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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 it 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 of 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. The deviation between experimental and estimated densities is within a ±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.

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 integrating renewable energy in the 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 the 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 mixtures 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 mol fraction methane and differed mainly in the content of nitrogen, carbon dioxide and high alkanes. In 2014, Hernández-Gómez *et al.* [4]

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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 the 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 for the mixture are in agreement with the idea of studying the behavior 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 shown in 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 is 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: $CH_4 + CO_2$ [9], $CH_4 + N_2$ [10], $N_2 + CO_2$ [11][12] and $N_2 + CO$ [13]. For some of these mixtures there are also speed of sound measurements available [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 dm^3 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 in 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 cm^3 ($k = 2$), measured at $T = 293.05$ K and 1.01134 bar.

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	$U(x_i)$/% ($k = 2$)			T_c/K	P_c/MPa
Methane	0.498 141	0.014	>99.999 5 mol%	Praxair	190.56[d]	4.60[d]
Carbon dioxide	0.099 916	0.040	>99.999 9 mol%	Air Liquide[a]	304.13[e]	7.38[e]
Nitrogen	0.352 028	0.006 2	>99.99 5 mol%	Carburos Metálicos[b]	126.19[f]	3.39[f]
Carbon monoxide	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] Reference [29].
[e] Reference [30].
[f] Reference [31].
[g] Reference [32].