J. Chem. Thermodynamics 68 (2014) 253–259

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Accurate thermodynamic characterization of a synthetic coal mine methane mixture

R. Hernández-Gómez [a], D. Tuma [b], M.A. Villamañán [a], M.E. Mondéjar [a], C.R. Chamorro [a,*]

[a] Grupo de Termodinámica y Calibración (TERMOCAL), Dpto. Ingeniería Energética y Fluidomecánica, Escuela de Ingenierías Industriales, Universidad de Valladolid, Paseo del Cauce, 59, E-47011-Valladolid, Spain

[b] BAM Bundesanstalt für Materialforschung und -prüfung, D-12200 Berlin, Germany

ARTICLE INFO

Article history:
Received 22 April 2013
Received in revised form 16 September 2013
Accepted 17 September 2013
Available online 27 September 2013

Keywords:
Coal mine methane
Density measurements
Single sinker densimeter
GERG-2008 equation of state

ABSTRACT

In the last few years, coal mine methane (CMM) has gained significance as a potential non-conventional gas fuel. The progressive depletion of common fossil fuels reserves and, on the other hand, the positive estimates of CMM resources as a by-product of mining promote this fuel gas as a promising alternative fuel. The increasing importance of its exploitation makes it necessary to check the capability of the present-day models and equations of state for natural gas to predict the thermophysical properties of gases with a considerably different composition, like CMM. In this work, accurate density measurements of a synthetic CMM mixture are reported in the temperature range from (250 to 400) K and pressures up to 15 MPa, as part of the research project EMRP ENG01 of the European Metrology Research Program for the characterization of non-conventional energy gases. Experimental data were compared with the densities calculated with the GERG-2008 equation of state. Relative deviations between experimental and estimated densities were within a 0.2% band at temperatures above 275 K, while data at 250 K as well as at 275 K and pressures above 10 MPa showed higher deviations.

1. Introduction

Coalbed methane (CBM) refers to all methane originated in coal seams by geological or biological processes. Depending on the production source of this fuel gas, it can be classified in several groups, each of them with specific reservoir characteristics, composition and extraction process. Thus, in order from highest to lowest methane concentration, we can identify virgin coalbed methane (VCBM), abandoned mine methane (AMM), coal mine methane (CMM) and ventilation air methane (VAM). CMM is obtained from working coal mines, either in advance of mining or from worked seams, by using drainage techniques. Although its composition depends significantly on the reservoir characteristics, it generally consists of a mixture of methane as the main compound (35% to 75% molar fraction) and higher alkanes, together with nitrogen, oxygen, carbon dioxide and, occasionally, water vapor [1].

Due to the rise of fuel prices in the last years caused by the advancing depletion of their reserves and increasing demand by the global economy, non-conventional and renewable fuels are gaining importance as an alternative to fossil fuels and also as a step to reduce the CO_2 emissions to the atmosphere. Among non-conventional fuels, coalbed methane arises as a potential energy resource in countries with an important coal production. As a by-product of mining, coalbed methane was traditionally used in local small-scale power production, but it can also contribute to the domestic and commercial gas supply.

The presence of CMM in coal mining is a challenge for working safety and from environmental reasons. On the one hand, the accumulation of the gas due to desorption from the distressed coal seam can affect the safety of the mine with an increase of the explosion risk. On the other hand, the uncontrolled release of this gas to the atmosphere can be even more harmful to the environment than CO_2 emissions, since the global warming potential (GWP) of methane is 25 times that of carbon dioxide [2]. Therefore, apart from the exploitation of a coal mining by-product, the controlled use of CMM reduces the overall greenhouse gases emissions and ensures safety in coal mines.

The significant difference in composition between CMM and natural gas, which manifests in a lower methane content and a corresponding higher content of carbon dioxide, nitrogen and other components of the first, makes it necessary to validate the performance of the existing equations of state for natural gases for gases with deviating compositions employing accurate experimental data of their thermophysical properties.

Experimental density data of different multi-component gas mixtures with common natural gas compositions have been previously measured by other authors. In 2007, Patil et al. [3] published experimental density data of a natural-gas-like mixture with a

* Corresponding author. Tel.: +34 983423756; fax: +34 983423363.
E-mail addresses: cescha@eis.uva.es, cescha@eii.uva.es (C.R. Chamorro).

0021-9614/$ - see front matter
http://dx.doi.org/10.1016/j.jct.2013.09.023

methane mole fraction of 91%. In 2011, McLinden [4] 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. However, no previous density data of synthetic mixtures with similar compositions to that of non-conventional gas fuels, such as biogas or CMM, can be found in the literature.

In this work, accurate experimental (p,ρ,T) data of a synthetic CMM mixture in the supercritical and gaseous state at temperatures ranging from (250 to 400) K and pressures up to 15 MPa are presented. The study was part of the research project EMRP ENG01 of the European Metrology Research Program for the characterization of non-conventional energy gases [5]. Densities were measured by using a single-sinker densimeter with magnetic suspension coupling. The experimental data were compared with the corresponding densities calculated from the GERG-2008 equation of state, which is the current reference equation of state for natural gas and other related mixtures and designated as ISO Standard (ISO 20765-2 [6]) for the calculation of thermodynamic properties of natural gases.

