MICRO AND NANOSENSORS FOR THE MULTIPARAMETRIC ANALYSIS OF NATURAL GAS QUALITY

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Introduction

Natural gas composition varies depending on its point of origin and on its manipulation during the distribution to end users. This change of composition, which must be accurately measured, affects the chemical and physical properties of the natural gas. There are two key parameters that depend on the composition of natural gas and that affect energy billing and industrial processes. First, the High Calorific Value (HCV), which is an indicator of the heat quantity supplied. Secondly, the Methane Number (MN), a parameter used to prevent knocking in gas engines.

Nowadays, the energy measurement of natural gas is carried out in an indirect way by means of gas chromatographs located in the head-end of the gas distribution network. This method, in spite of being highly accurate, prevents the integration of HCV measurement in domestic and industrial meters, due to its cost, complexity and size. In this way, great effort has been carried out to develop new technological solutions to measure in situ the HCV, NM and Wobbe Index. Up to now different analytical, calorimetric and correlative methods have been employed. Analytical methods use huge and expensive equipments such as gas chromatography and mass spectroscopy to calculate the properties of the gas from the composition of the gas mixture. Calorimetric methods estimate the heating value of the natural gas by a combustion process. As an example, COSA 9610TM system [1] is based on the analysis of the oxygen content in the flue gas after catalytic combustion of the sample. The fuel air mixture is oxidized in a combustion furnace in the presence of a catalyst at 800'C, and the oxygen concentration of the combusted sample is measured and correlated to the Wobbe Index of the gas. On the other hand, correlative methods take advantage of the existing relationship between some physical and chemical parameters and the properties of natural gas. Some examples of these systems are: EnCAl300 [2] which is a gas chromatograph based on microelectromechanical (MEMS) components, GasLabQ1 [2], which measures the infrared absorption and heat capacity of the gas mixture, GasPT2 [3] which determines the thermal conductivity, sound velocity and CO_2 concentration and EMC500 [4] which measures the thermal conductivity, heat capacity, density and CO_2 content in the gas. The main disadvantage of these devices is their high cost as many physical or chemical parameters have to be measured in order to infer an effective gas mixture and estimate the quality of natural gas.

The aim of this work is to implement a series of novel multiparametric techniques based on micro-nanotechnology to evaluate the quality of natural gas. The advantage of the method proposed is that the HCV or NM of the gas mixture are measured by indirect methods employing MEMS, this means that low cost and combustion-less process is carried out.

Furthermore, the integration of these low cost sensors in an intelligent network of sensor nodes is a promising solution regarding energy efficiency in domestic and commercial gas utilization. Thus, it is thought that the system proposed will result in a more rational use of energy and greater cost savings.

Experimental

Two different sensors were developed by means of microfabrication techniques. The major advantage of the fabrication process is that it is suitable for mass production and provides low cost sensors.

HCV sensor consists on a surface acoustic wave sensor (SAW). This sensor was fabricated on ST-cut quartz substrate, which is a piezoelectric material. The transmitting and receiving interdigital transducers (IDTs) were obtained by dc sputtering of aluminum followed by patterning with photolithographic technique. The IDTs consisted of 20 finger pairs and different delay lines (400, 800, 1200 µm), widths (5, 7.5, 10 µm) and lengths (400, 800, 1200 µm).

A thermal conductivity sensor is employed to determine the MN. This sensor was fabricated on silicon substrate, where Si_3N_4 thin film was deposited by LPCVD. In the next step, platinum resistance was deposited, with length (100, 200 µm) and width of 5,10 and 20 µm. Then, an annealing treatment in Ar at 500 ºC was carried out to stabilize the microsestruce of the platinum film. Finally, silicon etching was carried out in TMAH solution to remove the silicon beneath the resistance and obtain a micro-bridge.

