

Integration of biogas in the natural gas grid: thermodynamic characterization of a biogas-like mixture

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Abstract:

The composition of biogas may vary significantly due to the diversity of production sources, making essential to have a detailed knowledge of their thermophysical properties in order to develop and validate methods for the estimation of density, heat capacity and calorific value of biogas and biomethane. In this work the thermodynamic behavior of a synthetic biogas-like mixture, composed by methane (50%), carbon dioxide (35%), nitrogen (10%) and carbon monoxide (5%), is studied through accurate (p,ρ,T) experimental data obtained by using a single sinker densimeter with magnetic suspension coupling. The mixture was prepared by the gravimetric method at the Spanish National Metrology Institute (Centro Español de Metrología, CEM) and the accurate density measurements have been performed in the temperature range from (275 to 400) K and pressures up to 20 MPa. This work is part of the research project 'Metrology for Biogas' supported by the European Metrology Research Program. Experimental data are compared with the densities calculated with the GERG-2008 equation of state. Deviation between experimental and estimated densities is within a $\pm 0.2\%$ band at all temperatures, except at the lower temperature, 275 K, and pressures from (6 to 15) MPa, which shows a higher deviation.

Keywords: biogas; thermodynamic characterization; density; single sinker densimeter; GERG-2008.

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Highlights

Accurate density data of a 4 components synthetic biogas-like mixture are presented.

Experimental data are compared with the densities calculated from the GERG-2008 equation of state.

Relative deviations in density were within a 0.2% band at temperatures above 300 K.

Densities at 275K and pressures around 10 MPa showed higher deviations.

1. Introduction

The European Union has established that 20% of energy consumption should come from renewable sources by 2020, and that biofuels should provide at least 10% of transport petrol and diesel consumption by the same year [1]. This directive describes a framework for the promotion of energy from renewable sources, reducing CO₂ emissions and establishes the need of integrate renewable energy in existing transmission and distribution grids. A significant increase of the amount of biogas injected into natural gas networks is an urgent need to achieve this goal. Due to the diversity of sources of biogas and other non-conventional energy gases, their composition may vary significantly. The significant difference in composition between biogas and natural gas manifests in a lower methane content (50% to 80%) and a corresponding higher content of carbon dioxide (20% to 50%), with small amounts of other components as nitrogen, carbon monoxide and hydrogen. The biogas matrix presents serious challenges concerning the applicability of approaches used in the natural gas industry for measuring the moisture content and calculating gas properties, such as the density and calorific value. These problems are linked to the substantially higher carbon dioxide content of biogas.

Therefore it is essential to have a detailed knowledge of the thermophysical properties of biogas in order to solve technical and design problems during the transport and exploitation stages. The current models are based on binary mixture data and accurate experimental data on multicomponent mixtures are relatively scarce yet. A large number of very high accuracy experimental data over wide temperature and pressure ranges are needed to develop and validate methods for the estimation of density, heat capacity and calorific value of biogas and biomethane. Experimental density data of multicomponent natural-gas-like mixture have been previously measured by other authors. In 2007, Patil et al. [2] published experimental density data of a natural-gas-like mixture with a methane mole fraction of 91%. In 2011, McLinden [3] 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. In 2014, Hernández-Gómez et al. [4] published

density data of a synthetic Carbon Mine Methane (CMM) mixture. However, no many previous accurate density data of synthetic biogas-like mixtures with a content of methane less than 60% can be found in the literature. Moreover, CO is not present in anyone of the studied mixtures. The composition of biogas may vary significantly due to diversity of sources of production and according to different processes of biogas production is not unusual to find small amounts of CO [5], mainly in processes like biomass gasification. Therefore, the four components proposed are in agreement with the idea of studying the behaviour of a gas that represents a possible mixture of natural gas, biogas landfill and biomass gasification.

