

Characterization of a biomethane-like synthetic gas mixture through accurate density measurements from (240 to 350) K and pressures up to 14 MPa

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**Abstract:**

In this work the thermodynamic behavior of a synthetic four-component biomethane-like mixture, composed mainly of methane (96.48%), with small amounts of carbon dioxide (2.00%), nitrogen (1.50%), and traces of oxygen (0.02%), is studied using accurate ( $p, \rho, T$ ) experimental data. Two mixtures of identical nominal compositions were prepared by the gravimetric method at the Spanish National Metrology Institute (Centro Español de Metrología, CEM) and at the Slovak National Metrology Institute (Slovenský Metrologický Ústav, SMÚ). The composition was double checked by Gas Chromatography, at both NMI and at the beginning and end of the measurements. An additional test of the consistency of the given compositions was performed by measuring the density of both mixtures at selected points, with two different techniques, in two different laboratories. Accurate density measurements have been taken over a wide temperature range, from (240 to 350) K, and pressures up to 14 MPa, using a single-sinker densimeter with magnetic suspension coupling. Experimental data are compared with the densities calculated with the GERG-2008 and AGA8-DC92 equations of state. Deviations between experimental and GERG-2008-estimated densities are within a  $\pm 0.03\%$  band at all temperatures, which shows the outstanding performance of the current reference equation for natural gases when describing a biomethane-like mixture. Deviations between experimental and AGA-8-estimated densities are higher than 0.04% at 250 K for pressures greater than 10 MPa and also at 240 K for pressures higher than 9 MPa. This work is part of the research project ‘Metrology for Biogas’ supported by the European Metrology Research Program.

Keywords: biomethane; thermodynamic characterization; density; single-sinker densimeter; equations of state, GERG-2008.

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## 1. Introduction

Natural gas, as the fossil fuel with the lowest emission factor, has been identified as the fuel for the 21st century according to several influential institutions [1]. Hydrogen from renewables (power-to-gas) and synthetic natural gas (SNG) from bio-syngas or biogas can be injected into the natural gas grid, greening the gas network [2] and decreasing the net greenhouse gases emissions associated with fossil fuels use.

Biogas represents a renewable energy source obtained from the anaerobic digestion of biomass. Due to the diversity of the sources of biogas, their composition may vary significantly, with a methane content ranging from less than 50% to more than 80%, a relatively high carbon dioxide (20% to 50%) and nitrogen (up to 40 %) content, and small amounts of other components, such as water, oxygen, hydrogen, H<sub>2</sub>S, NH<sub>3</sub>, halogenated hydrocarbons, volatile organic contaminants and siloxanes.

Biogas can be upgraded to biomethane, expanding its utilization opportunities. The final use of this biomethane determines its composition and the type of upgrading process required. The most exigent quality requirements are faced when biomethane is intended to be injected into natural gas grids or to be used as a vehicle fuel, which often demands CH<sub>4</sub> concentrations > 96 %, CO<sub>2</sub> < 2 %, and O<sub>2</sub> < 0.2 % [3].

It is essential to have a detailed knowledge of the thermophysical properties of biogas and biomethane in order to solve technical and design problems during the transport and exploitation stages. A large number of very high accuracy experimental data over wide temperature and pressure ranges are needed to develop and validate equations of state for the estimation of the density, heat capacity and calorific value of biogas and biomethane.

This work studies the thermodynamic behavior of a synthetic biomethane-like mixture, composed of 96.48 % methane, 2.00 % carbon dioxide, 1.50 % nitrogen and 0.02 % oxygen, using accurate ( $p, \rho, T$ ) experimental data, at temperatures ranging from (240 to 350) K and

pressures up to 14 MPa, obtained using a single-sinker densimeter with magnetic suspension coupling. The experimental data are compared to the corresponding densities calculated from the GERG-2008 [4] equation of state, which is the current reference equation of state for natural gas and other related mixtures and designated as the ISO Standard (ISO 20765-2) [5] for the calculation of the thermodynamic properties of natural gases. A comparison of experimental data with the corresponding densities calculated using the AGA8-DC92 equation of state [6] is also presented.

The biomethane-like gas mixture was prepared by the Spanish National Metrology Institute (Centro Español de Metrología, CEM) using the gravimetric method according to ISO 6142 [7]. In order to ensure the accuracy of the mixture's composition, a second gas mixture of identical nominal composition was prepared by the Slovak National Metrology Institute (Slovenský Metrologický Ústav, SMÚ). The composition of both mixtures was double checked by Gas Chromatography (GC), at both NMI, and at the beginning and end of the measurements. An additional test of the consistency of the given compositions were performed by measuring the density of both mixtures at ambient temperature and low pressures, with two different techniques (an isochoric pycnometer at SMÚ and a single-sinker densimeter at the University of Valladolid). The objective of this redundant check of the compatibility of the given compositions for both mixtures, through GC and high accuracy density measurements, was to evaluate the capability of both NMI in preparing multicomponent gas mixtures using their usual procedures, and to evaluate the performance of the reference densimeters of the Slovak NMI and that of the University of Valladolid, within the general objectives of the research project 'Metrology for Biogas' supported by the European Metrology Research Program [8].

Experimental density data of synthetic multicomponent natural-gas-like mixtures have been previously measured by other authors. In 2007, Patil et al. [9] published experimental density data of a natural-gas-like mixture with a methane mole fraction of 91%. In 2011, McLinden [10] presented density data of four natural-gas-like mixtures with similar compositions, which

contained approximately 0.90 mole fraction methane and differed mainly in the content of nitrogen, carbon dioxide and high alkanes. Our group has published density and speed of sound measurements for a synthetic biogas-like mixture [11][12] composed of methane (50%), carbon dioxide (35%), nitrogen (10%) and carbon monoxide (5%), and for a Coal Mine Methane (CMM) mixture of 11 components, with 64 % of methane, 17 % of nitrogen and 17% of carbon dioxide as the main components [13][14].

