

FIBER OPTIC HYDROCARBON SENSORS BASED ON LONG PERIOD GRATINGS

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Abstract

We report the use of long period gratings (LPG) fabricated with electrical arc discharges from a fusion splicer for hydrocarbon detection in both fuel and atmospheric environment. In the fuel experiments, four different types of solvents are used. Wavelength shifts in the attenuation peak as longer as 10.3 nm, 2.6 nm, 50.6 nm, and 6.1 nm are obtained when different concentrations of turpentine, naphtha, thinner, and anhydrous alcohol, respectively, are added to the commercial Brazilian gasoline blend. The exposition of LPG to a mixture of butane and propane in air results in a wavelength shift of 0.6 nm in the attenuation peak. These results point to the prospect of using the LPG sensor for fuel quality control and for the detection of petroleum pollutant in atmospheric environment.

Key words: Butane-Propane or Gasoline detection, Long period grating, Hydrocarbon, Refractive index sensor

I. INTRODUCTION

The petroleum hydrocarbon detection demands some special characteristics of the sensors to be used. A passive electrical operation is one of the main characteristics because the hydrocarbon environment can be very inflammable, so it is interesting to have a sensor device which do not produce sparks.

Optical fiber sensors present such desirable characteristic for hydrocarbon detection, besides many others interesting ones for sensor applications like, e.g., immunity to electromagnetic interference, high sensitivity, spectral multiplexing [1], reduced weight, small volume, high fusion temperature and low attenuation. In this way, optical fiber sensors can result in safe, small size, low weight and remote devices.

There are two main types of optical fiber devices that can be used as fiber sensors: fiber Bragg grating (FBG) [2] and long period grating (LPG) [3]. Both of them are mainly produced by a periodic refractive index change in the core of an optical fiber. Although these two types of gratings could be used for hydrocarbon detection by measuring the refractive index changes in the surrounding medium, FBG will be sensitive only if the cladding fiber is reduced to allow the access to the core's evanescent field. However, this procedure makes the FBG a very frail device and the handling can easily breaks the grating. Unlike the FBG, the LPG couples light from core to cladding modes, which are very sensitive to refractive index changes of the external environment [3]-[4]. This characteristic allows their use without etching the cladding, being more attractive than FBG for that sensing purpose.

In this paper, we present a LPG sensor written by arc discharge for hydrocarbon detection, which relies on the refractive indexes changes of the grating surrounding media. The experiments are carried out with a LPG immersed in an external medium of gasoline blend and solvent mixtures, or air and butane-propane mixture. The changes in the refractive index of the external medium are obtained increasing the solvent concentration in pure and commercial gasoline samples, or adding the butane-propane mixture to air. The obtained results show that long period gratings can be applied for fuel quality control [5] and detection of gas presence in pipelines or small places. In Brazil the mixture of gasoline with solvents has legal validity for an anhydrous alcohol proportion between 20 and 25%, which depends of the Brazilian alcohol production. In our experiments, the used commercial gasoline samples show an alcohol proportion of 20%. Nevertheless, as some solvents have lower prices (about 60%) than gasoline, a common malpractice is to increase the solvents concentrations in the commercial gasoline that will be sold to car owners. Thus, procedures to verify the content of alcohol and diferent solvents in the fuel mixture are required to assure the legal limit and to protect the consumer's rights.

II. PRINCIPLE OF OPERATION

In 1996, Vengsarkar *et al* reported the principle of operation and some characteristics of long period gratings (LPG) [3]. In comparison with standard Bragg gratings, which have spatial periods in the order of a micrometer, the LPG present a longer spatial period for the refractive index modulation, in the order of hundreds of micrometers. The LPG operate by coupling the fundamental mode in the core fiber to co-propagating cladding modes. Standards Bragg gratings couple the fundamental mode with a counter-propagating mode in the core and the large change in the wave vector implies short periods for the grating. For a LPG, the small difference in the co-propagating wave vectors requires the longer spatial periods in the index modulation. The resonant wavelength of coupling to a particular cladding mode is given by [3]:

$$\lambda_m = (n_{co} - n_{cl}^m) \Lambda \quad (1)$$

where λ_m is the peak wavelength of the resonance band between the core mode and the cladding mode, n_{co} and n_{cl}^m are, respectively, the effective refractive index of the core mode and of the m -th order cladding mode, and Λ is the grating pitch. The interaction of the guided mode in the optical fiber happens to cladding modes, which are strongly affected by fiber imperfections, micro and macro bending, and by the boundary condition at the cladding-external medium interface. Thus, the light coupled from the core to the cladding modes leaks out the fiber, leaving several transmission dips in the transmission spectrum, each one corresponding to a specific coupling governed by equation (1).

LPG can be very sensitive to changes in the refractive index of the external medium. If the parameter to be measured affects the fiber surrounding refractive index, this alteration will also change the matching condition expressed by equation (1) and will lead to wavelength shifts of the resonance dips in the LPG transmission spectrum. Such displacement occurs because the effective indexes of the cladding modes are dependent on the refractive index of the core, cladding, and external medium. For comparison, in the case of Bragg gratings, the effective index of the mode in the core fiber depends on the core and the cladding refractive indexes. A change in the external medium index is only perceived when the cladding is almost entirely removed to expose the evanescent field of the core mode to the external medium index.

Chiang et al [6] presented analytical expressions to describe the shift at the resonance wavelength of a LPG in response to the etching of the fiber cladding or to the changes in the refractive index of the external environment. Thus, for external changes in the refractive index from n_{ex0} to n_{ex} , the wavelength shift $\delta\lambda_0$ is [6]:

$$\delta\lambda_0 \approx \frac{u_\infty^2 \lambda_0^3 \Lambda}{8\pi^3 n_{cl} \rho^3} \left[\frac{1}{(n_{cl}^2 - n_{ex0}^2)^{1/2}} - \frac{1}{(n_{cl}^2 - n_{ex}^2)^{1/2}} \right] \quad (2)$$

where u_∞ is the m -th root of the Bessel function J_0 [7], λ_0 is the resonance wavelength at n_{ex0} , Λ is the grating pitch, and ρ is the cladding radius.

Equation (2) shows that the LPG operation and the grating sensitivity are dependent on the cladding mode order, resulting in a higher sensitivity as u_∞ increases [6].

III. EXPERIMENTS

3.1 Fabrication

The LPG are produced using a technique similar to that described by [8]. A bare fiber without its protective coating is inserted between the electrodes of a commercial fusion splicer. A small weight is suspended in one of the fiber's extremities to keep a constant longitudinal tension. The other extremity of the fiber is mounted on a 5 μm resolution computer controlled translation stage. An electrical arc is applied with the fusion splicer, using an adequate current and time duration settings. After the discharge, the fiber is moved by the required period of the grating, before another arc is applied. After a suitable number of point-to-point discharges, a periodic pattern is engraved in the refractive index profile of the fiber, due to heating activated processes. An optical set-up, which uses an halogen lamp, a monochromator, objective lens, detector, and a personal computer, is employed during the writing process to monitor the transmission spectrum through the fiber. When the measured spectrum shows suitable characteristics to the intended application, the process is terminated. Usually 40-70 points were necessary to form a grating for the described sensor. The advantage of using the electrical arc is that no special fiber (hydrogenated or pre sensitized) is required. Furthermore, fusion splicers are very common in optical fiber laboratories.

3.2 Grating Parameters

The experiments was performed with two different LPG fabricated in a fiber with a cladding radius of 62.5 μm and a core radius of 4.5 μm . The fusion splicer arc parameters used in the writing process were current of 12 mA and fusing time of 0.5 s.

A LPG with a pitch of 649 μm and 53 points was employed for gasoline blend and solvent mixture characterizations. For this grating the stronger attenuation peak, in air, is located at 1586.4 nm. The experiments with butane-propane mixture was performed using a LPG with a pitch of 604 μm , 60 points of interaction, and two resonance peaks centered, in air, at 1559 nm and 1573 nm.