This work studies the thermodynamic behavior of a synthetic biogas-like mixture, composed by methane, carbon dioxide, nitrogen and carbon monoxide with the composition showed in the Table 1, through accurate (p, ρ, T) experimental data, at temperatures ranging from (275 to 400) K and pressures up to 20 MPa, obtained by using a single sinker densimeter with magnetic suspension coupling. The experimental data are compared with the corresponding densities calculated from the GERG-2008 equation of state [6], which is the current reference equation of state for natural gas and other related mixtures and designated as ISO Standard (ISO 20765-2 [7]) for the calculation of thermodynamic properties of natural gases. To achieve the highest accuracy in composition, the gas mixture was prepared by the gravimetric method according to ISO 6142 [8] by the Spanish National Metrology Institute (Centro Español de Metrología, CEM).

Using the same technique, our group has reported in the past density measurements on binary mixtures of the four components of this synthetic biogas-like mixture: $\text{CH}_4 + \text{CO}_2$ [9], $\text{CH}_4 + \text{N}_2$ [10], $\text{N}_2 + \text{CO}_2$ [11][12] and $\text{N}_2 + \text{CO}$ [13]. For some of these mixtures there are also available speed of sound measurements [14].

This work is part of the Joint Research Project 'Metrology for Biogas', funded by the European Metrology Research Program [15].

2. Experimental

2.1. Sample preparation

The synthetic biogas-like mixture was prepared gravimetrically at the Spanish National Metrology Institute (Centro Español de Metrología, CEM) and was supplied in a 5 dm³ aluminum alloy cylinder (CEM no.: 51858). The goal was to obtain a representative mixture of actual biogas, with known composition and with the smallest achievable uncertainty in composition. The composition of the mixture from gravimetric preparation according to ISO 6143 [16] is given in Table 1, together with the expanded uncertainty for each component (coverage factor, $k = 2$), the certified purity, supplier and critical parameters of each of the component gases. All substances were used without further purification.

The critical parameters of the mixture, estimated with the GERG-2008 equation of state [6] by using REFPROP software [17], were critical temperature 224.8 K and critical pressure 8.9352 MPa.

All components were introduced directly into the cylinder. The filling order was: carbon dioxide, carbon monoxide, nitrogen and methane (balance gas). 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 target composition of the synthetic mixture was considered to be sufficiently stable due to previous experience with mixtures of the same compounds and similar composition.

The composition of the mixture was validated by using the multi-point calibration according to the procedure described in ISO 6143 [16]. The composition of the three calibration reference materials were in the range ± 5 % of the targeted composition. In the validation procedure, a GC analyzer was used with a set of packed columns and TCDs designed for the analysis of natural gas samples (Agilent 6890N, Agilent Technologies, Santa Clara CA, USA). Table 2 gives the results of this analysis together with the expanded uncertainty.

Since the chromatographic method used is not optimized for CO analysis, large relative uncertainty and deviation are obtained for this component.

2.2. Apparatus Description

The 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. It is one of the state-of-the-art methodologies for high precision density measurements of fluids over wide temperature and pressure ranges [18]. This methodology was developed by Brachthäuser et al. [19] at 1993 to simplify the design of the previously developed two sinker densimeter [20], and was further improved by Klimeck et al. [21]. The single-sinker densimeter used on this work was especially designed for density measurements of pure gases and gaseous mixtures and has been previously described in detail by Chamorro et al. [10] and improved by Mondéjar et al. [22]. The high accuracy of this methodology is 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 sinker used in this experiment was a silicon cylinder with a real mass of 61.59181 ± 0.00016 g and a volume of 26.444 ± 0.003 cm³ ($k=2$), measured at 293.05 K and 1.01134 bar.

