

# A saturated liquid density equation in conjunction with the Predictive-Soave–Redlich–Kwong equation of state for pure refrigerants and LNG multicomponent systems

Khashayar Nasrifar, Mahmood Moshfeghian \*

*Department of Chemical Engineering, School of Engineering, Shiraz University, P.O. Box 1133 Shiraz 71345, Iran*

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## Abstract

An equation and a set of mixing rules for the prediction of liquid density of pure refrigerants and liquified natural gas (LNG) multicomponent systems have been developed. This equation uses the parameters of Mathias and Copeman [P.M. Mathias, T.W. Copeman, *Fluid Phase Equilib.* 13 (1983) 91–108] temperature dependent-term for the Predictive-Soave–Redlich–Kwong [T. Holderbaum, J. Gmehling, *Fluid Phase Equilib.* 70 (1991) 251–265] equation of state and hence it could be used together with this equation. The equation uses a characteristic parameter for each refrigerant; however, if it is not available, a value of zero is recommended. This model gives an average of absolute errors less than 0.42% for the prediction of liquid density of 28 pure refrigerants consisting of 2489 data points and 0.33% for 18 multicomponent LNG systems involving 132 data points. The model parameters were determined from pure component properties and reported. These parameters were then used without any adjustment to predict liquid density of multicomponent LNG mixtures and excellent results were obtained. The model was also compared with other available methods. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Liquid density equation; Equation of state; Refrigerant; LNG

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## 1. Introduction

Having known the hazardous effects of chloroflourocarbon (CFC) refrigerants to the atmosphere, the development and/or modification of available equations for accurately prediction of properties of alternative refrigerants are more pronounced. Two of these properties are vapor pressure and liquid density. Equations of states (EOSs) are commonly used for calculation of vapor pressure. Using the

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\* Corresponding author. Tel.: +98-71-30-3071; fax: +98-71-30-3071; e-mail: moshfeg@succ.shirazu.ac.ir

given temperature dependent term by Mathias and Copeman [1] for attractive parameters in EOSs, equations like Predictive-Soave–Redlich–Kwong (PSRK) [2] gives vapor pressures that deviate less than 0.5% from experimental data. This accuracy is enough for design purposes. There are also EOSs that predict accurately liquid density of pure components [3,4] or even their mixtures [5,6]. However, correlations are usually applied for design purposes. The EOSs, in spite of correlations, have narrower range of applicability specially at regions near critical point where deviations from experimental data become excessive. Nevertheless, they need the same number of parameters that are required for the calculation of other properties. Correlations are more accurate and reliable than EOSs, although they suffer from some shortcomings. Recently, Iglesias-Silva and Hall [7] have developed an excellent correlation for the prediction of liquid density of CFC and hydrofluorocarbon (HFC) refrigerants. This correlation requires two fitting parameters for each refrigerant in addition to the critical properties and as a result its accuracy is within the range of experimental data. However, they have not addressed the needed parameters for other widely used refrigerants such as light hydrocarbons or inorganic gases. Moreover, its extension to multicomponent systems has not been made. The corresponding state liquid density (COSTALD) correlation [8] and the modified Rackett correlation by Spencer and Danner (RSD) [9] are the two other widely used correlations for nearly all purposes including refrigeration. The former gives poor results for the calculation of liquid density of He and H<sub>2</sub> and the latter for multicomponent systems in addition to its inaccuracy for He and H<sub>2</sub>.

In order to compensate the faults from correlations and EOSs, an equation for the calculation of saturated liquid density of refrigerants is developed. This equation can be used in conjunction with the PSRK EOS [2].

