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Thermodynamic Research Improves Energy Measurement in Natural Gas[1]

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This paper gives a brief overview of existing energy measurement systems for natural gas and presents a novel correlative concept for determining the energy contained in a gas. In addition, it provides information on the development and application of a new fundamental reference equation of state. This equation greatly improves prediction of caloric properties and therefore allows optimization of the use of critical nozzles for metering natural gas flows of varying qualities. Laboratory tests of the new energy measurement system have shown that the target uncertainty of 0.2% for the calorific value is routinely reached. A feasibility study currently underway examines the possibility of building a reference calorimeter with an uncertainty of 0.05%.

KEY WORDS: calorific value; critical nozzles; energy; equation of state; Helmholtz free energy; natural gas; relative permittivity; speed of sound.

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.

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This paper first looks at some of today's most frequently used energy measurement systems, followed by an introduction to the components of a possible future system and a report on projects currently underway at Ruhrgas, Gasunie, and GERG (Groupe Européen de Recherches Gazières).

2. EXISTING ENERGY MEASUREMENT SYSTEMS

The measurement of electric power, P, or energy (= power × time) is relatively simple, $P = IU \cos\varphi$, where U is the voltage at both ends of a resistance, R, and I is the current passing through it. With alternating currents, $\cos\varphi$ is the so-called power factor and φ is the phase shift between current and voltage.

The equivalent relationship for determining the energy or heat content, Q, or power (=energy/time) of natural gas is $Q = V_r H_{sr}$. Present energy measurement systems for natural gas comprise volume metering, volume conversion from field conditions to reference conditions, and calorific value determination (see schematic in Fig. 1). V is the volume transmitted in a given time, t; the volume is converted from actual conditions to reference conditions (e.g., $T_r = 273.15$ K and $p_r = 101.325$ kPa).

$$V_r = V \frac{Z_r}{Z} \frac{T_r}{T} \frac{p}{p_r} \tag{1}$$

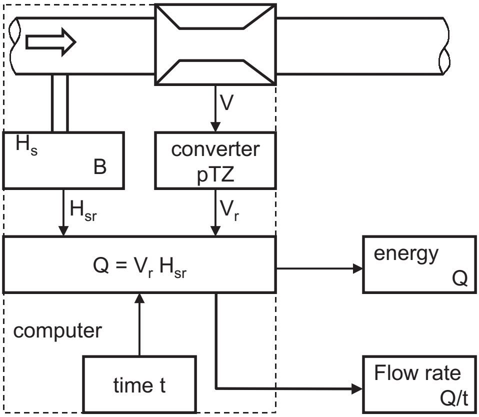

Fig. 1. Schematic of existing energy metering system.

where

p is the absolute pressure,

T is the thermodynamic temperature, and

Z is the compression factor.

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 metered volume. The energy is defined as the product of the calorific value and the volume, each under reference conditions.

Turbine flowmeters, ultrasonic flowmeters, etc. have to be calibrated at reference flow test facilities before being installed in the field. Considerable effort has gone into building these test facilities. One of them is *pigsar* [3], the German National Standard, which has an uncertainty of less than 0.15%. Orifice meters, usually built and operated according to accepted standards, may have experimental uncertainties of up to 0.6%. Regardless of the type of system used, however, installation effects may produce additional uncertainties, e.g., if the flow is not fully developed because of the piping configuration just upstream of the meter [4].

In volume conversion, thermal equations of state are used to calculate the compression factor [5, 6]. Based on Ruhrgas data, the composition range has been examined beyond the range of pipeline-quality gas [7, 8]. Figure 2 shows the uncertainty of two equations currently in use, which have been modeled primarily for pipeline-quality natural gas [5, 6]. The rms (root mean square) values of the differences between the experimental data and the calculated Z-values ($Z_{expt} - Z_{calc}$) for all experimental data within temperatures of 270 to 330 K and pressures of up to 12 MPa have been plotted for different natural gas samples numbered 1 to 27 representing the gases N51 to N75, N82, and N83 in Ref. [7].