For reducing the 'nonlinearity effect' present at any electronic balance, independently of its quality, and defined as a deviation of the balance's real curve versus the real load measured, the two calibrated masses are used. This load compensation system allows operating near to balance's zero point and to improve the accuracy of the measurement. The calibrated masses are made of tantalum and titanium. They have different mass but approximately the same volume (4.9 cm³), so the difference in weight between both of them is similar to the sinker mass (60 g approximately) and the air buoyancy effect is neglected. The two masses were provided by Rubotherm and their mass and volume were calibrated at the Mass Division of the Spanish National Metrology Institute (Centro Español de Metrología, CEM).

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

$$\rho = (m_{s0} - m_s) / V_s(T, P) \quad (1)$$

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 and 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 m^3 ; which is accurately 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). Pressure is measured by two Digiquartz transducers (Paroscientific model 2300A-101 and 43KR-HHT-101, Paroscientific, Inc., Redmond WA, USA) which cover pressure ranges up to 2 and 20 MPa, respectively.

2.3. Experimental Procedure

Six isotherms were recorded for this work at (275, 300, 325, 350, 375 and 400) K. Each isotherm was measured from a pressure of 20 MPa to 1 MPa by 1 MPa steps, followed by measurements of the sinker mass in vacuum. 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 gas industry.

Measurements couldn't be done at the lowest limit of the temperature range of densimeter (250 K) because it was close to the saturation curve of the studied mixture and the composition may change due to the condensation of the mixture components in the colder parts of the densimeter. The maximum pressure achieved on each of the isotherms was 20 MPa.

Before and after measurements on the studied biogas-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. [16]. Relative deviations of the experimental data from the

calculated densities were within a $\pm 0.02\%$ band, with an Absolute Average Deviation (AAD) of 0.011% at the nitrogen's measurements before biogas and 0.007% after.

As mentioned above, the sinker mass in vacuum was measured after each of the isotherms to check any misalignment suffered by the magnetic suspension coupling during the measurements. The maximum difference between the replicates of the sinker mass in vacuum at the same temperature was of 0.0065%, corresponding to a temperature of 400K. This good repeatability of the measurements in vacuum confirmed that there was not any misalignment during the measurements.

The single sinker densimeter is one of the most accurate methodologies for the measurement of the density of fluids; however this methodology presents some systematic errors, which affect the final density results. There are two main effects that 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. These two aspects will be discussed later on the results section.

2.4. Uncertainty of the measurements

Uncertainty in measurements of the single sinker densimeter used in this work was estimated by Mondéjar et al. [22] after performing several improvements on the equipment. The expanded uncertainty in density ($k = 2$) as a density function is given by equation 2.

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

Uncertainties in temperature and pressure were evaluated to be less than 4 mK and 0.015%, respectively ($k = 2$). The uncertainty in composition for the biogas-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 3.

$$u_T(\rho) = \left[u(\rho)^2 + \left(\left(\frac{\partial \rho}{\partial p} \right)_{T,x} u(p) \right)^2 + \left(\left(\frac{\partial \rho}{\partial T} \right)_{p,x} u(T) \right)^2 + \sum_i \left(\left(\frac{\partial \rho}{\partial x_i} \right)_{T,p,x_j \neq x_i} u(x_i) \right)^2 \right]^{1/2} \quad (3)$$

where p is the pressure, T is the temperature, and x_i is the mole fraction of each of the mixture components. Partial derivatives can be calculated with the GERG-2008 equation of state.

3. Results

Measurements were carried out at six different temperatures (275, 300, 325, 350, 375 and 400) K and decreasing pressure steps of 1 MPa from 20 to 1 MPa. Table 4 presents the experimental (p, ρ, T) data of the synthetic biogas-like mixture measured in this work. 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 4 also presents the relative deviation in density from the values calculated with the GERG-2008 equation of state (zero line) and the expanded uncertainty in density (coverage factor $k = 2$) of the experimental data, calculated by equation 2, which is given in absolute value and relative value like a percentage of the measured density. The relative uncertainty in density ($k = 2$) is less than 0.02% at the highest pressure and less than 0.30% at the lowest pressures for the biogas-like mixture measured.

