

## Application of an optical fiber sensor in the analysis of Brazilian gasoline conformity

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### Abstract

*The fuel quality control, in special the gasoline, is a matter of importance for the consumers, for the State and for the environment. In Brazil, this control is ruled by standard assays established according to Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, a governmental agency. As the conformity analysis demands for several tests in a specialized laboratory, the development of an alternative and faster procedure is an important subject of research. In this work, we describe the application of an optical fiber sensor, the long period grating, employed as an auxiliary tool to perform the gasoline conformity analysis. The results show that by correlating the sample refractive index, determined with the optical sensor, with the sample density, a parameter measured during the standard fuel assays, it becomes possible to distinguish between conform and non-conform gasoline samples. The proposed sensor is not affected by seasonal rules, as the presented results concern samples collected in different times of the year with different amounts of anhydrous alcohol in the gasoline composition.*

### Introduction

Gasoline is a complex blend of volatile and flammable liquid hydrocarbons derived from petroleum, whose molecular structure contains from 4 to 12 carbon atoms per molecule. Produced in refineries and distributed as fuel for motorized vehicles, the Brazilian gasoline presents paraffins, isoparaffins, naphthenes, olefins and aromatics, with distillation curve ranging from 30 °C to 220 °C [1]. Besides, a 23 % (v/v) of anhydrous ethanol is added to the gasoline to reduce the incomplete combustion as well as to enhance anti-knocking properties of the fuel. The Brazilian regulatory agency for petroleum production and commercialization, ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis), has established a national program for quality control of fuels (Portaria 309/2001) with the standard assays for the automotive gasoline in the national territory. Since 1999 up to 2007 the ANP, by means of the laboratories responsible for monitoring the quality of automotive fuels, supervised about 150.000 economic agencies, among them 30 % showed irregularities and 12 % were interdicted or suffered sanctions due to the non-conformity of the products [2].

Problems resulting from fuel quality are commonly associated with adulterations realized with the aim of increasing profits by decreasing the costs with its constituents. However, this practice can be harmful to the consumers increasing the demand for engine maintenance, to the State by means of the fiscal evasion, or to the environment. The continuous monitoring of the fuels, in special the automotive gasoline in the gas stations, is a very important issue to reduce the malpractices associated with the non-conformity of fuels. Nowadays, in the fuel monitoring, samples of gasoline are collected and evaluated by using the *American Society for Testing Materials* (ASTM) and/or *Technical Rules Brazilian Association* (ABNT) standard methods. For this purpose, a series of physicochemical tests are done, including the determination of samples anhydrous ethanol content, distillation curve, octane number, density, vapor pressure, gum, induction period, copper corrosivity, and hydrocarbon, sulfur and lead content, as well as gas chromatography analysis [3-4]. Nevertheless, such tests take some amount of time to be concluded and a specialist is required to do the analysis.

In an early work the results concerning to the study of gasoline adulteration pointed to the sample refractive index as a parameter that can be employed in the analysis of the automotive gasoline conformity [5]. In that work, the fiber optical based sensor employed a long period grating (LPG) as a transducer. The LPG consists of a periodic modulation in the core refractive index of an optical fiber produced along the fiber length with spatial

periods  $\Lambda$  (100-700  $\mu\text{m}$ ), which couples light from the fundamental core propagation mode to co-propagating cladding modes. This mode coupling results in attenuation dips in the fiber transmission spectrum, centered in wavelengths that are determined by the effective refractive indexes of the core and cladding modes and by the grating period. The device shows sensitivity to other external parameters like temperature and stress [6], however, when an adequate method to correct their influence in the LPG response is employed, the LPG sensitivity to the surroundings refractive index can be used to build a refractometer. The most interesting features of LPG for sensing application are the electrical passivity, immunity to electromagnetic interference, low attenuation, high fusion temperature, small volume, reduced weight, information wavelength coded and the possibility of real time response and application in a quasi-distributed monitoring system with the use of more than one LPG in the same link. These characteristics turn the device very attractive to be employed in hazardous and inflammable environments, industrials furnaces and transmission lines.

This work shows the results concerning to the LPG sensors applied to identify the gasoline conformity commercialized in several gas stations in Brazil. The device response was compared with the results obtained from the standard assays ruled by the governmental agency ANP.

