L. F. Baladão Journal of Engineering Research and Application *www.ijera.com*
ISSN : 2248-9622, Vol. 8, Issue 8 (Part -III) Aug 2018, pp 25-34

RESEARCH ARTICLE OPEN ACCESS

Comparison of the GERG-2008 and Peng-Robinson Equations of State for Natural Gas Mixtures

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ABSTRACT

This work compares two equations of state applicable to natural gas mixtures, namely the GERG-2008 equation of state (EoS), which was proposed as a high-accuracy reference model, and the traditional Peng-Robinson (PR) EoS. This comparison is done in terms of the accuracy of calculated properties such as pressure and density with respect to experimental data from the literature, as well as in vapor-liquid equilibria (VLE) calculations. It was found that the GERG-2008 EoS gives better results in comparison with PR for the calculation of density and pressure, generating deviations in the range from 0.1 to 1%. For the VLE calculations, the accuracy of GERG-2008 was slightly better than PR. However, this accuracy is accompanied with increased mathematical complexity, resulting in increased computational time: 2 to 6 times higher. This is due to the fact that the calculation of molar density of GERG-2008 requires an iterative calculation step for the liquid and vapor phases, which makes the resolution of the VLE calculation slower.

Keywords - Equation of state, GERG-2008, Natural gas, Multiparametric Equation, Peng-Robinson

DATE OF SUBMISSION:16-08-2018 DATE OF ACCEPTANCE: 30-08-2018

I. INTRODUCTION

The increasing global energy demand associated with environmental concerns has boosted the search for energy sources cleaner than petroleum and coal. Natural gas, despite being a non-renewable fuel, is now well stablished in the global energy market due to recent discoveries and exploitation of unconventional sources. In addition, among the most used non-renewables, natural gas causes the least environmental impact. Therefore, accurate calculations of thermodynamic properties for natural gas and other mixtures formed by its components are of great importance for basic engineering. Examples for this are processing, transport, and storage of liquefied natural gas.

During the 70's, empirical multiparametric equations of state became available and were employed as reliable sources of thermodynamic property data in scientific and engineering applications. The development of such equations continued over the past 20 years.

For the thermodynamic properties of mixtures, Helmholtz energy models based on multi-fluid approaches were introduced to obtain high accuracy. As a consequence, appropriate software tools became available, thus increasing the impact of precise empirical models property in practical applications [1].

The GERG-2008 EoS [2] was developed as an extension of the GERG-2004 equation of state [3] in order to constitute a reference model for natural gas and its mixtures. Both equations have the same mathematical formalism, differing only by the number of terms [2]. The GERG-2008 EoS is valid for all mixtures consisting of 21 components of natural gas (Table 1) in any arbitrary combination or concentration. The calculation of the thermodynamic properties of multicomponent mixtures by GERG-2008 EoS is based on equations developed for binary mixtures, covering a total of 210 pairs of substances.

In this study, the accuracy of the GERG-2008 EoS was evaluated in property calculation (either pressure or molar density) for binary and multicomponent mixtures with respect to experimental data from literature. The results were compared for reference with the standard Peng-Robinson EoS [4]. Moreover, the accuracy in vapor-liquid-equilibria (VLE) computations for 12 binary mixtures was comparatively assessed for both EoS.

Table 1. Components of Natural Gas Considered in GERG-2008

Component	**Formula**
methane	CH_4
nitrogen	N_2
carbon dioxide	CO_2
ethane	C_2H_6
propane	C_3H_8
n-butane	n-C_4H_{10}
isobutane	i-C_4H_{10}
n-pentane	n-C_5H_{12}
isopentane	i-C_5H_{12}
n-hexane	n-C_6H_{14}
n-heptane	n-C_7H_{16}
n-octane	n-C_8H_{18}
n-nonane	n-C_9H_{20}
n-decane	n-$C_{10}H_{22}$
hydrogen	H_2
oxigen	O_2
carbon monoxide	CO
water	H_2O
hydrogen sulfide	H_2S
helium	He
argon	Ar

II. MATHEMATICAL FORMULATION OF GERG-2008

The GERG-2008 EoS [2] is based on an explicit multi-fluid approximation of the reduced molar Helmholtz energy, α:

$$\alpha(\delta,\tau,x) = \alpha^o(\rho,T,x) + \alpha^r(\delta,\tau,x) \qquad (1)$$

The term α^o represents the properties of an ideal gas mixture for a given molar density (ρ), temperature (T) and molar composition of the mixture (x) with N components according to the following expression:

$$\alpha^o(\rho,T,x) = \sum_{i=1}^{N} x_i\left(\alpha_{oi}^o(\rho,T) + \ln(x_i)\right) \qquad (2)$$