As was mentioned before, there are two main effects that 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. [23], Cristancho et al. [24] and Kano et al. [25]. 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 under vacuum for each isotherm. In the case of the fluid specific effect, its magnitude depends on the magnetic behavior of the measured gas. The magnetic

susceptibility (χ_{BIOGAS}) of the biogas-like mixture used in this work was estimated to be of $-9.52 \cdot 10^{-9}$ by using an additive law, as proposed by Bitter [26]. 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 study by Richter et al. [27]. Previously, Klimeck et al. [28] 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 up to about 0.1% in density measurements could occur. Therefore, test measurements to check any adsorption effect on the experimental density value were carried out.

According to the experimental procedure, each isotherm is recorded in 120 hours, approximately. After that, the cell is evacuated and fresh mixture is introduced for measuring another isotherm. To check the sorption effects on the mixture composition for an isotherm measurement time, an adsorption test was carried out measuring a large number of replicates of one selected point. The test was performed at temperature of 350 K and pressure of 1 MPa and density measurements were continuously recorded during 120 hours. The results showed that the relative deviation in density from the GERG-2008 equation was near constant along the whole test. The difference observed in the trend of the relative deviation in density from the GERG-2008 equation of state between the first and the last measurement was 0.0045%, which is one order of magnitude lower than the uncertainty in density at the work pressure. Therefore it was concluded that the adsorption effect could be neglected in our 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 showed in Figure 2.

As it can be observed, the relative deviations are within a $\pm 0.2\%$ band. Only the pressure range from (6 to 15) MPa at the temperature of 275 K are out of this limits. The 275 K isotherm shows a crest in which the highest relative deviation from densities calculated from the GERG-2008 equation of state is 0.41% and it can be observed at 10 MPa. A qualitatively similar behavior was observed in the binary mixtures $\text{CH}_4 + \text{CO}_2$ [9] and $\text{CH}_4 + \text{N}_2$ [10] at the same pressures for the lower temperatures measured.

The results also showed that only the isotherms at (275 and 300) K have positive deviation from the equation of state. Data belonging to the isotherms over 300 K show negative deviation in density; however this isotherms are close to zero line, independently of pressure. Measurements at 325K revealed the highest negative deviation, but always below 0.2% range. According to Kunz and Wagner, the uncertainty of GERG-2008 in gas-phase density is 0.1% over the temperature range from (250 to 450) K at pressures up to 35 MPa [6]. This uncertainty estimate is valid for various types of natural gases, including natural gases rich in nitrogen, carbon dioxide or considerable amounts of heavier hydrocarbons, carbon monoxide or oxygen. Anyway, for gas mixtures with carbon dioxide mole fractions of 0.14 and more, GERG-2008 states that systematic deviations exceeding 0.3% may be observed at some states. The biogas-like mixture studied in this work has a high content of CO_2 (35%), so the behavior registered in the measurements agrees with the uncertainty claimed by GERG-2008 equation of state.

The statistical comparison of the data measured is given in Table 5, where *AAD* is the average absolute deviation defined in equation 4, *Bias* is the average deviation defined in equation 5, *RMS* refers to the root mean squared defined in equation 6, and *MaxD* represents the maximum relative deviation in the considered data set.

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| 10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right| \quad (4)$$

$$Bias = \frac{1}{n} \sum_{i=1}^n \left(10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right) \quad (5)$$

$$RMS = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right)^2} \quad (6)$$

5. Conclusions

Accurate density data of a synthetic biogas-like mixture were carried out by using a single-sinker densimeter with magnetic suspension coupling. The temperature range was from (250 to 400) K and pressures up to 20 MPa. The mixture was prepared gravimetrically at Spanish National Metrology Institute (Centro Español de Metrología, CEM). This work is part of the research project 'Metrology for Biogas' of the European Metrology Research Program.

Experimental densities 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 $\pm 0.2\%$ band. However, data at 275 K showed larger deviations up to 0.41% at pressures from (6 to 15) MPa.