## Experimental Setup

The experimental system used to verify the gasoline conformity employs a standard telecommunication optical fiber with a LPG ( $\Lambda = 595 \mu\text{m}$ , 60 interaction points), written by the point-to-point technique with the electrical arc of a splice machine (0.5 s, 12.5 mA). The fiber is inserted into a 15 ml glass cell with four openings [7], as shown in figure 1. Both fiber tips are clamped on holders to avoid changes in the fiber position and to keep constant the longitudinal tension. Light from a superluminescent led (central wavelength of 1550 nm, bandwidth of 52 nm) is coupled to one of the fiber extremities, while the other one is coupled to an optical spectrum analyzer (OSA Anritsu-MS9710B), with  $\pm 5 \text{ pm}$  of wavelength stability. The transmission spectra are recorded via RS 232 port of a personal computer with software to determine the central wavelength of the LPG resonant dips. The LPG wavelengths were measured for a set of 46 fuel samples (20 % or 25 % anhydrous alcohol content according to the Brazilian legislation), collected in several gas stations and previously analyzed at LACAUT-UFPR (Laboratório de Análise de Combustíveis Automotivos, Universidade Federal do Paraná), an ANP associated laboratory. Refractive indexes of the samples were measured with an Abbe refractometer (Bausch & Lomb),  $\pm 0.0001 \text{ nm}$  of resolution and  $\pm 0.0002 \text{ nm}$  of precision. During the whole experiment, the temperature was kept constant within  $20 \text{ }^\circ\text{C} \pm 0.5 \text{ }^\circ\text{C}$ .

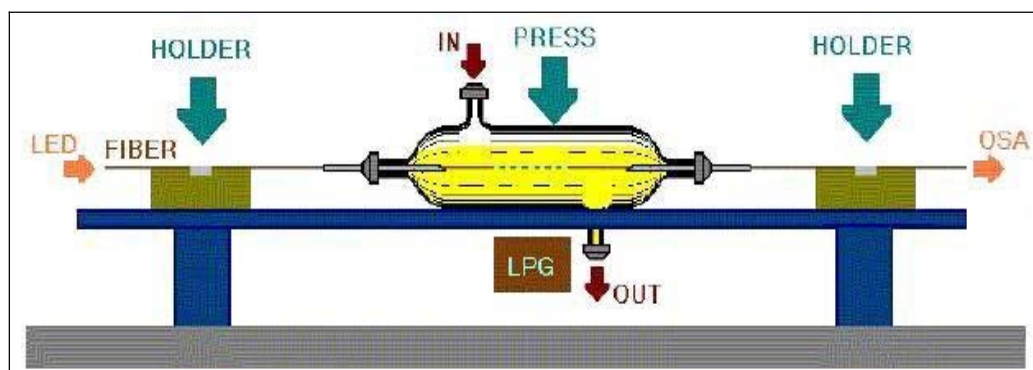
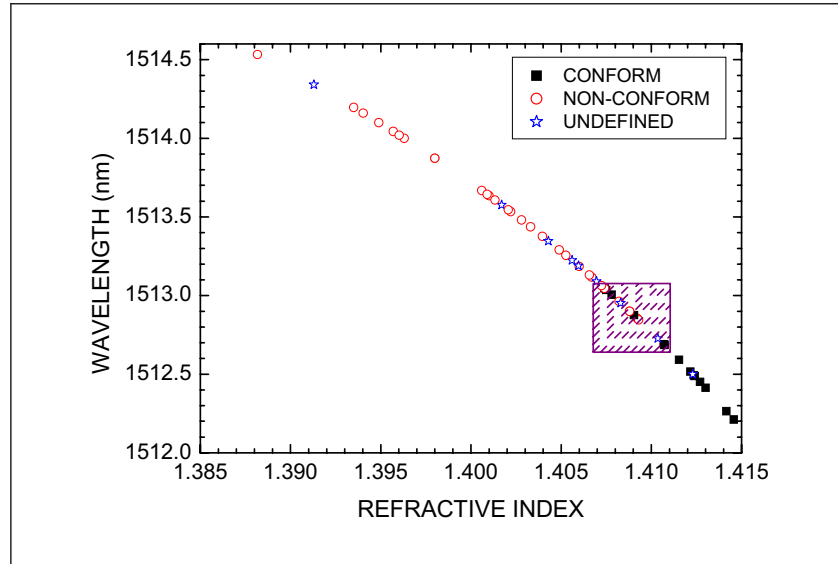


Figure 1: Experimental setup used in the gasoline characterization.