In (2), the reduced ideal gas state Helmholtz energy of component i is given by

$$\alpha_{oi}^o(\rho,T) = \ln\left(\frac{\rho}{\rho_{c,i}}\right) + \frac{R^*}{R}\Bigg(n_{oi,1}^o + n_{oi,2}^o\frac{T_{c,i}}{T} + n_{oi,3}^o\ln\left(\frac{T_{c,i}}{T}\right) + \sum_{k=4,6} n_{oi,k}^o\ln\left(\left|\sinh\left(\vartheta_{oi,k}^o\frac{T_{c,i}}{T}\right)\right|\right) - \sum_{k=5,7} n_{oi,k}^o\ln\left(\cosh\left(\vartheta_{oi,k}^o\frac{T_{c,i}}{T}\right)\right)\Bigg) \qquad (3)$$

where $\rho_{c,i}$ and $T_{c,i}$ are critical parameters of the pure components and R*/R = 8.314510/8.314472. The coefficients $n_{oi,k}^o$ and $\vartheta_{oi,k}^o$ in (3) are provided by Kunz and Wagner [2].

The residual part of the reduced Helmholtz free energy of the mixture (α^r) is given by

$$\alpha^r(\delta,\tau,x) = \sum_i^N x_i\alpha_{oi}^r(\delta,\tau) + \Delta\alpha^r(\delta,\tau,x) \qquad (4)$$

where $\delta \equiv \rho/\rho_r(x)$ is the reduced mixture density and $\tau \equiv T_r(x)/T$ is the inverse reduced mixture temperature. The reduced critical parameters of the mixture are combined by means of the following mixing rules:

$$\rho_r(x)^{-1} = \sum_{i=1}^{N} x_i^2\frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} 2x_ix_j\beta_{v,ij}\gamma_{v,ij}\cdot\frac{x_i+x_j}{\beta_{v,ij}^2x_i+x_j}\frac{1}{8}\left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}}\right)^3 \qquad (5)$$

$$T_r(x) = \sum_{i=1}^{N} x_i^2T_{c,i} + \sum_{i=1}^{N-1}\sum_{j=1+1}^{N} 2x_ix_j\beta_{T,ij}\gamma_{T,ij}\cdot\frac{x_i+x_j}{\beta_{T,ij}^2x_i+x_j}\left(T_{c,i}\cdot T_{c,j}\right)^{1/2} \qquad (6)$$

The first term in (4) is the contribution of pure species to the residual Helmholtz energy of component *i*, given by

$$\alpha_{oi}^r(\delta,\tau) = \sum_{k=1}^{K_{Pol,i}} n_{oi,k}\delta^{d_{oi,k}}\tau^{t_{oi,k}} + \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{oi,k}\delta^{d_{oi,k}}\tau^{t_{oi,k}}.\exp\left(-\delta^{c_{oi,k}}\right) \qquad (7)$$

The second term in (4) represents the departure function (deviation from the corresponding states principle) and is based on the contribution of the binary mixture of components *i-j* to the non-ideal behavior [2]:

$$\Delta\alpha^r(\delta,\tau,x) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_ix_jF_{ij}\alpha_{ij}^r(\delta,\tau) \qquad (8)$$

The function α_{ij}^r in (8) is given by

$$\alpha_{ij}^r(\delta,\tau) = \sum_{k=1}^{K_{Pol,i}} n_{ij,k}\delta^{d_{ij,k}}\tau^{t_{ij,k}} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_{ij}\delta^{d_{ij,k}}\tau^{t_{ij,k}}\cdot\exp\left(-\eta_{ij,k}(\delta - \varepsilon_{ij,k})^2 - \beta_{ij,k}(\delta - \gamma_{ij,k})\right) \qquad (9)$$

and can both represent a specific binary mixture or a group of binary mixtures (generalized departure function). All coefficients ($\beta_{v,ij}$, $\gamma_{v,ij}$, $\beta_{T,ij}$, $\gamma_{T,ij}$, $n_{ij,k}$) and exponents ($d_{oi,k}$, $t_{oi,k}$, $c_{oi,k}$, $d_{ij,k}$, $t_{ij,k}$, $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, $\gamma_{ij,k}$) are provided by Kunz and Wagner [2] and were adjusted with data for binary mixtures. The factor F_{ij} is fitted to binary data for each given mixture, and it is set to zero for the binary mixtures for which a departure function has not been developed. Pressure (or density as a function of ρ) can be calculated with the GERG-2008 EoS by means of the thermodynamic relation

$$\frac{P(\delta,\tau,x)}{\rho RT} = 1 + \delta\alpha_\delta^r \qquad (10)$$

where

$$\alpha_\delta^r \equiv \left(\frac{\partial \alpha^r}{\partial \delta}\right)_{\tau,x} \tag{11}$$

