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Thermodynamic research improves energy measurement of natural gas

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Abstract

The new energy measurement concept is based on the idea that three physical properties will be sufficient for characterising natural gas and providing the information required for energy conversion by way of correlation. The inferential or correlative system uses relative permittivity (ε), speed of sound (w) and CO_2 mole fraction (x_{CO_2}) as input parameters. For relative permittivity, a measurement unit (a re-entrant resonant cavity cell), has been optimised by National Engineering Laboratory (NEL) for both laboratory and field or on-line applications. With the new system, the calorific value measured at reference conditions agrees with other experimental results, Cutler–Hammer calorimeter and GC analysis, to within 0.1%.

Keywords: Energy conversion; Inferential method; Calorific value; Relative permittivity; Reference calorimeter

1. Introduction

Energy measurement is one of the central tasks in the gas industry. Compared with the measurement and billing of electrical energy, determining the energy contained in a gas involves a much greater effort and is far more complex because fluid mechanics and the thermodynamic and calorific properties of natural gases have to be taken into account.

Present energy measurement systems for natural gas comprise volume metering, volume conversion from field conditions to reference conditions and calorific value determination. The calorific value (H_{sr}) is either measured with a calorimeter or determined by compositional analysis using a process chromatograph [1,2]. At large gas receiving or delivery stations, this information is made available together with the volume measured by orifice plates, turbine flow meters or ultrasonic flow meters, etc. as shown in Fig. 1. The energy is defined as the product of the calorific value and the volume, each under reference conditions. The volume (V_f) measured under operating conditions (p_f, T_f), therefore, is converted to the volume (V_r) at reference conditions (p_r, T_r). The conversion factor (CF) $= V_r/V_f$ is determined from thermal equations of state which primarily calculate compression factors or densities [3,4].

This paper presents a novel correlative concept for determining the energy contained in a gas but using conventional volume measurement. It describes the development of the new concept, the selection of the components of a possible future energy measurement system, followed by some details of the newly developed system, especially the component for measuring relative permittivity which will basically replace the calorimeter in our present system (see Fig. 2). Information is provided on the laboratory tests of the new

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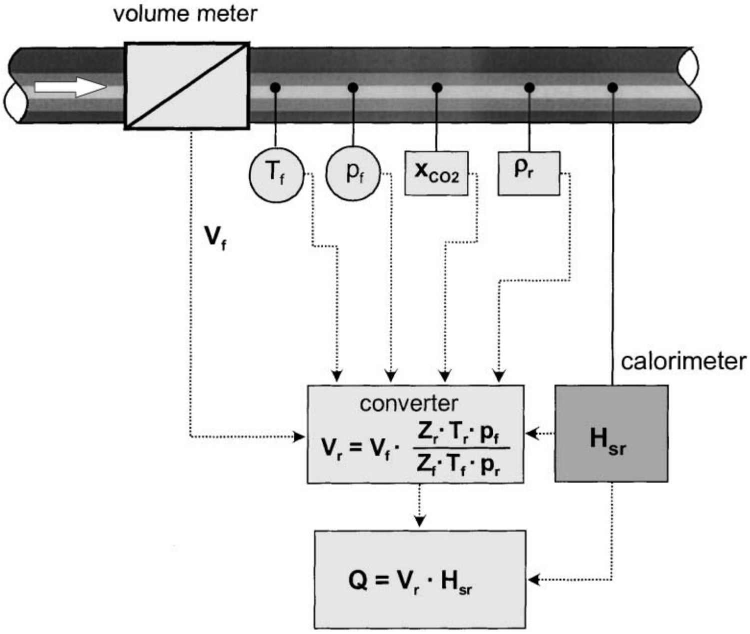

Fig. 1. Existing energy measurement system with a pTZ converter. The compression factor (*Z*) is determined from CO_2 content (x_{CO_2}), density (ρ) and superior calorific value (H_{sr}) at field or reference conditions (index *f* and *r*, respectively). For an ideal gas pressure (p) and temperature (T) only defines the conversion factor ($T_r p_f / T_f p_r$) for the volume (V_f) measured at field conditions. The uncertainty (ΔH_{sr})is approximately 0.4%.

