Petroleum Hydrocarbon Detection with Long Period Gratings

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Abstract— **We report the use of long period gratings (LPG) fabricated with electrical arc discharges from a splice machine for hydrocarbon detection in both fuel and air. In the fuel experiments, we used four different types of solvents. Wavelength shifts as longer as 10.3 nm, 2.6 nm, 50.6 nm, and 6.1 nm were obtained when different concentrations of Tozan®, naphtha, thinner, and anhydrous alcohol, respectively, were added in the commercial Brazilian gasoline. We also report a LPG application for butane detection in air.**

Index Terms— **butane or gasoline detection, petroleum hydrocarbon, long period grating, refractive index sensor.**

I. INTRODUCTION

THE petroleum hydrocarbon detection demands some special characteristics of the sensors that will be used. A passive electrical operation is one of the main characteristics because the hydrocarbon environment is very inflammable, so that no sparks can happen in the sensor device.

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

There are two main types of fiber optical devices that can be used as fiber sensors: fiber Bragg grating (FBG) [2] and long period grating (LPG) [3], and both of them can be produced by a periodic refractive index change in the core of an optical fiber. Although both types of grating could be used for hydrocarbon detection by measuring the refractive index changes in the surrounding medium, the first one will be sensitive only if the cladding fiber is reduced to allow the access to the evanescent field. This procedure makes the FBG a very frail device and the handling can easily breaks the grating. Unlike the FBG, the LPG couple light from core to cladding modes, which are very sensitive to refractive index changes of the external environment [3]-[4]. This characteristic allows its use with no cladding etching, being more attractive than FBG for this sensing purpose.

In this paper, we present a LPG sensor for petroleum hydrocarbon detection, which relies on the changes of refractive indexes of the surrounding media of the grating. The experiments were carried out with a LPG immersed in an external medium of gasoline and solvent mixtures, or air and butane. The changes in the refractive index of the external medium were obtained increasing the solvent concentration in pure and commercial gasoline samples, or increasing the butane concentration in air. The obtained results show that long period gratings could 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 up to 20 %. However, as some solvents have lower prices (about 60 %) than gasoline, a common malpractice is to increase the solvent concentration in the commercial gasoline that is sold to car owners. Procedures to verify the content solvents and mainly of the alcohol in the 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 [3]. In comparison with standard Bragg gratings, that 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 of the 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 a particular coupling to a cladding mode is given by [3]:

$$l_m = \left(n_{co} - n_{cl}^{m}\right)L \qquad (1)$$

Manuscript received March 24, 2003. This work was supported in part by the CAPES, CNPq, CTPETRO, Fundação Araucária (Brazilian Agencies), and from the Brazilian National Agency of Petroleum (PRH-ANP/MME/MCT 10 CEFET-PR).

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where l_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 L is the grating pitch. The interaction of the guided mode in the optical fiber occurs with a cladding mode, which is 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 mode leaks out the fiber, leaving several transmission dips in the transmission spectrum, each one corresponding to a specific coupling governed by (1).

LPG are sensitive when the refractive index of the external medium changes. If the parameter to be measured affects the refractive index, this will also change the matching condition expressed by (1) and will lead to wavelength shifts of the resonance dips in the LPG transmission spectrum. That 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 fiber's core depends on the core and cladding refractive indexes. A change on the external medium index only is perceived when the cladding is almost entirely removed, to expose the evanescent field of the core mode to the external index.

Chiang *et al* [6] presented analytical expressions to describe the shift in 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 $d l_0$ is [6]:

$$d l_0 \approx \frac{u_\infty^2\, l_0^3 L}{8p^3 n_{cl}\, r^3}\left[\frac{1}{\left(n_{cl}^2-n_{ex0}^2\right)^{1/2}}-\frac{1}{\left(n_{cl}^2-n_{ex}^2\right)^{1/2}}\right] \qquad (2)$$

where $u_¥$ is the m-th root of the Bessel function J_0 [7], l_0 is the resonance wavelength at n_{ex0}, L is the grating pitch, and r 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

A. *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 splicing machine. 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 computer controlled translation stage. An electrical arc is applied with the splicing machine, 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 fiber's refractive index profile, due to heating activated processes. An optical set-up is used 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 interrupted. 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, splicing machines are very common in optical fiber laboratories.

