BIOGAZ PROPERTIES

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A prototype software for the evaluation of the thermophysical properties of pure methane, carbon dioxide, and hydrogen sulfide and their mixtures has been developed.

The software performs a flash calculation. According to the input conditions (system temperature, pressure, and global composition), the output properties are density, enthalpy, entropy, heat capacities, viscosity and thermal conductivity in the fluid phases (vapor or liquid). In case of thermodynamic equilibrium, the software provides also the compositions of the phases in equilibrium, for both the fluid and solid phases.

The actual lowest temperature for the calculation is -140°C. This limit will be further decreased in order to match the operative conditions of cryogenic processes such as the biogas liquefaction. The highest value for the pressure, 700 bar, has been fixed according to the range of applicability of the models within the software.

The thermodynamic/transport models together with the calculation methods implemented in the software are listed. A part of the parameters within these models have been regressed with respect to a database of experimental values collected by means of a bibliographic research. Some qualitative comparisons between literature and calculated values have also been included in this report.

1. Introduction

A precise and reliable knowledge of the thermophysical properties is a key issue in dealing with the engineering and the optimization steps of an industrial process.

This work aimed at setting up a user-friendly software able of quickly supplying this knowledge to workers and engineers operating in the field of the biogas production, purification and liquefaction processes.

Biogas, a gas resulting from the anaerobic digestion of organic matter at temperature ranging from 30 up to 70 °C and pressures between 1 and 2 bar [1], typically refers to a gaseous mixture composed of 50-70 % methane, 20-40 % carbon dioxide, and lower quantities of oxygen, nitrogen, water, hydrogen sulfide, siloxanes, and volatile organic compounds, whose concentrations depend on the production process.

In order to create a demo version of the software prone to future improvements:

1. only hydrogen sulfide has been considered among all the remaining impurities. Therefore, biogas has been roughly considered being a ternary mixture of methane, carbon dioxide, and hydrogen sulfide;
2. a set of starting properties has been identified: it includes density, enthalpy, entropy, heat capacities, viscosity and thermal conductivity.

As a consequence, a basic architecture of the software has been realized and future developments will include the addition of other impurities and thermophysical properties.

2. Bibliographic research overview

The bibliographic research focused on the experimental values for the cited pure components and their mixtures (CH_4+CO_2, CH_4+H_2S, CO_2+H_2S, and CH_4+CO_2+H_2S).

Experimental values have been collected: i) searching with science direct and other searching tools in scientific journals and books; ii) searching among previous works of the Centre Thermodynamics of Processes, like GPA research reports and Ph.D. thesis; iii) consulting the following sources: the NIST database ThermoData Engine, [2], the Dortmund Data Bank database, [3], the GERG-2004 and GERG-2008 databases, [4]-[5].

For each mixture and each thermophysical properties of interest, the total number N of available literature values is listed in Table 1 along with the pressure and temperature ranges. The literature values involving Equilibria between two or more coexisting Phases (EPs) have been summarized in the last row of Table 1, where any distinction has been made with respect to the kind (solid, liquid, or vapor) of the equilibrium phases.

One notices at once the lack of experimental heat capacities, viscosities, and thermal conductivities for the mixtures involving hydrogen sulfide.

Table 1. Literature values for the multicomponent systems of interest.

Properties	**CH_4+CO_2**		**CH_4+H_2S**		**CO_2+H_2S**		**CH_4+CO_2+H_2S**	
	N	**Ranges**	**N**	**Ranges**	**N**	**Ranges**	**N**	**Ranges**
Density	2690	-80 – 300 °C	1227	-81 – 227 °C	1292	-25 – 227 °C	174	5 – 71 °C
		1 – 1000 bar		1 – 690 bar		1 – 606 bar		8 – 20 bar
Enthalpy	771	-57 – 149 °C	117	-79 – 93 °C	37	20 – 40 °C	103	-60 – 149 °C
		1 – 111 bar		1 – 138 bar		5 – 15 bar		1 – 138 bar
Heat capacity	242	40 – 151 °C						
		35 – 155 bar						
Viscosity	435	20 – 300 °C						
		1 – 1700 bar						
Thermal conductivity	432	-61 – 163 °C						
		1 – 706 bar						
EPs	1032	-182 – 31 °C	381	-154 – 93 °C	719	-96 – 101 °C	306	-88 – 60 °C
		0.3 – 85 bar		0.4 – 137 bar		0.7 – 90 bar		1 – 125 bar