3.3 Solvent Detection in Commercial Gasoline

The set-up shown in Fig.1 is used to measure the solvent sensitivity of the LPG in gasoline. The sensor is inserted into a specially designed glass recipient with four openings,

two of them used to pass the optical fiber with the LPG and the two others to insert and to drain the gasoline samples. With the LPG inserted into the recipient, the fiber ends are immobilized to avoid fiber-bending interference on the sensor response. Another parameter controlled to avoid errors on the sensor response was the temperature, which was maintained between 20.0 ± 1.5 °C. The glass recipient is also immobilized to avoid its movement. A LED source (central wavelength at 1530.3 nm and half bandwidth of 52.0 nm) and an Optical Spectrum Analyzer (0.1 nm resolution) are employed for the transmission spectrum measurements. The central wavelength of the LPG dip is obtained by adjusting a Gaussian line profile to the attenuation band of the transmission spectrum. The refractive indexes of the samples, after being drained from the glass recipient, are measured with an Abbe refractometer.

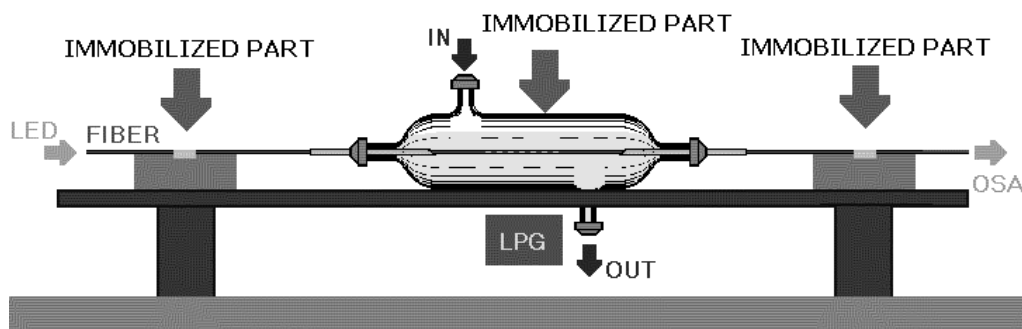


Figure 1: Experimental set-up used for the measurement of LPG sensitivity when different solvents are added to gasoline blend.

To study the LPG response when different petroleum hydrocarbon solvents are mixed to commercial gasoline, several amounts of anhydrous alcohol, naphtha, turpentine and thinner are added to it. Because we used only anhydrous alcohol in the experiments, it will be referred just as alcohol from now on. Table 1 shows some relevant refractive indexes obtained during this measurements.

One can verify from Table 1, that pure thinner has a refractive index ($n_{ex} = 1.4652$) greater than the fiber cladding, which accounts for the large shift of the wavelength when the proportion of thinner in commercial gasoline is increased (see Fig.2). Figure 2 also shows that alcohol and naphtha shift the attenuation peak towards higher wavelengths, indicating a reduction of the samples refractive index when these solvents are mixed in commercial gasoline, whereas turpentine shifts the attenuation peak towards lower wavelengths. It also can be seen that the LPG is more sensitive to alcohol addition in commercial gasoline than to naphtha addition.

Table 1: Refractive indexes obtained during the LPG response characterization.