The SGERG equation [5] is a gross method which uses three input properties to characterize the natural gas quality: calorific value and density at reference conditions and the carbon dioxide content. The AGA8 equation [6] on the other hand is a more detailed method which requires the complete gas composition. The graph shows that both equations basically describe the experimental data within an rms error of 0.05%. The advantage of the SGERG method is that it uses a truncated virial equation with only second and third virial coefficients and only requires a rough description of the gas composition. The AGA8 equation is somewhat more complicated but has the advantage of being valid and applicable outside the pressure and temperature ranges specified for the SGERG method.

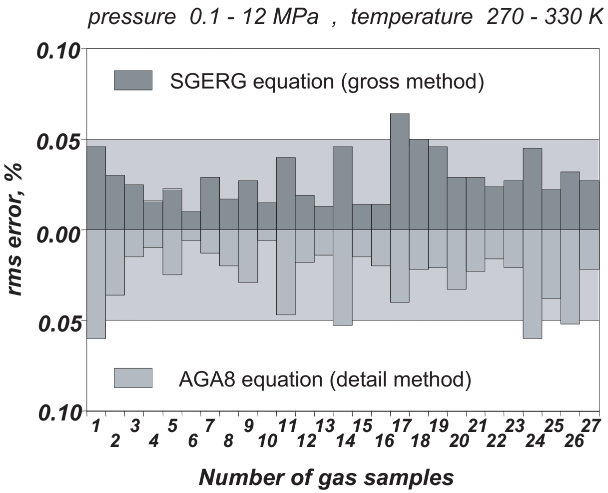

Fig. 2. Averaged uncertainties for compression factor of two equations given by the rms value for a number of pipeline-quality natural gas samples.

Energy measurement systems featuring a pTZ converter use the calorific value H_{sr} twice: in the volume conversion procedure and for calculating energy from the measured volume. This is why the sensitivity, $\delta Q/\delta H_{sr}$, of the metered energy to the calorific value is larger than 1. Accordingly, the uncertainty of the calorific value will contribute substantially to the final result. Also, the operating costs of using either a calorimeter such as the Cutler Hammer calorimeter or a process gas chromatograph to provide the detailed gas analysis for calculating the calorific value are quite substantial, so there is a need for an alternative way of determining the energy content, which is presented below.

3. FUTURE ENERGY MEASUREMENT

The new concept of energy measurement is based on a correlation of three physical properties with calorific values. A central feature of this concept is the availability of a high-accuracy caloric equation of state, yet it is more important for this method to have calculated values for the properties used which agree with the measured values within a given uncertainty band. The maximum acceptable uncertainty is governed by the sensitivity of these properties to the calorific value. In the feasibility study for a new energy measurement method, the AGA8 equation, also referred to as the

AGA8DC92 equation of state, was used. It employs the detail characterization method to specify gas composition.

Given some of the shortcomings of this equation—the AGA8 DC92 equation does not fulfill the requirements of 0.1% uncertainty for density, compression factor, and speed-of-sound calculations at temperatures below 270 K for diluted natural gases, enriched natural gases, and nitrogen fractions between 10 and 15 mole% [9, 10]—it was decided to set up a new reference equation of state. This new equation will improve the accuracy of critical nozzles in flow metering for natural gas with changing qualities, and it may modify the correlation used in the new energy concept. All these aspects (i.e., the new reference equation, its possible impact on nozzle flow metering, and the new concept of energy measurement under field conditions) will be discussed below.

3.1. Wide-Range Reference Equation of State for Natural Gas

At the end of an earlier project assessing available caloric equations of state [9], it was decided within the consortium of European gas companies to develop a wide-range reference equation of state for natural gases. The purpose is to set up the first accurate wide-range equation of state that can be applied in the gas and liquid phases and be used for vapor-liquid-equilibrium calculations. The goal is to achieve high accuracy for all thermal and caloric properties and to allow accurate predictions to be made within the experimental uncertainty also for vapor-liquid-equilibrium data such as pressure, temperature, and density. The reference equation will then be used as a database for all known and probably all future applications.

The range of application of the new reference equation is shown in Fig. 3. The AGA8 equation was more or less accurate enough in the 270 to 350 K temperature range, and the uncertainty for density and speed of sound was less than 0.1%. With the new reference equation, this highly accurate application range will now be extended down to, at least, 250 K. Outside this range, at both higher and lower temperatures, the thermodynamic properties should be predicted within the experimental uncertainty of the best data available.