3. Thermodynamic and transport properties models

Several types of Equation of State (EoS) have been proposed in the literature and are commonly used in the field of the natural gas. Examples are the AGA8-DC92 equation of Starling and Savidge, [6], cubic equations such as the Peng-Robinson EoS, [7], and the GERG-2008 EoS, [5].

The former is currently the international accepted standard for the gas phase. Nevertheless, many authors investigated its accuracy in describing densities and thermal properties of natural gases of different compositions, revealing several shortcomings in the liquid phase to a greater extent than in the gas phase, [5].

A critical assessment of the Peng-Robinson EoS has been illustrated in 1996 by Klimeck et al., [8]. Authors challenged the use of this equation in technical applications where high accuracy predictions of thermophysical properties are required, and generalized that cubic EoSs are not suitable for accurate descriptions of caloric properties in the homogeneous region and of saturated-liquid densities.

The GERG-2008 model is a Helmholtz energy-explicit equation based on the multi-fluid approximation concept. It means that a fundamental equation is used for each component, whereas the residual behavior of the mixture is taken into account with further equations in forms of correlations, whose structure and parameters are tuned according to available experimental values.

The main feature of the GERG-2008 equation is its ability of representing the literature thermal and caloric properties within their experimental accuracy. Furthermore, over the entire composition range, the model covers the gas phase, the liquid phase, the supercritical region, and the fluid-fluid equilibrium states for mixtures of 21 natural gas components, [5].

According to what stated above, the GERG-2008 equation of state has been chosen for the evaluation of the thermodynamic properties of interest in the fluid phases.

Concerning viscosity and thermal conductivity, the Friction Theory General (FTG) model, [9], and the Extended Corresponding State (ECS) model, [10], have been adopted, respectively. It should be noted that methane is chosen as reference fluid in [10].

Both models are valid over the thermodynamic states from dilute gas to the dense liquid and the supercritical region and are applicable to non polar as well as polar fluids.

The evaluation of viscosity and thermal conductivity by means of these models requires some thermodynamic properties such as density. As a consequence, the transport properties models are dependent on the equation used for describing the thermodynamic properties.

This feature leaded to the need of tuning the parameters within the FTG and ECS models in order to match the functional forms presented in [9] and [10] together with the GERG-2008 equation of state.

As a consequence, the application of the transport properties models (and also of the prototype software) is related to the normal validity range of the GERG-2008 EoS, namely temperatures from -210 to 430 °C and pressures up to 700 bar, [5].

As detailed in the abstract, the actual lowest temperature for the calculation is -140 °C. This limit has been chosen according to the applicability of the thermodynamic model adopted for representing the solid phases and coupled with the GERG-2008.

The model for the solid phase, known as “classic approach”, relates the solid fugacity to the liquid fugacity of a pure component, and together with the fluid fugacities it is necessary for evaluating the thermodynamic equilibrium. More information concerning the classic approach could be found in [11].

Having in mind the thermodynamic and transport properties models here briefly presented, the PTz flash calculation performed by the software can be executed via either the isofugacity condition (as described in [12]) or the minimization of the Gibbs free energy of mixing, [13]. The former method considers only fluid phases, thus the latter is best suited for the evaluation of the system thermodynamic state at low temperatures where also solid phases become stable.

