MefHySto
Metrology for Advanced Hydrogen Storage Solutions

Deliverable D3

Report on improved reference equations of state (EoS) used for modelling hydrogen injection up to 20 % vol. including traceable density measurements with a target uncertainty of between 0.03 % to 0.5 % to be used as a basis for accurate determination of calorific values of energy gases

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Lead Partner	UVa
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Table of Contents

Executive Summary

The aim of this report is to inform about the delivered scientific papers focusing on thermophysical properties of hydrogen-enriched natural gas mixtures with a hydrogen content of up to 20 % injected in the gas grids and hydrogen under geological storage conditions. These were outcomes of the work carried out in Work Package 2 within the EURAMET EMPIR Metrology for Advanced Hydrogen Storage Solutions - MefHySto 19ENG03 project.

This report also addresses the critical need for high-quality thermodynamic data to support the development of advanced hydrogen storage solutions. Two key applications are explored:

1. **Hydrogen Injection into Natural Gas Grids:** This method leverages existing gas infrastructure for storing and distributing renewable energy from sources like solar and wind converted into green hydrogen. However, accurate equations of state (EoS) are essential to estimate the properties of hydrogen-enriched natural gas mixtures and ensure reliable energy metering.
2. **Underground Geological Storage (UGS):** This approach maximizes storage capacity and allows for reversible storage of hydrogen. Yet, missing data on hydrogen behaviour under high pressures and temperatures hinders the safe and efficient utilization of UGS.

The current reference EoS (GERG-2008) exhibits limitations when applied to hydrogen-enriched natural gas mixtures. This report details research that contributes to overcoming these limitations:

- **Published Research:** Two peer-reviewed papers have been published, with a third under revision and two more planned for submission. These studies investigate the thermophysical properties of hydrogen mixtures with high accuracy.
- **H_2 + Natural Gas Blends:** The project identified significant changes in phase behaviour with increasing hydrogen content. This reduces hydrocarbon solubility, simplifying hydrogen extraction from UGS. A manuscript on this topic is under preparation.
- **Experimental Data:** Density measurements were conducted for hydrogen-enriched natural gas mixtures (up to 20% H_2) across a range of temperatures and pressures relevant to transportation. Deviations from GERG-2008 were observed and found to be more pronounced at lower temperatures. These findings emphasize the need for further research near the phase boundaries of such mixtures. A scientific paper detailing these investigations is currently under review by a peer-reviewed scientific journal.
- **H_2-Propane Mixtures:** Density data for three hydrogen-propane mixtures were published in the International Journal of Hydrogen Energy, revealing deviations from GERG-2008 that increase with pressure and propane content. Speed of sound measurements were also conducted, but publication was delayed due to various challenges.
- **Data Review**: A paper published in "Renewable Energy" comprehensively reviews existing data and models for the thermophysical properties of hydrogen mixtures. The review highlights the need for further data on specific binary systems, like hydrogen with water, hydrogen sulphide, and various hydrocarbons.

The project's findings provide valuable insights for improving existing EoS models and developing new ones specifically designed for hydrogen mixtures. This will be crucial for the safe and efficient implementation of advanced hydrogen storage solutions, paving the way for a clean energy future.

Background

Gas mixtures properties are required for understanding two advanced hydrogen storage solutions:

1) injection of hydrogen into the natural gas grid can be seen as a way of energy storage from renewable sources, such as solar PV and wind. It uses the existing natural gas infrastructure to store and distribute this energy carrier.

2) underground storage in geological cavities (UGS), where storage capacity and reversible storage options are maximized.

The feasibility, implementation, optimization, and metrological reliability of both solutions rely on the precise thermodynamic characterization of the gas. Hence, there is call for developing high-quality thermodynamic Equations of State (EoS) encompassing a wide range of compositions, concentrations, temperatures, and pressures. Those models require a minimum set of experimental properties for calibration and validation: 1) Vapour-Liquid Equilibrium data showing condensation conditions; 2) a volumetric property, i.e., density; 3) a caloric property, e.g., speed of sound. All three properties must be consolidated and cover a wide range of conditions.

Equations of state are needed to estimate the properties of the hydrogen-enriched natural gas mixtures and to obtain the energy content of the mixture from composition and volumetric flow measurements. Accurate density determination from equations of state is also of great interest to determine the calorific values of this kind of mixtures and to provide necessary information for correct evaluation of the measurements of volumetric flow meters and to convert them to mass and energy units.

The harmonisation of national gas regulations for hydrogen composition in the gas grid is lacking, as the accepted hydrogen levels can vary from (0.1–10) vol. %. If the rates of hydrogen in the grids are higher than 10 vol. %, there will be a risk of non-compliance of the energy meters used for fiscal billing purposes. The reduced accuracy of the meters originates from inaccurate specific thermodynamic data for mixtures of hydrogen and natural gas. Thus, high-accuracy thermophysical experimental data are required to validate and improve the established reference equation of state (EOS) for natural gas and related mixtures (e.g., GERG-2008 – ISO 20765-2) (Kunz and Wagner, 2012) and other reference EOS for more specific, hydrogen-related mixtures (Thol *et al.*, 2019; Beckmüller *et al.*, 2021).

Missing thermodynamic data for hydrogen under high pressure and temperatures (viscosities, densities, etc.) jeopardise the use of Underground Geological Storage of hydrogen. Phase behaviour of mixtures can also change dynamically during application. Quality measurement of gas mixtures (mixtures of hydrogen and hydrocarbons in changing compositions) must be significantly extended for the technologies described.

Thermophysical properties of natural gas mixtures with increased hydrogen content and of pure hydrogen with impurities are either limited or of disputed quality. This report provides evidence of peer-reviewed published papers and work delivering relevant thermophysical properties, with the highest achievable accuracy, that is needed for the design and operation of processes related to the production, transport, storage and use of hydrogen and hydrogen-enriched natural gas mixtures. The accuracy of the established reference EOS for natural gas and related mixtures (GERG-2008 - ISO 20765-2) (Kunz and Wagner, 2012) when used with hydrogen-enriched natural gas is also checked. The experimental data obtained in this project and described in this report will further support the improvement of the current reference EOS and the development of new EOS that are specifically designed for hydrogen-related mixtures.

1 Influence of the hydrogen content in the saturation curve of hydrogen-enriched natural gas mixtures.

1.1 Potential content of condensable hydrocarbons in H_2-enriched natural gas mixtures with H_2 concentration up to 50 % (DBI)

1.1.1 Introduction

Ensuring flow assurance in gas infrastructure transporting H_2-enriched natural gas mixtures necessitates avoiding multiphase flow at transport conditions. Determining the dew point line of natural gas at different H_2 concentrations is therefore crucial, as even small H_2 quantities can significantly alter the phase behaviour of these blends. However, a thorough understanding of this critical phenomenon is hindered by the scarcity of existing experimental data and discrepancies within the industry's most widely used models.

DBI Gas- und Umwelttechnik GmbH (DBI), a subsidiary of DVGW, which is the German organization responsible for gas property standardization, led activities A2.2.2 and A2.2.3 aimed at studying the phase behaviour (i.e., condensate formation and potential liquid hydrocarbon content) of H_2-enriched natural gas mixtures with H_2 concentrations up to 50 %.

An existing cylindrical microwave resonator housed at FUNGE-UVa is a new technique capable for high-pressure phase equilibria determination (Susial *et al.*, 2019). This apparatus was planned to support these activities by measuring the changes in the saturation curve of a natural gas sample with increasing hydrogen content. Gas blends for these particular measurements were to be gravimetrically prepared by BAM (see Section 1.2.2). The underlying principle involves detecting the shift in the dielectric constant, which occurs due to phase transition, and the corresponding discontinuity in the cavity's microwave resonance frequency. This technique had previously been successfully tested on highly concentrated condensing phases of the binary (CO_2 + CH_4) system (Susial *et al.*, 2019). However, due to the very low (trace-level) concentration of condensable phases in H_2-enriched natural gas mixtures and the limitations of the equipment's sensitivity at such low liquid levels within the vapor-liquid phase region, the microwave resonator technique was ultimately deemed unsuitable for this application.

While all measurements and data analysis have been completed, the publication of the scientific paper has been delayed due to disruptions caused by COVID-19 lockdowns and the created backlog. A final draft for submission is currently in preparation.

1.1.2 Methodology

Two synthetic natural gas mixtures were prepared by DBI. The first batch encompassed typical natural gas + 20 % H_2. The second was typical natural gas + 50 % H_2. They were made by the gravimetric procedure.

The phase behaviour of these mixtures was compared with the (classic cubic) models of Soave-Redlich-Kwong (SRK) (Soave, 1972) and Peng-Robinson (PR) (Peng and Robinson, 1973). DBI used its PRO II software to carry out the simulations. The phase diagrams of the gas saturated with

n-undecane, according to the Equations of State were calculated from the analytically determined gas composition of the gas used.

The potential content of condensable hydrocarbons (PHLC) in mixtures of hydrogen-natural gas was measured by DBI according to DIN EN ISO 6570 "Natural gas - Determination of the potential content of liquid hydrocarbon – Gravimetric method" at a given pressure and temperature.

With the addition of hydrogen, the phase and condensation behaviour changes. To study this influence, the corresponding hydrogen content (20 % and 50 %, respectively) is mixed to the natural gas and then saturated with the hydrocarbon. The phase diagrams and condensates are then calculated.