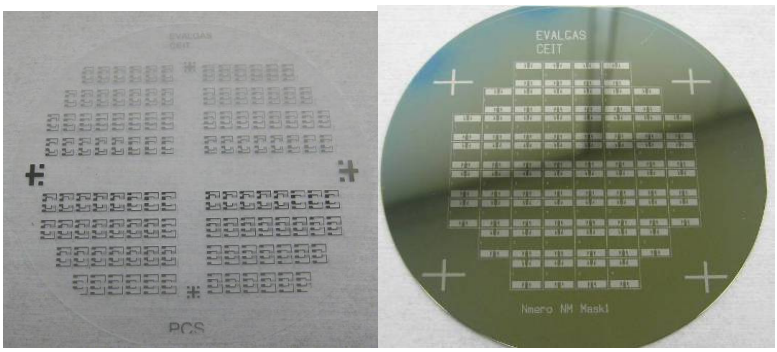

Figure 1. *ST-cut Quartz Wafer provided with HCV sensors (left) and silicon wafer with NM sensors (right).*

The microsensors were tested under 5 different mixtures of natural gas, obtained by varying the molar percentage of each component of the mixture (methane, ethane, propane, butane, CO_2 and N_2). This percentage was changed within the acceptable range established by legislation (NGTS standards). Table 1 shows the composition of the gas mixtures, which were acquired from AirLiquide SA as certified bottles.

COMPONENT (%)	**TEST 1**	**TEST 2**	**TEST 3**	**TEST 4**	**TEST 5**
Methane (CH_4)	75.00	84.30	89.75	91.80	98.45
Ethane (C_2H_6)	10.00	7.70	8.00	5.00	0.15
Propane (C_3H_8)	5.00	1.90	1.50	1.00	0.10
Buthane (C_4H_{10})	3.00	0.40	0.20	0.10	0.10
N_2	5.00	5.50	0.50	2.00	1.00
CO_2	2.00	0.20	0.05	0.10	0.20

Table 1. *Composition of the natural gas mixtures employed to calibrate the sensors.*

Results and Discussion

PROGAS software has been employed to calculate the physical parameters corresponding to each gas mixture. As shown in Table 2, the variation of the dynamic viscosity, density and thermal conductivity for the different samples is determined. Then, the HCV and NM of each gas is also calculated, in order to relate these key parameters to the physical properties of the gas.

	TEST 1	**TEST 2**	**TEST 3**	**TEST 4**	**TEST 5**	**N2**	**Ar**
Viscosity η (μPa)	109	110.1	107.8	109	109.3	173	210
Density ρ (kg/m3)	0.9025	0.7859	0.7523	0.7348	0.6912	1.184	1.784
Thermal conductivity λ (W/mK)	0.0307	0.0331	0.0337	0.0342	0.0354	0.024	0.016
PCS (kWh/m3) (1.013 bar,15ºC)	12.05	10.9	11.358	10.852	10.42	0	0
NM	48.9	69	78.2	82	93.3	0	0

Table 2. *Physical properties and key parameters of the gas mixtures calculated with the Progas software.*

First, a Surface Acoustic Wave (SAW) sensor is employed to measure the variation of viscosity of the natural gas. Due to the piezoelectric effect, when a sinusoidal voltage with frequency f is applied at the first IDT, a corresponding periodic mechanical strain pattern is produced. Only when the distance between the adjacent electrodes (p/2) is equal to half of the wavelength (λ/2), all vibrations interfere constructively. This causes acoustic waves propagating away from the IDT, in directions perpendicular to the electrodes [5]. The frequency that corresponds to this cumulative effect is called the resonance frequency and is calculated as follows:

$$f_0 = \frac{v_f}{\lambda} = \frac{v_f}{p} = \frac{3158 m/s}{p} \tag{1}$$

where v_f is the phase velocity of the acoustic wave in the ST-cut quartz and p is the period of the IDT.

The frequency (f_0) of the device taking into account the design of the IDTs are 157, 105 and 78.9 MHz for a width of 5 µm (p=20 µm), 7.5 µm (p=30 µm) and 10 µm (p=40 µm) respectively. Figure 2a shows the ideal response of the SAW sensor with the characteristic parameters: frequency and insertion losses. The viscosity and density of the surrounding medium affects the propagation of the wave, so a relation between the amplitude and frequency of the sensor and dynamic viscosity can be obtained. This relation could be later employed to determine the HCV of the mixture. Figure 2b shows the response of a sensor (10 µm width) under different samples with different dynamic viscosity.