To develop a new wide-range reference equation of state for natural gas, it was decided to perform experimental as well as theoretical work. The experimental part comprises density measurements at the Ruhr-Universität Bochum, speed-of-sound measurements at the Imperial College in London [11], and vapor-liquid-equilibrium measurements at Technische Universität Braunschweig [12]. Additional density measurements are underway for ethane and propane, while speed-of-sound measurements for methane + nitrogen and ethane + nitrogen mixtures as well as pressure,

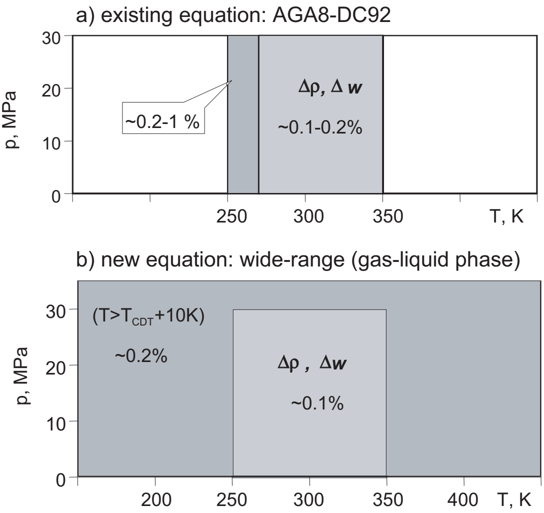

Fig. 3. Range of application for the AGA8 DC92 and the new reference equation of state.

temperature, and density measurements in the gas and liquid phases have already been made under vapor-liquid-equilibrium conditions for systems containing methane, ethane, and nitrogen.

Part of the theoretical work involves compiling and examining available literature data to be used in the development of or for testing the new equation of state. This correlation work is being done at Ruhr-Universität Bochum.

Ruhr-Universität Bochum [13] is pursuing the following structure/ elements for the new wide-range equation of state. They have developed reference quality equations of state for each of the main components methane, ethane, and nitrogen, which have an identical structure with 24 terms while the equation for carbon dioxide consists of 22 terms. Simple equations of states with an identical structure and 12 terms are used for secondary components like propane, *n*- and iso-butane, *n*-pentane, and iso-pentane. More simple, generalized equations are correlated at the same time for the minor components, i.e., hydrocarbons up to *n*-octane with only 3 substance-specific parameters. With the new equations, uncertainties for the density calculations are around 0.03, 0.1, and 0.2% for the main, secondary, and minor components, respectively (see Table I). Due to a lack of accurate speed-of-sound data in the liquid and supercritical regions for the secondary and minor components, the uncertainties here are much higher.

Table I. Typical Deviations of Density Calculated with the New Reference Equation from Accurate Experimental Data for Pure Components

	Gas	Liquid	Supercritical
Highly accurate EOS (main components)	±0.03%	±0.05%	±0.03%
Simple EOS (secondary components)	±0.1%	±0.1%	±0.1%
Generalized EOS (minor components)	±0.2%	±0.2%	±0.2%

The natural gas reference equation is explicit in the reduced Helmholtz energy, $\alpha = A/(RT)$. An important part of the development is the multi-fluid approximation used:

$$\alpha(\delta, \tau) = \alpha^0(\rho, T, X) + \sum_{i=1}^{k} x_i \cdot \alpha^r_{0i}(\delta, \tau) + \Delta\alpha^r(\delta, \tau, X) \tag{2}$$

It consist of the ideal gas part, α^0, the contribution of the pure fluid equations, $x_i \alpha^r_{0i}(\delta, \tau)$, and the departure function, $\Delta\alpha^r(\delta, \tau, X)$. The variables are defined as:

ρ is the density,

T is the temperature,

X is the mole fraction of all components in natural gas,

δ is the reduced density $(= \rho/\rho_n(X))$,

τ is the reduced temperature $(= T_n(X)/T)$, and

x_i is the mole fraction of component i.