1.1.3 Results and discussion

Figure 1 shows the calculated phase diagrams of a Russian-type natural gas mixture (0 % H_2), and of the same sample with 10 %, 20 % and 50 % H_2 concentration in the same natural gas mixture.

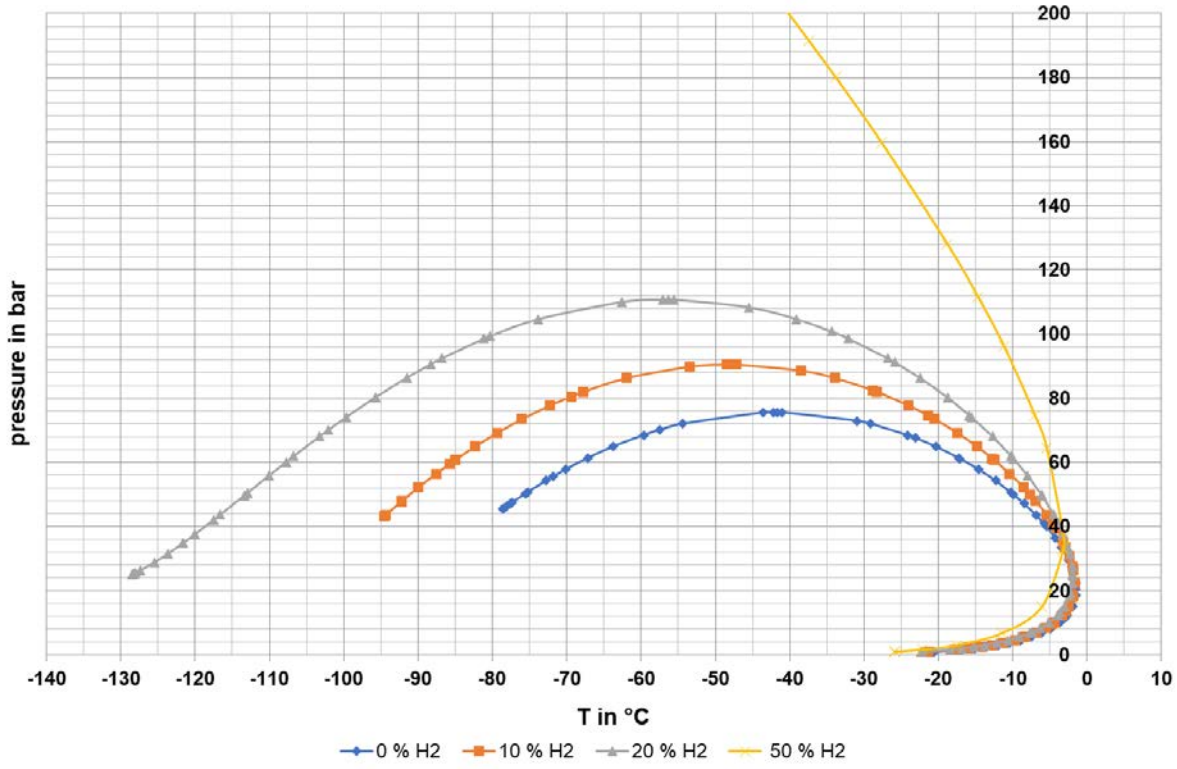


Figure 1: Phase envelope (*p* – *T* diagram) of a Russian-type natural gas mixture (0 % H_2), and the same sample with 10 %, 20 % and 50 % H_2 concentrations. SRK EoS predicted values.

In can be seen that H_2 concentrations above 20 % significantly change the phase diagram and condensation of the mixtures.

The minimum temperature at which condensation occurs at every pressure, the cricondentherm, decreases with increasing H_2 concentration.

Table 1: Calculated cricondentherm using the Equation of State of Soave-Redlich-Kwong (SRK) (Soave, 1972)

Hydrogen content [mole fraction]	Cricondentherm [°C]	Pressure [bar]
0 (= natural gas)	1.34	20.5
0.10	−1.68	22.4
0.20	−1.91	24.7
0.50	−3.60	36.5

The cricondenbar, i.e., the minimum pressure at which condensation occurs, multiphase onset, at every temperature, increases with increasing H_2 concentration. This has significant implications for the design of transport systems for H_2-enriched natural gas mixtures.

Figure 2 and Figure 3 show the solubility of higher hydrocarbons, and the calculated Potential Hydrocarbon Liquid Content (PHLC) of the mixtures under study.

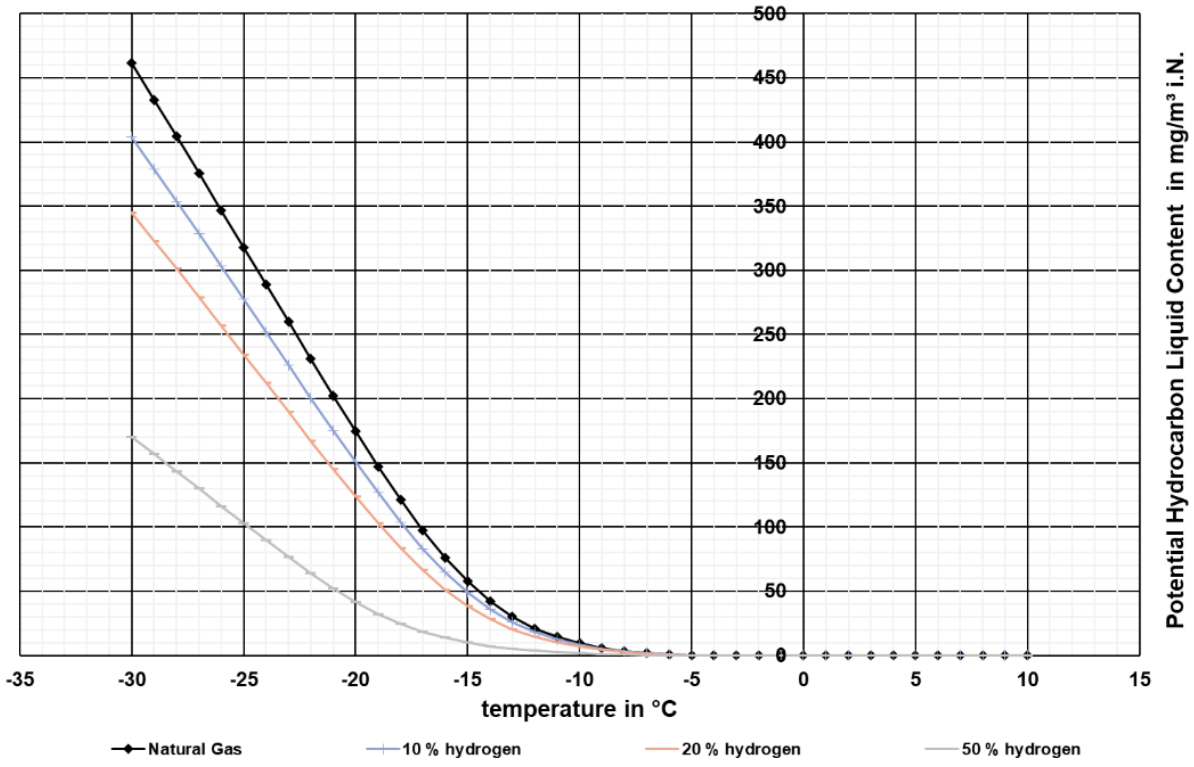


Figure 2: Calculated potential Hydrocarbon Liquid Content of a Russian-type natural gas mixture (0 % H_2), and the same sample with 10 %, 20 % and 50 % H_2 concentrations at 28 bar.

