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Online determination of natural gas properties

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Abstract

Methane number and Lower Heating Value (*LHV*) of natural gas are determined by the online measurement of thermal conductivity at two different temperatures. Natural gas is first considered as a ternary mixture of the most important components. A pseudo-ternary composition can then be calculated, using the thermal conductivity formula for mixtures derived from kinetic theory. A non-linear system is solved numerically using the Newton–Raphson method. A sensor based on thermal conductivity measurement has been developed and tested successfully for many natural gas compositions. ***To cite this article: C. Rahmouni et al., C. R. Mecanique 331 (2003).***
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Résumé

Caractérisation des propriétés du gaz naturel. L'indice de méthane et le pouvoir calorifique inférieur (*PCI*) du gaz naturel sont déterminés au moyen de la mesure de la conductivité thermique à deux niveaux de température. Dans un premier temps, le gaz naturel est assimilé à un mélange ternaire de ses composés les plus influents. Dans ce cas, il est possible de calculer une pseudo-composition (ternaire) en utilisant l'expression de la conductivité thermique des mélanges déduite de la théorie cinétique des gaz. Le système d'équation non linéaire afférant est résolu numériquement par une méthode de Newton–Raphson. Enfin, un capteur, basé sur la mesure de la conductivité thermique, a été conçu et testé avec succès sur différents gaz naturels. ***Pour citer cet article : C. Rahmouni et al., C. R. Mecanique 331 (2003).***
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Version française abrégée

Dans le cadre du suivi des variations de la qualité du gaz naturel, en termes de variation d'indice de méthane [1] et de pouvoir calorifique, pour des applications moteur stationnaires ou embarquées, nous avons conçu un *capteur*

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basé sur la mesure de la conductivité thermique à deux niveaux de température. Ce capteur s'appuie sur une approche différente de celles employées dans les travaux antérieurs [4–8].

En se basant sur l'expression de la conductivité thermique issue de la théorie cinétique des gaz [9–11] et en l'appliquant aux gaz naturels polyatomiques [12], on peut écrire cette quantité sous la forme de l'Éq. (2). Il est possible de traduire des variations de composition par des variations de conductivité thermique.

En effet, une analyse en composantes principales (ACP), utilisant une base de gaz naturels représentatifs de ceux distribués en Europe [16], permet d'éliminer d'une part les propriétés physiques redondantes et d'autre part, de restreindre le nombre de constituants influents du gaz naturel vis-à-vis de l'indice de méthane et du pouvoir calorifique. Ainsi, deux propriétés physiques *expliquent* à plus de 97 % l'indice de méthane et déterminent complètement le pouvoir calorifique. De même, l'ACP a permis de distinguer trois groupes dans le gaz naturel :

– un groupe constitué du méthane (CH_4), principal constituant du gaz naturel,
– un groupe *lourds* constitué de l'éthane (C_2H_6), du propane (C_3H_8) et du butane (C_4H_{10}),
– un groupe *inertes* constitué de l'azote (N_2) et du dioxyde de (CO_2).

Le gaz naturel est alors représenté par un mélange ternaire représentatif de ces trois groupes et la composition de ce pseudo-gaz peut être déterminée par la résolution numérique (de type Newton–Raphson) du système d'équations non linéaires, Éq. (5).

Le capteur mesure la conductivité thermique à 30 °C et à 80 °C au moyen de deux résistances thermiques placées chacune dans une cellule contenant le gaz. Le signal de sortie du capteur, fonction de la conductivité, est ensuite utilisé pour la résolution du système précédent. Enfin, l'indice de méthane et le pouvoir calorifique inférieur du gaz naturel sont déterminés à partir du pseudo-gaz. Les résultats sont en concordance avec les valeurs réelles de l'indice de méthane et du pouvoir calorifique et permettent d'anticiper une combustion détonante dans les moteurs. Cette approche donne également la possibilité d'utiliser divers couples de propriétés physiques telles que la viscosité dynamique et l'indice de réfraction.

1. Introduction

Knock rating of gaseous fuels is an important topic for SI gas engines because abnormal combustion can cause serious damages. Interconnection of natural gas networks, involving variation of composition, leads to variation in terms of methane number (*MN*), defined by Leiker et al. [1], and also leads to power fluctuations in terms of lower calorific value (*LHV*). *MN* characterizes the resistance to knock of gaseous fuels and is measured on a standard CFR engine under specified conditions [1–3]. A comparison between the unknown resistance to knock of a gaseous fuel with the knock resistance of a gaseous reference binary mixture (methane as an anti-knock component and hydrogen as a knock component) is made. The *MN* is then the percentage by volume of methane in the reference fuel that matches exactly the unknown gas mixture knock intensity.

