# Advanced thermodynamics of hydrogen and natural gas blends for gas transmission and distribution networks

## ARTICLE INFO

## ABSTRACT

The cubic, multiparameter and saft based equations of state (Peng-Robinson, AGA8, GERG-2008 and PC-SAFT) were used to predict thermo-physical properties of $H_2$-mixed with $N_2$, $CO_2$, $C_1$-$C_4$ as a $H_2$-enriched natural gas blend. The experimental data covers a range of 10–200 bara and temperatures 15 °C, 25 °C, and 45 °C with high accuracy and precision. These data were measured with the UK's unique hydrogen thermodynamic test rig situated at the TÜV SÜD National Engineering Laboratory (hereby referred to as NEL).

Based on our research, it has been determined that, under the mentioned experimental conditions, the AGA8 and GERG-2008 have the capability to predict thermophysical properties of $H_2$-enriched natural gas, and the Peng-Robinson can be used to predict with good accuracy the values of density and speed of sound of this complex mixture without attempting to tune binary interaction parameters. Although, PC-SAFT is preferable for the modelling of associating compounds, it showed acceptable and reliable results for $H_2$ containing mixtures as well.

## 1. Introduction

Recently, there has been a rapid advancement in energy transition technology to facilitate the reduction of carbon emissions across several industries. This is done to meet important targets outlined in the Paris Agreement, regional policies, and corporate sustainability targets [1]. Hydrogen ($H_2$) research has the potential to significantly impact sustainability, technological innovation, and social well-being from an energy infrastructure perspective.

The integration of $H_2$ into the natural gas (NG) system has been investigated in many recent projects as a potentially economical and environmentally friendly energy source [2]. The utilisation of $H_2$ as an alternative to fossil fuels, which compose a significant portion of global energy consumption, presents an environmentally advantageous alternative for mitigating $CO_2$ emissions. Substituting $H_2$ with fossil fuels can enhance air quality. In other words, this substitution will cause the reduction of sulphur dioxide ($SO_2$), nitrogen oxide ($NO_x$), and volatile organic compounds (VOCs) [3].

With the worldwide transition towards sustainable energy resources, the delivery of $H_2$ natural gas mixtures to consumers necessitates the presence of transportation infrastructure and facilities to ensure the secure and reliable distribution of $H_2$ from power plants to residential and industrial gas network grids. Therefore, this has significant implications for research on $H_2$ flow assurance.

Therefore, it is important to accurately estimate the thermodynamic and transport properties of $H_2$ when it is mixed with additional components from the natural gas system, which is necessary for designing efficient system operations. The thermophysical properties of $H_2$-enriched NG mixtures during transportation differ from those of pure NG mixtures, and these variances are influenced by factors such as density variations and changes in the speed of sound.

There is an urgent need for experimental data across an extensive range of temperature and pressure conditions in order to conduct a complete investigation into the thermodynamic modeling of $H_2$/NG mixtures. The lack of comprehensive data is a substantial challenge in evaluating and analysing the effectiveness and reliability of equation of state modeling in forecasting the thermophysical properties of fluids [3–5]. To evaluate equations of state (EoSs) used for $H_2$ application, such as cubic, multiparameter, and saft-based models, it is necessary to utilise experimental data from $H_2$/NG mixtures that are relevant to the gas transmission and distribution networks not only in the UK but also globally.

One of the most challenging aspects of modeling the transportation of $H_2$-mixtures is the successful utilisation of an EoS, which depends on multiple variables such as the range of components present, computational capacity, range of validity (in terms of pressure, temperature, and phase), and modelling preciseness for specific thermophysical properties. Several authors have published a comprehensive study of observations and modeling pertaining to the thermophysical properties of mixtures containing $H_2$ [6–8]. Currently, there is no thermodynamic model that can accurately forecast the properties of $H_2$-enriched fluids across the whole transportation and utilisation chain. This is because there is a trade-off between these variables for each EoS. This paper further investigates this challenge and presents some new experimental and thermodynamic modelling datasets.