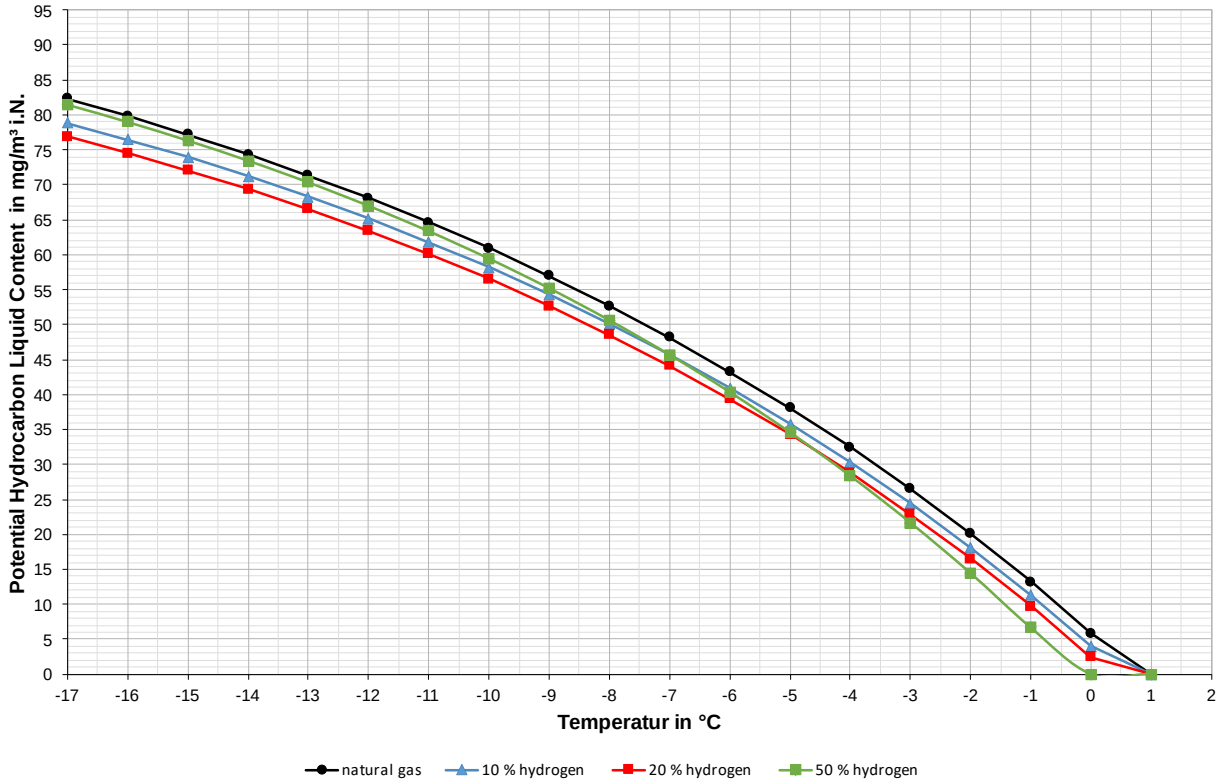


Figure 3: Potential Hydrocarbon Liquid Content of a Russian-type natural gas mixture (0 % H_2), and the same sample with 10 %, 20 % and 50 % H_2 concentrations at a saturation temperature of 0 °C and different separation temperatures (saturated with n-undecane)

The point of intersection with the *x*-axis in Figure 3 gives the hydrocarbon dew point (HCDT). With higher hydrogen contends (>20 % hydrogen) the hydrocarbon dew point (HCDT) decreases.

We can conclude from these comparisons:

- Addition of H_2 results in significant changes in phase behaviour.
- With higher hydrogen contents the phase behaviour changes significantly.
- Solubility of the hydrocarbons decreases with increasing hydrogen content.

These points are relevant for:

- Storage of hydrogen in porous structures (UGS) that are converted from natural gas to hydrogen storages cavities, and depleted gas fields used for gas storage. The decreased solubility of hydrocarbons in H_2-containing gases reduces the processing effort and has an influence on the measurement technology to be used.
- Standardisation in the field of hydrogen transport and measurement
- Pipelines – Single Phase Flow and Solubilisation of condensates in hydrogen or hydrogen/natural gas mixtures.

1.2 Experimental (p, ρ, T) data in two typical natural gas mixtures enriched with H_2 concentrations up to 20 % (FUNGE-UVa)

1.2.1 Introduction

In the course of decarbonization, the infrastructure for natural gas will experience an influx of hydrogen from various sources. Currently, the GERG-2008 equation of state (EoS) (Kunz and Wagner, 2012) serves as the ISO standard (ISO 20765-2) for calculating the thermodynamic properties of natural gas and related mixtures. However, hydrogen is considered a secondary component in the claims of this EoS due to the limited availability of consolidated data for mixtures with hydrogen, which was not a top priority at the time of establishment.

This work reports new experimental density results for three gravimetrically (according to ISO 6142-1) prepared natural gas mixtures with zero, 10 mol-%, and 20 mol-% hydrogen with a high-precision single-sinker densimeter with magnetic suspension coupling.

Some results were disseminated during the GAS ANALYSIS 2022 conference, held in Paris in May 2022, where the natural gas mixture and its blends with hydrogen up to 20 % were presented. The Final MefHySto workshop, held in Berlin in July 2023, and the Hydrogen Colloquium of the Competence Centre H2Safety at BAM held in Berlin in November 2023 offered adequate platforms for presenting all results, including the synthetic natural gas mixture and their blends with hydrogen.

One scientific paper has been submitted to the International Journal of Hydrogen Economy (Elsevier) presenting these results. It is currently under review. Publication has been delayed mainly for the following reasons:

1) Covid lockdowns´ disruptions in previous work, calibration of equipment, planned maintenance, that caused a delay in the planned activities.

2) Repair of Gas Pressure Control System: a malfunction arose with the gas pressure control system in UVa´s single sinker magnetic suspension, which necessitated immediate attention to maintain the reliability and accuracy of the experimental setup. This unforeseen issue involved delays in procuring critical parts, recommissioning the system, and performing new calibrations, ultimately resulting in a 9-month postponement of the planned schedule.

3) Experimental results have been compared with AGA8-DC 92 EoS- and GERG-2008 EoS-based predictions. Fruitful discussions with developers of the latter also caused a delay on preparing the drafts.

1.2.2 Methodology

Three synthetic natural gas mixtures were prepared at the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung, BAM). The batch encompassed BAM catalogue no. G 431 (H_2-free natural gas mixture, BAM cylinder no. 2030-200928), G 453 (H_2-enriched natural gas mixture, G 431 + 10 % H_2, 2036-201115), and G 454 (H_2- enriched natural gas mixture, G 431 + 20 % H_2, 2043-201124). The first mixture, G 431, is an 11-compound mixture that represents a high-calorific natural gas composed mainly of methane (> 97 %). The other two mixtures, G 453 and G 454, are made by dilution of hydrogen into the first one until a nominal composition of 10 and 20 mol-%, respectively. All mixtures were prepared by the gravimetric procedure according to the standard ISO 6142-1 (International Organization for Standardization, 2014), which yields the lowest uncertainty in the composition.

The experimental part of this work was accomplished with a single-sinker magnetic suspension densimeter. It consists of a pressurized diamagnetic CuCrZr cell containing a monocrystalline silicon sinker of calibrated volume (V_s = 226.4440 ± 0.0026 cm^3) surrounded by the sample gas, which buoyancy force is transmitted to an analytical microbalance (XPE205DR, Mettler Toledo GmbH) located above the cell at ambient pressure through a magnetic coupling device to avoid any mechanical friction (Mondéjar, Segovia and Chamorro, 2011; Lozano-Martín, Akubue *et al.*, 2020; Lozano-Martín, Mondejar *et al.*, 2020). This kind of setups is the most accurate to determine the density of a fluid over large range of temperatures and pressures, providing an absolute determination of the density without the need for calibration fluids.

The pressure of the fluid is determined by two quartz crystal transducers, both calibrated in certified facilities at UVa: one for the pressure range from (0 to 2) MPa (Digiquartz 2300A-101, Paroscientific Inc.) and the other for the range between (2 to 20) MPa (Digiquartz 43KR-HHT-101, Paroscientific Inc.). The estimated expanded (k = 2) uncertainty is $U(p)$ = (7.5·10^{-5}(p/MPa) + 4·10^{-3}) MPa for the lower pressure-scale transducer, and $U(p)$ = (6.0·10^{-5} (p/MPa) + 2·10^{-3}) MPa for the higher pressure-scale transducer.

The temperature of the cell, thermostatted by means of a thermal oil bath (Dyneo DD-1000F, Julabo GmbH) and an electrical heating cylinder around the cell connected to a temperature controller (MC-E, Julabo GmbH) is measured by two standard platinum resistance thermometers SPRT-25 (S1059PJ5X6, Minco Products Inc.) using an AC resistance bridge (ASL F700, Automatic Systems Laboratory). The SPRTs were also calibrated in Uva's accredited labs on the ITS-90 temperature scale, the estimated expanded (k = 2) uncertainty is $U(T)$ = 0.015 K.

The overall experimental expanded (k = 2) uncertainty for the three mixtures ranges from 0.029 to 0.078 kg·m^{-3}, i.e., from 0.034 to 0.61 %.

1.2.3 Results and discussion

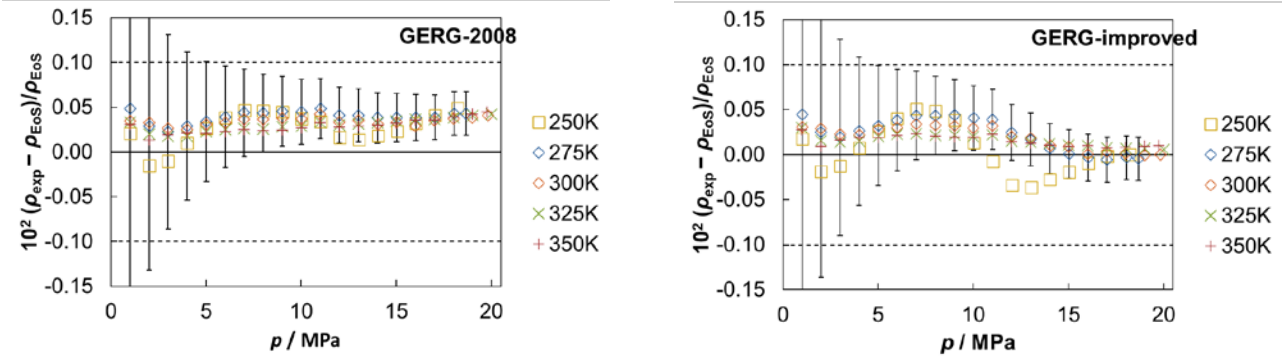


Figure 4: Relative deviations of experimental density ρ_{exp} data of the binary (H_2-free) natural gas mixture G 431 from density values calculated from (a) the GERG-2008 EoS (Kunz and Wagner, 2012); (b) the improved GERG-2008 EoS (Thol *et al.*, 2019; Beckmüller *et al.*, 2021), as a function of pressure from (1 to 20) MPa for different temperatures. Dashed lines indicate the expanded (k = 2) uncertainty of the corresponding EoS. Error bars exemplarily given on the 275 K data set indicate the expanded (k = 2) uncertainty of the experimental density.