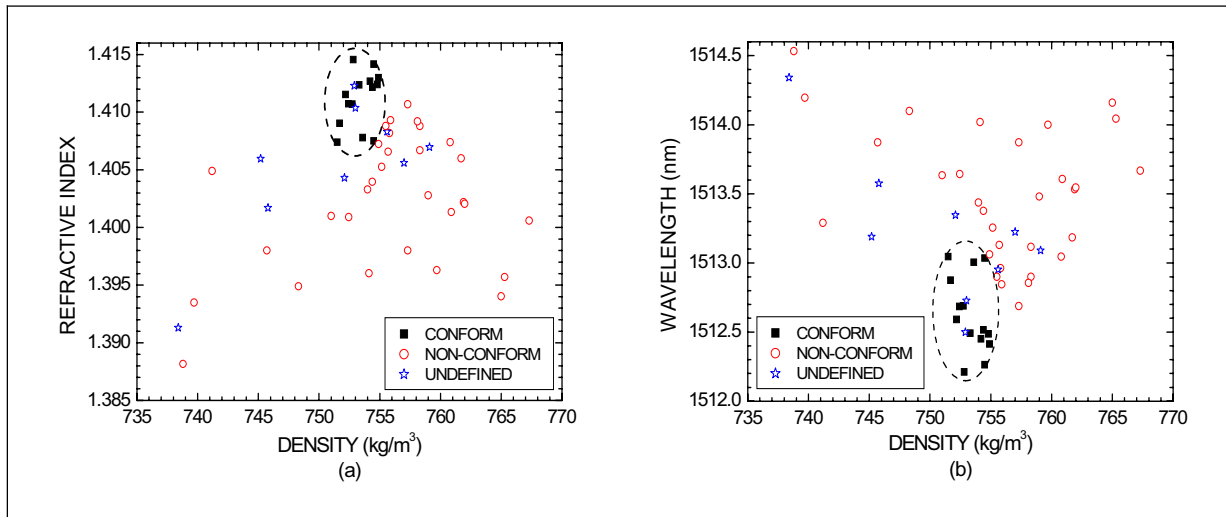
## Results and Discussions

Among the 46 analyzed samples, 10 are conform, 27 non-conform and 9 are undefined, as the anhydrous alcohol concentration is unknown or its properties are too close to the upper limit established by the ANP, and therefore requiring another analysis to be classified. Figure 2 shows that, for this set of samples, all the refractive indexes are within 1.3850 and 1.4150. This range corresponds to a wavelength shift about 2.4 nm of the LPG resonance. It also can be noted in that figure that some conform (■) and non-conform (○) samples belong to the same refractive index range (inside the square area), what shows the necessity of considering an additional parameter to analyze the samples concerning to the gasoline conformity. Considering the relationship between the refractive index and the LPG response with the sample density, figures 3(a) and 3(b) respectively, the

experimental points are now redistributed among new zones, the conform one delimited by the elliptical boundary in both figures. As can be seen from that figures, these zones contain all the samples classified as “conform”, and two samples classified as “undefined”. Between these two samples, one does not fulfill the “appearance” criterion, while the other one presents only 1 % more then the allowed anhydrous alcohol concentration in its composition. All the points outside the elliptical zones correspond to the “non-conform” samples.



**Figure 2:** Relationship between the refractive index and the LPG response for the gasoline samples.



**Figure 3:** Conformity analysis of gasoline with the aid of the sample density and: (a) refractive index, and (b) LPG response.

### Conclusions

The results presented in this work show the possibility of using the sample refractive index as a parameter to be considered in the conformity analysis of gasoline. Moreover, the LPG sensitivity to this parameter points to the prospect of using this device as an attractive sensor to be employed in an auxiliary conformity monitoring. The refractive index alone (or the LPG response) is not enough to perform the conformity analysis; however, by analyzing these parameters together the sample density (belonging to the ANP standards) allows performing this

determination. The proposed sensor is not affected by seasonal rules, as the presented results concern samples collected in different times of the year with different amounts of anhydrous alcohol in the gasoline composition.

### Acknowledgements

This work is partially supported by CAPES, CNPq, FINEP, and Fundação Araucária (Brazilian Agencies). R. Falate also acknowledges the NUFORE through her experiments that have been done at UTFPR laboratories.

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