## 2. Experimental and theoretical methods

In order to effectively develop and manage the technical processes within the gas-based energy industry, it is imperative to accurately depict the thermodynamic properties by assessing precise EoSs. The study utilised widely recognised equations of state, such as Peng-Robinson

**Table 1**

Molar composition of H₂-enriched natural gas used in this study.

| Component | CAS Number | Mole fraction |
|---|---|---|
| $H_2$ | 1333-74-0 | 0.05 |
| $N_2$ | 7727-37-9 | 0.01425 |
| $CO_2$ | 124-38-9 | 0.019 |
| $CH_4$ | 74-82-8 | 0.836 |
| $C_2H_6$ | 74-84-0 | 0.057 |
| $C_3H_8$ | 74-98-6 | 0.019 |
| n-$C_4H_{10}$ | 106-97-8 | 0.00285 |
| Iso-$C_4H_{10}$ | 75-28-5 | 0.0019 |

(PR) [9], GERG-2008 [10], AGA8 [11], and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) [12], to calculate the density and sound speed of a NG blend with addition of $H_2$ into the stream. The AGA8 and GERG-2008 models are specifically relevant for $H_2$ applications.

### 2.1. Experimental method

Density and speed of sound datasets of the $H_2$ containing gas mixture combined with nitrogen, carbon dioxide, methane, ethane, propane, n-butane and iso-butane which can be considered as a typical natural gas are provided for pressures between 10 and 200 bara and temperatures between 15 °C–45 °C and mole fractions described in Table 1.

A novel thermophysical properties test rig was deployed for the first time at the National Engineering Laboratory to precisely determine speed of sound and density in high pressure condition. In this specific study herein, the relative expanded uncertainties in experimental datasets (k = 2) $U$(exp) for the studied hydrogen/natural gas blends are within the range of $0.01 \leq U(exp) \leq 0.03$.

### 2.2. Equation of state modelling

The validity of GERG-2008 extends throughout a wide range of pressures and temperatures, encompassing 21 gas components. This includes the components that are the focus of this investigation, as indicated in Table 1.

The modelled thermodynamic properties of the fluids at specific temperatures (T) are determined using a multi-fluid approximation that incorporates the reduced residual Helmholtz energy derived from:

$$\frac{a(\rho, T, x)}{RT} = \widetilde{a}(\delta, \tau, x) = \widetilde{a}^{ig}(\rho, T, x) + \widetilde{a}^{res}(\delta, \tau, x). \tag{1}$$

Where $\widetilde{a}^{res}$ is reduced residual Helmholtz free energy and $\widetilde{a}^{ig}$ is related to ideal-gas contribution, $\rho$ is the mixture density, $T$ is the temperature, $x$ is the molar composition, $\tau$ is the inverse reduced temperature, and $\delta$ is the reduced density.

Other thermodynamic properties can be achieved analytically from terms $\widetilde{a}^{ig}$ and $\widetilde{a}^{res}$ and their derivatives. The GERG-2008 EoS use the quadratic mixing rules proposed by Klimeck [13] to determine terms $\rho_r$ and $T_r$:

$$\frac{1}{\rho_r(x)} = \sum_{i=1}^{N} \frac{x_i^2}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{2x_i x_j}{\rho_{c,ij}} \tag{2}$$

$$T_r(x) = \sum_{i=1}^{N} x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j T_{c,ij} \tag{3}$$

Where $\rho_{c,i}$ is the critical density and $T_{c,i}$ is the critical temperature for component $i$. The terms $\rho_{c,ij}$ and $T_{c,ij}$ are calculated by using some adjustable binary interaction parameters. More information has been given in Ref. [10].