The classical Peng-Robinson EoS [4] is given by

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{12}$$

where v is the molar volume. Mixture parameters a and b are given by Van der Walls mixing rules with binary interaction coefficients k_{ij}:

$$a = \sum_i \sum_j y_i y_j \sqrt{a_{ii} a_{jj}} \left(1 - k_{ij}\right) \tag{13}$$

$$b = \sum_i y_i b_i \tag{14}$$

as a combination of the component pure parameters, a_{ii} and b_i:

$$a_{ii} = 0{,}4572 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left(1 + m_i\left(1 - \sqrt{T/T_{c,i}}\right)\right)^2 \tag{15}$$

$$m = 0{,}37464 + 1{,}54226\omega_i - 0{,}26992\omega_i{}^2 \tag{16}$$

$$b_i = 0{,}07780 \frac{RT_{c,i}}{P_{c,i}} \tag{17}$$

where ω_i is the acentric factor.

III. RESULTS AND DISCUSSIONS

Accuracy in the calculation of either pressure $P = P(\rho, T, x)$ or density $\rho = \rho(P, T, x)$ were assessed for binary mixtures in vapor and liquid homogeneous phases and in the saturated state with respect to experimental data using the mean relative error (MRE)

$$MRE = \frac{1}{N_p} \sum_{j=1}^{N_p} \left|\hat{z}_j - z_j\right| / z_j \tag{18}$$

where N_p is the number of data points, z is the experimental value of the property of interest and $\hat{z}$ is the value obtained with the EoS (GERG-2008 or PR). Since GERG-2008 is implicit and non-linear in ρ, the fzero function of Matlab 7.8.0 (R2009a) was employed to calculate the density for given pressure, temperature and composition. The initial guess for the gas phase is the gas ideal density ($\rho = p/RT$) and for the liquid phase (homogeneous or saturated) the reference value of 30 mol/L was employed. The density roots of PR-EoS can be calculated by a standard polynomial method.

3.1 Calculation of P and ρ for binary mixtures

Tests were performed with some binary mixtures for the calculation properties for gas and liquid phases in both homogeneous and saturated states. Table 2 presents the experimental data employed in the tests.

Table 2. Mixtures Considered in p and ρ Calculations

Mix.	**Source**	**CH_4**	**N_2**	**C_2H_6**
A1$^{(a)}$	[5]	0.8994	0.1002	-
A2$^{(a)}$	[5]	0.8000	0.2000	-
B1$^{(b)}$	[6]	0.4988	0.5012	-
B2$^{(b)}$	[6]	0.3166	0.6834	-
B3$^{(b)}$	[6]	0.7137	0.28627	-
C1$^{(b)}$	[7]	0.6853	-	0.3147
C2$^{(b)}$	[7]	0.5022	-	0.4978
C3$^{(b)}$	[7]	0.3425	-	0.6575

$^{(a)}$ data for gas phase only
$^{(b)}$ data for gas and liquid phases

Table 3 shows the results of MRE for all mixtures considered. For the gas phase calculations (mixtures A1 and A2), both models are fairly accurate, with advantage to GERG-2008 (MRE around 0.2%). Nevertheless, as far as data included the liquid region (mixtures B1, B2, B3, C1, C2 and C3), PR-EoS performed significantly worse, with deviation up to 100%, whereas GERG-2008 still achieved a good precision for engineering calculations (up to 5%).

Table 3. MRE in the Calculation of Pressure Using the GERG-2008 and the Peng-Robinson EoS

Mix.	**T_{RANGE} (K)**	**MRE (%) GERG**	**MRE (%) PR**	**Number of data points**
A1$^{(a)}$	240 to 400	0.20	1.72	108
A2$^{(a)}$	240 to 400	0.18	1.69	129
B1$^{(b)}$	75 to 300	1.02	77.40	363
B2$^{(b)}$	75 to 300	1.91	53.22	112
B3$^{(b)}$	75 to 300	4.61	105.8	106
C1$^{(b)}$	100 to 320	0.43	25.82	144
C2$^{(b)}$	100 to 320	1.01	42.25	164
C3$^{(b)}$	100 to 320	0.71	42.45	106

$^{(a)}$ Accuracy of experimental data: ±0.001%
$^{(b)}$ Accuracy of experimental data: ±0.010%

The same analysis was made for the density calculation of the mixtures show in Table 2, given the pressure. For mixtures A1 and A2, the MRE for GERG-2008 was in the range of 0.20 to 0.25%, a result similar to that obtained by Kunz and Wagner [2]. GERG-2008 showed a significantly greater accuracy in relation to the Peng-Robinson in all cases. Table 4 summaries the results for all mixtures presented.