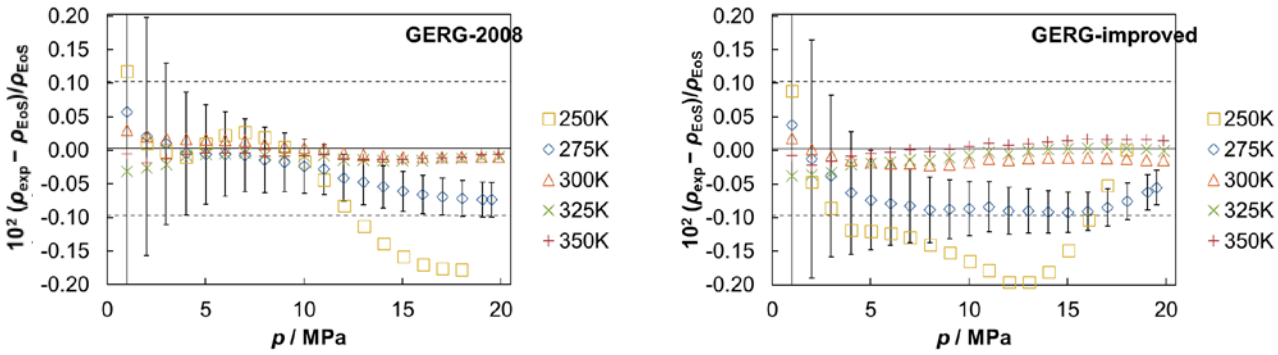


Figure 5: Relative deviations of experimental density ρ_{exp} data of the binary (H_2-enriched) natural gas mixture G 453 (G 431 + 10 % H_2) from density values calculated from (a) the GERG-2008 EoS (Kunz and Wagner, 2012); (b) the improved GERG-2008 EoS (Thol *et al.*, 2019; Beckmüller *et al.*, 2021), as a function of pressure from (1 to 20) MPa for different temperatures. Dashed lines indicate the expanded (k = 2) uncertainty of the corresponding EoS. Error bars exemplarily given on the 275 K data set indicate the expanded (k = 2) uncertainty of the experimental density.

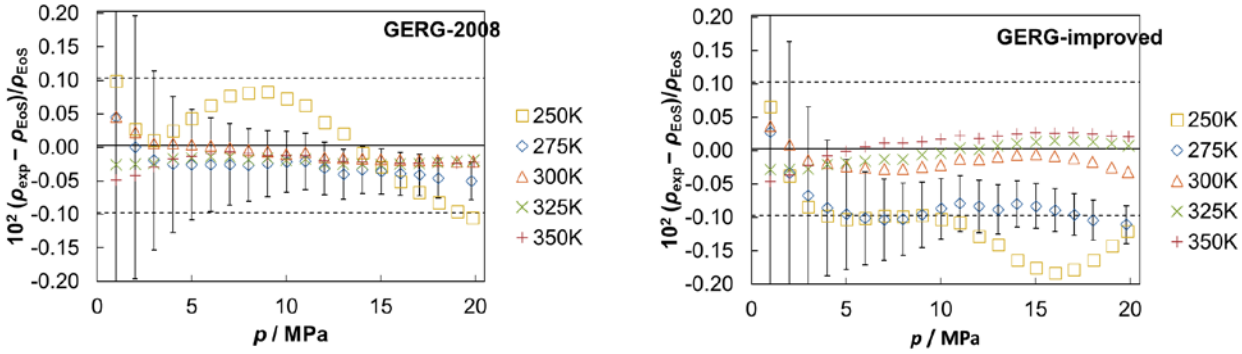


Figure 6: Relative deviations of experimental density ρ_{exp} data of the binary (H_2-enriched) natural gas mixture G 454 (G 431 + 20 % H_2) from density values calculated from (a) the GERG-2008 EoS (Kunz and Wagner, 2012); (b) the improved GERG-2008 EoS (Thol *et al.*, 2019; Beckmüller *et al.*, 2021), as a function of pressure from (1 to 20) MPa for different temperatures. Dashed lines indicate the expanded (k = 2) uncertainty of the corresponding EoS. Error bars exemplarily given on the 275 K data set indicate the expanded (k = 2) uncertainty of the experimental density.

Data comparisons with the Standard Helmholtz Energy Equation of State GERG-2008 (Kunz and Wagner, 2012) and with the improved GERG-2008 Equation of State (Thol *et al.*, 2019; Beckmüller *et al.*, 2021) are shown in Figure 4, Figure 5, and Figure 6. We can conclude from these comparisons:

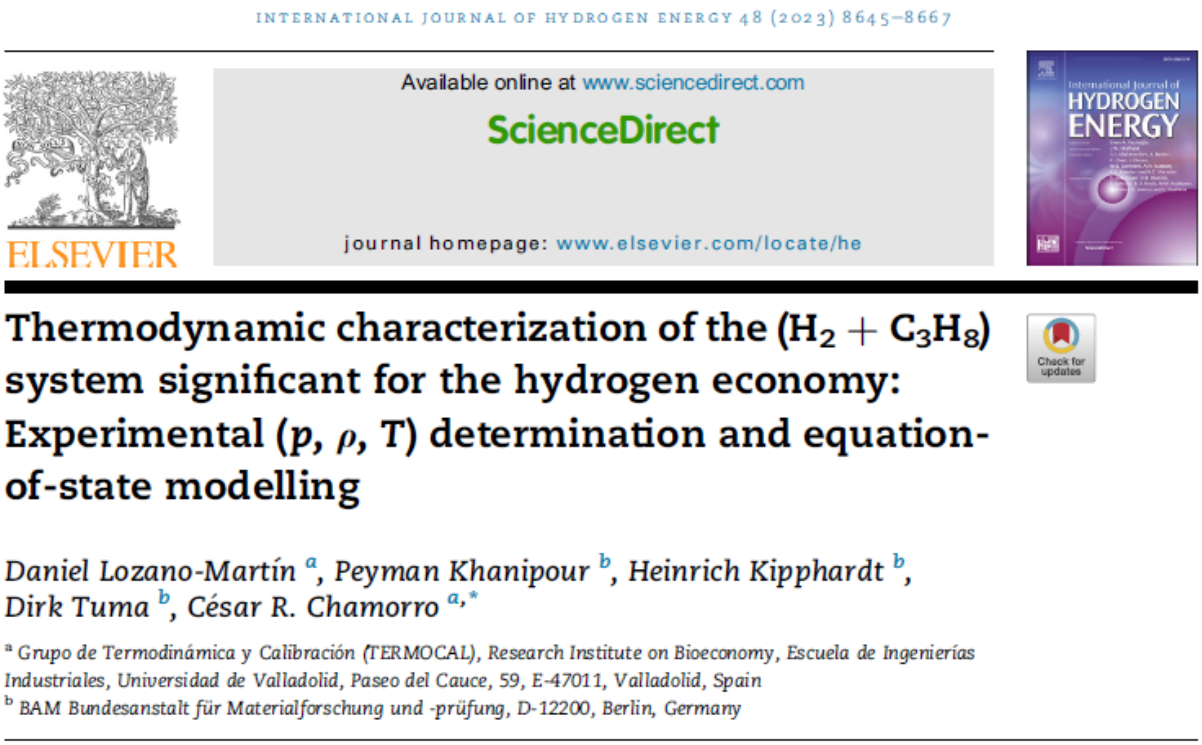
- Addition of H_2 results in a larger deviation.
- Most data are located within the assigned uncertainty boundary for density.
- Deviations are observed for EoS model at the two temperatures close to the phase boundary (i.e., 250 and 275 K).
- Deviations of the H_2-containing mixtures from the zero line are mainly negative.
- The approach "*GERG-improved*" works better than the *classic* GERG-2008 but not for the low temperatures (250 and 275 K).

The conclusions obtained from this study are only valid for natural gas mixtures composed mainly of methane when hydrogen is added up to 20 %. More research is needed to evaluate the performance of these reference EoS for H_2-natural Gas mixtures when the starting natural gas to which hydrogen is added has a different composition and/or the hydrogen added results in a concentration above 20 mol-%.

2 (p, ρ, T) and speed of sound data of three H_2 + C_3H_8 binary gas mixtures. (FUNGE-UVa)

2.1 (p, ρ, T) data of three H_2 + C_3H_8 binary gas mixtures

2.1.1 Introduction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Thermodynamic characterization of the (H_2 + C_3H_8) system significant for the hydrogen economy: Experimental (p, ρ, T) determination and equation-of-state modelling

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Figure 7. Snapshot of the first page of the published peer-reviewed scientific paper (Lozano-Martín *et al.*, 2023) reporting the density of three hydrogen-propane mixtures.

An open access scientific paper was published online the 15th of November 2022 in the International Journal of Hydrogen Energy (Elsevier) (Lozano-Martín *et al.*, 2023).