Solvent Proportion (%)	Alcohol	Naphtha	Turpentine	Thinner	Pure Gasoline	Commercial Gasoline
7.7	1.4197	1.4259	1.4258	1.4301	1.4470	1.4240
14.3	1.4170	1.4230	1.4272	1.4326		
20.0	1.4122	1.4216	1.4280	1.4333		
40.0	Not measured			1.4433		
60.0				1.4506		
75.0				1.4571		
87.0				1.4614		
100.0	1.3665	1.4059	1.4411	1.4652		

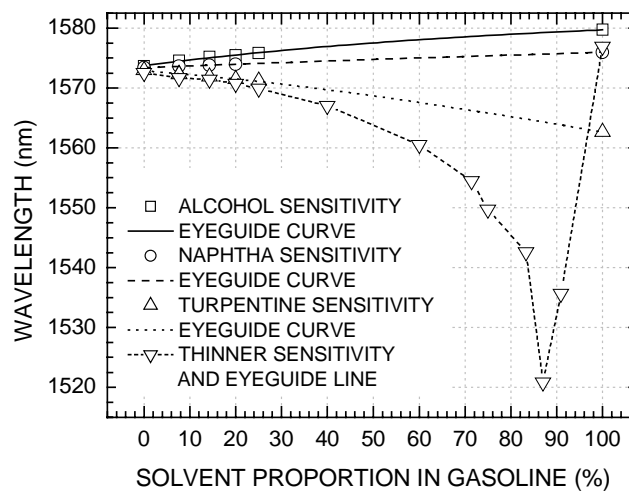


Figure 2: Grating response when four different solvents are added to commercial Brazilian gasoline. Alcohol and naphtha shift the attenuation peak towards longer wavelengths, whereas turpentine and thinner shift it towards shorter wavelengths. The lines through the data points are solely a visual aid. Uncertainty in measured points is typically less than symbol size.

The evolution of the LPG transmission spectrum when the refractive index of the external medium changes are shown in Fig.3. The observed changes are due to the increase of thinner proportion in commercial gasoline. For sake of comparison, are also shown the spectra when the external medium is air ($n=1.0000$), commercial gasoline ($n = 1.4274$), and pure thinner ($n=1.4652$). From graphs 2, 3 and table 1, it can be seen that for thinner concentration above 70 %, small concentration changes lead to larger resonance wavelength shifts, once such concentrations result in external medium refractive index close to the cladding one ($n=1.458$), so the best LPG sensitivity is reached [4].

Fig. 4 shows the curve of the grating sensitivity to changes in the external medium refractive index. It also shows the best fit of the analytical curve given by (2) for $n_{ex} < n_{cl}$, which agrees with the experimental data. The parameters used to the fitting were: (a) fixed parameters: $\Lambda = 649 \mu\text{m}$, $n_{ex0} = 1.0000$ (air), $\rho = 62.5 \mu\text{m}$, (b) $n_{cl} = 1.4640 \pm 0.0007$, $u_{\infty} = 14.46 \pm 0.38$, and $\lambda_0 = (1585.8 \pm 0.5) \text{ nm}$, as variable parameters. These results allow finding the value of the corresponding effective index (n_{cl}^m) and the order of the m -th cladding mode

coupled by the grating. The J_0 root closest to the u_∞ calculated value is 14.93, corresponding to the 5th order mode [9].

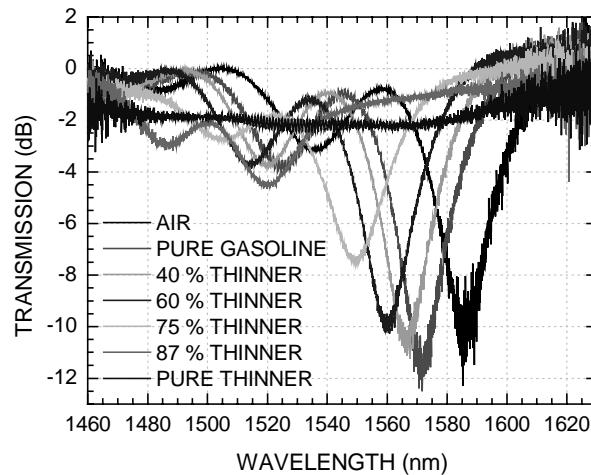


Figure 3: LPG response for different refractive indexes of the external environment. These spectra show the shift of the attenuation peak to higher energies as the refractive index increases, and the decrease of the amplitude of the attenuation peak for the refractive index close to 1.4614 (87 % thinner). After this value, the amplitude of attenuation peaks is very low.