Many techniques for determining *MN* and *LHV* of gaseous fuels are detailed in previous papers [4–8]. These methods need the measurement of physical properties by means of an expensive apparatus, which make the present work attractive. The commonly admitted error in the determination of methane number is ± 2 *MN* units, which represents the error produced by the algorithm METHANE developed by the Austrian company AVL, our reference *MN*.

Physical properties, such as thermal conductivity for monoatomic gases, have been described by the kinetic theory [9–11]. Molecules can be decribed, for dilute gases, by the equation of Maxwell–Boltzmann [9,10] dealing with interactions between colliding molecules.

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \mathbf{F} \cdot \nabla_v f = \left[\frac{\partial f}{\partial t}\right]_{\text{coll.}} \tag{1}$$

Solving this equation by the method of Chapman–Enskog gives an expression for monoatomic gas mixture thermal conductivity [10,11]. The extension to polyatomic gases, such as natural gas, has been suggested by Mason and Saxena [12] in order to take into account the energy exchanged by internal degrees of freedom of the molecules. The expression of polyatomic gas mixture thermal conductivity is then:

$$\lambda_m = \sum_{i=1}^{\nu} \lambda_i \left[1 + \sum_{\substack{k=1 \\ k \neq i}}^{\nu} G_{ik} \frac{x_k}{x_i} \right]^{-1} \tag{2}$$

$$G_{ik} = \frac{1.065}{2\sqrt{2}} \left(1 + \frac{M_i}{M_k} \right)^{-1/2} \left[1 + \left(\frac{\lambda_i^{(tr)}}{\lambda_k^{(tr)}} \right)^{1/2} \left(\frac{M_i}{M_k} \right)^{1/4} \right]^2 \tag{3}$$

where x_i and M_i are respectively the molar fraction and the molecular weight of species i. λ_i is the thermal conductivity of pure gas i whereas $\lambda_i^{(tr)}$ is the coefficient of *frozen* conductivity when no internal degrees of freedom but translational are concerned. These are defined in [13].

2. Determination of a pseudo-gas

A principal component analysis (PCA) has been performed on a square symmetric test gas matrix of 30 natural gases in terms of gas composition and gas physical property standardized data (correlation matrix between variables). The objective of PCA is to reduce the number of variables by transforming a number of (possibly) correlated variables into a (smaller) number of uncorrelated variables called principal components. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible.

The results first pointed out that 97.5% of the variability of methane number in the data is "summarized" (or 'reduced') on 2 factorial axis, each representing an optimal linear combination of the other variables. As well, it pointed out that almost 100% of the variability of *LHV* is summarized on 2 factorial axis.

Table 1 presents the variability of methane number, *LHV* and thermal conductivity according to the first two principal components (coefficient of correlation between the physical properties and the principal component i, cor_i). The total variability of each physical property for two axis is computed by summing the variability of each physical property taken alternatively for the first and the second principal component.

Another physical property could improve *MN* quality of determination.

Results for natural gas components are shown for the first two principal components u_1 and u_2 in Fig. 1. This figure indicates that natural gas can be represented by three different groups: (1) methane (CH_4), chief constituent of major natural gases; (2) *heavy* hydrocarbons C_2H_6, C_3H_8 and C_4H_{10}; (3) *inert* gases (N_2 and CO_2).

It has been shown that at least three factorial axis are necessary to correctly describe the test gas matrix. It is then possible to define a ternary pseudo-gas of influent natural gas components for which the physical properties are *conserved*. Thus, natural gas composition is well described in the most representative ternary pseudo-gas, CH_4–C_2H_6–N_2 [14].

Table 1
Variability of each physical property according to the two first principal components

	cor_1	cor_1	$\sum_{\alpha=1}^{2} cor_\alpha(j)$
MN	0.945	0.030	0.975
λ_{293}	0.905	0.083	0.988
λ_{393}	0.555	0.431	0.986
LHV	0.510	0.489	0.999

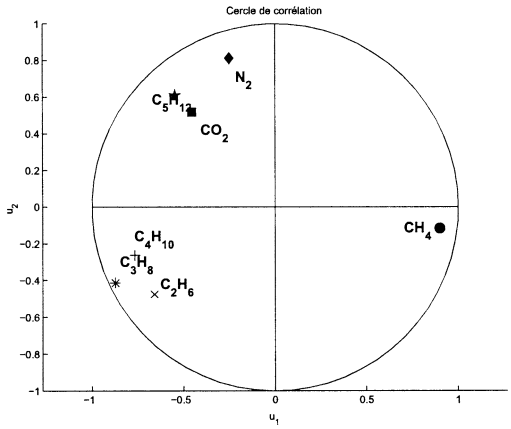

Fig. 1. *PCA* on natural gas components.

Fig. 1. *ACP* des composés du gaz naturel.