Hydrogen is a key option towards a decarbonization of the energy systems. However, large quantities of hydrogen at high pressure require to be stored underground in geological formations, where hydrocarbons are present. Therefore, a comprehensive understanding of the thermodynamic properties of H_2 + hydrocarbon blends is crucial for the design, operation, and metrological requirements of processes involving these mixtures.

The published paper reports accurate experimental (p, ρ, T) data for three hydrogen-propane mixtures with nominal compositions (amount of substance, mol/mol) of (0.95 H_2 + 0.05 C_3H_8), (0.90 H_2 + 0.10 C_3H_8), and (0.83 H_2 + 0.17 C_3H_8), at temperatures of (250, 275, 300, 325, 350, and 375) K, and pressures up to 20 MPa. Experimental density data were compared to the densities calculated from two reference equations of state: the GERG-2008 (Kunz and Wagner, 2012) and the AGA8-DC92 (Transmission Measurement Committee, 2017).

The most relevant conclusions are that 1) relative deviations from the GERG-2008 EoS are systematically larger than those from the AGA8-DC92; 2) most deviations are within the ±0.5 % assigned uncertainty boundary with 5 % of propane; 3) but deviations are higher than 0.5 % for the mixtures with 10 % and 17 % of propane, especially at low temperatures and high pressures.

2.1.2 Method

The three (H_2 + C_3H_8) mixtures investigated were prepared at the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung, BAM by the gravimetric procedure according to the standard ISO 6142-1 (International Organization for Standardization, 2014), which yields the lowest uncertainty in the composition.

The experimental part of this work is accomplished with a single-sinker magnetic suspension densimeter. This technique is founded on the Archimedes' principle which relates the buoyancy force experimented by a sinker of known volume submerged in a fluid with the density of this fluid. It is a primary technique, which means that it works without calibration fluids if an independent determination of the mass and volume of the sinker is available. The equipment consists of a pressurized diamagnetic CuCrZr cell containing a monocrystalline silicon sinker of calibrated volume (V_s = 226.4440 ± 0.0026 cm^3) surrounded by the sample gas, which buoyancy force is transmitted to an analytical microbalance (XPE205DR, Mettler Toledo GmbH) located above the cell at ambient pressure through a magnetic coupling device to avoid any mechanical friction (Mondéjar, Segovia and Chamorro, 2011; Lozano-Martín, Akubue, *et al.*, 2020; Lozano-Martín, Mondejar, *et al.*, 2020). This kind of setups are the most accurate to determine the density of a fluid over large range of temperatures and pressures, providing an absolute determination of the density without the need for calibration fluids.

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The temperature of the cell, thermostatted by means of a thermal oil bath (Dyneo DD-1000F, Julabo GmbH) and an electrical heating cylinder around the cell connected to a temperature controller (MC-E, Julabo GmbH) is measured by two standard platinum resistance thermometers SPRT-25 (S1059PJ5X6, Minco Products Inc.) using an AC resistance bridge (ASL F700, Automatic Systems Laboratory). The SPRTs were also calibrated in UVa's accredited labs on the ITS-90 temperature scale, the estimated expanded (k = 2) uncertainty is $U(T)$ = 0.015 K.

The overall experimental relative expanded (k = 2) uncertainty for the three mixtures ranges from 0.11 % for the (0.90 H_2 + 0.10 C_3H_8) mixture at the highest experimental density up to 1.7 % for the (0.95 H_2 + 0.05 C_3H_8) at the lowest measured density.

2.1.3 Results and Discussion

The densities of the experimental points determined in this study span from ρ = 1.316 kg m^{-3} (T = 375 K, p = 1 MPa, x_{H2} = 0.95) up to ρ = 45.006 kg m^{-3} (T = 300 K, p = 20 MPa, x_{H2} = 0.90). Data comparisons with the Standard Helmholtz Energy Equation of State GERG-2008 (Kunz and Wagner, 2012) are shown in Figure 8, Figure 9, and Figure 10.

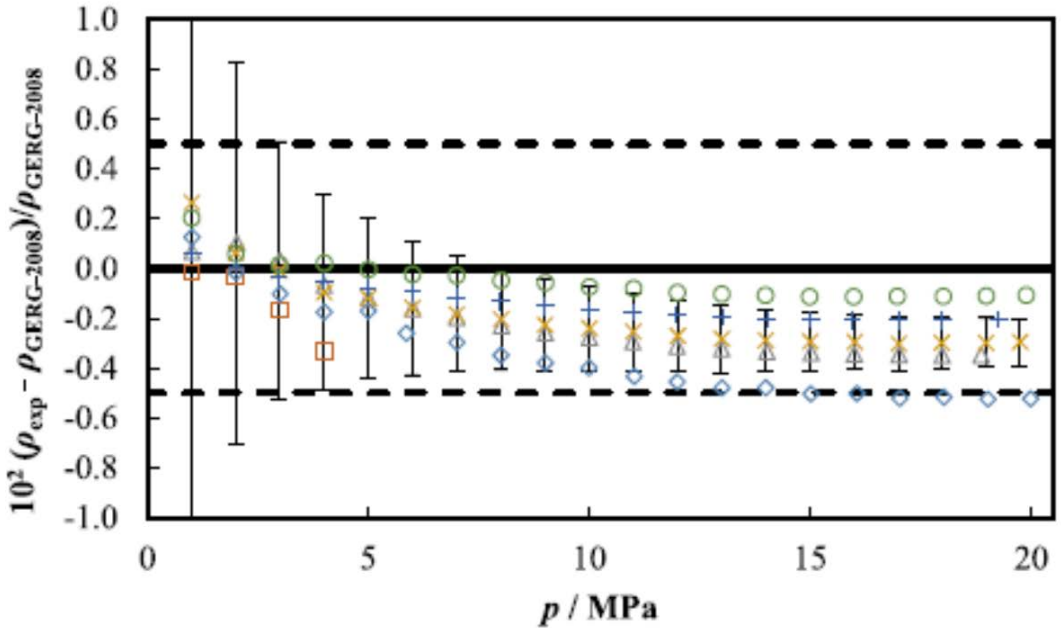


Figure 8. Relative deviations of experimental density ρ_{exp} data of the binary (0.95 H_2 + 0.05 C_3H_8) mixture from density values calculated from the GERG-2008 (Kunz and Wagner, 2012) as a function of pressure from (1 to 20) MPa for different temperatures of (□ 250 K, ◇ 275 K, Δ 300 K, × 325 K, + 350 K, ○ 375 K). Dashed lines indicate the expanded (k = 2) uncertainty of the corresponding EoS. Error bars exemplarily given on the 325-K data set indicate the expanded (k = 2) uncertainty of the experimental density.

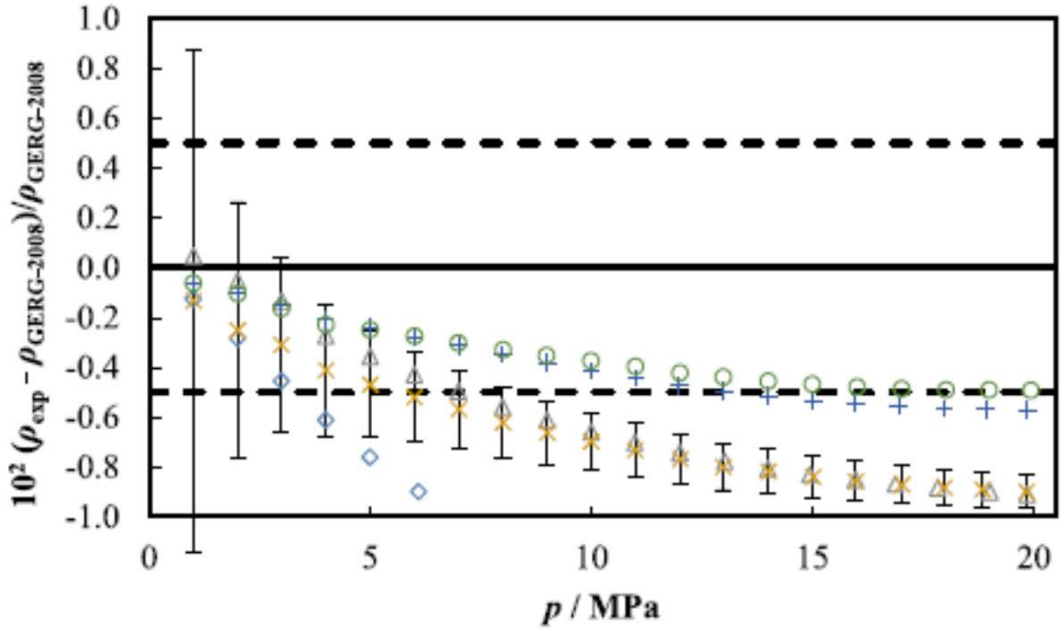


Figure 9. Relative deviations of experimental density ρ_{exp} data of the binary (0.90 H_2 + 0.10 C_3H_8) mixture from density values calculated from the GERG-2008 (Kunz and Wagner, 2012) as a function of pressure from (1 to 20) MPa for different temperatures of (□ 250 K, ◇ 275 K, Δ 300 K, × 325 K, + 350 K, ○ 375 K). Dashed lines indicate the expanded (k = 2) uncertainty of the corresponding EoS. Error bars exemplarily given on the 325-K data set indicate the expanded (k = 2) uncertainty of the experimental density.