$T_n(X)$ and $\rho_n(X)$ are reducing functions which depend only on the composition [13]. For the methane+nitrogen system, this model gives liquid densities within ±0.2% (see Fig. 4) and gas densities within 0.1% (see Fig. 5). In general, the properties in the liquid phase and under vapor-liquid-equilibrium conditions are already calculated within the experimental uncertainty. In the gas phase some improvements are still necessary to meet the stated target uncertainty as given in Fig. 3, especially at moderate pressures of up to 10 MPa and for certain pipeline-quality natural gases.

3.2. Flow Metering with Critical Nozzles

Critical nozzle flow metering has been a well-known concept for a long time [17, 18]. In principle, gas flow through a choked nozzle can be calculated from the stagnation conditions assuming, e.g., a one-dimensional isentropic ($s_0 = s^*$) and adiabatic flow (total enthalpy $h_0 = h^*$). The nozzle is considered choked or under critical-flow conditions if the flow velocity in the nozzle throat is equal to the local speed of sound. This condition denotes the maximum/critical mass flow rate through the nozzle:

$$\dot{m} = \rho^* a^* A^* \tag{3}$$

where

ρ^* is the density in the throat,

a^* is the speed of sound of the fluid in the throat, and

A^* is the cross-sectional area in the throat.

A^* is defined by the geometry of the nozzle, while ρ^* and a* can be calculated from the stagnation conditions for which the flow velocity is zero, i.e., the pressure, p_0, and the temperature, T_0.

Critical nozzles can be calibrated to account for two-dimensional effects (e.g., boundary layer effects) and also for differences from a strictly isentropic and adiabatic flow. These effects are accounted for by the

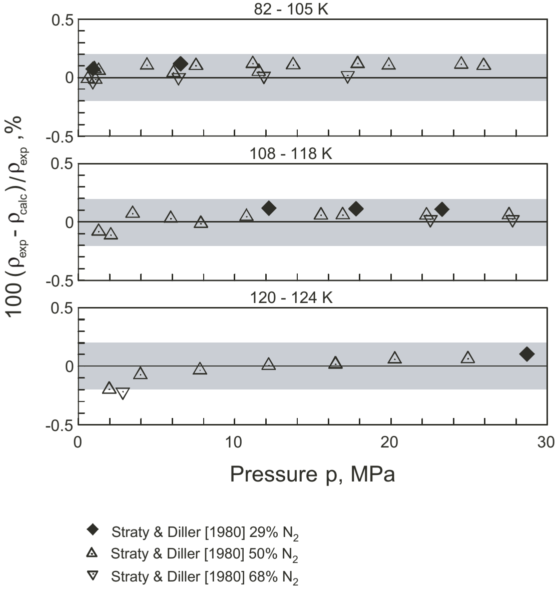

Fig. 4. Uncertainty of the new reference equation for liquid densities for the methane + nitrogen system

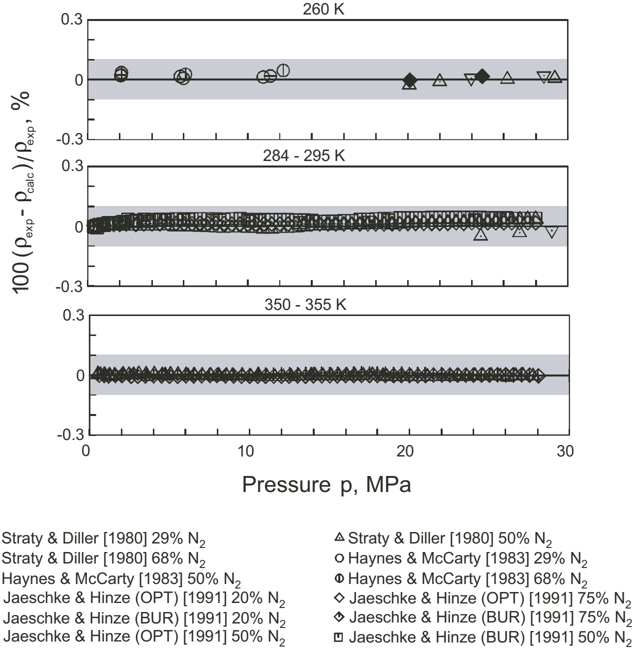

Fig. 5. Uncertainty of the new reference equation for gas densities for the methane + nitrogen system

discharge coefficient, C, defined as the ratio of the actual mass flow (calibration), $\dot{m}_{expt}$, to the calculated mass flow, $\dot{m}_{cal}$.

