v/v. The FSR strongly depends on the spectral characteristics and sensitivity of the employed CLPG. A device with narrower fringes leads to a lower uncertainty in the determination of the dip wavelength, consequently resulting in a better resolution although at the expense of FSR. Another feature to be considered is that an increase in the sensitivity is followed by an improvement in the resolution, though it can compromise the FSR. The resolution is obtained dividing the OSA limit detection (± 5 pm)

by the sensitivity. The sensor average sensitivity was 73.8 pm / % v/v resulting in an average resolution of 0.07 % v/v in the determination of oil concentration in oil-biodiesel blends.

4. CONCLUSION

This work shows two approaches for CLPG based refractometric optical sensor that can be employed in the determination of concentrations in fuel blends with high refractive indices at room temperature, a common drawback for LPG-based sensors. Despite the measurements were carried out with fuel blends, it is also possible to apply the proposed approaches to determinate concentrations of different liquid samples. To enable the CLPG use as a wavelength coded sensor for a specific application, the temperature of operation and sensor calibration curve must be previously established. This temperature depends on the samples refractive indices and thermo-optic coefficients, as well as on the sensor free spectral range. The partial immersion of the CLPG in the samples provides a sensor able to evaluate BX blends when the device is intensity coded. This configuration can be employed to determine concentrations in substances with high refractive indices, when the substance heating is not advisable. Despite the poor resolution presented by such sensor configuration when compared with the wavelength encoded device, the use of a CLPG with higher refractive index sensitivity can improve the sensor performance.

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