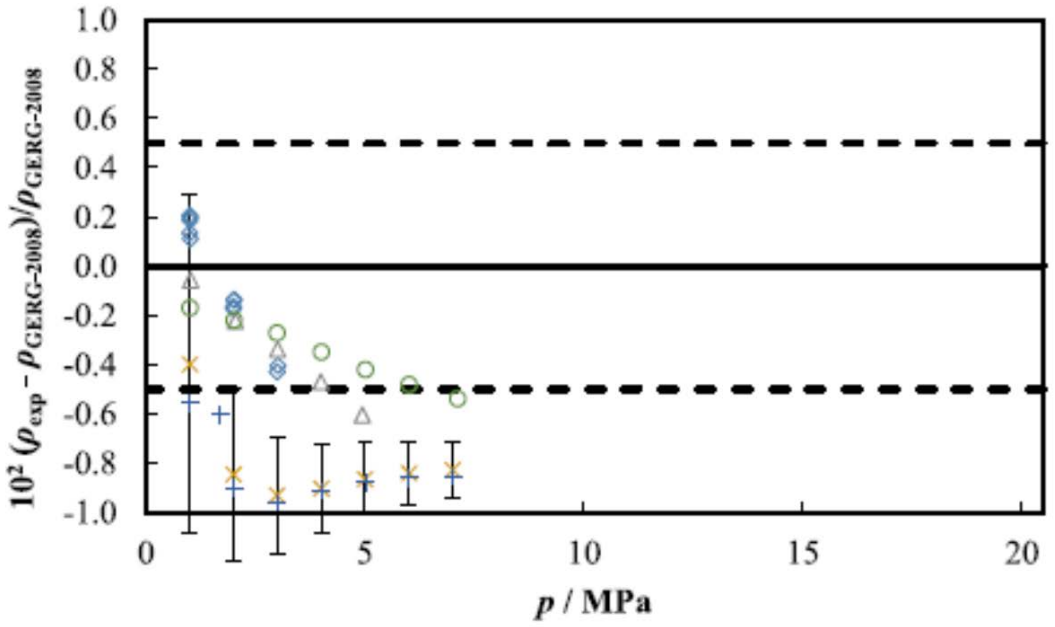


Figure 10. Relative deviations of experimental density ρ_{exp} data of the binary (0.83 H_2 + 0.17 C_3H_8) mixture from density values calculated from the GERG-2008 (Kunz and Wagner, 2012) as a function of pressure from (1 to 20) MPa for different temperatures of (□ 250 K, ◇ 275 K, Δ 300 K, × 325 K, + 350 K, ○ 375 K). Dashed lines indicate the expanded (k = 2) uncertainty of the corresponding EoS. Error bars exemplarily given on the 325-K data set indicate the expanded (k = 2) uncertainty of the experimental density.

The relative deviations tend to increase with the pressure, as well as with the propane content, in all the cases investigated. On the contrary, the higher the temperature, the better becomes the agreement with the model. Most deviations are within the ±0.5 % assigned uncertainty boundary with 5% of propane, but deviations are higher than 0.5 % for the mixtures with 10% and 17% of propane, especially at low temperatures and high pressures.

The sets of new experimental data have also been processed by the application of two different statistical equations of state: the virial equation of state, and the PC-SAFT equation of state, respectively.

2.2 Speed of sound data of three H_2 + C_3H_8 binary gas mixtures

2.2.1 Introduction

The introduction of hydrogen into the existing natural gas grid is a practical alternative for the transport and storage of energy produced from the surplus electricity of renewable sources, such as wind, solar and hydraulic power. Hydrogen is regarded a key option towards a decarbonization of the energy systems. However, large quantities of hydrogen at high pressure require to be stored underground in geological formations, where hydrocarbons are present. Therefore, a comprehensive understanding of the thermodynamic properties of H_2 + hydrocarbon blends is crucial for the design, operation, and metrological requirements of processes involving these mixtures. Speed of sound is a caloric thermodynamic property that can be measured with high precision in gases deploying steady-state acoustic techniques as the one used here. This property enables the validation and/or

improvement of the Equations of State in a wide range of thermodynamic states with very low uncertainty.

This work gathered accurate experimental speed of sound data for three hydrogen-propane mixtures with nominal compositions (amount of substance, mol/mol) of (0.95 H_2 + 0.05 C_3H_8), (0.90 H_2 + 0.10 C_3H_8), and (0.83 H_2 + 0.17 C_3H_8), at temperatures of (273.16, 300, 325, and 350) K and pressures up to 20 MPa. The experimental speed of sound data were compared to those calculated from three reference equations of state: the GERG-2008 (Kunz and Wagner, 2012), the improved GERG-2008 Equation of State (Thol *et al.*, 2019; Beckmüller *et al.*, 2021), and the AGA8-DC92 Equation of State (Transmission Measurement Committee, 2017).

The results have been disseminated during the European Conference of Thermophysical Properties ECTP 2023 conference, held in Venice in September 2023. It offered the adequate platform for presenting these results.

Although all measurements and data analysis are completed, the publishing of the scientific paper has been delayed mainly for the following reasons:

1) Disruptions caused by Covid-19 lockdowns in previous work, equipment calibration, and planned maintenance resulted in a delay in the planned activities.

2) Hydrogen permeation presented a challenging experimental obstacle due to the high diffusivity of the gas through all materials compared to propane. Consequently, the concentration of propane inside the resonator increased over time. Since the rig's thermostat is adiabatic, and the resonator material is stainless steel with low thermal conductivity, the thermal equilibrium time needed to measure the speed of sound is no shorter than 10 hours after a pressure change during an isotherm set of measurements. This time is sufficient to noticeably change the composition inside the high-sensitivity, low-uncertainty acoustic resonator, invalidating the constant concentration condition. This obstacle was overcome by repeating every speed of sound measurement twice after a few hours, with the duration increasing as the temperature decreases. The permeated amount of hydrogen was linear with time at the same thermodynamic state. Hence, the speed of sound could be extrapolated to the same time origin when the composition was constant. This correct approach implied a one-and-a-half times longer extension of the planned time to finish the activity in accordance with the Gantt Chart.

3) Repair of both acoustic transducers, due to the high velocities (i.e., high frequencies required), which in turn imposed higher stresses on them, necessitating immediate attention to maintain the reliability and accuracy of the experimental setup. Due to the extended measuring time caused by the employed strategy to deal with hydrogen permeation, repairs and maintenance shifts of those acoustic transducers had to happen twice, resulted in an additional two months. This unforeseen issue involved delays in procuring critical parts, recommissioning the system, and performing new calibrations, ultimately resulting in a 9-month postponement of the planned schedule.

All these three reasons brought the end of the activity A2.3.3 almost to the end of the project.

2.2.2 Method

The three (H_2 + C_3H_8) mixtures investigated were prepared at the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung, BAM by the gravimetric procedure according to the standard ISO 6142-1 (International Organization for Standardization, 2014), which yields the lowest uncertainty in the composition.

The speed of sound was measured using a spherical stainless-steel acoustic resonator designed for measurements of pure gases and their mixtures (Pérez-Sanz *et al.*, 2014; Lozano-Martín *et al.*, 2021; Segovia *et al.*, 2022, 2024). The resonator is a spherical cavity of a nominal internal radius of 40 mm made of grade 321 austenitic stainless steel. It consists of two aligned hemispheres welded by electron beam. There are two transducers located in the northern hemisphere forming an angle of 90º, which play the roles of source and detector. These transducers are capacitors made of two conductive surfaces (steel and a gold layer) separated by a dielectric polyimide membrane. When the electrical signal is supplied to one of these transducers, using a wave generator, the membrane is induced to vibrate. The acoustic pressure vibrations impact the membrane of the detector transducer and the electrical signal produced is pre-amplified and supplied to a lock-in amplifier.

The acoustic cavity is contained within a stainless-steel vacuum vessel, which in turn is submerged in an ethanol-containing Dewar cooled by a thermal bath (FP89-ME, Julabo). The thermal control of the vessel at the desired set point is achieved by three temperature loops encompassing band resistors and 25 Ω Standard Platinum Resistance Thermometers (SPRTs). The latter are located at the base and side of the vessel and at the top copper block from which the acoustic cavity is suspended. The thermal gradient between hemispheres is not worse than 1 mK, with an achievable better temperature stability. Two Standard Platinum Resistance Thermometers (25.5 Ω SPRT 162D, Rosemount) calibrated on the ITS-90 and located in the north and south hemispheres are plugged into an AC resistance bridge (F18 automatic bridge, ASL) to measure the temperature of the gas inside with an expanded (k = 2) uncertainty from calibration of $U(T)$ = 4 mK.

The pressure inside of the resonant shell is gauged by two piezoelectric quartz transducers located at the top of the inlet gas tube: one calibrated for the pressure range (0 to 2) MPa, (2003A-101-CE, Paroscientific Digiquartz); and the other for the pressure range (2 to 20) MPa, (43KR-101-CE, Paroscientific Digiquartz). The expanded (k = 2) uncertainty from their calibration is estimated to be $U(p) = (8 \cdot 10^{-5}\ (p/\text{Pa}) + 200)$ Pa, and the pressure readings are corrected considering the hydrostatic column of the gas.

The overall relative expanded (k = 2) uncertainty of the speed of sound $U_r(w_{exp})$ equal to 250 parts in 10^6 (0.025 %).