The results obtained are within the limits of uncertainty claimed by the GERG-2008 equation of state, which is up to 0.1%; exactly the 60% of data measured are lower than this limit. However, for mixtures with a high content of carbon dioxide, like the studied mixture, the deviations from the equation of state can be higher than 0.3%, but only at the temperature of 275 K and pressures around 10 MPa this fact has been registered.

Acknowledgments

Support for this work came from project ENE2013-47812-R of the Spanish Ministry of Economy and Competitiveness, from project VA391A12-1 of the Junta de Castilla y León, and from the research project ENG54, 'Metrology for Biogas' of the European Metrology Research Program.

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Figures

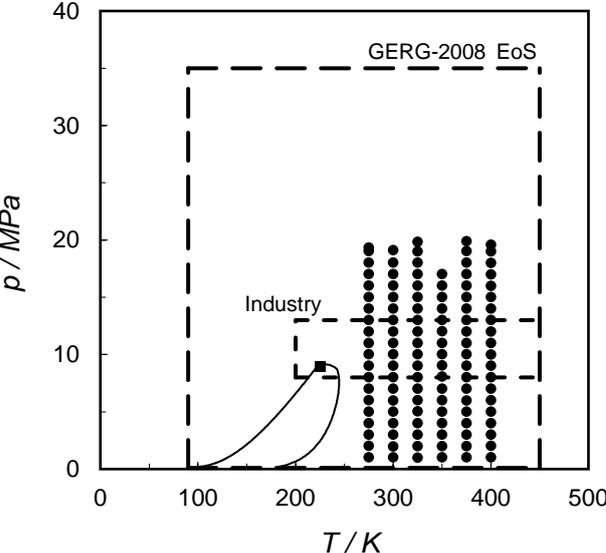


Figure 1. p-T phase diagram showing the experimental points measured in this work (●), the calculated saturation curve for the biogas like mixture, the critical point (■), the temperature and pressure ranges of validity of the GERG-2008 equation of state (dashed line) and the area of interest for the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