$$C = \dot{m}_{expt} / \dot{m}_{cal} \tag{4}$$

As long as a calibrated nozzle is used within the range of its calibration (i.e., pressure and temperature) and above all for the specified gas or natural gas quality, the uncertainty of the measured result for $\dot{m}$ obtained using the calibrated value for C may be comparable to the results after calibration with the test facility. Thus, the uncertainty of $\dot{m}$ is essentially the uncertainty of $\dot{m}_{expt}$, as the uncertainty of $\dot{m}_{cal}$ is compensated by the calibration procedure for a given gas.

The uncertainty of the calculated mass flow rate, $\dot{m}_{cal}$, from Eq. (3) for a one-dimensional flow is given by the experimental uncertainty for the stagnation conditions (pressure, temperature) and the accuracy of the equation of state used. The influence of the thermodynamic properties on a one-dimensional isentropic nozzle flow rate under critical conditions is often expressed by the critical flow factor, C^*, [18].

$$C^* = \rho^* a^* \sqrt{RT_0}/p_0 \tag{5}$$

The uncertainty of the critical mass flow factor or rate is determined by the uncertainty of the equation of state used. Stewart et al. [19] investigated this for pure gases, methane, nitrogen, etc. using the reference equations from Setzmann and Wagner [20] and Span *et al.* [21], respectively. For methane the resulting uncertainty is approximately 0.1%. For nitrogen the uncertainty of the theoretical mass flow rate is approximately 0.3% at stagnation temperatures below 300 K. This uncertainty results from the relatively high uncertainties in the calculated speed-of-sound data for temperatures below 250 K. Stagnation temperatures of less than 300K correspond to a critical temperature of less than 250 K.

For natural gases the AGA8 DC92 equation [6] was applied to calculate the critical mass flow rate using the ideal heat capacity from a previous paper [22]. A project by the Groupe Européen de Recherches Gazières (GERG) examined the accuracy of various equations of state against experimental data [9]. The conclusion was that the above method is at present the most accurate way of calculating the thermal and caloric properties of natural gas. There are, however, some deficiencies for temperatures below 270 K with regard to density and speed of sound (see Fig. 3). Therefore, for the given situation the uncertainty of the calculated critical flow rate is approximately 0.3% for natural gas [19] and may be as high as 0.6% [23] depending on the stagnation conditions (high pressure, low temperature).

An experimental examination at the high pressure test facility in Dorsten, Germany, confirmed the above estimate. For a nozzle diameter of $d = 9.94$ mm and stagnation conditions of $p_0 = 3.63$ MPa and $T_0 = 292$ K, the calculated mass flow agrees with the experimental value within -0.26% [24]. In this comparison the discharge coefficient, C, was taken from ISO 9300 and the uncertainty of the experimental value was 0.15%. The mass flow calculated in accordance with ISO 9300 agrees with the measured value within -0.59%.

An improvement or confirmation of the present situation is only possible with the new reference equation and/or with additional experimental results for mass flow rates, preferably for a variation of nozzle diameters, stagnation conditions, and above all, for different gas qualities. Once critical nozzles have been tested under these conditions, it will be possible to use them for varying gas qualities with more or less the same uncertainty as if the nozzle were calibrated directly for the gas quality in question. This will pave the way to using critical nozzles not only on special test rigs but also in the field. This way, by an *in-situ* comparison of a meter with the reading of a critical nozzle, installation effects can directly be identified and compensated. This will reduce the work necessary to investigate installation effects for existing or future metering devices.

3.3. Energy Conversion Under Field Conditions

The new energy measurement concept is based on the idea that three physical properties will be sufficient to characterize the natural gas and provide the information required for energy conversion by way of correlation. A similar concept had been applied with the SGERG equation to calculate density and compression factor values of natural gases [5].