2.2.3 Results and Discussion

For the four isotherms T = (273.16, 300, 325, and 350) K and at pressures between p = (0.25 up to 10) MPa, the speed of sound data have been calculated for three binary (H_2 + C_3H_8) mixtures with nominal hydrogen mole fractions $x(H_2)$ = (0.95, 0.90 and 0.83), considering the first two (0,2) and (0,3) radial acoustic modes. Results of the richest hydrogen blend (0.95 H_2 + 0.05 C_3H_8) are shown in Figure 11.

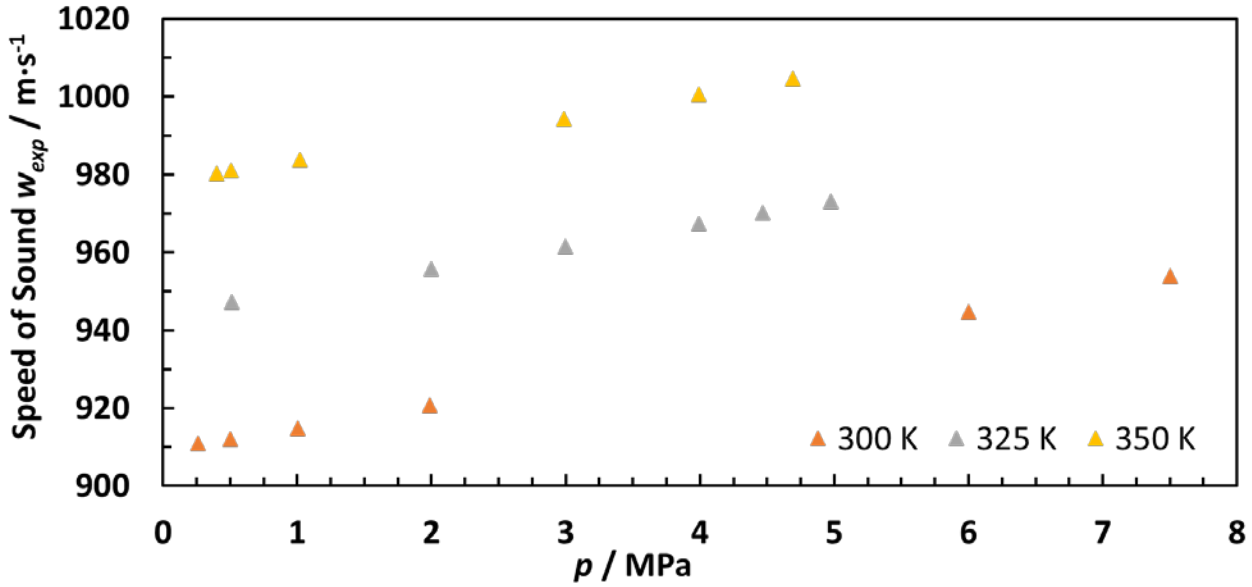


Figure 11. Experimental speed of sound data of the binary (0.95 H_2 + 0.05 C_3H_8) mixture as a function of pressure from (1 to 8) MPa for different temperatures.

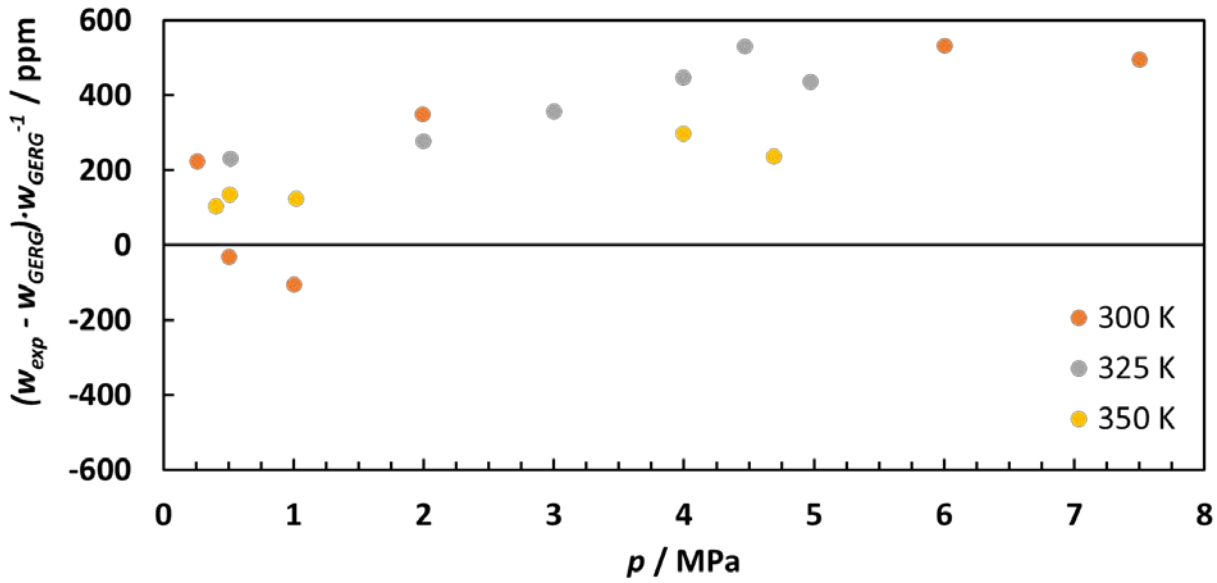


Figure 12. Relative deviations of experimental speed of sound data of the binary (0.95 H_2 + 0.05 C_3H_8) mixture from density values calculated from the GERG-2008 (Kunz and Wagner, 2012) as a function of pressure from (1 to 8) MPa for different temperatures.

The relative deviations shown in Figure 12 tend to increase with the pressure in all the cases investigated. Most deviations are within the ±0.5 % (5000 ppm) assigned uncertainty boundary with 5 % of propane.

3 (p, ρ, T) and speed of sound data of three H_2 + CO binary gas mixtures. (FUNGE-UVa)

This activity was included in Task 2.3, which aimed to contribute to the improvement of the current reference equation of state (EoS) and/or the development of new ones by determining the experimental thermodynamic properties of selected binary mixtures. These mixtures were chosen following a literature review and consultation with stakeholders.

The first selection was a (H_2 + C_3H_8) mixture –set C– of cylinders-. Both density and speed of sound measurements were executed and discussed (see Section 2 above).

The second set of cylinders –set D– targeted (H_2 + CO) mixtures with mole fractions of H_2 of 0.90, 0.75, and 0.60. This selection was based on the identification of this system as having the most limited available experimental data among the H_2 + (CH_4, CO_2, N_2, and CO) binary mixtures. While a binary-specific equation of state explicit in Helmholtz energy was recently presented for this system (Beckmüller *et al.*, 2021), the authors concluded that the (H_2 + CO) system required more accurate data within single-phase regions. Only a few density data points (Townend and Bhatt, 1931) were used to fit a departure function, and only one speed of sound data set (van Itterbeek and van Doninck, 1949) was found for validation purposes.

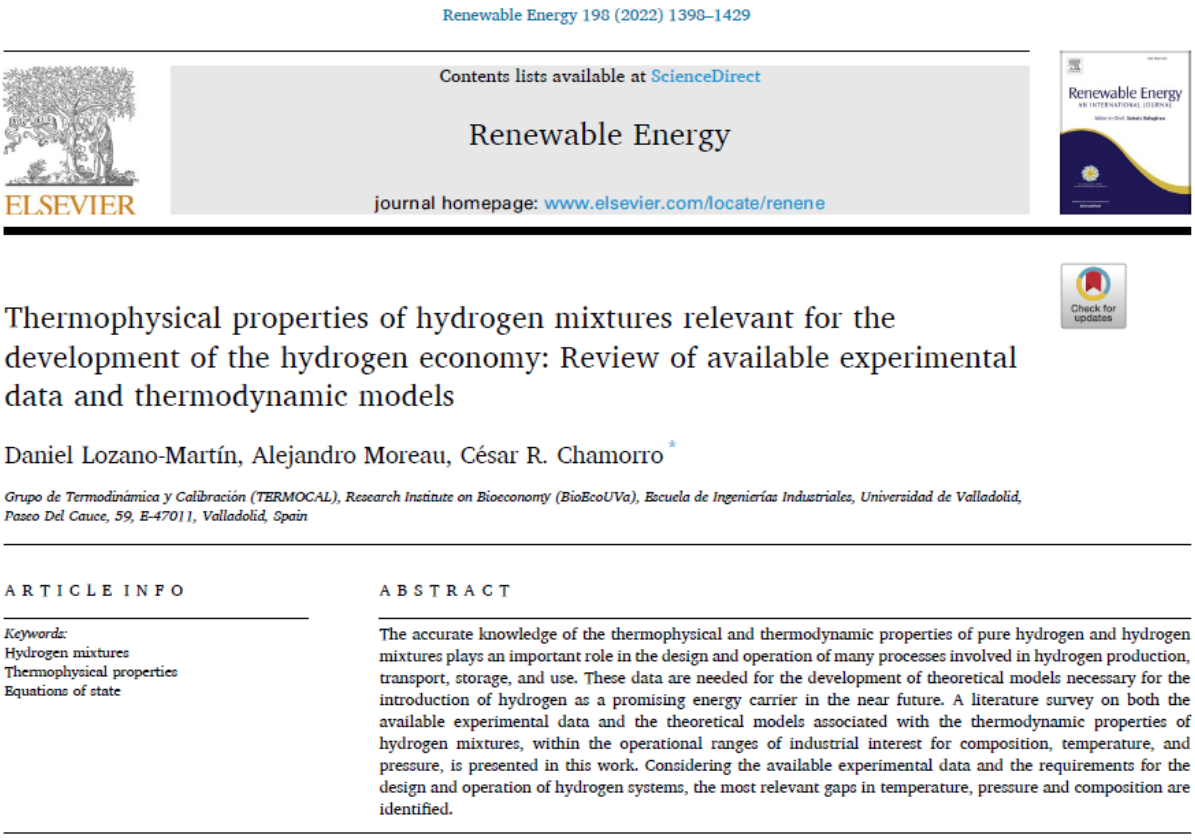
These limitations prompted the WP2 team to select the (H_2 + CO) binary system. However, density measurements proved to be particularly challenging from the onset of the campaign. Issues with repeatability and unexpected density values with deviating trends over time suggested changes in gas composition that could not be explained by adsorption, permeation, or degassing. A potential explanation might lie in an unintended Mond process or carbonyl method (Richter, 2023), where Nickel exposed to pure CO at temperatures between (50–60) ºC reacts to form the toxic gas nickel tetracarbonyl $Ni(CO)_4$ (Morrison *et al.*, 2018) within the equipment. This, in turn, could alter the composition and density of the gas mixtures within the measuring cell. Notably, parts of the apparatus are made of austenitic stainless steel 316L, which contains significant amounts of nickel (10–14) % (American Iron and Steel Institute, 1976). This unforeseen behaviour necessitated methodological changes beyond the scope of this project, ultimately preventing the measurement of the (H_2 + CO) system under the project's conditions.