## 2. The PSRK EOS

For pure components, the PSRK EOS [2,10,11] is in essence the same as the SRK EOS [12] except that the Mathias and Copeman temperature dependent term [1] is used instead of the conventional temperature dependent term in the *a*-parameter of the SRK EOS. This substitution improves greatly the prediction of vapor pressures. The PSRK EOS is expressed by:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \quad (1)$$

where *b* and *a* are given by:

$$b = 0.08664 \frac{RT_C}{P_C} \quad (2)$$

$$a = 0.42748 \frac{R^2 T_C^2}{P_C} f(T_r) \quad (3)$$

where *f*(*T<sub>r</sub>*) is the Mathias and Copeman [1] temperature dependent term and *T<sub>r</sub>* = (*T*/*T<sub>C</sub>*) is reduced temperature. It is defined by:

$$f(T_r) = \left[ 1 + c_1(1 - \sqrt{T_r}) + c_2(1 - \sqrt{T_r})^2 + c_3(1 - \sqrt{T_r})^3 \right]^2, T_r < 1 \quad (4)$$

Table 1  
Global constants in Eq. (7)

$d_1$	1.1688
$d_2$	1.8177
$d_3$	−2.6581
$d_4$	2.1613

and

$$f(T_r) = \left[1 + c_1(1 - \sqrt{T_r})\right]^2, T_r > 1 \quad (5)$$

### 3. The proposed liquid density equation

After examining a large number of correlations, the following equation is proposed. It has been formulated empirically in order to be satisfied at critical conditions. The equation is expressed by:

$$\frac{\rho_s}{\rho_c} = \rho_0 \left[1 + \delta(f(T_r) - 1)^{1/3}\right] \quad (6)$$

and  $\rho_0$  is defined by:

$$\rho_0 = 1 + d_1 \left(1 - \frac{T_r}{f(T_r)}\right)^{1/3} + d_2 \left(1 - \frac{T_r}{f(T_r)}\right)^{2/3} + d_3 \left(1 - \frac{T_r}{f(T_r)}\right) + d_4 \left(1 - \frac{T_r}{f(T_r)}\right)^{4/3} \quad (7)$$

where  $\rho_s$  and  $\rho_c$  are respectively, saturated and critical molar liquid density,  $f(T_r)$  is given by Eq. (4),  $\delta$  is a characteristic parameter for each component and  $d_1$ ,  $d_2$ ,  $d_3$  and  $d_4$  are global constants independent of refrigerants which are given in Table 1. The procedure for determination of the global constants and characteristic parameter is explained in the following sections.

### 4. The proposed mixing rules

In order to use Eq. (6) for predicting liquid density of mixtures, some mixture value for  $\rho_c$ ,  $\delta$ ,  $f(T_r)$  and  $T_c$  must be specified. After evaluating several mixing rules for the prediction of liquid density of LNG mixtures, the following mixing rules have been proposed:

$$T_{cm} = \sum_i^{NC} X_i T_{ci} \quad (8)$$

$$\delta_m = \sum_i^{NC} X_i \delta_i \quad (9)$$

$$f_m(T_r) = \sum_i^{NC} \sum_j^{NC} X_i X_j f_{ij}(T_r) \quad (10)$$

where

$$f_{ij}(T_r) = \sqrt{f_i(T_r)f_j(T_r)} \quad (11)$$

and

$$\rho_{\text{Cm}}^{-3/4} = \sum_i^{NC} X_i \rho_{\text{Ci}}^{-3/4} \quad (12)$$

in Eqs. (8)–(12)  $X$  is mole fraction.

## 5. Results and discussion

The name of refrigerants, their formula, number, temperature ranges, number of points and sources for parameter estimation are given in Table 2. Before calculating the liquid densities,  $c_1$ ,  $c_2$  and  $c_3$