Using the thermal conductivity formula for ternary gases at a fixed temperature T, we have:

$$\lambda_m = \sum_{i=1}^{3} \frac{\lambda_i(T)}{\sum_{j=1}^{3} x_j G_{ij}(T)} x_i \overset{\text{notation}}{=} s^t x \tag{4}$$

where G_{ij} is defined by Eq. (3), $x = (x_1, x_2, x_3)$ and $s = (s_1, s_2, s_3)$ with

$$s_i = \frac{\lambda_i(T)}{\sum_j^3 x_j G_{ij}(T)}, \quad i = 1, 2, 3$$

By definition of a ternary gas ($\sum_i x_i = 1$) and considering thermal conductivity at two temperatures T_1 and T_2, let Φ be the vector $\Phi = (\lambda_m(T_1); \lambda_m(T_2))$. Determining a pseudo-gas composition x is equivalent to the solution of the following nonlinear system

$$\begin{pmatrix} \lambda_m(T_1) - s_3(T_1) \\ \lambda_m(T_2) - s_3(T_2) \\ 1 \end{pmatrix} = \begin{pmatrix} s_1(T_1) - s_3(T_1) & s_2(T_1) - s_3(T_1) & 0 \\ s_1(T_2) - s_3(T_2) & s_2(T_2) - s_3(T_2) & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \tag{5}$$

This solution may be obtained by the Newton–Raphson method.

3. *MN* and *LHV* sensor

The sensor consists in two cells, each containing a heating resistor and a thermal conductivity detector. Temperature is fixed at 30 °C for the first cell and 80 °C for the second one. The output signal of each thermal conductivity detector is used for the numerical solution of (5). *MN* is then calculated from the software METHANE, using the pseudo-gas composition. The *LHV* is deduced from the knowledge of the *LHV* of each compound of the pseudo-gas [15]. Results for *MN* and *LHV* are illustrated on Fig. 2.

The error made on the determination is below ±2 *MN* units and below 1% for *LHV*. This methodology is valid for the thermal conductivity range:

$$322\ \text{W/(m}\cdot\text{K)} \leqslant \lambda_{m1} \cdot 10^4 \leqslant 344\ \text{W/(m}\cdot\text{K)}, \qquad T = 30\,^\circ\text{C}$$
$$398\ \text{W/(m}\cdot\text{K)} \leqslant \lambda_{m2} \cdot 10^4 \leqslant 420\ \text{W/(m}\cdot\text{K)}, \qquad T = 80\,^\circ\text{C}$$

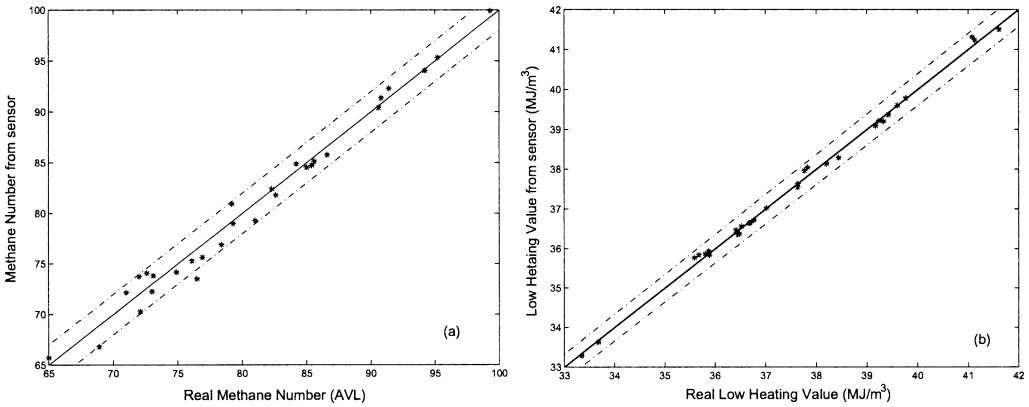

Fig. 2. Properties of natural gas determined from the sensor.

Fig. 2. Propriétés du gaz naturel déterminées par le capteur (a) Methane number–indice de méthane (b) *LHV–PCI*.

The sensor, based on the measurement of thermal conductivity, is a good compromise in terms of accuracy and cost-effective. At last, the sensor is capable of measuring simultaneously important properties such as *MN* and *LHV* unlike other methods.

4. Conclusion

Principal component analysis has shown that two physical properties describe 97% of the variation of *MN* and almost 100% of the variation of *LHV* of the test gas matrix. It is also shown that natural gas can be reduced to its most influent components. The sensor developed on this basis was capable of measuring *MN* and *LHV* with respectively an error of less than ± 2 *MN* units and 1%. This sensor presents the advantage to measure simultaneously, in a cost-effective way, *MN* and *LHV* with a good accuracy. It can also determine combustion properties such as Wobbe index and the stoichiometric air–fuel ratio. This methodology could be extended to other couples of physical properties such as viscosity and refraction index, improving its accuracy.

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