3.3.1. Feasibility Study

In two feasibility studies conducted by Ruhr-Universität Bochum [25] and the Van der Waals–Zeeman Institute, Amsterdam [26], 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 suitable for appropriately characterizing 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, $\Delta inp(expt)$.

If natural gases are treated as four-component mixtures consisting of methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2) and the sum of the other hydrocarbons, three input properties can produce sufficient information to characterize the gas composition. This kind of approach was already used for the SGERG equation [5]. However, in the approach selected 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 ethane up to *n*-octane via a second-order

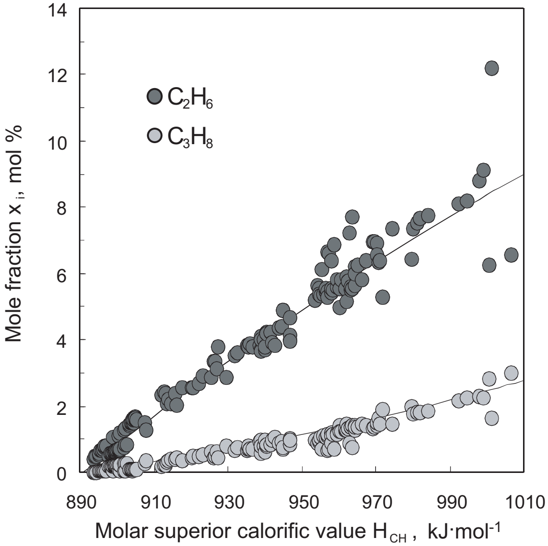

Fig. 6. Ethane and propane percentage mole fractions as a function of the superior calorific value, H_{CH}, of the equivalent hydrocarbon gas for 210 natural gas samples

expansion in the molar calorific value, H_{CH}, of the equivalent hydrocarbon gas.

$$x_i = \{a_{1,i}(H_{CH} - H_{CH4}) + a_{2,i}(H_{CH} - H_{CH4})\}x_{CH} \tag{6}$$

where subscript i denotes ethane, propane, etc. The coefficients $a_{1,i}$ and $a_{2,i}$ were correlated previously [27]. An example for ethane and propane as a function of the molar calorific value H_{CH} is shown in Fig. 6 for approximately 200 natural gases (Fig. 2 in Ref. 28). Here, H_{CH} is calculated using ISO 6976 [1] for the equivalent hydrocarbon gas which is obtained by deleting the mole fractions of the inerts, nitrogen, carbon dioxide, etc. and renormalizing the mole fractions of the hydrocarbons.

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

- T_f, p_f, $x_{\mathrm{CO_2}}$, ρ_r or w_r, ε_r
- T_f, p_f, $x_{\mathrm{CO_2}}$, ρ_r or w_f, ε_f

Pressure, p_f, and temperature, T_f, are necessary to define the operating/field conditions for the flow meter (subscript f). Mole fraction CO_2,

x_{CO_2}, density, ρ, or speed-of-sound, w, and relative permittivity, ε, are the proposed input properties for determining the gas composition. For density and speed of sound, instruments were available while for the permittivity, ε, a new system was developed and tested [29].

A flow diagram for calculating the gas composition which is then used to determine the energy conversion factor under field conditions (i.e., superior calorific value $H_{s,r}$, Z or ρ_r, and Z_f or r_f) is given in Ref. 28. For the iterative method to be used, the input properties must be known. Moreover, the method requires an equation or formula to calculate these properties from a given gas composition. For density and speed of sound, the AGA8 DC92 equation is employed. At reference conditions (low pressure) and normal field conditions of approximately 5 MPa, the AGA8 DC92 equation is sufficiently accurate, while for other state conditions (e.g., high pressure), an improved reference equation may be necessary. For the relative permittivity a truncated virial expansion in molar density, ρ_m, is used.

$$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{\rho_m}=A_\varepsilon+B_\varepsilon\rho_m \tag{7}$$

A_ε and B_ε are the first and second dielectric virial coefficients. The term on the left-hand side is also called the Clausius–Mossotti function for the molar polarisability.