Speed of sound measurements of the three (H_2 + CO) mixtures were not measured during the time of the project due to delays described in Heading 2.2.1. In light of the aforementioned Mond process and the complete lack of speed of sound data at the studied temperatures, we can hypothesize that these measurements might also have proven challenging or even insurmountable.

4 Thermophysical properties of hydrogen mixtures relevant for the development of the hydrogen economy: a review. (FUNGE-UVa)

4.1 Introduction

Considering the impact of Covid-19 lockdown during the measuring campaign and the unforeseen delays described previously, the FUNGE-UVa team decided to contribute to the main objectives and impact of WP2 by publishing a review of all available experimental data and models related with the thermophysical properties of H_2 mixtures (Lozano-Martín, Moreau and Chamorro, 2022). It is an open-access paper was published online the 24th of August 2022 in Renewable Energy (Elsevier).



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Thermophysical properties of hydrogen mixtures relevant for the development of the hydrogen economy: Review of available experimental data and thermodynamic models

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ABSTRACT

The accurate knowledge of the thermophysical and thermodynamic properties of pure hydrogen and hydrogen mixtures plays an important role in the design and operation of many processes involved in hydrogen production, transport, storage, and use. These data are needed for the development of theoretical models necessary for the introduction of hydrogen as a promising energy carrier in the near future. A literature survey on both the available experimental data and the theoretical models associated with the thermodynamic properties of hydrogen mixtures, within the operational ranges of industrial interest for composition, temperature, and pressure, is presented in this work. Considering the available experimental data and the requirements for the design and operation of hydrogen systems, the most relevant gaps in temperature, pressure and composition are identified.

Figure 13. Snapshot of the first page of the published peer-reviewed scientific paper (Lozano-Martín, Moreau and Chamorro, 2022) reviewing literature thermophysical properties of H_2 mixtures.

4.2 Method

The work presents a review of both the experimental data and models for the thermodynamic properties of hydrogen mixtures needed in industry and by the energy sector for the development of the hydrogen economy. The components of the studied mixtures were selected from among the main components involved in the processes to obtain, transport and use hydrogen with current and

foreseeable technologies. The paper is focused on VLE, density, speed of sound and other caloric properties of binary hydrogen mixtures, as these constitute the main experimental data needed for the improvement of existing reference equations of state and the development of new ones. Phase equilibrium data are limited to VLE data. Liquid-liquid, solid-liquid, or solid-vapor equilibrium data are not considered in this review. The purpose of the work was to summarize the available experimental data and theoretical models, to evaluate their quality, and to identify knowledge gaps, providing suggestions for future research into H_2 mixtures. 176 references were studied to compile this review.

4.3 Results and discussion

The current reference equation of state for hydrogen was proposed in 2009 (Leachman *et al.*, 2009). The equation of state is explicit in the Helmholtz free energy, with 14 terms, and is valid for temperatures from the triple point (13.957 K) to 1000 K and for pressures up to 2000 MPa. Another important equation of state for hydrogen, with reference quality, was developed in 2000 (Klimeck, 2000) specifically designed for the development of the multicomponent GERG-2008 equation of state (Kunz and Wagner, 2012). This equation of state was developed by using multi-property fitting and optimization methods. It has an individually optimized structure with 14 terms. This equation is valid for temperatures of (14 to 700) K and pressures up to 300 MPa.

Only the methane + hydrogen binary system, of the 20 possible binary mixtures of hydrogen with the rest of the components considered (Kunz and Wagner, 2012), has a binary specific departure function included in the current GERG-2008 EoS. A recent study (Beckmüller *et al.*, 2021) has developed four equations of state for the binary systems of hydrogen with methane, nitrogen, carbon dioxide, and carbon monoxide. Nevertheless, the authors recognized that new highly accurate data for these systems are still required for further improvements and a more comprehensive validation, especially for the binary system hydrogen + carbon monoxide. For the rest of the binary systems, the amount of experimental data available is very limited and of disputed quality. New experimental data will enable the development of new generalized departure functions and reducing functions of the mixture density and temperature, dependent on the composition, for several H_2 binary mixtures.

There is a real need for density and speed of sound data for the binary systems of hydrogen with water, hydrogen sulphide, helium, and argon, as well as all the linear hydrocarbons from ethane to decane, including iso-butane and iso-pentane. Accurate prediction of the fluid-liquid phase equilibrium and dew point calculations for mixtures, including heavier hydrocarbons and hydrogen, is crucial as well.

Besides the experimental data of binary mixtures, which are relevant for the development of new equations of state, it is also important to check the capability of the current or newly developed EoS with multicomponent mixtures containing hydrogen. In this sense, it is important to determine the density, speed of sound or phase equilibrium properties of ternary or multicomponent mixtures containing hydrogen.

It is necessary to obtain high-quality experimental data of binary mixtures of hydrogen with other components at high pressures (over 70 MPa) or at very low temperatures (below 20 K), respectively.

Studying the effect of traces and small amounts of impurities in the behaviour of pure hydrogen or hydrogen mixture is also needed.

5 Conclusions

Two scientific papers have been published in peer-reviewed journals, and a third one is currently under revision. Two additional papers are under preparation, with a short-term submission time scheduled. However, characterizing one particular binary system, namely (H_2 + CO), was deemed impossible within the scope of the project due to inherent challenges linked to the nature of the mixture.

Addition of H_2 results in significant changes in the phase behaviour of H_2 + natural gas blends. The solubility of hydrocarbons decreases with increasing hydrogen content, reducing the processing effort of hydrogen withdrawal from underground geological storage of hydrogen. Phase behaviour and condensation studies of H_2-enriched natural gas mixtures were completed. A manuscript reporting the data is under preparation.

Experimental density data were measured for three H_2-enriched synthetic natural gas mixtures with H_2 concentration up to 20 % in a range of temperatures and pressures representative of the transport of such blends in the gas network. Deviations with the Standard Helmholtz Energy Equation of State (GERG-2008) increase with H_2 concentration. These deviations are significant at lower temperatures. These results prompted to further studies at temperatures close to the phase boundary of those mixtures. A scientific paper detailing these investigations is currently under review by a peer-reviewed scientific journal. Additionally, these results have been disseminated at an International Conference and at the final workshop of the MefHySto Project.

Accurate experimental density data for three hydrogen-propane mixtures in a range of temperatures and pressures representative of the transport of such blends in the gas network were published in the International Journal of Hydrogen Energy. The relative deviations with the Standard Helmholtz Energy Equation of State (GERG-2008) tend to increase with the pressure, as well as with the propane content, in all the cases investigated. On the contrary, the higher the temperature, the better becomes the agreement with the model. Most deviations are within the ±0.5 % assigned uncertainty boundary with 5 % of propane; but deviations are higher than 0.5 % for the mixtures with higher concentration of propane, especially at low temperatures and high pressures. The speed of sound of these mixtures has also been measured. Publication was delayed by Covid-19 related lockdown disruption, hydrogen permeation through the rig materials, and more frequent maintenance shutdowns of the acoustic transducers caused by the high speeds of sound in H_2-enriched gas mixtures.

A paper published in Renewable Energy reviews all available experimental data and models related to the thermophysical properties of H_2 mixtures. There is a real need for density and speed of sound data for the binary systems of hydrogen with water, hydrogen sulphide, helium, and argon, as well as all the linear hydrocarbons from ethane to decane, including iso-butane and iso-pentane. Accurate prediction of the fluid-liquid phase equilibrium and dew point calculations for mixtures, including heavier hydrocarbons and hydrogen, is crucial as well.

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