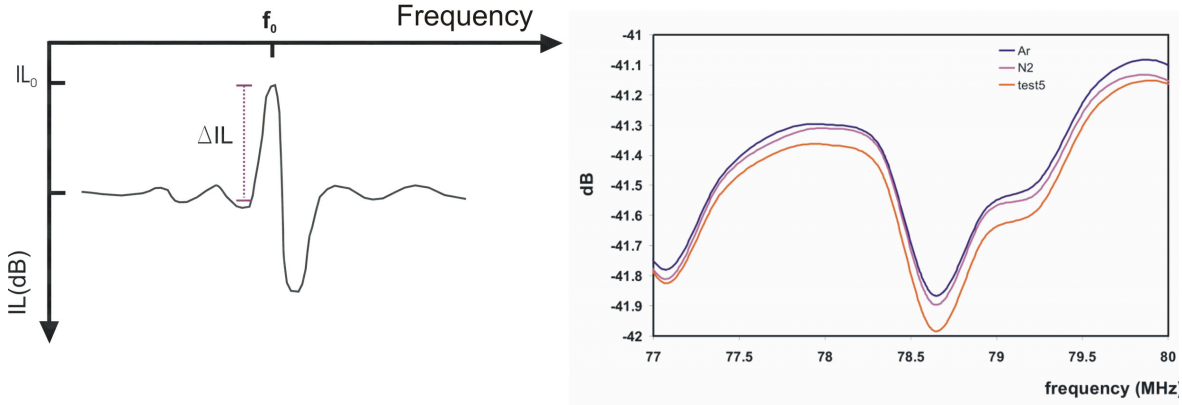

Figure 2. *Electrical signal of a SAW sensor (left) and response to different gas mixtures of a SAW sensor with f0=78.9 MHz.*

The resonance frequency of the device remains constant, but the insertion losses of the sensor changes due to the test gas. A logarithmic relationship between the product of dynamic viscosity and density of the gas with the amplitude of insertion losses is obtained as depicted in Figure 3.

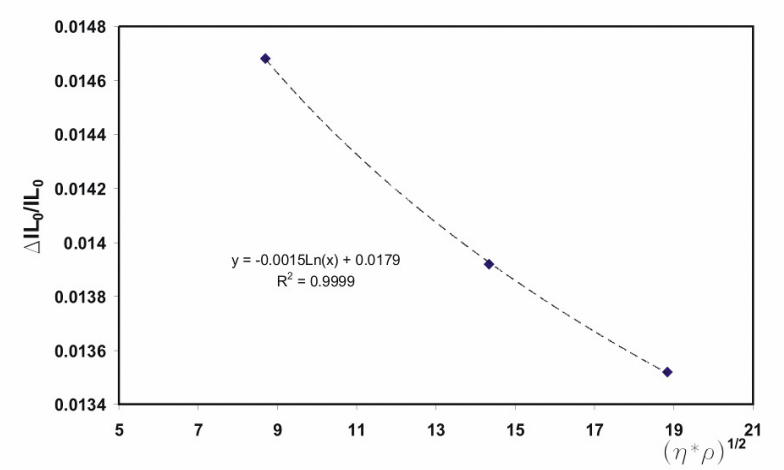

Figure 3. *Amplitude of insertion losses of the SAW sensor under different test gas mixtures.*

As shown in Figure 3, the amplitude of insertion losses (ΔIL/IL0) decreases when the gas mixture presents a bigger η*ρ. This means that a higher density and viscosity of the gas gives rise to the signal attenuation. In this way, if the higher molecular weight hydrocarbons are present in a greater percentage in the gas mixture, the sensor signal will be decreased.

On the other hand, a thermal conductivity sensor is employed to determine the methane number of the gas mixture. This sensor integrates two thermoresistors: one in thermal equilibrium with the gas (R reference) and the other self-heated to a temperature higher than that of the gas (R sensor). A low current of 1 mA is supplied to R reference assuring null self-heating to calculate gas temperature, while a constant current of 50 mA is supplied to R sensor. The heat generated in R sensor is dissipated to the surrounding gas and the output voltage of the resistance can be related to the thermal conductivity of the gas.