Table 2  
Refrigerants experimental data<sup>a</sup> used for fits

Refrigerant no.	Name	Chemical formula	NPTS	T Range (K)
50	methane	CH <sub>4</sub>	64	92–188
170	ethane	C <sub>2</sub> H <sub>6</sub>	56	155–300
290	propane	C <sub>3</sub> H <sub>8</sub>	48	190–365
600	<i>n</i> -butane	<i>n</i> -C <sub>4</sub> H <sub>10</sub>	52	225–420
600a	<i>i</i> -butane	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	47	215–400
1150	ethylene	C <sub>2</sub> H <sub>4</sub>	61	140–276
1270	propylene	C <sub>3</sub> H <sub>6</sub>	45	185–355
702	normal hydrogen	H <sub>2</sub>	65	15–30.8
704	helium	He	33	2.5–4.6
720	neon	Ne	67	24.6–42
728	nitrogen	N <sub>2</sub>	60	64–123
732	oxygen	O <sub>2</sub>	55	74–150
744	carbon dioxide	CO <sub>2</sub>	67	217–299
740	argon	A	65	84–147
717	ammonia	NH <sub>3</sub>	60	218–398
11	trichlorofluoromethane	CCl <sub>3</sub> F	60	248–463
12	dichlorodifluoromethane	CCl <sub>2</sub> F <sub>2</sub>	60	203–378
13	chlorotrifluoromethane	CClF <sub>3</sub>	67	158–297
13B1	bromotrifluoromethane	CBrF <sub>3</sub>	67	178–333
14	carbon tetrafluoride	CF <sub>4</sub>	68	133–218
22	chlorodifluoromethane	CHClF <sub>2</sub>	65	198–363
23	trifluoromethane	CHF <sub>3</sub>	63	163–291
113	trifluorotrichloroethane	CCl <sub>2</sub> FCClF <sub>2</sub>	60	267–473
114	dichlorotetrafluoroethane	CClF <sub>2</sub> CClF <sub>2</sub>	61	233–408
142b	chlorodifluoroethane	CH <sub>3</sub> CClF <sub>2</sub>	64	218–398
152a	difluoroethane	CH <sub>3</sub> CHF <sub>2</sub>	61	208–363
123	dichlorotrifluoroethane	CHCl <sub>2</sub> CF <sub>3</sub>	63	283–444
134a	tetrafluoroethane	CH <sub>2</sub> FCF <sub>3</sub>	53	228–364

<sup>a</sup> The source is ASHRAE [13] except for R-123 and R-134a that is Dupont [14].

must be determined for each refrigerant. They have been determined such that the summation of absolute relative errors in calculating vapor pressures by the PSRK EOS and those from experimental data of Table 2 at the same temperature are minimized. Therefore, the objective function used for optimization of vapor pressures is:

$$\Omega_P = \sum_i^{\text{NPTS}} \left| \frac{P_{\text{CAL}i}}{P_{\text{EXP}i}} - 1 \right|. \quad (13)$$

The optimization has been performed by the use of a nonlinear regression package [15]. Using the above procedure,  $c_1$ ,  $c_2$  and  $c_3$  for 28 refrigerants have been determined. Table 3 shows the refrigerants, the relevant  $c_1$ ,  $c_2$ ,  $c_3$  and the average of absolute percent deviation (AAPD) for calculating the vapor pressures. As it is seen trifluoromethane (R-23) with an AAPD equal to 0.47 has the most error for the calculation of vapor pressures and carbon dioxide (R-744) has the least with an

Table 3

The characteristic parameters, constants of Eq. (4) and the relevant AAPD<sup>a</sup> for the calculation of vapor pressure of pure refrigerants by the PSRK EOS