B. *Grating Parameters*

We used for the experiments two different LPG fabricated in a fiber with a cladding radius of 62.5 µm and a 4.5 µm core radius. The arc parameters were 12 mA for the current and a fusing time of 0.5 s.

A LPG with a pitch of 649 µm and 53 points was used in gasoline and solvent mixture characterizations. For this grating the stronger attenuation peak in air is at 1586.4 nm. The experiments with butane were performed with a LPG with a pitch of 639 µm, 55 points of interaction, and a resonance peak at 1503.97 nm in air.

C. *Solvent Detection in Commercial Gasoline*

To measure the solvent sensitivity of the LPG in gasoline we used the setup showed in Fig. 1. The sensor was inserted into a specially designed glass recipient with four exits, two of them used to pass the optical fiber and the other two ones to add and to drain the gasoline samples. After the LPG had been inserted into the recipient, the fiber ends were held 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 was pressed to avoid its movement. An LED source (central wavelength at 1530.3 nm and half bandwidth of 52.0 nm) and an Optical Spectrum Analyzer (0.1 nm resolution) were employed for the transmission spectrum measurements. The refractive indexes of the samples that were drained of the glass recipient were measured with an Abbe refractometer.

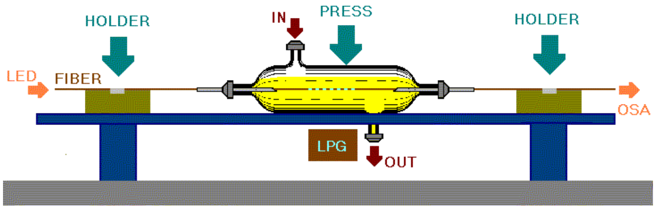

Fig. 1. Experimental setup used for the measurement of LPG sensitivity when different solvents are added in gasoline.

Four types of petroleum hydrocarbon solvents were chosen: Tozan® (in Brazil this solvent is known as *raz*), naphtha, thinner and anhydrous alcohol. Because we used only anhydrous alcohol in the experiments, it will be referred just as alcohol from now on.

To know the LPG response when different solvents were mixed to the commercial gasoline, several amounts of alcohol, naphtha, *raz* and thinner were added to it (see Fig. 2). One can verify that thinner has a refractive index greater than the fiber cladding, what it is justified because of the large shift on wavelength when the proportion of thinner in commercial gasoline is increased. It is also showed that alcohol and naphtha shift the attenuation peak towards higher wavelengths, indicating a reduction of the refractive index of the samples when these solvents are mixed in commercial gasoline, whereas *raz* shifts the attenuation peak towards lower wavelengths. It also can be seen that the LPG is more sensitive to alcohol insertion in commercial gasoline than to naphtha insertion.

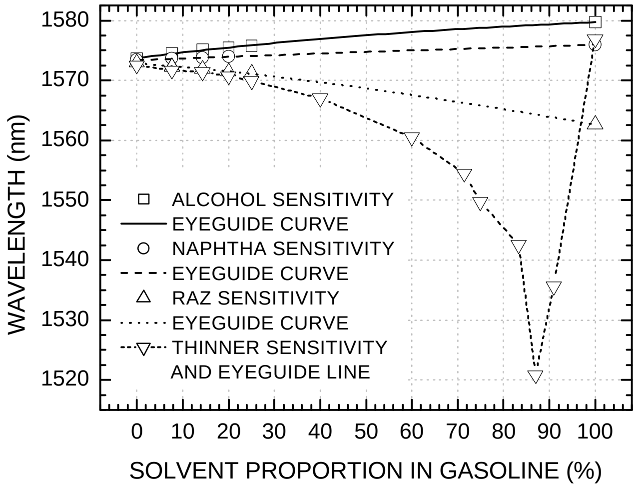

Fig. 2. Grating response when four different solvents are added in commercial Brazilian gasoline. Alcohol and naphtha move the attenuation peak to lower energies, whereas *raz* and thinner move it to higher energies. The lines through the data points are only guides for the eyes. Uncertainty in measured points is typically less than symbol size.