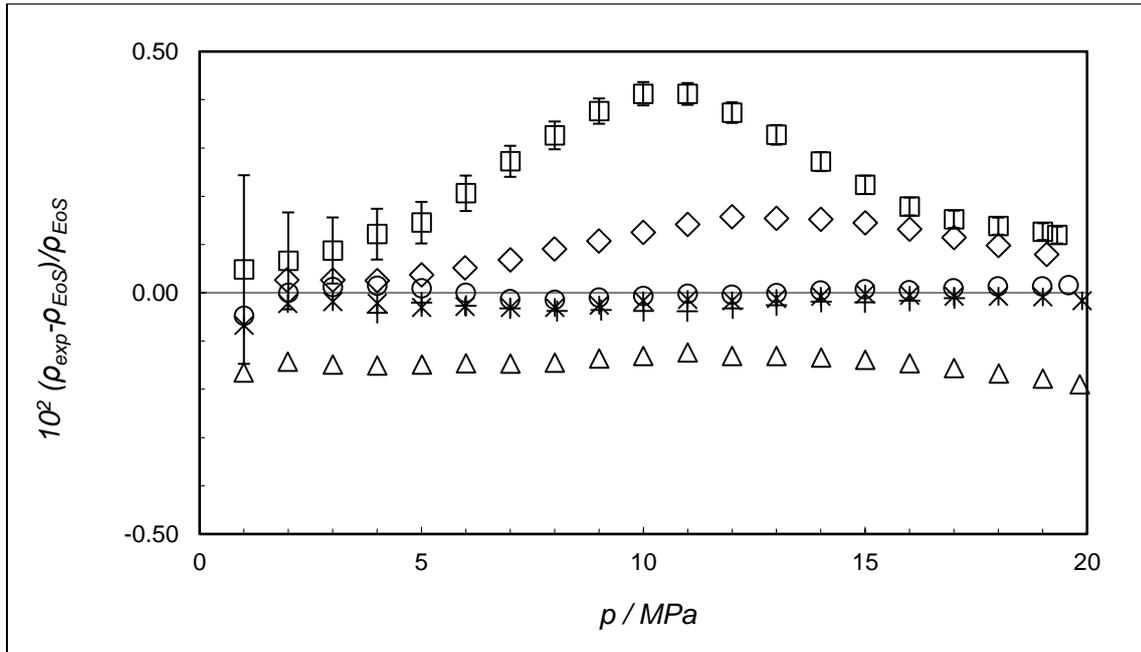


Figure 2. Relative deviations in density of experimental (p, ρ, T) data of the synthetic biogas ρ_{exp} from density values calculated from the GERG-2008 equation of state ρ_{EoS} versus pressure: \square 275 K; \diamond 300 K; \triangle 325 K; $+$ 350 K; $*$ 375 K; \circ 400 K. Error bars on the 275 K isotherm indicate the expanded uncertainty ($k = 2$) of the experimental data.

Tables

Table 1. Composition of the synthetic biogas-like mixture and purity, supplier and critical parameters of the individual component gases.

Component	Concentration (mole fraction)		Specified purity of the component	Supplier	Critical parameters of the component	
	x_i	$U(x_i)/\%$			T_c / K	P_c / MPa
CH ₄	0.498 141	0.014	> 99.999 5 mol %	Praxair	190.56 ^d	4.60 ^d
CO ₂	0.099 916	0.040	> 99.999 9 mol %	Air Liquide ^a	304.13 ^e	7.38 ^e
N ₂	0.352 028	0.006 2	> 99.99 5 mol %	Carbueros ^b	126.19 ^f	3.39 ^f
CO	0.049 915	0.10	> 99.998 mol %	Praxair ^c	132.86 ^g	3.49 ^g

^a AL Air Liquide España S.A., Madrid, Spain

^b Air Products Group, Barcelona, Spain

^c Praxair España S.L., Madrid, Spain

^d Ref. [29]

^f Ref. [30]

^g Ref. [31]

^h Ref. [32]

Table 2. Results of the GC analysis of the synthetic biogas-like mixture.

Component	Concentration (mole fraction)	Relative deviation between gravimetric preparation and first GC analysis	
	x_i	$U(x_i)/\%$ ($k = 2$)	%
Methane	0.500 220	2.9	0.417
Nitrogen	0.099 905	1.7	-0.011
Carbon dioxide	0.352 260	0.48	0.066
Carbon monoxide	0.051 236	5.2	2.646

Table 3. Results from the mass and volume calibration with its uncertainty ($k = 2$) of tantalum and titanium masses used in the load compensation system.

Magnitude	Tantalum calibrated mass	Titanium calibrated mass
Real mass	82 g + 88.343 mg \pm 0.100 mg	22 g + 399.677 mg \pm 0.070 mg
Conventional mass	82 g + 94.748 mg \pm 0.100 mg	22 g + 397.072 mg \pm 0.070 mg
Volume (cm ³)	4.9240 \pm 0.0007	4.9706 \pm 0.0007
Density (kg·m ⁻³)	16670.9 \pm 2.5	4506.5 \pm 0.6

Table 4. Experimental (p, ρ, T) measurements for the synthetic biogas, relative deviations from the GERG-2008 equation of state and expanded uncertainty in density $U(\rho_{\text{exp}})$ ($k = 2$), where T is the temperature (ITS-90), p the pressure, ρ_{exp} the experimental density and ρ_{EoS} the density calculated from the GERG-2008 equation of state.