Refrigerant	NPTS	$\delta \times 10^2$	$c_1$	$c_2$	$c_3$	AAPD <sup>a</sup>
CH <sub>4</sub>	64	−2.20	0.5857	−0.7206	1.2899	0.29
C <sub>2</sub> H <sub>6</sub>	56	1.26	0.7178	−0.7644	1.6396	0.26
C <sub>3</sub> H <sub>8</sub>	48	−0.38	0.7863	−0.7459	1.8454	0.21
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	52	0.00	0.8787	−0.9399	2.2666	0.43
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	47	3.87	0.8288	−0.8285	2.3201	0.43
C <sub>2</sub> H <sub>4</sub>	61	−4.05	0.7172	−0.8757	1.8771	0.41
C <sub>3</sub> H <sub>6</sub>	45	4.98	0.7647	−0.6111	1.3958	0.26
H <sub>2</sub>	65	−22.38	0.2053	−0.4241	−0.1032	0.09
He	33	30.11	−0.0590	−0.6527	0.4271	0.07
Ne	67	−5.59	0.6208	−1.5052	2.7912	0.32
N <sub>2</sub>	60	−3.08	0.5867	−0.4459	0.8926	0.12
O <sub>2</sub>	55	0.95	0.5914	−0.7127	1.4829	0.37
CO <sub>2</sub>	67	0.98	0.8679	−0.7135	2.6563	0.04
A	65	−3.59	0.5391	−0.5686	1.1338	0.14
NH <sub>3</sub>	60	5.88	0.9618	−0.9524	2.1480	0.38
CCl <sub>3</sub> F	60	0.55	0.8611	−0.9711	2.4291	0.37
CCl <sub>2</sub> F <sub>2</sub>	60	1.24	0.8143	−0.6838	1.7469	0.22
CClF <sub>3</sub>	67	−0.16	0.7956	−0.6096	1.6819	0.35
CBrF <sub>3</sub>	67	2.24	0.8032	−0.6106	1.5152	0.25
CF <sub>4</sub>	68	−1.53	0.8099	−0.6134	1.6465	0.21
CHClF <sub>2</sub>	65	0.45	0.8867	−0.7232	1.8186	0.28
CHF <sub>3</sub>	63	6.90	1.0145	−1.2356	2.8585	0.47
CCl <sub>2</sub> FCClF <sub>2</sub>	60	−0.28	0.9803	−1.0880	2.6255	0.40
CClF <sub>2</sub> CClF <sub>2</sub>	61	−3.15	0.9217	−0.5981	1.5593	0.23
CH <sub>3</sub> CClF <sub>2</sub>	64	4.54	0.8742	−0.0861	−0.7367	0.35
CH <sub>3</sub> CHF <sub>2</sub>	61	6.07	0.9231	−0.1238	−0.8003	0.34
CHCl <sub>2</sub> CF <sub>3</sub>	63	1.07	1.0041	−1.0020	2.7005	0.22
CH <sub>2</sub> FCF <sub>3</sub>	53	0.96	1.0708	−0.9536	2.3776	0.22

$$^a \text{AAPD} = \frac{100}{\text{NPTS}} \sum_i^{\text{NPTS}} \left| \frac{P_{\text{CAL}i}}{P_{\text{EXP}i}} - 1 \right|.$$

Table 4

Ability of different methods for the calculation of liquid density of pure refrigerants

Refrigerant	NPTS	T Range (K)	Source	AAPD <sup>a</sup>				
				This work with $\delta = 0$	This work with $\delta^b$	COSTALD	RSD	ISH
CH <sub>4</sub>	84	92–190	[13,16]	1.12	0.25	0.14	0.29	0.10
C <sub>2</sub> H <sub>6</sub>	90	95–300	[13,16]	0.74	0.36	0.09	0.23	0.24
C <sub>3</sub> H <sub>8</sub>	96	90–365	[13,16]	0.26	0.21	0.16	0.41	0.41
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	81	140–420	[13,16]	0.19	0.19	0.12	0.19	0.15
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	89	115–400	[13,16]	2.29	0.70	0.20	0.31	0.39
C <sub>2</sub> H <sub>4</sub>	79	110–276	[13,16]	2.13	0.72	0.45	0.63	0.33
C <sub>3</sub> H <sub>6</sub>	87	90–360	[13,16]	3.13	0.46	0.58	0.71	0.40
H <sub>2</sub>	87	14–32	[13,16]	7.51	1.28	1.24	0.81	0.63
He	69	2.2–5.1	[13,16]	12.36	0.96	3.66	2.92	0.57
Ne	77	24.6–44	[13,16]	2.86	0.25	0.33	0.52	0.20
N <sub>2</sub>	77	64–125	[13,16]	1.54	0.22	0.27	0.39	0.19
O <sub>2</sub>	87	55–154	[13,16]	0.55	0.51	0.24	0.45	0.27
CO <sub>2</sub>	83	217–301	[13,16]	0.56	0.19	0.43	0.45	0.17
A	80	84–150	[13,16]	1.69	0.27	0.13	0.50	0.20
NH <sub>3</sub>	87	198–403	[13,16]	3.76	0.47	1.36	0.40	0.12
CCl <sub>3</sub> F	88	200–463	[13,16]	0.49	0.18	0.45	0.55	0.08
CCl <sub>2</sub> F <sub>2</sub>	114	150–378	[13,16,17]	0.82	0.19	0.40	0.75	0.22
CClF <sub>3</sub>	92	91–301	[13,16]	0.20	0.19	0.12	0.27	0.24
CBrF <sub>3</sub>	85	170–333	[13,16]	1.34	0.33	0.15	0.18	0.14
CF <sub>4</sub>	91	100–223	[13,16]	0.84	0.12	0.04	0.17	0.10
CHClF <sub>2</sub>	125	120–368	[13,16–18]	0.48	0.22	0.27	0.20	0.19
CHF <sub>3</sub>	78	150–294	[13,16]	4.27	0.77	0.63	0.60	0.33
CCl <sub>2</sub> FCClF <sub>2</sub>	93	240–483	[13,16]	0.26	0.15	0.23	0.19	0.26
CClF <sub>2</sub> CClF <sub>2</sub>	84	190–410	[13,16]	1.76	1.53	1.78	1.66	0.88
CH <sub>3</sub> CClF <sub>2</sub>	92	200–400	[13,16,19]	3.07	0.70	0.67	1.08	0.49
CH <sub>3</sub> CHF <sub>2</sub>	118	170–371	[13,16,20]	3.81	0.27	0.53	0.43	0.32
CHCl <sub>2</sub> CF <sub>3</sub>	86	200–455	[14,21]	0.53	0.24	0.36	0.33	0.22
CH <sub>2</sub> FCF <sub>3</sub>	90	200–370	[14,21,22]	0.47	0.20	0.27	0.27	0.16
Average				2.00	0.42	0.52	0.54	0.28