Using the same technique, our group has also reported density measurements for the binary mixtures of three of the four components of this synthetic biomethane-like mixture:  $\text{CH}_4 + \text{CO}_2$  [15],  $\text{CH}_4 + \text{N}_2$  [16] and  $\text{N}_2 + \text{CO}_2$  [17], [18]. Speed of sound measurements are also available for some of these mixtures [19].

## **2. Experimental**

### **2.1. Sample preparation**

Two synthetic biomethane gas mixtures of identical nominal composition, designated as CEM-92365 and SMÚ-0009F\_6, were prepared by the gravimetric method according to ISO 6142 [7] at CEM and SMÚ respectively. The goal was to obtain a representative mixture of an actual biomethane with known composition and the smallest achievable uncertainty in its composition. The composition of the said mixtures is given in Table 1 and Table 2, together with the expanded uncertainty for each component (coverage factor,  $k = 2$ ), the certified purity, the supplier and the critical parameters of each of the component gases. All substances were used without further purification. Mixtures were supplied in 5 dm<sup>3</sup> aluminum alloy cylinders with an initial pressure of 10 MPa.

The biomethane mixture CEM-92365 was prepared at CEM from a premixture of carbon dioxide, oxygen and nitrogen (balance gas), which were introduced directly into a cylinder in

that order. The premixture was homogenized, partially transferred to a 5 dm<sup>3</sup>, aluminum-alloy cylinder and diluted with pure methane. The mass of the gas portions were determined using a high-precision balance (Mettler Toledo PR10003, Mettler-Toledo GmbH, Greifensee, Switzerland). After the last gas portion had been added and weighed, the cylinder was finally homogenized by a rolling procedure. The critical parameters of the mixture, estimated with the AGA8-DC92 equation of state [6], using REFPROP software [20], were critical temperature 191.98 K and critical pressure 4.77 MPa. The molar mass of the mixture was 16.7855 kg·kmol<sup>-1</sup>.

The biomethane mixture 0009F\_6 was prepared at SMU using a similar procedure in two steps. In a first step, a premixture containing carbon dioxide, nitrogen and oxygen was prepared. In a second step, the final mixture was prepared from the premixture and methane. All components were introduced directly into the cylinder. After each filling, the masses of the gas portions were determined using an automated system for 5 dm<sup>3</sup> cylinders, with a built-in high-precision balance comparator (Sartorius CC 10000, AG Gottingen Germany). The critical parameters of the mixture, estimated with the AGA8-DC92 equation of state using REFPROP software, were critical temperature 192.07 K and critical pressure 4.78 MPa. The molar mass of the mixture was 16.8093 kg·kmol<sup>-1</sup>.

## **2.2. Checking of the mixture composition and long term stability**

The composition of both mixtures was checked by Gas Chromatography, just after its preparation, at the corresponding NMI where each mixture was prepared, according to ISO 6143 [21].

An additional test of the consistency of the given compositions was performed by measuring the density of both mixtures at ambient temperature, around 295 K, and low pressures (0.2, 0.5 and 1.0) MPa, with two different techniques: an isochoric pycnometer at SMÚ (SMÚ-Pyc)

and a single-sinker densimeter at the University of Valladolid (UVa-SSD). The main objective of this test was to evaluate the capability of both NMI in preparing multicomponent mixtures using their usual procedures, and the evaluation of the capabilities in density determination of the SMÚ and the University of Valladolid, in the framework of the general objectives of the research project 'Metrology for Biogas' supported by the European Metrology Research Program.

The primary SMÚ Standard Densimeter is a special stainless steel pycnometer manufactured by Vakuu Praha under the special requirements and specifications defined by the SMU. It uses the gravimetric method for density determination. The inner volume of the pycnometer under standard conditions is 1.688160 dm<sup>3</sup>. The volume dependence on temperature and pressure is taken into account through the thermal and mechanical properties of the material. Accurate measurements of ( $m$ ,  $T$ ,  $p$ ) are performed with specific instrumentation and the results are traceable to the SMÚ National Standards of Mass, Pressure and Temperature. The mass of added gas is calculated as the difference between the evacuated and the filled pycnometer. Weighing is carried out via continual scanning of mass readings, using an analytical microbalance (Sartorius, model CCE 1005). The pycnometer is not thermostated, so its working temperature is the laboratory room temperature. Temperature stability is improved by putting the pycnometer into an isolating chamber. The temperature is measured using four NTC thermistor sensors situated at different point inside the pycnometer. The pressure is measured using a deadweight piston gauge (SMU, model A03) connected to the pycnometer through a differential pressure transducer (Rosemount, model 3051S1). The atmospheric pressure is recorded using a precision barometer (Paroscientific, model 740-168). The pressure range is 5 MPa. Expanded uncertainties ( $k = 2$ ) in the three measured or calculated magnitudes are  $U(\rho) < 0.1 \%$ ,  $U(p) < 0.01 \%$  and  $U(T) < 50 \text{ mK}$ .



The UVa single-sinker densimeter is based on the Archimedes' principle, by which the buoyancy force acting on a sinker immersed in a fluid is proportional to the density of that fluid. A detailed description of this densimeter is given in the next section.

The density of both mixtures (CEM-92365 and SMÚ-0009F\_6), at ambient temperature, 295 K, and low pressures (0.2, 0.5 and 1.0) MPa, were measured using the two different techniques.

The results are presented in Table 3. The compatibility of the density results of each laboratory with the reference value of density given by the GERG-2008 equation of state is also presented in Table 3. The compatibility factor used,  $I(\rho_{exp}, \rho_{GERG})$ , is defined as:

$$I(\rho_{exp}, \rho_{GERG}) = \left| \rho_{exp} - \rho_{GERG} \right| / \sqrt{U(\rho_{exp})^2 + U(\rho_{GERG})^2} \quad (1)$$

The compatibility of the density results of each laboratory with the other has also been calculated through the differences of their results with the reference equation of state, using the compatibility factor,  $I(\rho_{UVa}, \rho_{SMÚ})$ , defined as:

$$I(\rho_{UVa}, \rho_{SMÚ}) = \left| (\rho_{exp,UVa} - \rho_{GERG}) - (\rho_{exp,SMÚ} - \rho_{GERG}) \right| / \sqrt{U(\rho_{UVa})^2 + U(\rho_{SMÚ})^2} \quad (2)$$

The compatibility factors of experimental density results with the GERG-2008 equation of state, which have an uncertainty of 0.1%, were always smaller than 0.40. The compatibility factors of density results obtained at each laboratory with the results obtained at the other were always smaller than 0.20. The results obtained show a perfect agreement between the SMÚ and UVa density measurements.