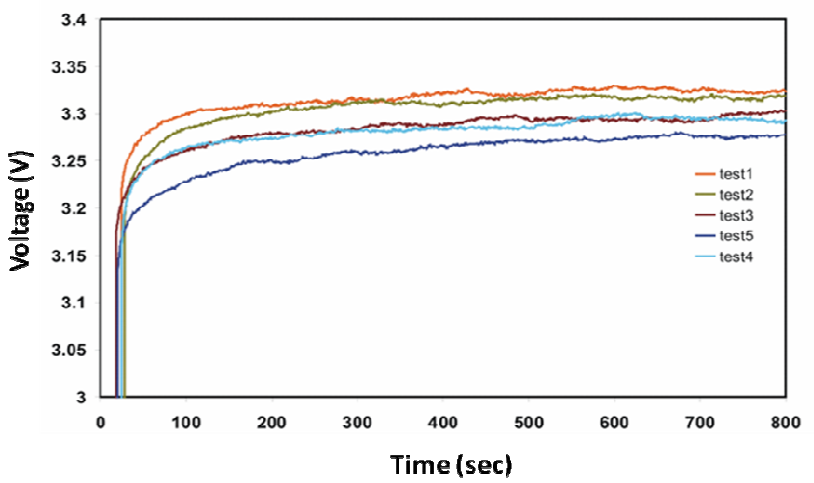

Figure 4. *Voltage variation of the R sensor supplied with a constant current of 50 mA under different natural gas mixtures.*

Figure 4 shows the voltage evolution of the sensing resistance when the sample is tested under different natural gas mixtures. It takes about 10 min stabilizing the output signal, where equilibrium with the gas is achieved. The samples characterized with a higher thermal conductivity dissipate more heat and a decrease in the output signal and the temperature achieved by the resistance is produced.

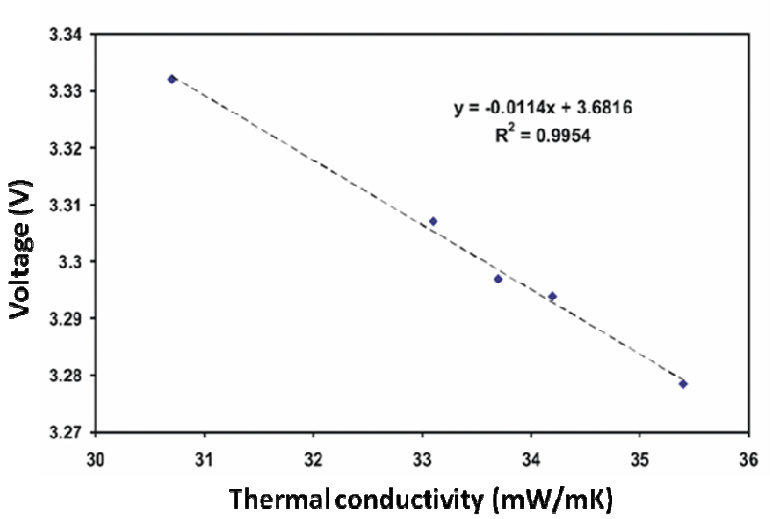

Figure 5. *Voltage variation as a function of thermal conductivity of the gas for different natural gas mixtures.*

For the range of thermal conductivities considered (0.0307-0.0354 W/mK), the microsensor gives an output signal of 48 mV and a good linearity. Furthermore, the thermal conductivity of the gas mixture can be related to the MN, so a linear relationship is described for the MN and output voltage, given by Equation 2.

$$NM = -838.94 \cdot V + 2844.2 \quad (2)$$

Conclusions

In this work two fundamental parameters of natural gas have been determined by means of indirect measurements. For this purpose, two physical properties of the mixture have been controlled: the dynamic viscosity of the gas and the thermal conductivity. Two low cost sensors have been fabricated by thin film technology and tested under different natural gas compositions. These microsensors provide an accurate relationship between the parameter to be determined and the physical property measured. Thus, the work has successfully shown that some quality parameters of natural gas such as HCV and MN can be determined by this low cost and combustion-less process. These sensors can also be integrated into an intelligent sensor network for developing a smart metering system that will result in a more rational use of energy and greater cost savings.

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