$$^a \text{AAPD} = \frac{100}{\text{NPTS}} \sum_i^{\text{NPTS}} \left| \frac{\rho_{\text{CAL}i}}{\rho_{\text{EXP}i}} - 1 \right|.$$

<sup>b</sup> Values of  $\delta$  are given in Table 3.

AAPD of 0.04. Consequently, the PSRK EOS calculates the vapor pressures of the 28 refrigerants within 0.47% of experimental data.

In order to calculate the liquid density of the refrigerants using Eq. (6), the global constants and characteristic parameter for each of the refrigerants must be determined. The global constants  $d_1$ ,  $d_2$ ,  $d_3$  and  $d_4$  and the characteristic parameters,  $\delta$ , have been optimized in a two step procedure. The objective function applied for the optimization is:

$$\Omega_p = \sum_i^{\text{NPTS}} \left( \frac{\rho_{\text{CAL}i}}{\rho_{\text{EXP}i}} - 1 \right)^2 \quad (14)$$

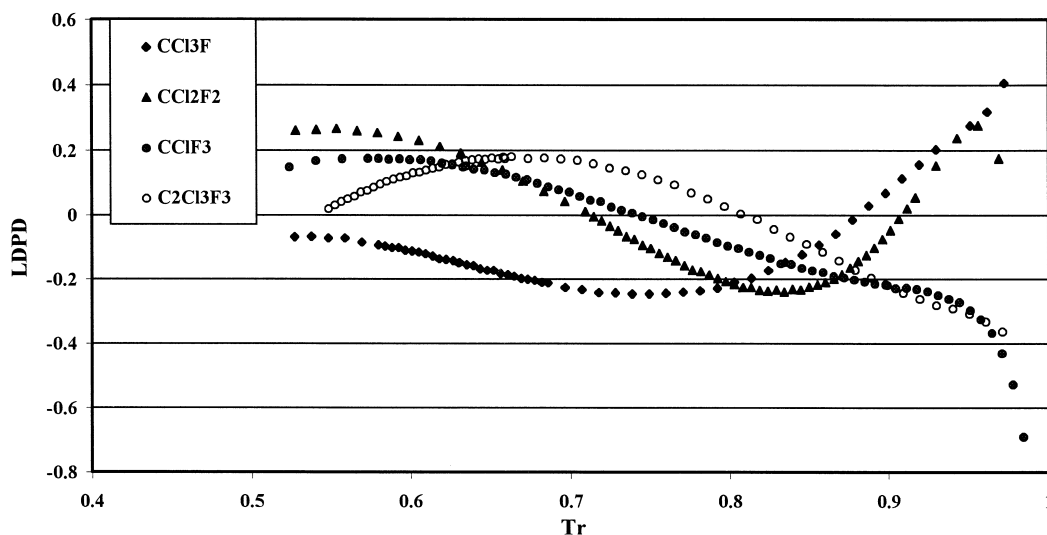


Fig. 1. Liquid density percent deviation of this work as a function of reduced temperature for some of the chlorofluorocarbon refrigerants (experimental data from Ref. [13]).

In the first step  $\delta$  has been taken equal to zero and for nearly 600 data points including a series of refrigerants  $d_1$ ,  $d_2$ ,  $d_3$  and  $d_4$  have been determined. Then in determining  $\delta$ , Eq. (14) has been optimized for each refrigerant using Eq. (6). Again the nonlinear regression package [15] has been applied. The global constants are given in Table 1 and the characteristic parameters included in Table 3.

Table 4 compares the calculations of liquid density of the proposed model, the COSTALD, RSD and Iglesias-Silva and Hall (ISH) [7] correlations. Having a courteous comparison, the parameters for

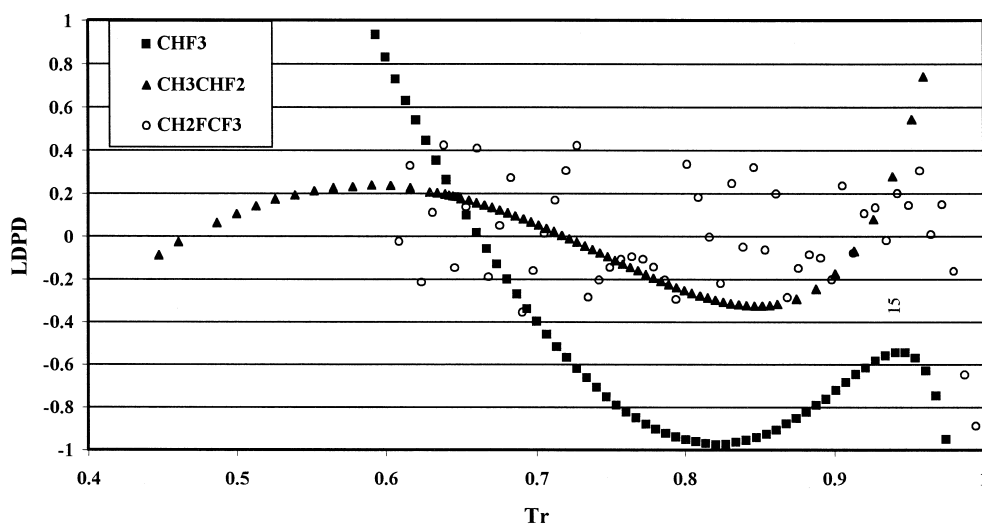