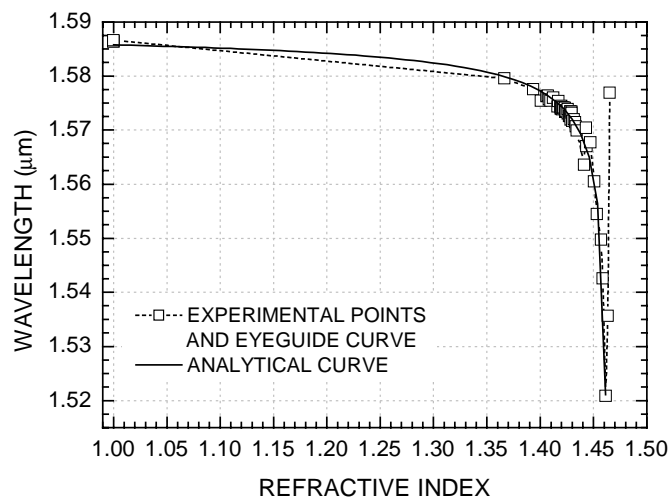


Figure 4: Grating sensitivity to changes in the external medium refractive index. Experimental points are in good accordance with the analytical curve given by (2). Uncertainty in measured points is typically less than symbol size. The dotted line through the experimental points is solely a visual aid.

The main product added to commercial Brazilian gasoline is anhydrous alcohol with an allowed proportion of 20%. Figure 5 shows the LPG response for a mixture of alcohol in both commercial (open circles) and pure gasoline (full circles). The data from pure gasoline can be fitted by the empirical equation $y = a - bc^x$, which corresponds to the solid line. When the alcohol proportion in commercial gasoline is increased, the grating response agrees with the characteristic (or empirical) curve. However, other solvent additions to a commercial gasoline sample changes the sample volume and consequently decrease the alcohol proportion in this mixture, resulting in the other curves of fig. 5. As it can be seen from that figure, only the

legal commercial gasoline blend matches the characteristic curve when alcohol is added to the sample.

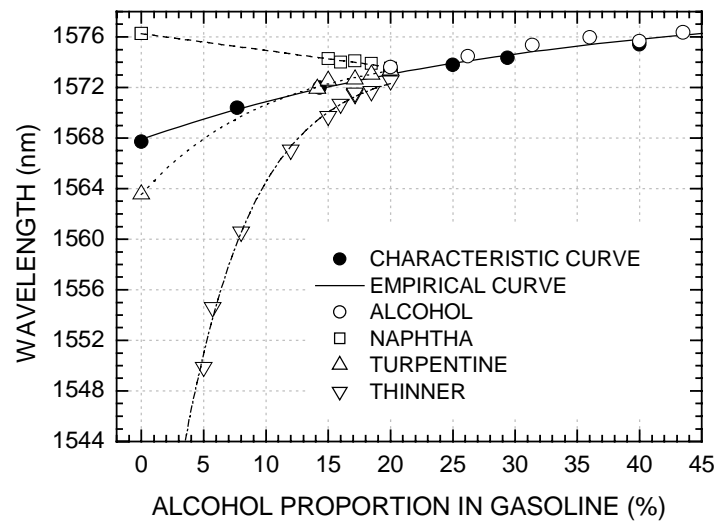


Figure 5: LPG attenuation peak wavelength versus alcohol proportion in gasoline sample when: Alcohol is added to pure gasoline (● experimental points, – empirical curve); Alcohol (○), Naphtha (□), Turpentine (△) and Thinner (▽) are added to commercial gasoline. The lines through the data points are solely a visual aid.

3.4 Butane-Propane Detection

The experimental set-up for butane-propane detection is similar as the one used for the liquid gasoline and solvents characterizations. The grating is fixed under constant longitudinal strain, and the butane-propane sample is injected inside the glass recipient. A superluminescent LED with 1546.68 nm central wavelength and 53.12 nm half bandwidth is used as light source. The Optical Spectrum Analyzer has a wavelength stability of ± 5 pm, and the resolution was set to 0.07 nm.