Finally, to test the long term stability of the mixtures, a final GC analysis was performed at SMÚ for both mixtures, with the remaining gas after the density measurements. The

composition of the mixtures was validated using multi-point calibration, according to the procedure described in ISO 6143 [21]. A GC analyzer (model: Star 3800, Varian Chromatography Systems, Walnut Creek CA, USA) was used with a set of packed columns and TCDs designed for the analysis of natural gas samples. The results of this second GC analysis are presented in Table 4. All the components fulfilled the validation criteria.

### 2.3. Apparatus Description

The single-sinker densimeter is based on Archimedes' principle, by which the buoyancy force acting on a sinker immersed in a fluid is proportional to the density of that fluid. The methodology, developed by Brachthäuser et al. [22] in 1993 to simplify the design of the previously developed two sinker densimeter [23], further improved by Klimeck et al. [24], is one of the state-of-the-art methodologies for high precision density measurements of fluids over wide temperature and pressure ranges [25]. The single-sinker densimeter used on this work was especially designed for density measurements of pure gases and gaseous mixtures. It has previously been described in detail by Chamorro et al. [16] and by Mondéjar et al. [26]. The wide temperature and pressure ranges of this methodology are achieved due to the fact that there is no contact between the measuring fluid and the high-accuracy microbalance thanks to the presence of a magnetic suspension coupling between the sinker and the balance hook.

The density of the fluid is given by the following expression:

$$\rho = (m_{s0} - m_s) / V_s(T, p)$$

(3)

where the difference between the sinker mass in vacuum  $m_{s0}$  and the sinker mass in the pressurized fluid,  $m_{sf}$ , is expressed in *kg* and refers to the buoyancy force experienced by the sinker. It is measured by an accurate microbalance (Mettler Toledo AT261, Mettler Toledo GmbH, Gießen, Germany).  $V_s(T, p)$  is the volume of the sinker immersed in the fluid in  $\text{m}^3$ ; which is known as a function of temperature and pressure.

The temperature of the fluid is determined by two platinum resistance thermometers (model Minco S1059PJ5X6, Minco Products, Inc., Minneapolis MN, USA) connected to an AC comparator resistance bridge (ASL model F700, Automatic Systems Laboratories, Redhill, England). The pressure is measured by two Digiquartz transducers (Paroscientific model 2500A-101 and 43KR-HHT-101, Paroscientific, Inc., Redmond WA, USA) covering pressure ranges up to 3 and 20 MPa, respectively.

#### **2.4. Experimental Procedure**

Eight isotherms were recorded for this work at (240, 250, 260, 275, 295, 300, 325 and 350) K. Each isotherm was measured from a pressure of 14 MPa to 1 MPa by 1 MPa decreasing pressure steps, followed by measurements of the sinker mass in a vacuum. Pressure was decreased by opening an automated air-operated relief valve. In order to check the stability of the mixture composition after several decreasing pressure steps, some points at low pressures were repeated with fresh mixture introduced directly from the bottle. The repeatability of the results proves the negligible influence of the decreasing pressure procedure in the mixture composition. All measured points of the studied biogas-like mixture are represented in Figure 1 together with the saturation curve and the range of validity of the GERG-2008 equation of state and the range of importance for the gas industry.

Before and after measurements on the studied biometahane-like mixture, test measurements with nitrogen were carried out in the whole working range of the apparatus to validate its operation by comparing the experimental results with the densities calculated from the reference equation of state for nitrogen by Span et al. [27]. Relative deviations of the nitrogen test density data from the values calculated with the reference equation of state were within a  $\pm 0.02\%$  band.

## 2.5. Uncertainty of the measurements

Mondéjar et al. [26] estimated the uncertainty in the measurements of the single-sinker densimeter used in this work after performing several improvements on the equipment. The expanded uncertainty in density ( $k = 2$ ) as a density function is given by equation 4.

$$U(\rho) = 2,3 \cdot 10^{-2} + 1,1 \cdot 10^{-4} \cdot \rho$$

(4)

Uncertainties in temperature and pressure were estimated to be less than 4 mK and 0.015%, respectively ( $k = 2$ ). The uncertainty in composition for the biomethane-like mixture studied in this work is given in Table 1.

To calculate the overall standard uncertainty in density  $u_T(\rho)$  the uncertainties of density, temperature, pressure, and composition of the mixture must be considered, as expressed in equation 5.

$$u_T(\rho) = \left[ u(\rho)^2 + \left( \left( \frac{\partial \rho}{\partial p} \right)_{T,x} u(p) \right)^2 + \left( \left( \frac{\partial \rho}{\partial T} \right)_{p,x} u(T) \right)^2 + \sum_i \left( \left( \frac{\partial \rho}{\partial x_i} \right)_{T,p,x_j \neq x_i} u(x_i) \right)^2 \right]^{1/2}$$

(5)

where  $p$  is the pressure,  $T$  is the temperature, and  $x_i$  is the mole fraction of each of the mixture's components. Partial derivatives can be calculated with the GERG-2008 equation of state.

### 3. Results

Measurements of the density for the CEM-92365 mixture (see composition in Table 1) were carried out at eight different temperatures (240, 250, 260, 275, 295, 300, 325 and 350) K and decreasing pressure steps of 1 MPa from 14 to 1 MPa. Table 5 presents the experimental ( $p$ ,  $\rho$ ,  $T$ ) data. The state point magnitudes on each isotherm were calculated as the average of the last ten measured values of the corresponding magnitude for each pressure step. Table 5 also presents the expanded uncertainty in density (coverage factor  $k = 2$ ) of the experimental data, calculated by equation 4. The relative deviation in density from the values calculated with the GERG-2008 and the AGA8-DC92 equations of state are also calculated and presented in Table 5.