Fig. 2. Liquid density percent deviation of this work as a function of reduced temperature for some of the hydrofluorocarbon refrigerants (experimental data from Refs. [13,14]).

all of the correlations were determined using the experimental data of Table 2 and Eq. (14). To show the predictability of the methods, some other experimental data not used for fits to those used for fits were added. As can be seen this work calculates the liquid densities with an average of AAPD (AAAPD), i.e., the AAPD for all refrigerants including all experimental data points, equal to 0.42. The maximum deviation occurs for R-114 with an AAPD of 1.53 and the least for R-14 with an AAPD of 0.12. The AAAPD of COSTALD, RSD and ISH correlations are 0.52, 0.54 and 0.28 for the same number of data points, respectively. Obviously, the ISH correlation is the best, this work is the next and COSTALD and RSD are the third and the fourth. However, this superiority is in the expense of one more estimation parameter for each refrigerant. ISH correlation has two fitting parameters while the three others have one. Table 4 also compares the model results with optimized  $\delta$  and for the case in which  $\delta$  is zero. Clearly,  $\delta$  improves the results of the model; however, the AAAPD when  $\delta$  is taken zero is still less than 2.00 and without considering He and H<sub>2</sub>, the AAAPD is 1.49. In other words, Eq. (6) have the ability to calculate the liquid density of the refrigerants within 1.49% of experimental data and still not any other parameters in excess of those required for the calculation of vapor pressure or any other pure component properties by the PSRK EOS will be necessary. However, in this case the liquid density results for He and H<sub>2</sub> are not satisfactory.