The evolution of the LPG transmission spectrum when the refractive index of the external medium changes, is showed in Fig. 3. The changes were obtained by means of the increase of thinner proportion in commercial gasoline. For sake of comparison, it is also showed the spectra when the external medium is air (n = 1.0000), commercial gasoline (n = 1.4274), and thinner (n = 1.4652). From Fig. 3 it can be seen that small changes of the external medium refractive index above 1.4433 result in larger resonance wavelength shifts, once this index are close to the cladding one, 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 (2) for $n_{ex}<n_{cl}$, which agrees with the experimental data. The parameters used to the fitting were: (a) fixed parameters: L = 649 µm, n_{ex0} = 1.0000 (air), r = 62.5 µm, (b) n_{cl} = 1.4640 ± 0.0007, $u_{¥}$ = 14.46 ± 0.38, and l_0 = (1585.8 ± 0.5) nm, as variable parameters. These results allow finding both the value of the effective index of the m-th cladding mode (n_{cl}^{m}) and the order of the cladding mode that was being used in our measurements. The best value to $u_{¥}$ from the roots of Bessel function is 14.93, which is possible considering the error estimated, thus the correspondent mode order is 5.

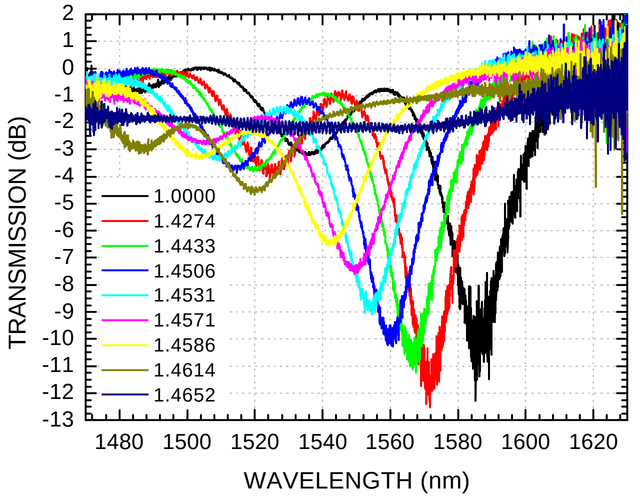

Fig. 3. LPG response for different refractive indexes of the external environment. These spectra show the shift of the attenuation peak to higher energies as the refractive index increases, and the decrease of the amplitude of the attenuation peak for the refractive index close to 1.4614. After this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

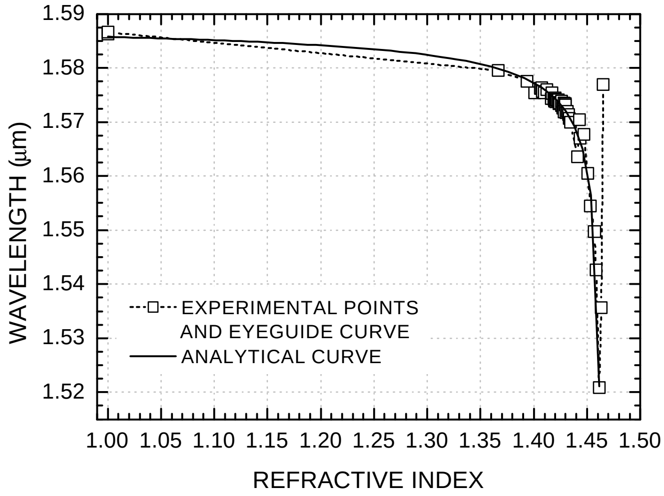

Fig. 4. Grating sensitivity to changes in the external medium refractive index. Experimental points are in good accordance with the analytical curve given by (2). Uncertainty in measured points is typically less than symbol size.