Table 4. MRE in the calculation of density for the GERG-2008 and the Peng-Robinson EoS

Mix.	**T_{RANGE} (K)**	**MRE (%) GERG**	**MRE (%) PR**	**Number of data points**
A1[(a)]	240 to 400	0.24	1.72	108
A2[(a)]	240 to 400	0.20	1.84	129
B1[(b)]	75 to 300	0.17	6.43	363
B2[(b)]	75 to 300	0.31	6.24	112
B3[(b)]	75 to 300	0.35	6.41	106
C1[(c)]	100 to 320	0.17	3.32	144
C2[(c)]	100 to 320	0.95	3.64	164
C3[(c)]	100 to 320	0.63	3.31	106

[(a)] Accuracy of experimental data: ±0.015%
[(b)] Accuracy of experimental data:: ±0.100%
[(c)] Accuracy of experimental data: ±0.010%

3.2 Calculation of p and ρ for multicomponent mixtures

In addition to binary mixtures, tests were conducted to evaluate the accuracy of GERG-2008 equation of state for some multicomponent mixtures in the gas phase with experimental data found in the literature (Table 5).

Table 5. Mole Fractions of Mixtures D1, D2, D3, D4 and D5 in the Gas Phase [8]

Mol. Frac.	**D1**	**D2**	**D3**	**D4**	**D5**
CH_4	0.9650	0.9064	0.8130	0.8120	0.8590
N_2	0.0027	0.0313	0.1357	0.0570	0.0101
CO_2	0.0059	0.0047	0.0099	0.0759	0.0150
C_2H_6	0.0181	0.0455	0.0329	0.0431	0.0850
C_3H_8	0.0040	0.0083	0.0064	0.0089	0.0230
n-C_4H_{10}	0.00102	0.0016	0.0010	0.0015	0.0035
i-C_4H_{10}	0.00099	0.0010	0.0010	0.0015	0.0035
n-C_5H_{12}	0.00032	0.0004	-	-	0.0005
i-C_5H_{12}	0.00047	0.0003	-	-	0.0005
n-C_6H_{14}	0.00063	0.00040	-	-	-

Mixtures D1, D2, D3, D4 and D5 were tested from 225 at 350 K and pressures up to 35 MPa, resulting in values of MRE from 0.02 to 0.38%, showing that, although the GERG-2008 equation is based on a binary mixing rule, it produces good results also for multicomponent mixtures. Table 6 summarizes the results of MRE for the evaluated systems.

Table 6. MRE in the Calculation of Pressure Using the GERG-2008 EoS for the Studied Mixtures

Mix.	**T_{RANGE} (K)**	**MRE GERG -2008 (%)**	**Number of data points**
D1	225 to 350	0.17	66
D2	225 to 350	0.38	67
D3	225 to 350	0.07	66
D4	225 to 350	0.02	71
D5	225 to 350	0.08	65

* Accuracy of experimental data: ±0.020%

For mixtures of Table 5, the MRE in calculating the density was 0.03 to 0.32%. Table 7 summarizes the results of MRE for the evaluated systems.

Table 7. MRE in the Calculating the Density for the Mixtures Using the GERG-2008 EoS

Mix.	**T_{RANGE} (K)**	**MRE GERG-2008 (%)**	**Number of data points**
D1	225 to 350	0.16	66
D2	225 to 350	0.32	67
D3	225 to 350	0.04	66
D4	225 to 350	0.03	71
D5	225 to 350	0.06	65

* Accuracy of experimental data: ±0.025%

3.3 VLE calculations

Tests were conducted to compare the accuracy of bubble-point pressure (P^b) and vapor phase mole fraction (y) resulting from VLE calculations for some binary mixtures with the GERG-2008 and Peng-Robinson EoS. Computations were made using the isofugacity criterion with the Rachford-Rice algorithm implemented in Matlab 7.8.0 (R2009a).

For this test, 12 mixtures were considered: CO_2 + n-C_4H_{10} [9], n-C_4H_{10} + n-$C_{10}H_{22}$ [10], n-C_5H_{12} + n-C_6H_{14} [11], C_3H_8 + n-$C_{10}H_{22}$ [12], C_2H_6 + n-C_5H_{12} [13], C_2H_6 + C_3H_8 [14], H_2S + n-$C_{10}H_{22}$ [15], H_2 + n-C_4H_{10} [16], CH_4 + n-C_4H_{10} [17], CH_4 + n-C_6H_{14} [18], N_2 + CO_2 [19] and N_2 + n-C_4H_{10} [9].

