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Full Length Article

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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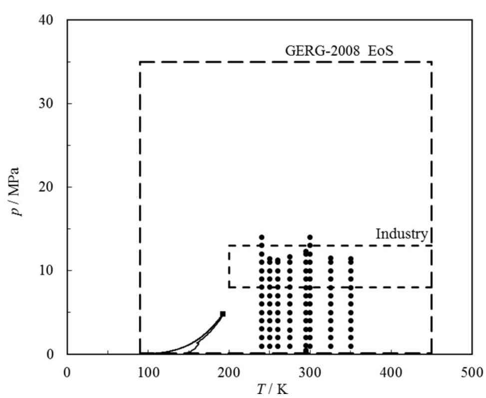
HIGHLIGHTS

- Accurate density data of a four component synthetic biomethane-like mixture are presented.
- Experimental data are compared to the densities calculated from the GERG-2008 and AGA8-DC 92 equations of state.
- Relative deviations in density from the GERG-2008 equation of state were within a 0.03% band.
- Relative deviations in density from the AGA8-DC92 equation of state were slightly bigger.

GRAPHICAL ABSTRACT



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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,ρ,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 ±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

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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.

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%–50%) and nitrogen (up to 40%) content, and small amounts of other components, such as water, oxygen, hydrogen, H_2S, NH_3, 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_4 concentrations >96%, CO_2 < 2%, and O_2 < 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, ρ, 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 mol 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: $CH_4 + CO_2$ [15], $CH_4 + N_2$ [16] and $N_2 + CO_2$ [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 Tables 1 and 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^3 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^3, 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 $kg\cdot kmol^{-1}$.

The biomethane mixture 0009F_6 was prepared at SMU using a similar procedure in two steps. In a first step, a premixture