There are two main effects that may affect the measurements and therefore must be evaluated: the force transmission error (FTE) due to the magnetic coupling and the adsorption of gas molecules on the cell and sinker surfaces.

The force transmission error (FTE) has been discussed in detail by McLinden et al. [28]. This FTE consists of two terms: the apparatus effect and the fluid specific effect. In this work, the

apparatus effect of the FTE was accounted for by measuring the sinker mass in a vacuum for each isotherm. In the case of the fluid specific effect, its magnitude depends on the magnetic behavior of the measured gas. Oxygen is a paramagnetic gas and its magnetic susceptibility is two orders of magnitude greater than the magnetic susceptibility of the three other components of the mixture. Nevertheless, due to the small amount of oxygen in the mixture its influence in the final value of the magnetic susceptibility of the mixture is negligible. The magnetic susceptibility ( $\chi_{\text{BIOMETHANE}}$ ) of the biomethane-like mixture used in this work was estimated to be of  $-8.52 \cdot 10^{-9}$  using an additive law, as proposed by Bitter [29]; practically the same value of the magnetic susceptibility of pure methane ( $-9.07 \cdot 10^{-9}$ ). Since this value is relatively low, the fluid magnetic behavior would be negligible in relation to the apparatus effect and therefore the fluid specific effect was not considered in our measurements.

Adsorption and desorption of gas molecules on the measuring cell walls or the sinker surface was recently studied by Richter et al. [30]. Previously, Klimeck et al. [31] reported that this effect could only affect the accuracy of the measurements near the saturation curve or at very low gas densities, since only the adsorption on the sinker, and not that on the cell walls, had to be considered. However, Richter reported that, due to sorption effects, the composition of the measured gas could be modified inside the cell and significant errors of up to about 0.1% in density measurements could occur. A detailed adsorption test for our densimeter was performed in a previous work [11]. Results showed that the adsorption effect for a methane, nitrogen, carbon dioxide and carbon monoxide mixture could be neglected in our measurements. The components of the biomethane mixture studied in this work are the same, except for the carbon monoxide which is not present in the current mixture, and for the small amount of oxygen, so it can be concluded that the adsorption effect may also be neglected in these measurements.

#### **4. Discussion of the results**

The relative deviations of experimental density data from the density calculated with the GERG-2008 equation of state for each of the isotherms are shown in Table 5 and Figure 2.

As can be observed, the relative deviations are within a  $\pm 0.03\%$  band, the higher one being of 0.027% for the density at the lower temperature (240 K) and at a pressure of 8 MPa. All these deviations are smaller than the experimental uncertainty of the data. They are also smaller than the uncertainty of the GERG2008 itself, which states that for gas-phase density for natural gases and many other mixtures consisting of the 21 natural gas components considered in the equation, is 0.1 % over the temperature range from (250 to 450) K at pressures up to 35 MPa. These deviations are even smaller than the stated uncertainty of the reference equation of state for pure methane [32], which in density is 0.03%, for pressures below 12 MPa and temperatures below 350 K. It can be concluded that the GERG-2008 equation of state represent the experimental density data of this biomethane mixture with an uncertainty much smaller than the assumed general uncertainty of the equation of state for natural gas mixtures in general. In fact, it has an uncertainty of the same order of magnitude as that of the reference equation of state for pure methane.

In previous works, relatively big deviations in density from the GERG equation of state were observed for the binary mixtures  $\text{CH}_4 + \text{CO}_2$  [15] and  $\text{CH}_4 + \text{N}_2$  [16], especially for the lower temperatures and pressures around 10 MPa. In the biomethane mixture studied in this work, the amount of  $\text{CO}_2$  and  $\text{N}_2$  is so small that this behavior is not detected.

The relative deviations of experimental density data from the density calculated with the AGA8-DC92 equation of state for each of the isotherms are also shown in Table 5 and Figure 3. The relative deviations are lower than 0.04% except for 250 K and pressures higher than 11 MPa, and for 240 K and pressures higher than 9 MPa. The highest deviation is 0.11% for 240 K

and 14 MPa. In general, deviations from AGA8-DC92 are still small, but greater than deviations from the GERG-2008 equation of state.

The statistical comparison of the experimental data with GERG-2008 and AGA8-DC92 equations of state is given in Table 6, where *AAD* is the average absolute deviation defined in equation 6, *Bias* is the average deviation defined in equation 7, *RMS* refers to the root mean squared defined in equation 8, and *MaxD* represents the maximum relative deviation in the considered data set.

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| 10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right|$$

(6)

$$Bias = \frac{1}{n} \sum_{i=1}^n \left( 10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right)$$

(7)

$$RMS = \sqrt{\frac{1}{n} \sum_{i=1}^n \left( 10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right)^2}$$

(8)



The AAD of experimental data from the GERG-2008 equation of state is 0.0071 %, while the AAD of experimental data from the AGA8-DC92 equation of state is 0.0174 %. The statistical parameters of the deviation of experimental data from the Peng-Robinson equation of state [33], widely used in industry, are also presented in Table 6. Densities from the Peng-Robinson equation of state were also calculated through the REFPROP software. In this case, the AAD is much higher: 0.875 %. The maximum relative deviation from the Peng-Robinson equation of state is near 5% at 240 K and 14 MPa.

## 5. Conclusions

Accurate density data of a synthetic biomethane-like mixture were obtained by using a single-sinker densimeter with magnetic suspension coupling. The temperature range was from (240 to 350) K and pressures up to 14 MPa.

The mixture was prepared gravimetrically at the Spanish National Metrology Institute (Centro Español de Metrología, CEM). Another mixture of the same nominal composition was prepared at the Slovak National Metrology Institute (Slovenský Metrologický Ústav, SMÚ) for comparison purposes of the mixture preparation capabilities of the two NMI and the density measurement techniques of SMÚ and University of Valladolid. The results obtained show a perfect agreement between the SMÚ and CEM mixture preparation capabilities and between the SMÚ and UVA density measurements. This inter-comparison was part of the general objectives of the research project ‘Metrology for Biogas’ of the European Metrology Research Program.