D. Alcohol Detection in Pure and Commercial Gasoline

The main solvent added in commercial Brazilian gasoline is anhydrous alcohol with a 20 % allowed proportion. Fig. 5 shows the LPG response for a mixture of alcohol in both the commercial and pure gasoline. The data from pure gasoline can be fitted by the empirical equation $y = a - b \cdot c^{x}$, which corresponds to the solid line.

E. Butane Detection

The experimental set-up for butane detection is similar as the one used for the liquid gasoline and solvents characterizations. The glass recipient was replaced by a glass box with a 1 dm^3 volume. The grating was fixed under constant longitudinal strain 4 mm above the bottom of the box, and the butane sample was injected inside it. The whole set-up was covered with a glass lid to avoid gas losses during the measurements. A superluminescent LED with a 1546.68 nm central wavelength and a 53.12 nm half bandwidth was used as ligth source. The OSA resolution was set to 0.07 nm.

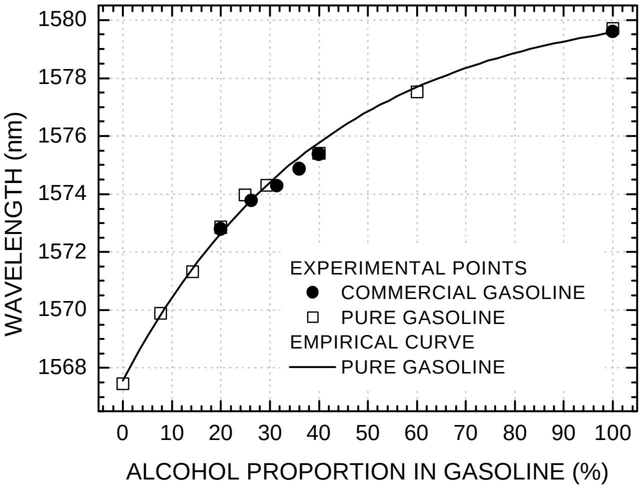

Fig. 5. LPG sensitivity when different alcohol concentrations are added in both commercial and pure gasoline. Uncertainty in measured points is typically less than symbol size.

Fig. 6 shows the LPG response for butane detection along a time span of 55 minutes. The points from 0 to 500 seconds (1503.97 nm) correspond to the LPG in air. As the injection process evolves from 500 to 1500 seconds, the peak attenuation moves towards lower wavelengths, with a wavelength shift of 0.09 nm. The gas injection was interrupted at 1500 seconds and air was allowed to fill the recipient.

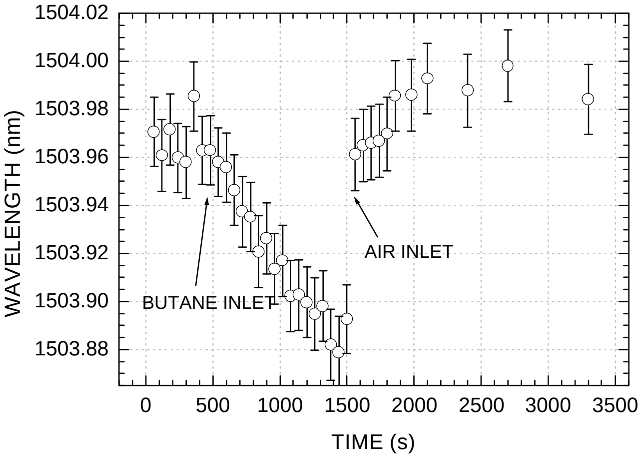

Fig. 6. LPG temporal response when the butane concentration is changed.

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 move the attenuation peak to lower energies, whereas thinner and *raz* lead to an inverse shift. The most effective solvent among the used ones to change the commercial gasoline refractive index towards lower values is alcohol, while thinner is the most efficient to increase this refractive index. LPG were also investigated as a butane gas sensor. The results show that a possible application of LPG is to determine the presence of hydrocarbon vapor in atmosphere, or inside a specific pipeline.

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

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