4. Qualitative comparison between literature values and software

In this section, two examples are given with respect to the qualitative comparison between experimental values and values calculated from the software for the same input conditions. In the following figures, black filled circles and lines represent experimental and calculated values, respectively.

Figure 1 shows the comparison between calculated and experimental densities for three mixtures of methane and carbon dioxide in the range $-23 \leq T \leq 170$ °C, and for methane mole fractions of 0.4, 0.6, and 0.8.

Figure 2 illustrates the comparison between calculated and experimental compositions in the fluid phases at the solid-liquid-vapor equilibrium in the methane-carbon dioxide-hydrogen sulfide mixture at -66.7 °C and 19.2 bar. The whole ternary diagram has been completed including all the binary equilibrium as calculated by the software.

It should be stated that the calculated values presented in Figures 1-2 have been obtained coupling several outputs of the software. For instance in Figure 2, the global input composition has been modified in the whole composition range in order to explore all the possible thermodynamic behaviors at the input temperature and pressure.

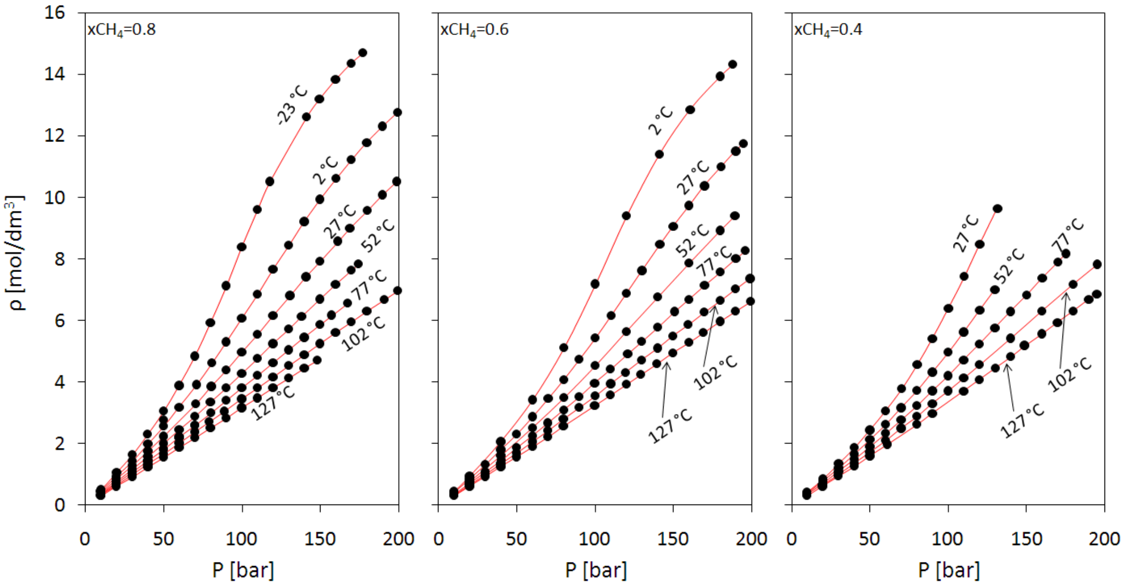

Figure 1. Qualitative comparison between experimental and calculated densities for the CH_4-CO_2 system for three different CH_4 mole fractions and from -23 °C up to 127 °C.
● : experimental densities [14]; — : calculated densities.