Experimental densities obtained by means of the Single Sinker Densimeter, from (240 to 350) K and pressures up to 14 MPa, were compared with the densities calculated from the GERG-2008 equation of state, which is the current reference equation of state for natural gas and

related mixtures. Relative deviations between experimental data and estimates are within a  $\pm 0.030\%$  band, smaller than the experimental uncertainty of the density data, and much smaller than the assumed uncertainty of the GERG-2008 equation of state for this kind of mixtures. This shows the outstanding performance of the current reference equation of state for natural gases when describing a biomethane-like mixture.

A comparison with the AGA8-DC92 equation of state was also performed. Deviations were still very small, but higher than the deviation from the GERG-2008. The maximum relative deviation from the Peng-Robinson equation of state is near 5% at 240 K and 14 MPa. These results demonstrate that the cubic equation of state of Peng and Robinson, due to its simple mathematical structure, is not suitable for an accurate description of thermal properties in the homogeneous region.

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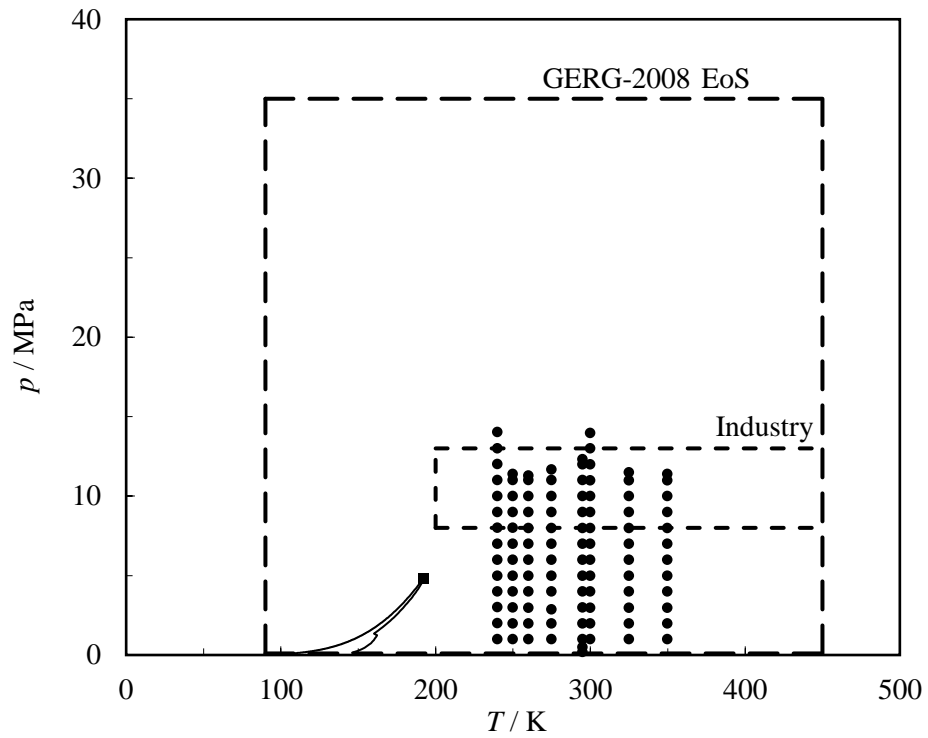


Figure 1.  $p$ - $T$  phase diagram showing the experimental points measured in this work (●), the calculated saturation curve for the biomethane-like mixture CEM-92365, the critical point (■), the temperature and pressure ranges of validity of the GERG-2008 equation of state (dashed line) and the area of interest for the transport and compression of gas fuels (thin dashed line).



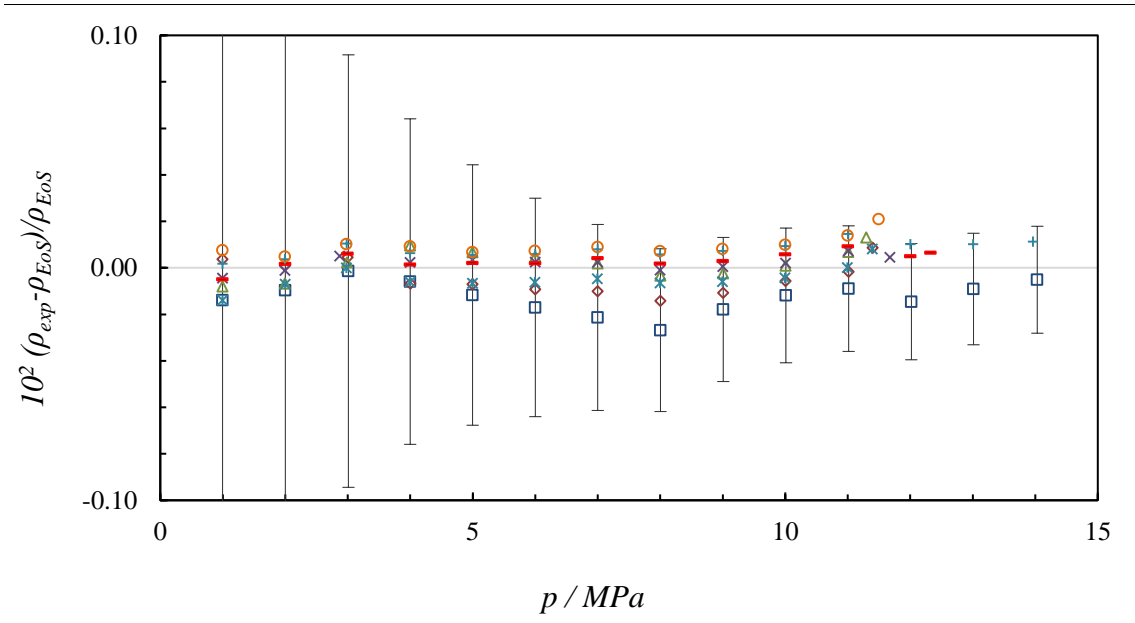


Figure 2. Relative deviations in density of experimental ( $p, \rho, T$ ) data of the synthetic biomethane-like mixture CEM-92365  $\rho_{\text{exp}}$  from density values calculated from the GERG-2008 equation of state  $\rho_{\text{EoS}}$  versus pressure:  $\square$  240 K;  $\diamond$  250 K;  $\triangle$  260 K;  $\times$  275 K;  $-$  295 K;  $+$  300 K;  $\circ$  325 K and  $\ast$  350 K. Error bars on the 240 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental data.