Table 8 shows the average accuracies (MRE for P^b and y along a given isotherm) of GERG-2008 and Peng-Robinson EoS for the 12 mixtures considered.

Examples of the VLE diagrams with the experimental isotherms (P-T-x-y data) from the literature and the results of the models are shown in Fig. 1 (CO_2 + n-C_4H_{10}), Fig. 2 (n-C_4H_{10} + n-$C_{10}H_{22}$), Fig. 3 (n-C_5H_{12} + n-C_6H_{14}) and Fig. 4 (C_3H_8 + n-$C_{10}H_{22}$).

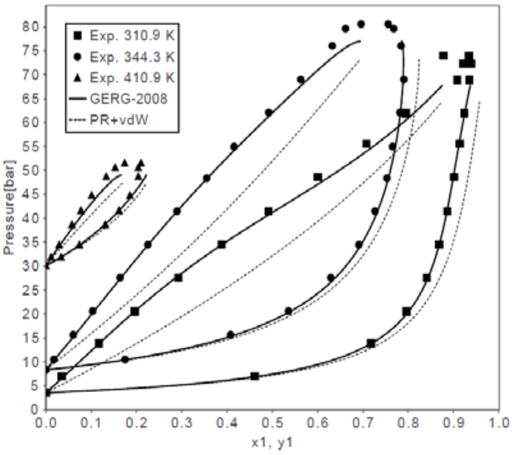

Figure 1. P-T-x-y data for the mixture CO_2 (1) + n-C_4H_{10} (2) [9] at 310.9 K, 344.3 K, 410.9 K and results for the GERG-2008 and Peng-Robinson EoS

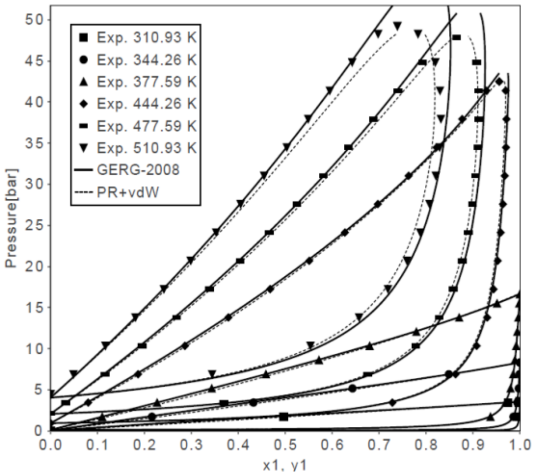

Figure 2. P-T-x-y data for the mixture n-C_4H_{10} (1) + n-$C_{10}H_{22}$ (2) [10] at 310.93 K, 344.26 K, 377.59 K, 444.26 K, 510.93 K and results for the GERG-2008 and Peng-Robinson EoS

It can be concluded that the GERG-2008 model is generally more accurate (overall MRE of 0.03856 for P^b and 0.01184 for y) than Peng Robinson (overall MRE of 0.07843 for P^b and 0.01715 for y) in the considered temperature range for these examples. Exceptions are the mixtures C_3H_8 + n-$C_{10}H_{22}$ (Figure 4) and C_2H_6 + C_3H_8 for which both models are similar in terms of MRE for P^b but the average MRE in y for PR (0.00710) is smaller than for GERG-2008 (0.01082).

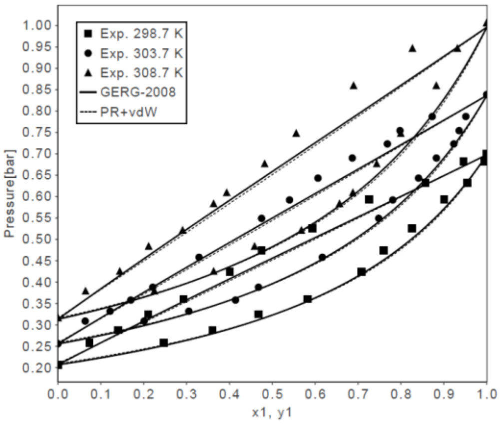

Figure 3. P-T-x-y data for the mixture n-C_5H_{12} (1) + n-C_6H_{14} (2) [11] at 298.7 K, 303.7 K, 308.7 K and results for the GERG-2008 and Peng-Robinson EoS