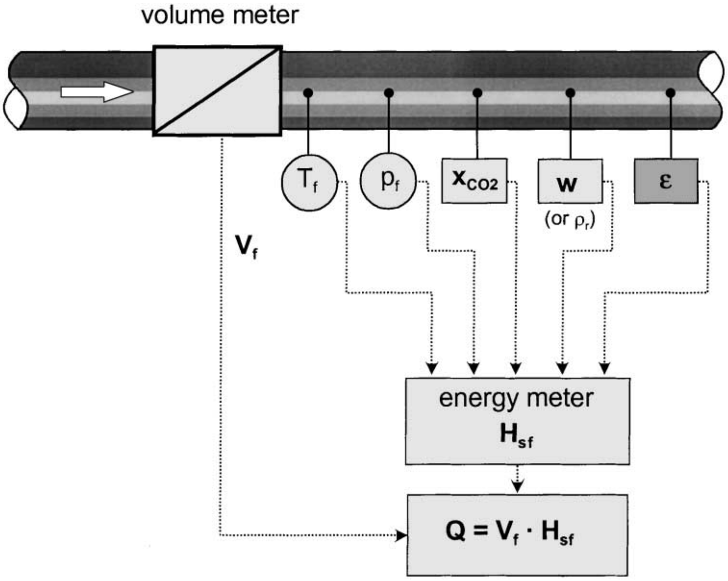

Fig. 2. Future energy measurement system based on a correlative, inferential energy determination from CO_2 content (x_{CO_2}), speed of sound (w) and dielectric permittivity (ε). The expected uncertainty under field conditions including conversion is $\Delta H_{sf} = 0.3\%$. The volume (V_f) is measured a field conditions (pressure (p_f) and temperature (T_f)).

energy measurement system and the field test with a simplified data acquisition system.

2. Development of a new energy measurement system

The new energy measurement concept is based on the idea that three physical properties will be sufficient for characterising natural gas and providing the information required for energy conversion by way of correlation. In other words, this is an inferential method which determines the calorific value and the conversion factor for energy conversion. A similar approach has already been adopted with the SGERG equation for calculating the density and compression factor values of natural gases [3]. A central feature of this concept is the availability of an accurate caloric equation of state to calculate values for the properties used in agreement within the measurement uncertainty of the properties. Using this information, a correlation is developed between three physical properties and the calorific value of natural gases. The AGA8 equation [4], also referred to as the AGA8 DC92 equation of state, was used to calculate the caloric properties of natural gases. For other properties, e.g. transport properties, simple equations were applied.

2.1. Feasibility study

In two feasibility studies conducted by Ruhr-Universität Bochum [5] and the Van der Waals-Zeeman Institute, Amsterdam [6], physical properties were checked for their suitability. The results presented below have been taken from the study by Ruhr-Universität Bochum. The selection criteria were: low measurement uncertainty, high sensitivity to gas composition (e.g. methane, ethane, nitrogen and carbon dioxide) and low cross-correlation between input properties. From the practical point of view, the following requirements are important: availability of measurement method, low capital expenditure and low operating and maintenance costs.

Possible physical properties were checked as input parameters to determine if they are suited for appropriately characterising binary mixtures of methane + nitrogen or ethane or carbon dioxide. In principle, any property which changes with composition is useful in determining the composition of a binary mixture as long as the variation of an input property (Δinp) to produce a change in mole fraction of CH_4 of 0.1 mol% is smaller than the experimental uncertainty of that input property (Δinp (expt)).

Natural gases may be treated as four-component mixtures consisting of methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2) and the sum of the other hydrocarbons. In that case three input properties can produce sufficient information to characterise the gas composition. An approach of this type was already used for the SGERG equation [3]. However, in the approach adopted here, the mole fraction of the equivalent hydrocarbon gas (the sum of all hydrocarbons including methane) (x_{CH}) is explicitly correlated to the mole fractions of the alkanes from ethane up to *n*-octane via a second-order expansion in the molar calorific value (H_{CH}) of the equivalent hydrocarbon gas.

$$x_i = \{a_{1,i}(H_{\mathrm{CH}} - H_{\mathrm{CH_4}}) + a_{2,i}(H_{\mathrm{CH}} - H_{\mathrm{CH_4}})^2\}x_{\mathrm{CH}} \quad (1)$$

where subscript *i* denotes ethane, propane, etc. The coefficients $a_{1,i}$ and $a_{2,i}$ were correlated previously [7]. An example for ethane and propane as a function of the molar calorific value (H_{CH}) is shown in Fig. 3 for