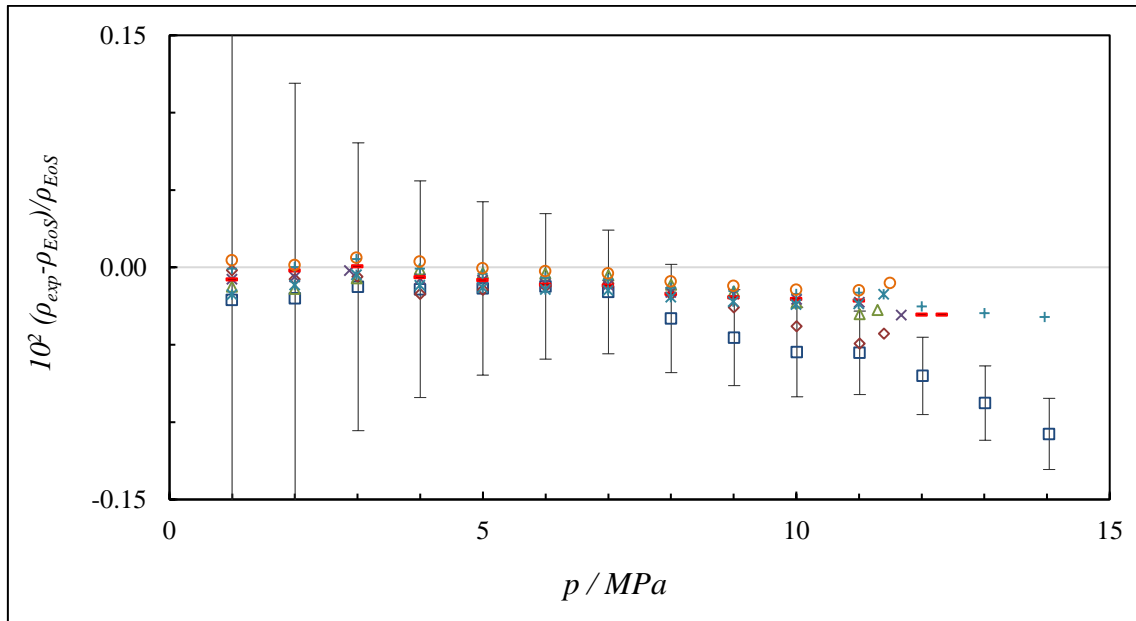


Figure 3. Relative deviations in density of experimental ( $p, \rho, T$ ) data of the synthetic biomethane-like mixture CEM-92365  $\rho_{\text{exp}}$  from density values calculated from the AGA8-DC92 equation of state  $\rho_{\text{EoS}}$  versus pressure:  $\square$  240 K;  $\diamond$  250 K;  $\triangle$  260 K;  $\times$  275 K;  $-$  295 K;  $+$  300 K;  $\circ$  325 K and  $*$  350 K. Error bars on the 240 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental data.

1 Table 1. Composition of the synthetic biomethane-like mixture CEM-92365 ( $M = 16.7855 \text{ kg}\cdot\text{kmol}^{-1}$ ,  $T_c = 191.98 \text{ K}$ ,  $p_c = 4.77 \text{ MPa}$ ) and purity,  
 2 supplier, molar mass and critical parameters of the individual component gases.

3

Component	Concentration (mole fraction)		Specified purity of the component mol %	Supplier	Molar Mass $M / \text{kg}\cdot\text{kmol}^{-1}$	Critical parameters of the component	
	$x_i$	$U(x_i)$				$T_c / \text{K}$	$P_c / \text{MPa}$
Methane	0.964 772	0.000 055	> 99.999 5 mol %	Air Liquide <sup>a</sup>	16.0428 <sup>d</sup>	190.56 <sup>d</sup>	4.60 <sup>d</sup>
Carbon dioxide	0.020 008	0.000 030	> 99.998 mol %	Air Liquide <sup>a</sup>	44.0098 <sup>e</sup>	304.13 <sup>e</sup>	7.38 <sup>e</sup>
Nitrogen	0.015 021	0.000 025	> 99.999 7 mol %	Carbueros Metálicos <sup>b</sup>	28.01348 <sup>f</sup>	126.19 <sup>f</sup>	3.39 <sup>f</sup>
Oxygen	0.000 197 4	0.000 002 8	> 99.999 8 mol %	Contse <sup>c</sup>	31.9988 <sup>g</sup>	154.58 <sup>g</sup>	5.04 <sup>g</sup>

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5 <sup>a</sup> AL Air Liquide España S.A., Madrid, Spain

6 <sup>b</sup> Air Products Group, Barcelona, Spain

7 <sup>c</sup> Contse S.A., Madrid, Spain

8 <sup>d</sup> Ref. [32]

9 <sup>e</sup> Ref. [34]

10 <sup>f</sup> Ref. [27]

11 <sup>g</sup> Ref. [35]

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15 Table 2. Composition of the synthetic biomethane-like mixture SMÚ-0009F\_6 ( $M = 16.8093 \text{ kg}\cdot\text{kmol}^{-1}$ ,  $T_c = 192.07 \text{ K}$ ,  $p_c = 4.78 \text{ MPa}$ ) and purity and  
16 supplier of the individual component gases.