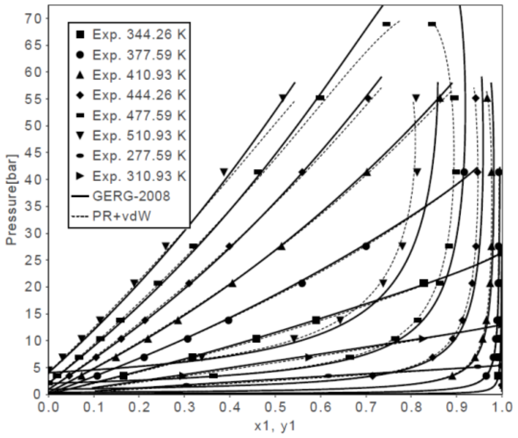

Figure 4. P-T-x-y data for C_3H_8 (1) + n-$C_{10}H_{22}$ (2) [12] and results for the GERG-2008 and Peng-Robinson (vdW) EoS at 277.59 K, 310.93 K, 344.26 K, 377.59 K, 410.93 K, 444.26 K, 477.59 K and 510.93 K

Additionally, at specific temperatures for the mixtures H_2S + n-$C_{10}H_{22}$, CH_4 + n-C_6H_{14} e N_2 + n-C_4H_{10}, the average MRE for P^b was 0.07082 (GERG-2008) and 0.09229 (PR), but it was 0.02432 (GERG-2008) and 0.01320 (PR) for y.

Table 8. Average Accuracies in the Calculation of P^b and y for All Mixtures Using the GERG-2008 and Peng-Robinson EoS

Mixture	EoS	MRE (P^b)	MRE (y)
CO_2 + n-C_4H_{10}[a]	GERG-2008	0.03733	0.01631
	PR-EoS	0.13416	0.03020
n-C_4H_{10} + n-$C_{10}H_{22}$[b]	GERG-2008	0.01895	0.00430
	PR-EoS	0.04063	0.01045

n-C_5H_{12} + n-C_6H_{14}[c]	GERG-2008	0.03169	0.00914
	PR-EoS	0.03775	0.01096
C_3H_8 + n-$C_{10}H_{22}$[d]	GERG-2008	0.02427	0.00536
	PR-EoS	0.02495	0.00179
C_2H_6 + n-C_5H_{12}[e]	GERG-2008	0.01475	0.00800
	PR-EoS	0.05843	0.02220
C_2H_6 + C_3H_8[f]	GERG-2008	0.02231	0.01707
	PR-EoS	0.01816	0.01317
H_2S + n-$C_{10}H_{22}$[g]	GERG-2008	0.07301	0.00108
	PR-EoS	0.09878	0.00263
H_2 + n-C_4H_{10}[h]	GERG-2008	0.06845	0.01217
	PR-EoS	0.24560	0.06071
CH_4 + n-C_4H_{10}[i]	GERG-2008	0.03396	0.00358
	PR-EoS	0.09171	0.01350
CH_4 + n-C_6H_{14}[j]	GERG-2008	0.07740	0.04542
	PR-EoS	0.07825	0.02166
N_2 + CO_2[l]	GERG-2008	0.04043	0.02258
	PR-EoS	0.05967	0.02789
N_2 + n-C_4H_{10}[m]	GERG-2008	0.04776	0.04133
	PR-EoS	0.10794	0.02372

[a] Tables I, II and III of [9]. Experimental data accuracy: T=±0.05 °C, Pressure up to 800 psig, P=0.1 psi, Pressure above 800 psig, P=2 psi and x,y=0.003.

[b] Table II of [10]. Experimental data accuracy: T=0.1 °F, P=0.2 psi and x,y=0.002.

[c] Table 3a of [11]. Experimental data accuracy: T=0.2 K, ^{t}=±0.068 KPa and x,y=0.03.

[d] Table II of [12]. Experimental data accuracy: T=0.03 °F, P=0.1 psi and x,y=0.001.

[e] Table II of [13]. Experimental data accuracy: T=0.03 °F, ^{t}=0.1 psi and x,y=0.005.

[f] Tables I, II, III, IV, V, VI and VII of [14]. Experimental data accuracy: T=0.015 K and Pressure of 5 MPa, P=0.5 KPa.

[g] Table II of Reamer [15].

[h] Tables 1, 2, 3, 4 and 5 of [16]. Experimental data accuracy: T=±0.015 °C, P=±0.05 atm and x,y=±0.04.

[i] Table II of [17]. Experimental data accuracy: T=±0.02 °C, P=0.1% and x,y=0.00001.