Measurements of the calorific value for the same synthetic CMM mixture have been carried out using several high-precision calorimeters, within the scope of the Joint Research Project EMRP ENG01 and are presented in a separate paper [7]. Furthermore, the speed-of-sound of a similar CMM mixture will be characterized by using a spherical acoustic resonator and results will be published later on.

2. Experimental

2.1. Sample preparation

The synthetic coal mine methane mixture was prepared gravimetrically at the Bundesanstalt für Materialforschung und -prüfung (BAM) and was supplied in a 5 dm^3 aluminum cylinder (BAM no.: 087). The goal was to obtain a representative mixture of actual CMM, with known composition and with the smallest achievable uncertainty in composition. The composition of the mixture from gravimetric preparation according to ISO 6142 [8] is given in table 1, together with the expanded uncertainty in composition 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 [9] by using REFPROP software [10], were $T_c = 207.1$ K and $p_c = 6.86$ MPa.

In order to obtain the uncertainties given in Table 1, the preparation of the CMM mixture required a multi-step method via pre-mixtures. Altogether, four pre-mixtures had to be prepared (in 10 dm^3 aluminum cylinders) which contained all components except carbon dioxide and methane that could be introduced directly into the final cylinder with the target composition (BAM no.: 7078–111005, volume: 10 dm^3). The corresponding compositions are given in table 1. Pre-mixture A (BAM no.: 7039-110912) contained n-pentane and isopentane in methane. The liquid pentanes were introduced into evacuated minicylinders (volume: 25 cm^3, arranged in a parallel configuration according to ISO 6142 [8]) and transferred into the recipient cylinder by evaporation that is directly followed by purging the transfer system with the calculated amount of methane. In the next step, pre-mixture A was diluted with methane which resulted in pre-mixture B (BAM no.: 7064–110920). Pre-mixture C (BAM no.: 7083–110926) contributed ethane, propane, n-butane, and isobutane. Propane, n-butane, and isobutane were filled in the same way via minicylinders and ethane as purging gas. In the next step, pre-mixture C was completed with methane. Pre-mixture D (BAM no.: 7045-110823) was a binary mixture of oxygen and nitrogen that were filled subsequently.

The filling sequence of the final CMM mixture (BAM no.: 7078-111005) was: carbon dioxide, pre-mixture B, pre-mixture C, pre-mixture D, methane (balance gas).

All substance transfers during the filling procedure were done by using temperature and pressure (or saturation pressure) differences only. No mechanical devices like, for example, a compressor, were employed here. The mass of the gas portions added directly into the 10 dm^3 recipient cylinders during the filling was determined using a high-precision mechanical gas balance (Voland model HCE 25, Voland Corp., New Rochelle NY, USA), whereas an electronic analytical balance (Sartorius CCE 2004, Sartorius AG, Göttingen, Germany) was used to determine the mass of minor components in smaller containers.

After the last gas portion had been added and weighed, the respective cylinder was finally homogenized by a procedure of subsequent heating and rolling. The target composition of the synthetic CMM was considered to be sufficiently stable due to the experience with mixtures of the same compounds and similar composition. The prepared final CMM mixture was decanted into the mentioned evacuated 5 dm^3 aluminum cylinder (BAM no.: 087). At this stage, the composition of the sample cylinder was

TABLE 1
Composition of the synthetic coal mine methane (CMM) 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
Oxygen	0.00504128	0.026	99.9995 vol.-%	Westfalen	154.58	5.04
Nitrogen	0.17031942	0.011	99.9999 vol.-%	Westfalen[a]	126.19	3.39
Methane	0.64207992	0.008	99.9995 mol-%	Linde[f]	190.56	4.60
Carbon dioxide	0.17312271	0.010	99.9995 vol.-%	Air Liquide[d]	304.13	7.38
Ethane	0.00846613	0.053	99.990 vol.-%	Scott Specialty Gases	305.32	4.87
Propane	0.00078154	0.052	99.990 vol.-%	Scott Specialty Gases[b]	369.89	4.25
i-Butane	0.00010716	0.052	99.95 vol.-%	Messer[c]	407.81	3.63
n-Butane	0.00005710	0.053	99.98 vol.-%	Scott Specialty Gases	425.13	3.80
i-Pentane	0.00001723	0.200	>99.7% (GC)	Sigma–Aldrich	460.35	3.38
n-Pentane	0.00000752	0.200	>99.8% (GC)	Sigma–Aldrich[e]	469.70	3.37

[a] Westfalen AG, Hörstel, Germany.
[b] Scott Specialty Gases Netherlands BV, Breda, The Netherlands.
[c] Messer Group GmbH, Krefeld, Germany.
[d] Air Liquide AG, Düsseldorf, Germany.
[e] Sigma–Aldrich Chemie GmbH, Steinheim, Germany.
[f] Linde AG, Unterschleißheim, Germany.