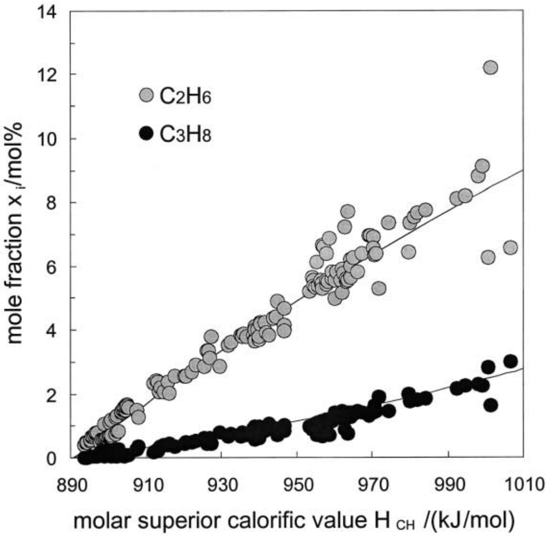

Fig. 3. Ethane and propane percentage mole fractions as a function of the superior calorific value (H_{CH}) of the equivalent hydrocarbon gas for 200 natural gas samples.

approximately 200 natural gases. Here, H_{CH} is calculated using ISO 6976 [1] for the equivalent hydrocarbon gas which is obtained by deleting the mole fractions of the inert gases, nitrogen, carbon dioxide, etc. and re-normalising the mole fractions of the hydrocarbons.

The feasibility study concluded that either of the two combinations of input parameters may be selected:

$T_f, p_f, x_{CO_2}, w_r, \varepsilon_r$

$T_f, p_f, x_{CO_2}, \rho_r, \varepsilon_r$

Pressure (p_f) and temperature (T_f) are necessary for defining operating or field conditions for the volume flow metered (subscript f). Mole fraction CO_2 (x_{CO_2}), density (ρ) or speed of sound (w) and relative permittivity (ε) are the input properties proposed for determining the gas composition. The subscript (r) refers to predetermined reference conditions. Instruments were available for CO_2 content, density and speed of sound, while a new system had to be developed and tested for permittivity (ε) [8].

2.2. Test of correlation method

A correlation method for calculating the gas composition which is then used to determine the energy conversion factor under field conditions (i.e. superior calorific value (H_{sr}) and conversion factor (CF)) was developed. A flow diagram is given in [9]. For the iterative method to be used, the input properties must be known. Moreover, the method requires an equation to calculate these properties from a given gas composition. For density and speed of sound, the AGA8 DC92 equation is employed [4,10]. For relative permittivity, a truncated virial expansion in molar density (ρ_m) is used. The term on the left-hand side of Eq. (2) is called the Clausius–Mossotti function for molar polarisability.

$$\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{1}{\rho_m} = A_\varepsilon + B_\varepsilon \rho_m \tag{2}$$

A_ε and B_ε are the first and second dielectric virial coefficients. In the feasibility study, values for these coefficients were taken from the literature [11,12], whereas, the final values used were fitted to our own experimental results.

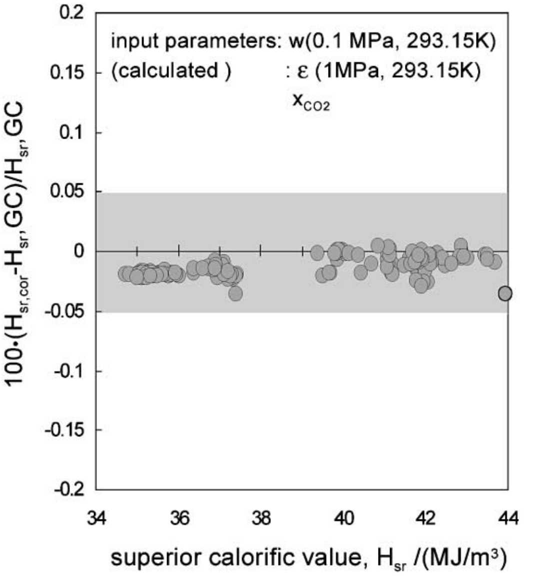

Fig. 4. Deviations of superior calorific value, correlated from input data, from values derived from GC analysis at reference conditions ($T_r = 273.15$ K, $p_r = 0.101325$ MPa). Relative permittivity (ε), speed of sound (w) and CO_2 mole fraction (x_{CO_2}) are calculated from GC analysis.