Fig. 6 shows the changes in the LPG higher wavelength attenuation peak when a butane-propane mixture was added to the atmospheric environment. The detection is made along a span of 600 s, with two gas insertions in this period. As the injection process evolves, the peak attenuation shifts towards shorter wavelengths, with a maximum shift of 0.06 nm in the first gas insertion. The same behavior is noticed when the gas is kept in contact with the LPG in a closed environment along time intervals up to 5 minutes. After this interval, the box is opened and the LPG recovers the air wavelength in a short time interval (less than 1 minute). This results allows to attribute the wavelength shift to the refractive index change and not to temperature changes resulting from the gas injection. Apparently the smaller wavelength shift on the second gas insertion comes from a thick film of heavier hydrocarbons on the LPG surface, which are present in commercial gas mixture.

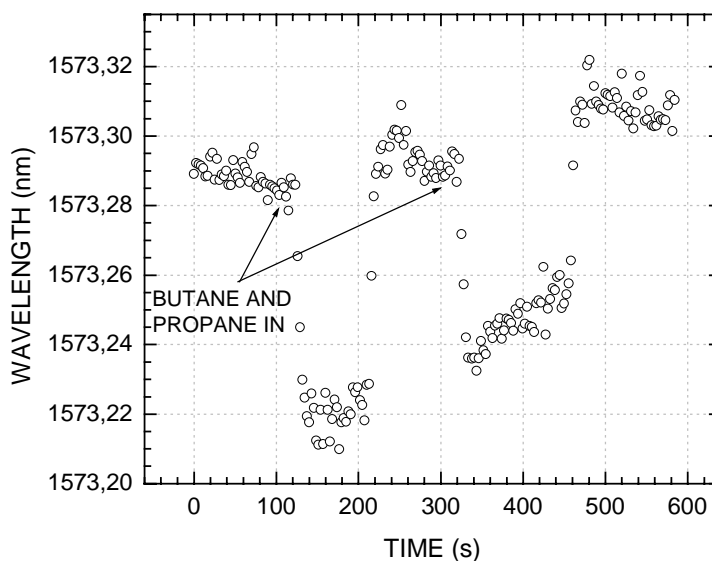


Figure 6: LPG temporal response when the butane concentration was changed.

IV. CONCLUSION

We report the petroleum hydrocarbon sensitivity of long period gratings. The LPG sensitivity for different hydrocarbon solvents points out to the use of this type of optical gratings to determinate the hydrocarbon concentrations when two different solvents are mixed. A LPG attenuation peak wavelength shift of 65.5 nm was obtained for refractive index changes between 1.0000 and 1.4614. We also verify that naphtha and alcohol shift the attenuation peak to longer wavelengths, whereas thinner and turpentine lead to an inverse shift. Among the used solvents, alcohol is the most effective to reduce the refractive index of commercial gasoline, whereas thinner is the most efficient to increase this refractive index. In spite of the fact that a suitable mixture of a set of solvents could lead to a refractive index equal to the legal gasoline blend, an extra alcohol addition to this sample allows to identify such illegal blend. Long period gratings was also investigated as a butane-propane gas sensor. The results show that a possible application of LPG is to determine the presence of hydrocarbon vapor in closed environments, or inside a specific pipeline or tank. An important characteristic of the LPG sensor is the detection on the spectral domain, not influenced by intensities changes of the source.

All the results obtained in the fuel characterization were carried out using the same grating over a period of several months. It implies that as long as the grating integrity is preserved the sensor can be reutilized. For in field applications a suitable enclosure and proper packing must be developed. For gas detection the reproducibility should be better studied to verify the problem arising from heavy hydrocarbon deposition over the fiber surface. In spite of the mentioned drawback a commercial version can be built with the current optical sensor technology.

A patent request has been filled for solvent determination in fuel blends.

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