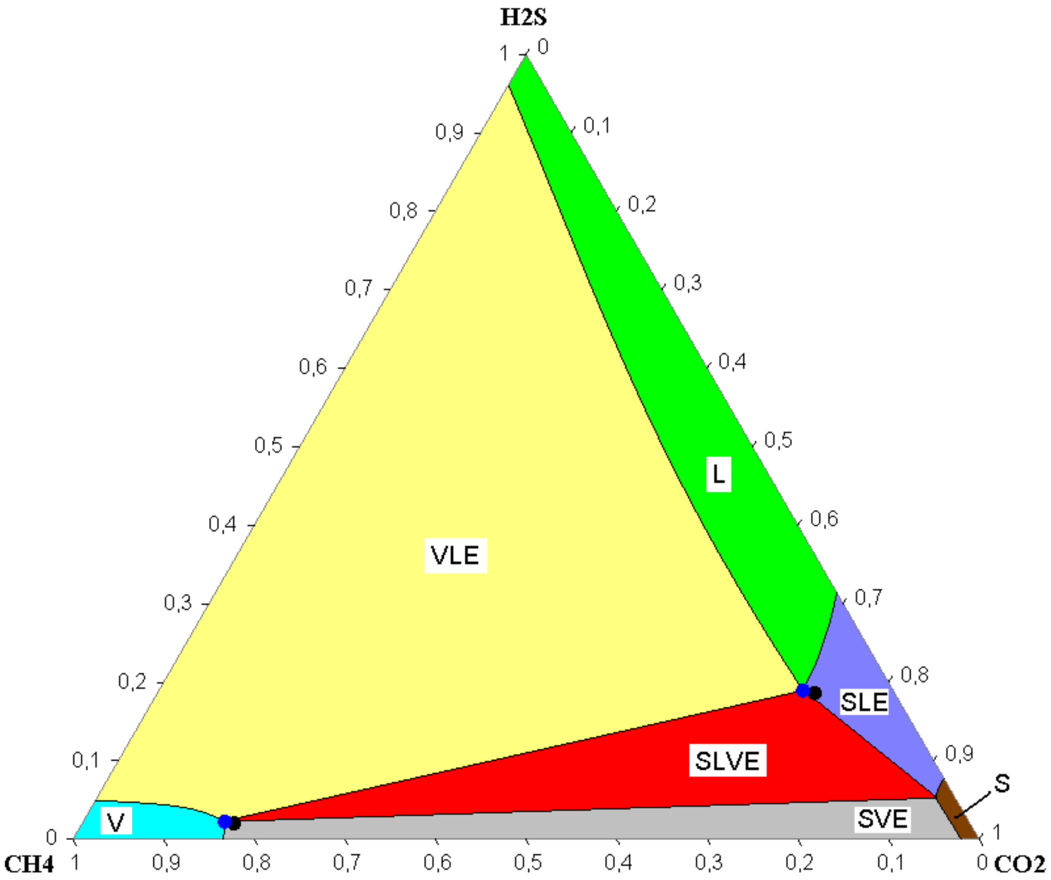

Figure 2. Qualitative comparison between experimental and calculated fluid compositions at solid-liquid-vapor equilibrium for the CH_4-CO_2-H_2S system at -66.7° C and 19.2 bar. ● : experimental fluids compositions, [15]; ● : calculated fluids compositions. Calculated areas: 🟥: solid-liquid-vapor equilibrium; ⬜: solid-vapor equilibrium; 🟪: solid-liquid equilibrium; 🟨: vapor-liquid equilibrium; 🟫: solid phase; 🟦: vapor phase; 🟩: liquid phase.

5. Outlook and future challenges

The prototype software here briefly presented satisfies the demands on easily-accessible description of thermophysical properties of interest in the field of biogas production and purification processes.

It could be a rather appealing tool for small and medium enterprises which do not always have access to high-cost packages for the evaluation of such properties.

The potential of the software has already been illustrated to ENGiE, and the companies Air Liquide and EReIE have already proved their interest. Other industrial groups will be contacted and urged in order to proceed with the development of the software.

Considering the components treated in the present work, the software can also be applied in the field of natural gas, and other substances (water, light hydrocarbons) and their correspondent mixtures could be added in order to match the special customer needs.

Furthermore, adding the evaluation of other properties, like diffusion coefficient, speed of sounds, and the Joule-Thomson coefficient, the sizing of industrial units could be also contemplated and incorporated.