Overall, to use GERG-2008, it is needed to have the values of some important parameters as specified in Table 2 where these values were

**Table 2**

Fluid GERG-2008 model parameters between components in binary condition used in this study [10].

| Component (i-j pair) | BetaT | GammaT | $F_{ij}$ | BetaV | GammaV |
|---|---|---|---|---|---|
| $H_2$-$IC_4$[a] | 1.0 | 1.8953 | 0.0 | 1.0 | 1.1476 |
| $H_2$-$NC_4$[a] | 1.0 | 2.5093 | 0.0 | 1.0 | 1.2329 |
| $H_2$-$N_2$[a] | 1.0569 | 1.1757 | 0.0 | 1.0282 | 0.97012 |
| $H_2$-$CO_2$[a] | 1.0612 | 1.7829 | 0.0 | 1.106 | 1.1528 |
| $H_2$-$C_3$[a] | 1.0 | 2.3082 | 0.0 | 1.0 | 1.074 |
| $H_2$-$C_2$[a] | 1.0718 | 1.902 | 0.0 | 1.1 | 1.1061 |
| $H_2$-$CH_4$[b] | 1.0 | 1.3526 | 1.0 | 1.0 | 1.0187 |
| $IC_4$-$NC_4$[a] | 0.99992 | 1.0014 | −0.055124 | 0.99912 | 1.0004 |
| $IC_4$-$N_2$[a] | 0.99287 | 1.2845 | 0.0 | 0.98642 | 1.1006 |
| $IC_4$-$CO_2$[a] | 1.0233 | 0.92998 | 0.0 | 1.0766 | 1.0819 |
| $IC_4$-$C_3$[a] | 0.99801 | 1.0053 | −0.055161 | 0.99924 | 1.0012 |
| $IC_4$-$C_2$[a] | 1.0 | 1.0333 | 0.26063 | 1.0 | 1.0066 |
| $IC_4$-$CH_4$[a] | 0.98032 | 1.1611 | 0.77104 | 1.0112 | 1.0543 |
| $C_4$-$N_2$[a] | 0.99452 | 1.3049 | 0.0 | 0.99608 | 1.1469 |
| $C_4$-$CO_2$[a] | 1.0182 | 0.9115 | 0.0 | 1.1748 | 1.2224 |
| $C_4$-$C_3$[a] | 1.0003 | 1.0074 | 0.031257 | 0.9998 | 1.0033 |
| $C_4$-$C_2$[a] | 0.99913 | 1.0348 | 0.28157 | 0.99916 | 1.0062 |
| $C_4$-$CH_4$[a] | 0.99417 | 1.1716 | 1.0 | 0.97911 | 1.0454 |
| $N_2$-$CO_2$[c] | 1.0059 | 1.1077 | 1.0 | 0.97779 | 1.0476 |
| $N_2$-$C_3$[a] | 1.0027 | 1.2013 | 0.0 | 0.97442 | 1.081 |
| $N_2$-$C_2$[d] | 1.0077 | 1.0987 | 1.0 | 0.97888 | 1.0424 |
| $N_2$-$CH_4$[e] | 0.9981 | 0.97927 | 1.0 | 0.99872 | 1.014 |
| $CO_2$-$C_3$[a] | 1.0336 | 0.90877 | 0.0 | 0.9969 | 1.0476 |
| $CO_2$-$C_2$[a] | 0.98632 | 0.90095 | 0.0 | 0.99748 | 1.0329 |
| $CO_2$-$CH_4$[f] | 1.0226 | 0.97567 | 1.0 | 0.99952 | 1.0028 |
| $C_3$-$C_2$[a] | 0.9962 | 1.0147 | 0.13042 | 0.99761 | 1.003 |
| $C_3$-$CH_4$[g] | 0.98968 | 1.0987 | 1.0 | 1.0048 | 1.0385 |
| $C_2$-$CH_4$[h] | 0.99634 | 1.0497 | 1.0 | 0.99755 | 1.0066 |