T/K	p/MPa	$\rho_{\text{exp}} / \text{kg}\cdot\text{m}^{-3}$	$10^2(\rho_{\text{exp}}-\rho_{\text{EoS}})/\rho_{\text{EoS}}$	$U(\rho_{\text{exp}}) / \text{kg}\cdot\text{m}^{-3}$ ($k = 2$)	$10^2 U(\rho_{\text{exp}}) / \rho_{\text{exp}}$
275.007	19.3239	360.865	0.120	0.063	0.017
275.002	19.0023	356.476	0.127	0.062	0.017
275.000	17.9983	341.807	0.138	0.061	0.018
275.002	17.0006	325.781	0.152	0.059	0.018
275.001	16.0001	308.168	0.179	0.057	0.018
274.999	14.9983	288.893	0.224	0.055	0.019
275.007	13.9978	267.942	0.272	0.052	0.020
275.008	12.9972	245.547	0.327	0.050	0.020
275.009	11.9972	222.071	0.373	0.047	0.021
275.012	10.9983	198.123	0.412	0.045	0.023
275.012	9.99881	174.283	0.413	0.042	0.024
275.009	8.99925	151.158	0.377	0.040	0.026
275.008	7.99932	129.186	0.326	0.037	0.029
275.006	6.99860	108.589	0.272	0.035	0.032
275.004	5.99808	89.433	0.206	0.033	0.037
275.001	4.99823	71.694	0.145	0.031	0.043
275.004	3.99601	55.230	0.121	0.029	0.053
275.007	2.99757	39.984	0.088	0.027	0.069
275.008	1.99549	25.730	0.066	0.026	0.100
275.014	0.99870	12.470	0.048	0.024	0.195
299.976	19.0856	289.280	0.063	0.055	0.019
299.973	17.9999	273.672	0.080	0.053	0.019
299.972	16.9982	258.475	0.098	0.051	0.020
299.969	15.9983	242.593	0.114	0.050	0.020
299.969	14.9975	226.084	0.132	0.048	0.021
299.968	13.9980	209.120	0.145	0.046	0.022
299.969	12.9974	191.822	0.152	0.044	0.023
299.971	11.9981	174.424	0.154	0.042	0.024
299.971	10.9978	157.097	0.157	0.040	0.026
299.970	9.99794	140.008	0.142	0.038	0.027
299.968	8.99798	123.323	0.125	0.037	0.030
299.971	7.99731	107.139	0.107	0.035	0.032
299.969	6.99791	91.571	0.091	0.033	0.036

299.971	5.97679	76.312	0.068	0.031	0.041
299.969	4.99731	62.315	0.051	0.030	0.048
299.969	3.99724	48.660	0.037	0.028	0.058
299.968	2.99690	35.626	0.025	0.027	0.076
299.971	1.96316	22.782	0.026	0.026	0.112
299.967	0.99651	11.312	0.027	0.024	0.214
324.982	19.8362	251.082	-0.190	0.051	0.020
324.984	18.9986	240.804	-0.178	0.049	0.021
324.982	18.0039	228.234	-0.168	0.048	0.021
324.981	16.9998	215.189	-0.156	0.047	0.022
324.980	15.9962	201.844	-0.146	0.045	0.022
324.983	14.9990	188.339	-0.139	0.044	0.023
324.981	14.0028	174.683	-0.134	0.042	0.024
324.980	13.0000	160.847	-0.131	0.041	0.025
324.980	11.9991	147.023	-0.131	0.039	0.027
324.980	10.9971	133.261	-0.124	0.038	0.028
324.981	9.99690	119.644	-0.131	0.036	0.030
324.982	8.99917	106.264	-0.136	0.035	0.033
324.980	7.99979	93.115	-0.145	0.033	0.036
324.980	6.99818	80.238	-0.147	0.032	0.040
324.983	5.99694	67.692	-0.146	0.030	0.045
324.985	5.00732	55.631	-0.149	0.029	0.052
324.986	3.99756	43.686	-0.151	0.028	0.064
324.986	2.99738	32.221	-0.149	0.027	0.082
324.987	1.98270	20.959	-0.143	0.025	0.121
324.986	0.98892	10.281	-0.165	0.024	0.235
349.970	17.0042	187.005	-0.010	0.044	0.023
349.970	15.9967	175.555	-0.006	0.042	0.024
349.968	14.9883	163.964	-0.005	0.041	0.025
349.970	14.0069	152.587	-0.011	0.040	0.026
349.969	12.9956	140.818	-0.016	0.038	0.027
349.969	12.0140	129.390	-0.020	0.037	0.029
349.969	10.9907	117.515	-0.019	0.036	0.031
349.971	10.0021	106.099	-0.025	0.035	0.033
349.970	9.04426	95.137	-0.033	0.033	0.035
349.969	8.05425	83.936	-0.038	0.032	0.038
349.969	6.99697	72.151	-0.037	0.031	0.043
349.969	5.99725	61.194	-0.036	0.030	0.049
349.969	4.99854	50.445	-0.038	0.029	0.057
349.970	3.99816	39.894	-0.033	0.027	0.069
349.970	2.99810	29.569	-0.027	0.026	0.089