The calculation method was tested on the same, approximately 200 gas samples as used in Fig. 3. The input parameters (speed of sound, relative permittivity and mole fraction CO_2) were calculated from a GC analysis. The correlated superior calorific value is compared to the value calculated from the GC analysis in Fig. 4. The maximum differences are below 0.04%. They result from systematic errors in the correlation and do not include any experimental uncertainties.

2.3. Re-entrant cavity for relative permittivity

The National Engineering Laboratory (NEL), East Kilbride, UK [8] has developed a re-entrant cavity operated as a LC resonator (L: inductance, C: capacitance). It is based on the concept described by Goodwin et al. [13]. A schematic is given in Fig. 5. The re-entrant cavity comprises two main components, an inner part with a bulbous shape and an outer part or shell into which the inner part is assembled by means of a finely threaded connection. The complete permittivity cell assembly is designed to be mounted in an external pressure containment vessel. Hence, the larger part of the resonator structure is completely

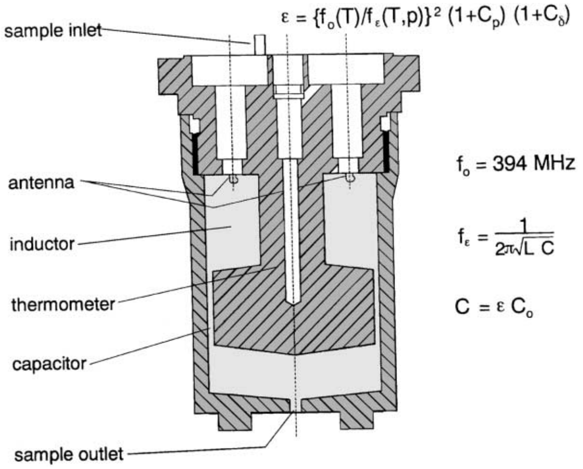

Fig. 5. Schematic of the re-entrant cavity operated as a LC resonator. L is the inductance and C the capacitance of the resonator.

immersed in the test gas and not subjected to large dilating forces. The dimensions of the new cavity have been optimised to provide a high-quality factor and to minimise the effect of gaseous adsorption through an enlarged annular gap. Silver and gold plating were used to further reduce the influence of gaseous adsorption as well as to enhance the electrical conductivity of the internal surface layers and thereby improve the quality factor to around 2300. The quality factor is defined as $Q = f/\Delta f$, where f is the central frequency of the resonance curve and Δf the half-width. The resonance frequency of the evacuated cavity is approximately 394 MHz.

Provided that the Q value is kept above 1000, Goodwin's theoretical model can be replaced by the following general model which is applicable to an absolute uncertainty better than 1 ppm at ambient conditions [8,14].

$$\varepsilon_r(T,p) = (f_0(T)/f_\varepsilon(T,p))^2(1 + C_p) \cdot (1 + C_\delta) \qquad (3)$$

where $f_0(T)$ is the resonant frequency of the evacuated cavity at temperature T, $f_\varepsilon(T,p)$ is the resonant frequency at the conditions of measurement, C_p is the correction factor for dilation due to pressure, and C_δ is the correction factor for effective dilation due to the change in penetration depth.

For the specific cell geometry and material (beryllium–copper alloy), the correction factor has been shown to be $C_p = (6.6 \pm 0.6) \times 10^{-12}p$, where p is the absolute pressure in Pa. At the maximum operating pressure of 10 MPa the correction reaches 66 ppm. The correction factor C_δ results from the penetration depth of the electromagnetic field into the metallic surface of the cavity. The effective depth of penetration of the field, the so-called *skin-depth*, can be related to the quality factor, $Q_0(T)$, of the evacuated cell and the relative permittivity, ϵ_r, of the enclosed dielectric media. The correction factor for the dilation of the specific cavity due to *skin-depth* has shown to be $C_\delta = (4.32 \times 10^{-5} + 6.47\ Q_0(T)^{-1})\ (\epsilon_r^{1/4}-1)$. For a relative permittivity of 1.1 (e.g., a natural gas at 10 Mpa) the correction factor reaches 69 ppm. The uncertainty in the factor C_p is $\pm\ 0.1C_p$ and in the factor $C_\delta \pm 0.05\ C_\delta$.