[j] Table I of [18]. Experimental data accuracy: T=±0.0.028 to ±0.11 °C, P=±0.14 atm and x,y=0.002.

[l] Table 1 of [19]. Experimental data accuracy: T=±0.02 K, pressures less than 0.7 MPa (P=0.0007 MPa), pressures between 0.7 and 3.5 MPa (P=0.0035 MPa), pressures between 3.5 and 10.14 MPa (P^{sat}=0.01 MPa), pressures greater than 10.14 (P=0.017 MPa) and x,y=±0.002.

[m] Tables IV and V of [9]. Experimental data accuracy: T=±0.05 °C, Pressure up to 800 psig, P=0.1 psi, Pressure above 800 psig, P=2 psi and x,y=0.003.

IV. CONCLUSIONS

The GERG-2008 equation of state is presented in the literature as a reference model to calculate thermodynamic properties of natural gas [2]. The results for calculating pressure and density were superior to those obtained by Peng-Robinson equation of state for all mixtures. Importantly, the density calculations for both equations of state were more precise than the calculation of the pressure in the liquid phase, for the conditions tested in this work.

It is noted that the GERG-2008 EoS works well for calculating the density regardless of the mixture phase and the obtained results confirm those obtained by Kunz and Wagner [2]. With respect to pressure, most of the results are in accordance with the precision obtained for density, except for mixtures at low temperatures, since the model can return negative values or, contrarily, display more than one volumetric root for a given pressure, depending on the problem conditions.

For the VLE calculations, the general accuracy of GERG-2008 was slightly superior. The Peng-Robinson EoS performed better only at some particular temperature conditions. Nevertheless, this higher precision is achieved at the expense of a 2 to 6 times higher computational time than a traditional cubic EoS (Peng-Robinson). This is effect is due to the fact that the calculation of molar density of GERG-2008 requires an iterative calculation for the liquid and vapor phases in an inner loop, which makes the resolution of the VLE calculation slower.

ACKNOWLEDGEMENTS

The first author would like to thank CAPES (Brazil) for the financial support.

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APPENDIX

Table A1. Accuracies in the Calculation of P^b and y for All Mixtures Using the GERG-2008 and Peng-Robinson EoS

Mixture	**T (K)**	**EoS**	**AARD$_P$**	**AAD$_y$**
CO_2 + n-C_4H_{10}	310.70	GERG	0.01883	0.00958
		PR-EoS	0.17671	0.03694
	344.30	GERG	0.01868	0.00698
		PR+vdW	0.16439	0.04026
	410.90	GERG	0.07449	0.03238
		PR-EoS	0.06139	0.01339
	310.93	GERG	0.05658	0.00045
		PR-EoS	0.02253	0.00042

n-C_4H_{10} + n-$C_{10}H_{22}$	344.26	GERG	0.01715	0.00028
		PR-EoS	0.02896	0.00054
	377.56	GERG	0.00685	0.00037
		PR-EoS	0.03382	0.00154
	444.26	GERG	0.00864	0.00188
		PR-EoS	0.04580	0.01989
	477.59	GERG	0.01033	0.00809
		PR-EoS	0.04830	0.01619
	510.93	GERG	0.01413	0.01471
		PR-EoS	0.06435	0.02412
n-C_5H_{12} + n-C_6H_{14}	298.70	GERG	0.02964	0.00811
		PR-EoS	0.03530	0.01019
	303.70	GERG	0.02404	0.00860
		PR-EoS	0.03000	0.00882
	308.70	GERG	0.04138	0.01071
		PR-EoS	0.04794	0.01388
C_3H_8 + n-$C_{10}H_{22}$	277.59	GERG	0.01300	0.00011
		PR-EoS	0.05044	0.00009
	310.93	GERG	0.03094	0.00044
		PR-EoS	0.00614	0.00038
	344.26	GERG	0.01350	0.00079
		PR-EoS	0.01539	0.00047
	377.59	GERG	0.02714	0.00141
		PR-EoS	0.02004	0.00029
	410.93	GERG	0.01530	0.00427
		PR-EoS	0.02671	0.00080
	444.26	GERG	0.00951	0.00763
		PR-EoS	0.02338	0.00170
	477.59	GERG	0.03376	0.01354
		PR-EoS	0.01594	0.00457
	510.93	GERG	0.05100	0.01467
		PR-EoS	0.04156	0.00602
C_2H_6 + n-C_5H_{12}	277.59	GERG	0.01736	0.00372
		PR-EoS	0.02465	0.00346
	310.93	GERG	0.01534	0.00460
		PR-EoS	0.05220	0.01831
	344.26	GERG	0.01676	0.00785
		PR-EoS	0.05524	0.01724
	377.59	GERG	0.00383	0.00727
		PR-EoS	0.05110	0.02062
	410.93	GERG	0.01636	0.01182
		PR-EoS	0.07414	0.02745
	444.26	GERG	0.01883	0.01274
		PR-EoS	0.09324	0.04613
C_2H_6 + C_3H_8	195.00	GERG	0.06565	0.00558
		PR-EoS	0.03355	0.00401
	210.00	GERG	0.03578	0.02236
		PR-EoS	0.01548	0.01848
	225.00	GERG	0.02367	0.02310
		PR-EoS	0.01058	0.01771
	235.00	GERG	0.01061	0.01468
		PR-EoS	0.02334	0.01125
	245.00	GERG	0.00852	0.02227
		PR-EoS	0.01368	0.01801
	255.40	GERG	0.00473	0.00953
		PR-EoS	0.01497	0.00489