[a] KW0 Generalised mixture model.
[b] KW7 Kunz and Wagner model for the methane-hydrogen mixture.
[c] KW5 Kunz and Wagner model for the nitrogen-$CO_2$ mixture.
[d] KW6 Kunz and Wagner model for the nitrogen-ethane mixture.
[e] KW3 Kunz and Wagner model for the methane-nitrogen mixture.
[f] KW4 Kunz and Wagner model for the methane-$CO_2$ mixture.
[g] KW2 Kunz and Wagner model for the methane-propane mixture.
[h] KW1 Kunz and Wagner model for the methane-ethane mixture.

suggested by Kunz, Kilmeck, Wagner and Jaeschke in 2007 [14]. As you can see in Table 2, BetaT represents the binary interaction parameter for temperature; GammaT characterises the departure of the real gas mixture's behaviour from that of an ideal mixture in terms of temperature; $F_{ij}$ shows the fitting parameters used in the GERG-2008 EoS; BetaV accounts for the interaction between components regarding volume effects; GammaV quantifies the non-ideality in the volume behaviour of the mixture.

SAFT-based EoS employs statistical thermodynamics and is derived from Wertheim's cross-interaction theory. It offers an accurate depiction of the interactions between molecules that are similar or dissimilar. The model versions vary in how they handle polarity. One instance of a non-polar original SAFT is PC-SAFT EoS but an SAFT-based EoS that incorporates polarity considerations through the utilisation is PCP-SAFT.

The PC-SAFT model addresses molecules as chains consisting of spherical segments with square-well pair potentials for each segment [15]. It also accounts for dispersion attraction between entire chains. By incorporating specific interactions like hydrogen bonding into the Helmholtz energy terms, the original PC-SAFT model is well-suited to describe both associative and non-associative contributions [12].

Residual Helmholtz free energy can be used to calculate a number of properties that result from differentiation. According to the SAFT equations, the reduced residual Helmholtz free energy ($\widetilde{a}^{res}$) for a mixture of associated or non-associated molecules is:

$$\widetilde{a}^{res} = \widetilde{a}^{hc} + \widetilde{a}^{disp} + \widetilde{a}^{assoc} \tag{4}$$

Where $\widetilde{a}^{hc}$ is contribution of hard-chain system, $\widetilde{a}^{disp}$ is contribution due
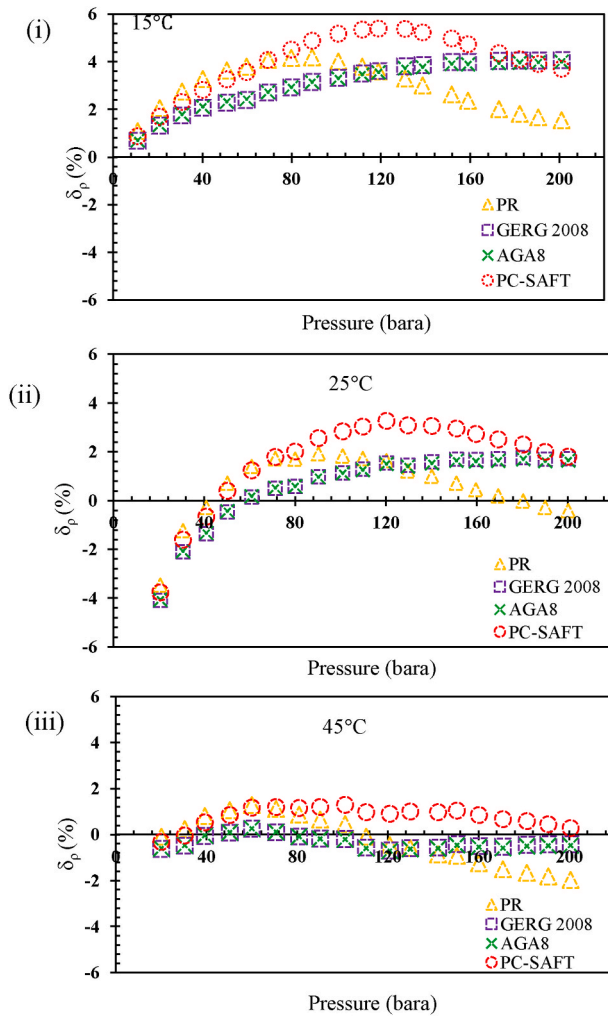
**Fig. 1.** Relative deviation in thermophysical property (density) values predicted by thermodynamic models, $\rho_{model}$, from experimental results, $\rho_{exp}$, for H$_2$-enriched natural gas mixture at a range of temperatures and pressures: i-iii show the results of modelling by PR, GERG2008, AGA8, and PC-SAFT for density at 15, 25, and 45 °C, respectively.