The re-entrant cavity was designed to operate at temperatures from 280 to 360 K at pressures to 10 Mpa allowing a relative permittivity range from 1.0 to 1.1. The cavity was used to measure a consistent set of data for the dielectric virial coefficient of the major natural gas components, thus providing the necessary coefficients for Eq. (2) to calculate relative permittivity values.

3. Test of new energy measurement system

3.1. Laboratory measurements

For the laboratory test of the energy system the following physical properties were measured simultaneously:

- Speed of sound with a domestic ultrasonic flow meter.
- CO_2 mole fraction with an infrared absorption device.
- Relative permittivity with the re-entrant cavity developed by NEL.

The resonant frequency of the permittivity cell cavity was determined by examination of the transmission amplitude response using a swept-frequency analyser (Hewlett-Packard HP8752C, 1.3 GHz max.). The stability of the instrument was maintained by using an oven-controlled oscillator giving a reference frequency stability of around one part in 10^8. The temperature was regulated to better than 10 mK. The uncertainty in temperature measurement is estimated to be 5 mK. Pressure measurements were made with a set of four quartz oscillator pressure transducers (Paroscientific) covering an operational range of up to 14 MPa in four overlapping sub-ranges. The uncertainty in pressure measurement is estimated to be 0.02%.

The complete energy measurement system was tested to verify the envisaged 0.2% uncertainty for the superior calorific value (H_{sr}) allowing uncertainties for the physical input properties of $\Delta w = 0.1\%$, $\Delta(\varepsilon - 1) = 0.1\%$ and $\Delta x_{CO_2} = 0.4$ mol%. The correlation Eq. (2) for molar polarisability based on the dielectric virial coefficient from this work and the AGA8 DC92 equation to calculate speed of sound and molar densities as a function of p, T and x_i were employed to determine the superior calorific value from the input data.

The results for 10 natural gases are given in Fig. 6. For the speed of sound and the CO_2 mole fraction, the data were measured at ambient conditions and relative permittivity was measured at $T = 293.15$ K and $p = 1$ MPa. The results for $H_{sr,cor}$ (volume at reference conditions) agree to within better than 0.05% with the calorific value calculated from the GC analysis. Moreover, the superior calorific value based on the volume at assumed field/operating conditions ($T_f = 283.15$ K, $p_f = 5$ MPa) (H_{sf}), i.e. the energy conversion factor for H_{sf} = energy conversion factor for H_{sr}, also agrees to within 0.1% with the calculated results obtained from the GC analysis (see Fig. 7). For this comparison, the conversion factor (CF) for $H_{sf,GC}$ from the gas analysis and for $H_{sf,cor}$ from the correlation method was calculated from the AGA8 DC92 equation.

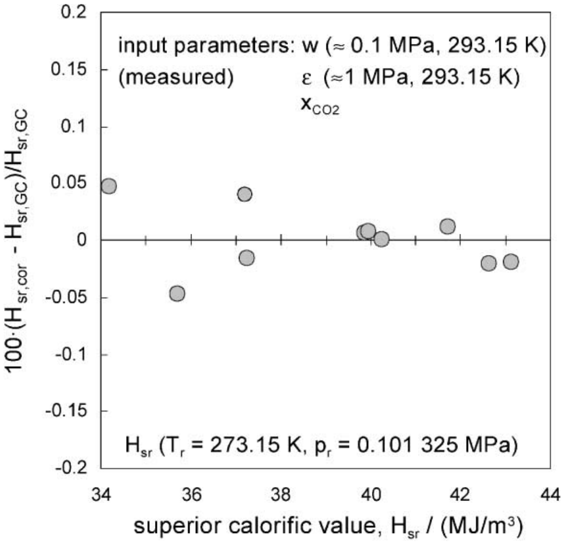

Fig. 6. Deviations of superior calorific value, correlated from input data, from values derived from GC analysis at reference conditions ($T_r = 273.15$ K, $p_r = 0.101325$ MPa). Relative permittivity (ε), speed of sound (w) and CO_2 mole fraction (x_{CO_2}) are measured simultaneously in the laboratory.