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Component	Concentration (mole fraction)		Specified purity of the component	Supplier
	$x_i$	$U(x_i)$		
Methane	0.963 897	0.000 019	>99.995	Air Liquid - Alphagaz
Carbon dioxide	0.020 833	0.000 064	>99.999 5	Messer Austria GmbH
Nitrogen	0.015 059	0.000 032	>99.999 9	Air Products SA/NV
Oxygen	0.000 210 1	0.000 001 3	>99.999 9	Air Products SA/NV

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21 Table 3. Experimental ( $p, \rho, T$ ) measurements for the synthetic biomethane-like mixtures CEM-92365 (composition as in Table 1) and SMÚ-0009F\_6  
 22 (composition as in Table 2), performed with the isochoric pycnometer at SMÚ (SMÚ-Pyc) and with the single-sinker densimeter at UVa (UVa-  
 23 SSD). Expanded uncertainty in density  $U(\rho_{exp})$  ( $k = 2$ ), deviations of the experimental data from the GERG-2008 ( $\rho_{exp} - \rho_{GERG}$ ), compatibility of the  
 24 experimental density results with the density calculated from the GERG-2008 ( $I(\rho_{exp}, \rho_{GERG})$ ) and compatibility between UVa and SMÚ density  
 25 results ( $I(\rho_{UVa}, \rho_{SMÚ})$ ) calculated through the deviations of the respective experimental data from the GERG-2008.

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Mixture	Densimeter	$T/K$	$p/MPa$	$\rho_{exp} / \text{kg}\cdot\text{m}^{-3}$	$U(\rho_{exp}) / \text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$\rho_{exp} - \rho_{GERG}$	$I(\rho_{exp}, \rho_{GERG})$	$I(\rho_{UVa}, \rho_{SMÚ})$
CEM-92365	SMÚ-Pyc	295.430	1.00079	6.9595	0.005	-0.0034	0.40	
CEM-92365	SMÚ-Pyc	296.535	0.50495	3.4670	0.005	-0.0015	0.24	
CEM-92365	SMÚ-Pyc	296.858	0.20212	1.3776	0.005	-0.0019	0.37	
CEM-92365	UVa-SSD	295.072	0.99737	6.9473	0.024	-0.0003	0.01	0.12
CEM-92365	UVa-SSD	295.072	0.49895	3.4447	0.024	0.0003	0.01	0.07
CEM-92365	UVa-SSD	295.071	0.19840	1.3641	0.023	0.0019	0.08	0.16
SMÚ-0009F_6	SMÚ-Pyc	296.538	1.00613	6.9820	0.005	-0.0008	0.09	
SMÚ-0009F_6	SMÚ-Pyc	293.990	0.50096	3.4723	0.005	-0.0043	0.71	
SMÚ-0009F_6	SMÚ-Pyc	293.913	0.20107	1.3882	0.005	0.0001	0.02	
SMÚ-0009F_6	UVa-SSD	295.067	0.99787	6.9615	0.024	0.0003	0.01	0.05

SMÚ-0009F_6	UVa-SSD	295.067	0.49925	3.4520	0.024	0.0005	0.02	0.20
SMÚ-0009F_6	UVa-SSD	295.066	0.19892	1.3698	0.023	0.0020	0.09	0.08

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30 Table 4. Results of the GC analysis of the remaining synthetic biomethane-like mixtures CEM-92365 (gravimetric composition as in Table 1) and  
 31 SMÚ-0009F\_6 (gravimetric composition as in Table 2) performed at SMÚ at the end of the complete density measurements. Compatibility of the GC  
 32 analysis values with the original gravimetric composition.

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Component	CEM-92365 mixture			SMÚ-0009F_6 mixture		
	Concentration (mole fraction)		Compatibility with gravimetric composition	Concentration (mole fraction)		Compatibility with gravimetric composition
	$x_i$	$U(x_i)$	$I$	$x_i$	$U(x_i)$	$I$
Methane	0.965 0	0.002 9	0.08	0.964 7	0.002 9	0.28
Carbon dioxide	0.019 89	0.000 20	0.58	0.021 02	0.000 24	0.75
Nitrogen	0.015 066	0.000 076	0.56	0.015 068	0.000 064	0.13
Oxygen	0.000 202	0.000 004	0.94	0.000 210	0.000 004	0.02

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37 Table 5. Experimental ( $p, \rho, T$ ) measurements for the synthetic biomethane-like mixtures CEM-  
 38 92365 (composition as in Table 1), expanded uncertainty in density  $U(\rho_{exp})$  ( $k = 2$ ), and relative  
 39 deviations (%) of the experimental data from the GERG-2008 and AGA8-DC92 equations of  
 40 state.

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$T/K$	$p/MPa$	$\rho_{exp} / \text{kg}\cdot\text{m}^{-3}$	$U(\rho_{exp}) / \text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$10^2(\rho_{exp}-\rho_{GERG})/\rho_{GERG}$	$10^2(\rho_{exp}-\rho_{AGA})/\rho_{AGA}$
240.036	14.0327	199.686	0.046	-0.005	-0.108
240.036	13.0115	185.834	0.044	-0.009	-0.088
240.035	12.0157	170.462	0.043	-0.015	-0.070
240.036	11.0136	153.256	0.041	-0.009	-0.055
240.035	10.0111	134.819	0.039	-0.012	-0.055
240.036	9.00772	116.063	0.036	-0.018	-0.045
240.035	8.00338	97.936	0.034	-0.027	-0.033
240.036	7.00018	81.121	0.032	-0.021	-0.016
240.037	5.99991	65.872	0.031	-0.017	-0.012
240.036	4.99832	52.096	0.029	-0.012	-0.014
240.037	3.99804	39.680	0.028	-0.006	-0.014
240.036	3.01080	28.561	0.026	-0.001	-0.013
240.037	2.00120	18.181	0.025	-0.010	-0.020
240.036	0.99687	8.700	0.024	-0.014	-0.021
250.006	11.3984	139.630	0.039	0.009	-0.043
250.004	11.0121	133.656	0.038	-0.002	-0.049
250.005	10.0075	117.975	0.037	-0.006	-0.038
250.007	9.00463	102.468	0.035	-0.011	-0.026
250.006	8.00415	87.577	0.033	-0.014	-0.017
250.005	7.00128	73.505	0.032	-0.010	-0.010
250.005	5.99952	60.417	0.030	-0.009	-0.012