	270.00	GERG	0.00721	0.02198
		PR-EoS	0.01552	0.01785
H_2S + n-$C_{10}H_{22}$	277.59	GERG	0.12138	0.00076
		PR-EoS	0.17253	0.00073
	310.93	GERG	0.08095	0.00054
		PR-EoS	0.09786	0.00051
	344.26	GERG	0.06172	0.00044
		PR-EoS	0.05704	0.00040
	377.59	GERG	0.05502	0.00061
		PR-EoS	0.07736	0.00139
	410.93	GERG	0.06412	0.00106
		PR-EoS	0.09111	0.00371
	444.26	GERG	0.05489	0.00304
		PR-EoS	0.09675	0.00906
H_2 + n-C_4H_{10}	327.65	GERG	0.05782	0.00203
		PR-EoS	0.26764	0.03654
	344.25	GERG	0.03939	0.00280
		PR-EoS	0.25103	0.05186
	360.95	GERG	0.06672	0.00439
		PR-EoS	0.24256	0.06650
	377.55	GERG	0.09288	0.01167
		PR-EoS	0.23756	0.07762
	394.25	GERG	0.08546	0.03995
		PR-EoS	0.22921	0.07101
CH_4 + n-C_4H_{10}	144.26	GERG	0.05897	0.00001
		PR-EoS	0.13449	0.00001
	155.38	GERG	0.07238	0.00002
		PR-EoS	0.12194	0.00001
	166.50	GERG	0.04153	0.00003
		PR-EoS	0.09641	0.00002
	177.62	GERG	0.03677	0.00008
		PR-EoS	0.07281	0.00007
	189.06	GERG	0.02501	0.00002
		PR-EoS	0.05515	0.00002
	190.58	GERG	0.02407	0.00002
		PR-EoS	0.11991	0.02519
	199.88	GERG	0.02444	0.00007
		PR-EoS	0.11277	0.02253
	210.94	GERG	0.01948	0.00158
		PR-EoS	0.10905	0.02719
	222.07	GERG	0.02359	0.00401
		PR-EoS	0.09311	0.02143
	233.18	GERG	0.02145	0.00750
		PR-EoS	0.07616	0.01952
	244.28	GERG	0.02353	0.00876
		PR-EoS	0.07422	0.02130
	255.38	GERG	0.03467	0.00843
		PR-EoS	0.06591	0.01807
	277.59	GERG	0.03562	0.01606
		PR-EoS	0.06024	0.02008
CH_4 + n-C_6H_{14}	310.93	GERG	0.06018	0.02507
		PR-EoS	0.05625	0.02352
	344.26	GERG	0.05229	0.00822
		PR-EoS	0.05622	0.00828
	377.59	GERG	0.07164	0.03554
		PR-EoS	0.05531	0.01421

	410.93	GERG	0.08158	0.05809
		PR-EoS	0.07325	0.01704
	444.26	GERG	0.12133	0.10017
		PR-EoS	0.15023	0.04527
$N_2 + CO_2$	250.00	GERG	0.01831	0.00274
		PR-EoS	0.04979	0.01164
	270.00	GERG	0.06254	0.04242
		PR-EoS	0.06955	0.04413
$N_2 + n\text{-}C_4H_{10}$	310.70	GERG	0.05911	0.01721
		PR-EoS	0.15387	0.02805
	410.90	GERG	0.03641	0.06544
		PR-EoS	0.06200	0.01938

L. F. Baladão"Comparison of the GERG-2008 and Peng-Robinson Equations of State for Natural Gas Mixtures"International Journal of Engineering Research and Applications (IJERA) , vol. 8, no.8, 2018, pp 25-34