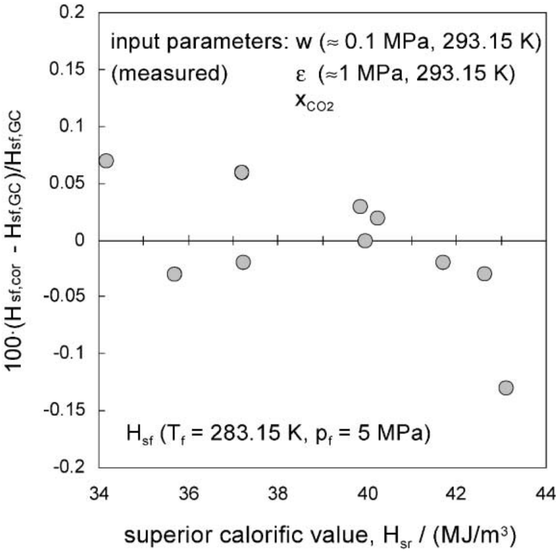

Fig. 7. Deviations of superior calorific value, correlated from input data, from values derived from GC analysis at fictitious field conditions ($T_f = 283.15$ K, $p_f = 5$ MPa). Relative permittivity (ε), speed of sound (w) and CO_2 mole fraction (x_{CO_2}) are measured simultaneously in the laboratory.

3.2. Field measurements

Two major modifications were made to adapt the laboratory equipment to field applications. For the speed of sound measurements the domestic ultrasonic flow meter, which is no longer manufactured, was replaced by a speed of sound sensor of Instromet International. This sensor is based on a time of flight principle and uses components of the ultrasonic flow meter of the same company.

The relative permittivity measurement was modified as to enable the re-entrant cavity to be operated as an accurate self-resonant device suitable for field or on-line applications. The main features of this

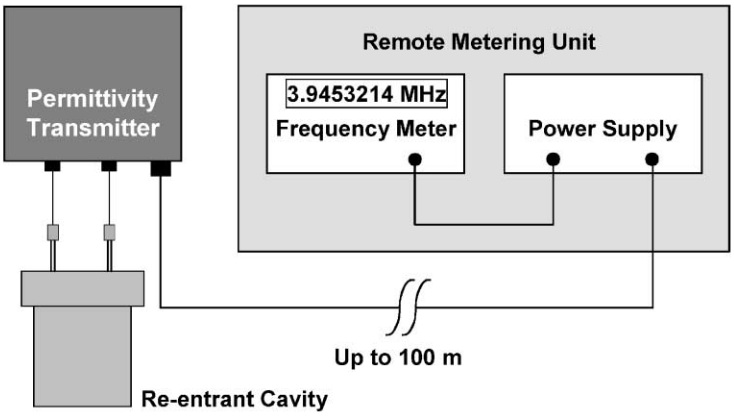

Fig. 8. Schematic of the re-entrant cavity cell operated as a self-resonant device.

development can be seen in Fig. 8. A driver circuit was designed and developed by NEL [15].The field instrument consists of a permittivity transmitter and a remote metering unit. It provides a means of exciting and maintaining the re-entrant cavity in electronic resonance at its natural resonance frequency. It transmits a precisely scaled frequency back to the remote metering unit which is precisely one-hundredth of the resonance frequency.

The frequency related to the resonant frequency of the permittivity cell cavity is counted with a frequency meter (Agilent 53131A universal counter). The counter is fitted with a temperature-stabilised reference frequency source. The stability is better than one part in 10^7. The instrumentation for the field test is installed in an container close to a gas transmission pipeline. The container is air-conditioned keeping temperature changes below 5 K. The uncertainty in temperature measurement is less than 0.05 K, that is, 0.02% (Rosemount, PT100). Pressure is measured with a quartz oscillator pressure transducer (Rosemount, type 3051). The uncertainty in pressure measurement is estimated to be 0.05%.

Six of the 10 natural gases for which results are shown in Fig. 6 under laboratory conditions have been investigated again with the field equipment installed in the container. As before, the speed of sound and the CO_2 mole fraction were measured at ambient conditions and relative permittivity was measured at $T = 293.15$ K and $p = 1$ MPa (see Fig. 9). The results for $H_{\mathrm{sr,cor}}$ (volume at reference conditions) agree to within better than 0.1% with the calorific value calculated from the GC analysis and with the previous results measured with the laboratory equipment.