250.005	4.99861	48.321	0.029	-0.007	-0.014
250.005	4.00185	37.192	0.027	-0.007	-0.017
250.006	3.00029	26.850	0.026	0.005	-0.006
250.003	1.99700	17.237	0.025	0.001	-0.008
250.004	0.99678	8.314	0.024	0.004	-0.002
260.005	11.2979	123.303	0.037	0.013	-0.027
260.004	11.0098	119.423	0.037	0.007	-0.030
260.003	10.0060	105.932	0.035	0.001	-0.023
260.003	9.00538	92.699	0.034	-0.002	-0.015
260.001	8.00153	79.861	0.032	-0.003	-0.011
260.002	6.99989	67.637	0.031	0.002	-0.005
260.003	5.99891	56.081	0.030	0.005	-0.004
260.004	4.99823	45.209	0.028	0.007	-0.004
260.004	3.99670	34.995	0.027	0.010	-0.001
259.999	2.98638	25.325	0.026	0.002	-0.007
259.992	1.99650	16.424	0.025	-0.007	-0.014
260.003	0.99628	7.957	0.024	-0.008	-0.012
274.980	11.6736	111.682	0.036	0.005	-0.031
274.979	11.0066	104.211	0.035	0.007	-0.023
274.978	10.0063	93.045	0.034	0.002	-0.021
274.977	9.00261	82.016	0.033	0.001	-0.017
274.975	7.99969	71.273	0.031	-0.001	-0.016
274.975	6.99955	60.915	0.030	0.003	-0.011
274.975	5.99819	50.945	0.029	0.002	-0.010
274.976	4.99762	41.410	0.028	0.003	-0.008

274.974	3.99706	32.307	0.027	0.002	-0.007
274.974	2.87228	22.582	0.026	0.005	-0.002
274.974	1.99782	15.376	0.025	-0.001	-0.006
274.975	0.99652	7.488	0.024	-0.004	-0.008
295.071	12.3259	102.498	0.035	0.007	-0.030
295.070	12.0005	99.490	0.035	0.005	-0.030
295.071	11.0035	90.278	0.033	0.009	-0.021
295.071	10.0001	81.042	0.032	0.006	-0.020
295.071	9.00057	71.945	0.031	0.003	-0.019
295.072	7.99777	62.973	0.030	0.002	-0.017
295.072	6.99760	54.222	0.029	0.004	-0.012
295.071	5.99858	45.705	0.028	0.002	-0.011
295.073	4.99717	37.416	0.027	0.002	-0.008
295.072	3.99670	29.396	0.027	0.002	-0.006
295.073	2.99691	21.649	0.026	0.006	0.001
295.073	1.99822	14.175	0.025	0.002	-0.002
295.072	0.99737	6.947	0.024	-0.005	-0.007
299.917	13.9642	113.821	0.036	0.011	-0.032
299.918	13.0053	105.385	0.035	0.010	-0.030
299.918	12.0023	96.492	0.034	0.010	-0.025
299.919	11.0024	87.613	0.033	0.015	-0.016
299.918	10.0011	78.751	0.032	0.009	-0.017
299.919	9.00065	69.988	0.031	0.007	-0.015
299.918	7.99770	61.339	0.030	0.006	-0.013
299.919	6.99768	52.887	0.029	0.008	-0.008

299.917	5.99793	44.634	0.028	0.006	-0.007
299.918	4.99729	36.594	0.027	0.006	-0.004
299.918	3.99663	28.787	0.026	0.006	-0.001
299.918	2.98122	21.111	0.026	0.010	0.006
299.918	1.99594	13.899	0.025	0.004	0.000
299.919	0.99701	6.826	0.024	0.002	-0.001
324.941	11.4964	80.266	0.032	0.021	-0.010
324.941	11.0003	76.562	0.032	0.014	-0.015
324.942	9.99904	69.108	0.031	0.010	-0.014
324.942	8.99827	61.701	0.030	0.008	-0.012
324.941	7.99816	54.366	0.029	0.007	-0.009
324.942	6.99651	47.108	0.029	0.009	-0.004
324.942	5.99693	39.968	0.028	0.007	-0.002
324.941	4.99675	32.946	0.027	0.007	-0.001
324.943	3.99672	26.058	0.026	0.009	0.004
324.944	2.98084	19.206	0.025	0.010	0.006
324.942	1.99719	12.717	0.025	0.005	0.001
324.943	0.99662	6.269	0.024	0.008	0.005
349.934	11.3955	71.090	0.031	0.008	-0.017
349.935	10.9953	68.487	0.031	0.000	-0.023
349.935	9.99688	62.005	0.030	-0.004	-0.024
349.933	8.99559	55.521	0.030	-0.006	-0.022
349.934	7.99648	49.082	0.029	-0.006	-0.019
349.935	6.99605	42.678	0.028	-0.005	-0.015
349.933	5.99517	36.327	0.027	-0.006	-0.014

349.932	4.99644	30.058	0.027	-0.007	-0.013
349.932	3.99621	23.857	0.026	-0.006	-0.011
349.932	2.98105	17.652	0.025	0.000	-0.005
349.932	1.99801	11.732	0.025	-0.007	-0.011
349.932	0.99633	5.799	0.024	-0.014	-0.018

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43 Table 6. Statistical parameters, AAD, Bias, RMS and MaxD, of the relative deviation (%) of experimental  
44 data with respect to the GERG-2008, AGA8-DC92 and Peng Robinson equations of state.

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Statistical parameter	Value		
	GERG-2008	AGA8-DC92	Peng-Robinson
AAD	0.0071	0.0174	0.8751
Bias	0.0005	-0.0169	-0.3194
RMS	0.0085	0.0244	1.1841
MaxD	0.0268	0.1076	4.9308

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