349.969	1.99245	19.417	-0.021	0.025	0.129
349.972	0.99733	9.601	-0.042	0.024	0.251
374.957	19.8820	194.414	-0.016	0.044	0.023
374.954	19.0010	185.997	-0.009	0.043	0.023
374.957	18.0023	176.300	-0.007	0.042	0.024
374.956	17.0016	166.458	-0.007	0.041	0.025
374.955	15.9964	156.468	-0.005	0.040	0.026
374.956	14.9968	146.445	-0.003	0.039	0.027
374.956	13.9982	136.360	-0.007	0.038	0.028
374.958	12.9981	126.219	-0.012	0.037	0.029
374.956	11.9977	116.060	-0.016	0.036	0.031
374.953	10.9982	105.923	-0.014	0.035	0.033
374.956	9.99764	95.796	-0.017	0.034	0.035
374.957	8.99869	85.730	-0.026	0.032	0.038
374.957	7.99840	75.725	-0.030	0.031	0.041
374.957	6.99822	65.812	-0.030	0.030	0.046
374.956	5.97550	55.783	-0.029	0.029	0.052
374.957	4.99988	46.329	-0.030	0.028	0.061
374.957	3.99768	36.750	-0.022	0.027	0.074
374.956	2.99773	27.330	-0.018	0.026	0.095
374.956	1.98112	17.903	-0.022	0.025	0.139
374.957	0.99719	8.929	-0.067	0.024	0.269
400.017	19.5829	173.337	0.016	0.042	0.024
400.015	18.9863	168.193	0.013	0.042	0.025
400.015	17.9829	159.462	0.013	0.041	0.025
400.016	16.9838	150.669	0.009	0.040	0.026
400.015	15.9871	141.817	0.006	0.039	0.027
400.017	14.9885	132.885	0.008	0.038	0.028
400.017	13.9877	123.875	0.005	0.037	0.030
400.018	12.9963	114.906	-0.001	0.036	0.031
400.017	11.9908	105.789	-0.004	0.035	0.033
400.017	10.9922	96.729	-0.002	0.034	0.035
400.017	9.99231	87.655	-0.007	0.033	0.037
400.017	8.99825	78.654	-0.010	0.032	0.040
400.018	7.99877	69.635	-0.014	0.031	0.044
400.018	6.99680	60.644	-0.013	0.030	0.049
400.018	5.99664	51.732	0.000	0.029	0.055
400.018	4.99736	42.892	0.009	0.028	0.065
400.018	3.99723	34.120	0.015	0.027	0.078
400.017	2.99727	25.434	0.012	0.026	0.101
400.019	1.99728	16.842	0.000	0.025	0.148

400.019

0.99723

8.351

-0.048

0.024

0.286

Table 5. Statistical parameters of the deviation of experimental data with respect to the GERG-2008 equation of state.

Statistical parameter	Value
AAD	0.0875
Bias	0.0209
RMS	0.1289
MaxD	0.413