3.3.2. *Re-Entrant Cavity for Relative Permittivity*

The National Engineering Laboratory (NEL), East Kilbride, United Kingdom [29] has developed a re-entrant cavity operated as an LC resonator (L: inductance, C: capacitance). It is based on the concept described by Goodwin *et al.* [30] who reported a Q value ($Q=f_0/\Delta f$; f_0 is the central frequency of the resonance curve and Δf is the half width) of 920 and 240 for brass and Inconel cavities, respectively. Provided that the quality factor, Q, is held above 1000, the theoretical model of Goodwin *et al.* can be replaced by the following general model which is applicable to an absolute uncertainty better than 1 ppm at ambient conditions [29, 31].

$$\varepsilon_r(T,p)=(f_0(T)/f_\varepsilon(T,p))^2\,(1+C_p)\cdot(1+C_\delta) \tag{8}$$

where

$f_0(T)$ is the resonant frequency of the evacuated cavity at temperature T,

$f_e(T,p)$ is the resonant frequency at the conditions of measurement,

C_p is the correction factor for dilation due to pressure, and

C_d 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 $C_p = (6.6 \pm 0.6)\ 10^{-12}\ p$, 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_d 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 $C_d = (4.32 \times 10^{-5} + 6.47 Q_0(T)^{-1})(\varepsilon_r^{1/4} - 1)$. For a relative permittivity of 1.1 (e.g., a natural gas at 10 MPa) the correction factor reaches 69 ppm.

The 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 uncertainty in temperature is 10 mK, that for pressure is 0.02%, and that for the relative permittivity at 293 K and 0.1 MPa is 1 ppm. The uncertainty in the factor C_p is $\pm 0.1 C_p$ and in the factor $C_\delta \pm 0.05 C_\delta$.

The dimensions of the new cavity have been optimized to provide a high quality factor. Silver and gold plating were used to enhance the electrical conductivity of the internal surface layers and improve the quality factor to around 2300. The principal resonance frequency of the evacuated cavity is approximately 394 MHz. The dimensions of the annular gap have been selected to minimize the effect of gaseous adsorption on the measurement of permittivity. 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 (see Fig. 7). The complete permittivity cell assembly is designed to be mounted into an external pressure containment vessel. Hence, the larger part of the resonator structure is completely immersed in the test gas and not subjected to large dilating forces.

The re-entrant 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. (7) to calculate relative permittivity values.

3.3.3. 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 built by NEL.

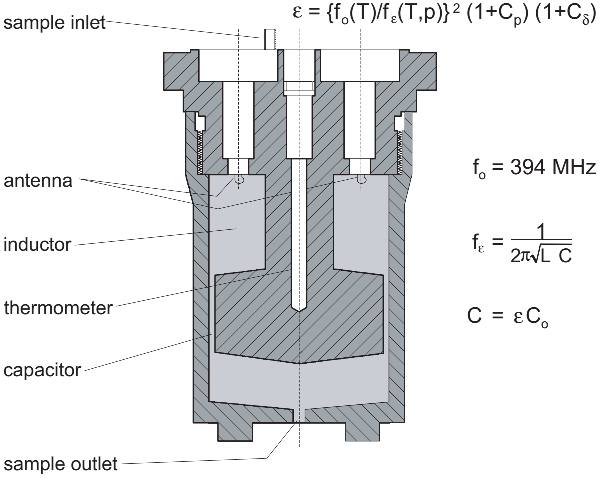

Fig. 7. Schematic of the re-entrant cavity operated as an LC resonator.