The long-term stability of the system is under investigation. The calorific value results obtained are being compared with the reading of a calorimeter of Ruhrgas and the reading of a GC operated by

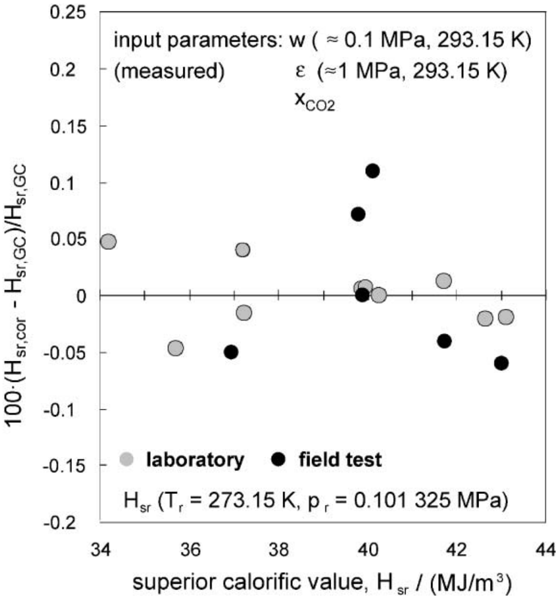

Fig. 9. Deviations of superior calorific value, correlated from input data, from values derived from GC analysis at reference conditions ($T_r = 273.15$ K, $p_r = 0.101325$ MPa). Relative permittivity (ε), speed of sound (w) and CO_2 mole fraction (x_{CO_2}) are measured simultaneously on-line under field conditions.

Gasunie. At the same time, other systems are being tested in the container.

4. Verification of calorific value

In Figs. 6, 7 and 9 the reading of the new energy measurement system, i.e. the calorific value (based on the volume at reference or field/operating conditions) has been compared with the calorific value calculated from GC analysis using the data provided by ISO 6976 [1]. The uncertainty of the calorific value from GC analysis is made up by the uncertainty in the analysis and the uncertainty of the basic data in ISO 6976. This results in an total uncertainty of approximately 0.2–0.3% for the calorific value of the gases used in testing the equipment.

The best that can presently be achieved for the calorific value of mixtures in the certification process in Germany is about 0.2% (95% confidence limit) [16]. Gases needed in calibration or verification procedures have "to be certified by a process which provides an uncertainty on the certified calorific value which is significantly less than the uncertainty requirement for the calorific values to be measured by the instrument. To achieve this, the uncertainty of the certified calorific value shall be not more than one-half of the uncertainty specified for the application" [2].

To verify a uncertainty of 0.1–0.2% for the calorific value determined with the new energy measurement system requires among other things a calorimeter which is "maintained or operated by a national standard institute or an accredited laboratory, which provides traceability to recognised national metrological standards" [2] and has an uncertainty of 0.05–0.1%. Therefore, a study was carried out by Advantica Technologies (formerly BG Technology),UK, Physikalisch Technische Bundesanstalt (PTB), Ruhrgas AG and SNAM, Italy, to determine the possibility/feasibility of developing a reference calorimeter with an uncertainty better than 0.05% (for two standard deviations, i.e. for a 95% confidence limit).

A detailed investigation was done on two calorimeter configurations, the Rossini-type [17,18] and the Alexandrov-type [19] calorimeter, which included improvements and refinements. A detailed uncertainty analysis has demonstrated that an uncertainty of 0.05% can be achieved. A follow-up project was proposed to develop a reference calorimeter to measure the superior calorific value of pure gases (methane, ethane, propane and butane) and a gas mixture. The original project team will be joined by Enagas, Spain, Gaz de France and Laboratoire National d'Essais of the Bureau National de Métrologie in France to build such a calorimeter.

5. Conclusion

A new energy metering system has been devised and developed. The correlative or inferential system uses speed of sound, relative permittivity and CO_2 mole fraction as input parameters. The following results were achieved:

- The measurement of relative permittivity with the re-entrant cavity has been optimised.
- The calorific value measurements made under laboratory conditions agree with the GC results to within 0.05%.
- The results of measurement with the field instrument which uses a driver circuit to operate the re-entrant cavity as a self-resonant device agree to within 0.1% with the GC analysis.

A contract between seven partners is being negotiated to develop and build a reference calorimeter traceable to national metrological standards.

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