**Fig. 2.** Relative deviation in thermophysical property (SoS) values predicted by thermodynamic models, SoS$_{model}$, from experimental results, SoS$_{exp}$, for H$_2$-enriched natural gas mixture at a range of temperatures and pressures: i-iii show the results of modelling by PR, GERG2008, AGA8, and PC-SAFT for SoS at 15, 25, and 45 °C, respectively.

to dispersion attraction from the square-well attractive potential, $\tilde{a}^{assoc}$ is contribution arising from associating interactions. Then, there are further equations that can be used to determine thermophysical properties that has been derived from partial derivatives of reduced residual Helmholtz free energy [16].

The computed relative deviations in modelled densities and SoS values compared to experimental thermophysical properties values for the H$_2$-enriched natural gas within the pressure range below 200 bara and temperatures at 15 °C, 25 °C, and 45 °C is provided in Figs. 1 and 2, respectively.

## 3. Results and discussion

In this work, brand-new experimental density and speed of sound datasets for hydrogen-enriched natural gas mixtures have been utilised. The experimental datasets covered a pressure range of 10–200 bara pressure and temperature conditions of 15, 25, and 45 °C. The purpose of this statistically analyse was to assess the reliability and accuracy of the modelling data obtained from the PR, GERG-2008, AGA8, and PC-SAFT EoS models.

Fig. 1 presents the relative deviations of the predicted densities modelled by the mentioned EoSs from experimental datasets. As you can see in Table 3, the average absolute relative deviations (AARDs)
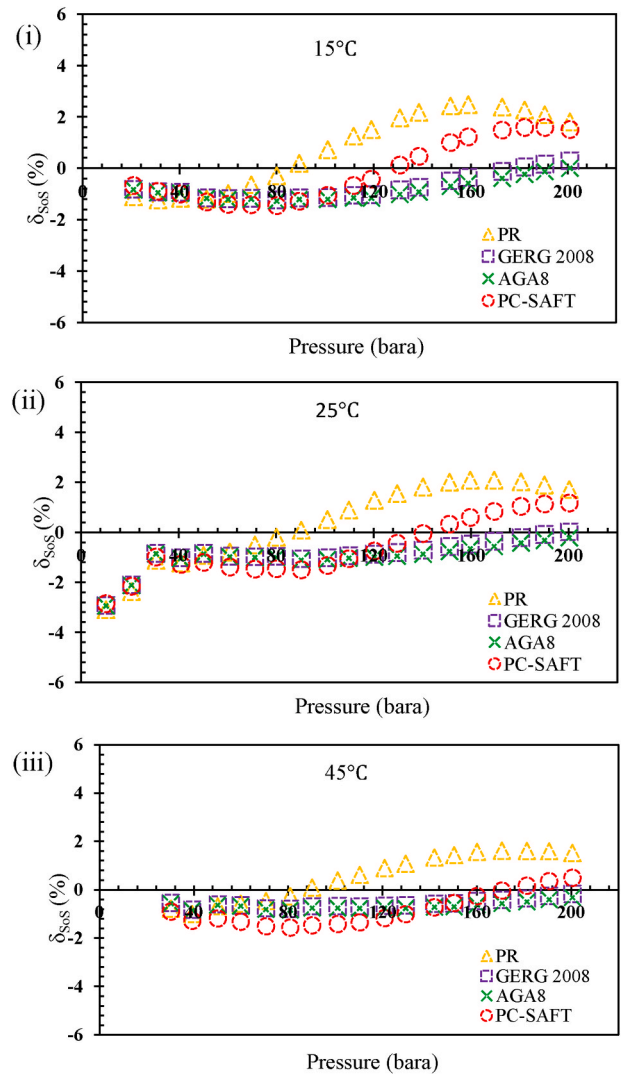
**Table 3**
The AARDs between density and speed of sound experimental datasets and modelling outputs of different studied equations of state.