Figs. 1 and 2 show deviation plots for two categories of the refrigerants. Fig. 1 presents liquid density percent deviation (LDPD) as a function of reduced temperature for some of the CFC refrigerants. Hence, LDPD is defined by:

$$\text{LDPD} = 100 \left( \frac{\rho_{\text{CAL}}}{\rho_{\text{EXP}}} - 1 \right) \quad (15)$$

As can be seen the maximum LDPD through the reduced temperature range are 0.41,  $-0.32$ ,  $-0.69$  and  $-0.36$  for CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub>, CClF<sub>3</sub> and C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>, respectively. These maximums occur near critical points. Fig. 2 demonstrates the LDPD of HFC refrigerants as a function of reduced temperature. The maximum LDPD of HFCs are  $-0.95$ , 0.74 and 0.88 for CHF<sub>3</sub>, CH<sub>3</sub>CHF<sub>2</sub> and CH<sub>2</sub>FCF<sub>3</sub>, respectively. It is seen that LDPD of CHF<sub>3</sub> changes fast through the given temperature range. Surprisingly, the LDPD plot for CH<sub>2</sub>FCF<sub>3</sub> is different from the others. It shows a scatter plot. This can be explained if it is noted that the source of experimental data for CH<sub>2</sub>FCF<sub>3</sub> is different from the source of other refrigerants. The ASHRAE [13] experimental data were smoothed whereas the Dupont [14] data were not.

In order to predict the liquid density of multicomponent systems, Eqs. (8)–(12) have been proposed as mixing rules. Eighteen LNG multicomponent systems have been considered for evaluation of Eq. (6) and their mixing rules. Table 5 shows the multicomponent systems, temperature ranges, sources and their code name. Table 6 presents the liquid density predictions by Eq. (6) and the proposed mixing rules. In addition, Table 6 shows the liquid density predictions of COSTALD, RSD and the Chain-of-Rotator-Group-Contribution (CORGC) EOS [26]. The CORGC has shown its versatility for the prediction of liquid density of LNG systems [5]. For using the CORGC EOS the group parameters of Pults et al. [26] has been used along with the mixing rules given by Nasrifar and Moshfeghian [5]. Yet, the ISH correlation has not been extended to multicomponent systems and so was not used for the comparison. For this comparison, the pure refrigerant parameters optimized in this work for the three correlations are used. As can be seen, the proposed model with its mixing rules predicts the liquid density of LNG multicomponent systems better than the CORGC EOS and the two correlations.