The realization of software involved the regression of some parameters according to existing experimental values. Considering the lack of some data, it is the authors opinion that further experimental investigation, for instance regarding the heat capacities and the transport properties of mixtures of hydrogen sulfide, could increase the knowledge of the behavior of these mixtures and than the accuracy of the calculated properties.

Finally, the software could also be modified in order to perform other kind of evaluations, such as isenthalpic/isentropic calculations, or to provide a rapid access to phase diagrams, like isothermal/isobaric cross sections, or pressure-enthalpy and temperature-entropy diagrams.

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7. References

[1]. Mao, C.; Feng, Y.; Wang, X.; Ren, G., “Review on research achievements of biogas from anaerobic digestion”, *Renew. Sustainable Energy Rev., vol. 45, pp. 540-555,* **2015**

[2]. Linstrom, PJ.; Mallard, W.G., NIST Chemistry WebBook, NIST Standard Reference Database Number 69**,** *National Institute of Standards and Technology,* Gaithersburg MD, 20899, http://webbook.nist.gov

[3]. Dortmund Data Bank, Mixture Properties, *Version 1.3.0.211,* http://www.ddbst.com, **2004,**

[4]. Kunz, O.; Klimeck, R.; Wagner, W.; e M. Jaeschke, “The GERG-2004 wide-range equation of state for natural gases and other mixtures”, *GERG TM15*, **2007**

[5]. Kunz, O.; Wagner, W., “The GERG-2008 wide range equation of state for natural gases and other mixtures: an extension of the GERG-2004”, *J. Chem. Eng. Data, vol. 57, pp. 3032-3091,* **2012**

[6]. Starling, K.E.; Savidge, J.L., “Compressibility factors of natural gas and other hydrocarbon gases”, *Transmission Measurement Committee Report N°8, 2nd ed., American Gas Association, Washington, DC,* **1992**

[7]. D. Peng and D. Robinson, "A new two parameters equation of state", *Industrial and Engineering Chemistry Fundamentals, vol. 15, pp. 59-64,* **1976**

[8]. Klimeck, R.; Span, R.; Kleinrahm, R.; Wagner, W., “Fundamental equation for calorific properties. Collecting of data and test of existing equation”, *Final Report to GERG WG 1.3, Ruhr-University Bochum, Bochum, Germany,* **1996**

[9]. Quinones-Cisneros, S.E.; Deiters, U.K., “Generalization of the friction theory for viscosity modeling”, *J. Phys. Chem. B, vol. 110, pp. 12820-12834,* **2006**

[10]. Mathias, P.M.; Parekh, V.S.; Miller, E.J., “Prediction and correlation of thermal conductivity of pure fluids and mixtures, including the critical region”, *Ind. Eng. Chem. Res., vol. 41, pp. 989-999,* **2002**

[11]. Prausnitz, J.M.; Lichtenthaler, R.N.; de Azevedo, E.G., “Molecular Thermodynamics of Fluid-Phase Equilibria”, *Prentice Hall, 3rd ed., Upper Saddle River, New Jersey,* **1998**

[12]. Michelsen, M.L., “The isothermal flash problem. Part II. Phase-split calculation”, *Fluid Phase Equilibria, vol. 9, pp. 21-40,* **1982**

[13]. Baker, L.E.; Pierce, A.C.; Luks, K.D., “Gibbs energy analysis of phase equilibria”, *Society of Petroleum Engineers Journal, vol. 22, pp. 731-742,* **1982**

[14]. Mondejar, M.E.; Fernandez-Vicente, T.E.; Haloua, F.; Chamorro, C.R., “Experimental determination of P-ρ-T data for three mixtures of carbon dioxide with methane for thermodynamic characterization of non-conventional energy gases”, *J. Chem. Eng. Data, vol. 57, pp. 2581-2588,* **2012**

[15]. Langé, S., “Purification of natural gas by means of a new low temperature distillation process”, *Ph.D. Thesis, Politecnico di Milano, Chemical Department,* **2015**