| Equation of state | $\delta_\rho$ (%) | | | $\delta_{SoS}$ (%) | | |
|---|---|---|---|---|---|---|
| | 15 °C | 25 °C | 45 °C | 15 °C | 25 °C | 45 °C |
| PR | 2.94 | 1.15 | 0.93 | 1.47 | 1.41 | 0.97 |
| GERG-2008 | 3.09 | 1.44 | 0.39 | 0.79 | 0.89 | 0.57 |
| AGA8 | 3.05 | 1.40 | 0.41 | 0.86 | 0.99 | 0.66 |
| PC-SAFT | 4.02 | 2.29 | 0.81 | 1.08 | 1.15 | 0.93 |

calculated from the relative deviations between experimental and modelling outputs in entire range of temperature for the PR, GERG-2008, AGA8 and PC-SAFT are 1.67 %, 1.64 %, 1.62 %, and 2.37 %, respectively. The lower AARDs values confirm the high accuracy of PR, AGA8 and GERG-2008 density predictions for the H$_2$/NG mixture of this study.

In addition, the relative deviation of modelled speed of sound values have been shown in Fig. 2. The speed of sound AARDs of PR, GERG-2008, AGA8 and PC-SAFT are 1.28 %, 0.75 %, 0.84 %, and 1.06 %,

respectively. The reliability of these models can be concluded from the small AARDs values for sound speed prediction particularly for AGA8 and GERG-2008 EoSs.

## 4. Conclusions

In this study, the density and sound speed of a mixture of $H_2$, $N_2$, $CO_2$, $CH_4$, $C_2H_6$, $C_3H_8$, n-$C_4H_{10}$, and iso-$C_4H_{10}$ were measured experimentally at various temperatures and pressures. The present work aimed to assess the accuracy and reliability of four equations of state: PR, GERG-2008, AGA8, and PC-SAFT EoSs, in relation to the variances in fluid's densities and speed of sound values for different pressure and temperature operating conditions observed in experimental datasets. Our observations indicate that the use of GERG-2008 and AGA8 EoSs as multiparameter models resulted in lower AARDs for speed of sound. This demonstrates the effectiveness of these EoSs in predicting the thermophysical properties of $H_2$ containing streams, despite the asymmetric nature of these systems and the complexity of modeling hydrogen's quantum behavior.

It is noteworthy that the values of $\delta_\rho$ can be accurately predicted using PR, GERG-2008, and AGA8 EoSs, with AARDs below 1.67 %, except for PC-SAFT, which exhibits a 2.37 % error. However, the reliability for speed of sound prediction is notably higher and acceptable, with values less than 1.28 % for all evaluated EoSs.

Typically, the most suitable option would be a prominent EoS that accurately forecasts thermophysical properties without the need for adjustment. Enforcing the alignment of an EoS with specific data should not be carried out without taking into account the capabilities of that EoS.

This study demonstrates the efficacy of AGA8 and GERG-2008 in accurately and reliably predicting the thermophysical properties, specifically density and speed of sound, of natural gas enriched with $H_2$. Moreover, PR and PC-SAFT exhibit significant potential for predicting the density of $H_2$/NG mixtures by improving the fluid model parameters and fine-tuning them using innovative methods. This is the focus of our ongoing research in the near future.

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