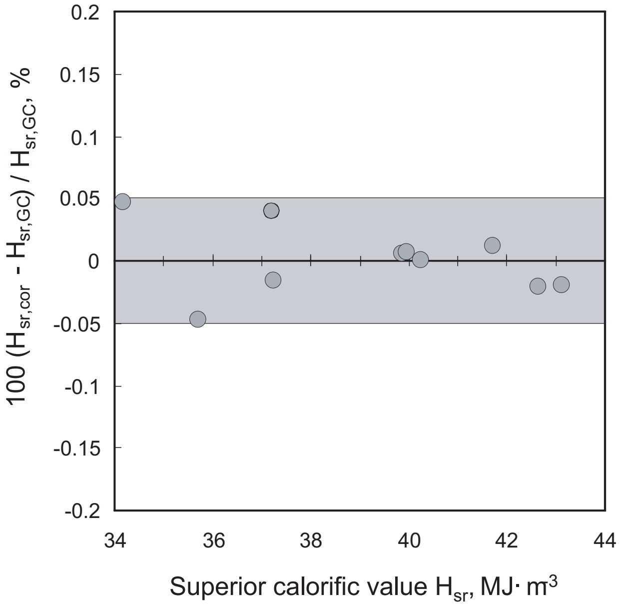

Fig. 8. Deviations of superior calorific value, correlated from input data, from values derived from GC analysis at reference conditions ($T_r = 273.15$ K, $p_r = 0.101325$ MPa). Relative permittivity, speed-of-sound, and CO_2 mole fraction are measured simultaneously.

Tests of the complete energy measurement system is essential to verify the envisaged 0.2% uncertainty for the superior calorific value, $H_{s,r}$, 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. (7) for the molar polarizability based on the dielectric virial coefficient from this work and the AGA8 DC 92 equation to calculate speed of sound and molar densities as a function of p, T, and x_i were employed to evaluate the superior calorific value from the input data.

The results for ten natural gases are given in Fig. 8. For the speed-of-sound and the CO_2 mole fraction, the data were measured at ambient conditions and the relative permittivity was measured at $T = 293.15$ K and $p = 1$ MPa or $p = 5$ MPa. The results for $H_{sr,\,\mathrm{cor}}$ (volume at reference conditions) agree better than 0.05% with the calorific value calculated from the GC analysis. Moreover, the superior calorific value based on the volume at fictitious field/operating conditions ($T_f = 283.15$ K, $p_f = 5$ MPa), H_{sf} , i.e., the energy conversion factor $= H_{sr}\rho_f/\rho_r$, agrees also within 0.1% with the calculated results obtained from the GC analysis (see Fig. 9). In both cases,

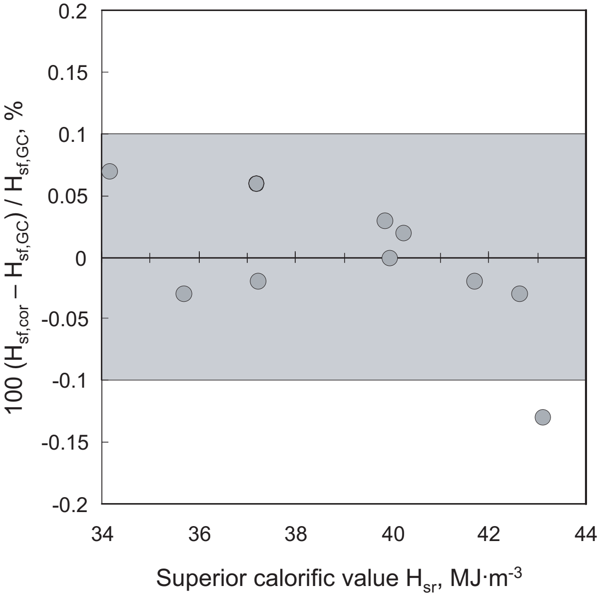

Fig. 9. Deviations of superior calorific value, correlated form input data, from values derived from GC analysis at fictitious field conditions ($T_f = 283.15$ K, $p_f = 5$ MPa). Relative permittivity, speed-of-sound, and CO_2 mole fraction are measured simultaneously.

for $H_{sf,\,\mathrm{GC}}$ from the gas analysis or $H_{sf,\,\mathrm{cor}}$ from the correlation method, the densities ρ_f and ρ_r are calculated from the AGA8 DC92 equation.

It should be noted that the existing method for calculating the superior calorific value [1] and density or the speed of sound [6, 22] from a detailed gas analysis was not examined. As regards density and speed of sound, investigations will follow in the reference equation project (see Section 3.1). With respect to the calorific value, the possibility of building a reference calorimeter for natural gases with an uncertainty of 0.05% on the basis of two standard deviations to test calculated superior calorific values from the GC analysis is being investigated.

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