Table 5

List of LNG multicomponent systems used for comparisons

System <sup>a</sup>	T Range (K)	Source	Code name
$(0.0475 - 0.4924)\text{N}_2 + (0.5075 - 0.9525)\text{C}_1$	95–140	[23]	LDS1
$0.0593\text{N}_2 + 0.9407\text{C}_2$	105–120	[23]	LDS2
$(0.0201 - 0.0674)\text{N}_2 + (0.9326 - 0.9798)\text{C}_3$	105–115	[23]	LDS3
$(0.3546 - 0.6800)\text{C}_1 + (0.3199 - 0.6454)\text{C}_2$	105–140	[23]	LDS4
$(0.2954 - 0.8579)\text{C}_1 + (0.1420 - 0.7046)\text{C}_3$	105–130	[23]	LDS5
$(0.7798 - 0.9278)\text{C}_1 + (0.0721 - 0.7798)i\text{-C}_4$	120–130	[23]	LDS6
$0.0593\text{N}_2 + 0.8907\text{C}_1 + 0.04998n\text{-C}_4$	110–125	[24]	LDS7
$0.8604\text{C}_1 + 0.0460\text{C}_2 + 0.0470\text{C}_3 + 0.0457i\text{-C}_4$	115–135	[24]	LDS8
$0.049\text{N}_2 + 0.8060\text{C}_1 + 0.0468\text{C}_2 + 0.0482\text{C}_3 + 0.05i\text{-C}_4$	115–130	[24]	LDS9
$(0.7644 - 0.9737)\text{C}_1 + (0.0080 - 0.0073)\text{C}_2 + (0.0034 - 0.02612)\text{C}_3$	105–125	[25]	LDS10
$(0.0505 - 0.338)\text{N}_2 + (0.3414 - 0.8409)\text{C}_1 + (0.1086 - 0.3206)\text{C}_2$	105–120	[25]	LDS11
$(0.497 - 0.0995)\text{N}_2 + (0.7977 - 0.9055)\text{C}_1 + (0.0497 - 0.1028)\text{C}_3$	105–120	[25]	LDS12
$0.0425\text{N}_2 + 0.8130\text{C}_1 + 0.0475\text{C}_2 + 0.0487\text{C}_3$	105–120	[25]	LDS13
$0.85443\text{C}_1 + 0.05042\text{C}_2 + 0.04038\text{C}_3 + 0.02577i\text{-C}_4 + 0.02901n\text{-C}_4$	105–120	[25]	LDS14
$0.0490\text{N}_2 + 0.8060\text{C}_1 + 0.0468\text{C}_2 + 0.0482\text{C}_3 + 0.05i\text{-C}_4$	105–120	[25]	LDS15
$0.0554\text{N}_2 + 0.7909\text{C}_1 + 0.0560\text{C}_2 + 0.0500\text{C}_3 + 0.0477n\text{-C}_4$	105–110	[25]	LDS16
$0.0425\text{N}_2 + 0.8130\text{C}_1 + 0.0475\text{C}_2 + 0.0487\text{C}_3 + 0.0242i\text{-C}_4 + 0.0241n\text{-C}_4$	105–120	[25]	LDS17
$0.8513\text{C}_1 + 0.0576\text{C}_2 + 0.0481\text{C}_3 + 0.0430n\text{-C}_4$	115–135	[24]	LDS18

<sup>a</sup> C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, n-C<sub>4</sub> and i-C<sub>4</sub> stand for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, n-C<sub>4</sub>H<sub>10</sub> and i-C<sub>4</sub>H<sub>10</sub>, respectively.

Table 6

Ability of different methods for the calculation of liquid density of multicomponent LNG systems

Code name	NPTS	AAPD <sup>a</sup>			
		This work	CORGC	COSTALD	RSD
LDS1	21	0.68	0.48	1.08	1.26
LDS2	4	0.62	0.55	0.03	0.50
LDS3	6	0.71	0.96	0.22	1.30
LDS4	20	0.17	0.21	0.05	0.73
LDS5	20	0.11	0.18	0.48	0.90
LDS6	4	0.88	0.37	1.51	1.72
LDS7	4	0.17	1.60	0.75	0.79
LDS8	5	0.28	1.02	0.42	0.31
LDS9	4	0.15	1.11	0.71	0.70
LDS10	10	0.19	0.19	0.32	0.99
LDS11	7	0.39	0.51	0.80	1.00
LDS12	4	0.25	0.15	0.74	0.54
LDS13	4	0.20	0.13	0.46	0.11
LDS14	4	0.10	0.14	0.41	0.30
LDS15	4	0.23	0.84	0.77	0.30
LDS16	2	0.40	0.31	0.81	0.12
LDS17	4	0.21	0.23	0.67	0.21
LDS18	5	0.30	0.24	0.33	0.23
Average		0.33	0.43	0.55	0.81

$$^a \text{AAPD} = \frac{100}{\text{NPTS}} \sum_i^{\text{NPTS}} \left| \frac{\rho_{\text{CAL}i}}{\rho_{\text{EXP}i}} - 1 \right|.$$

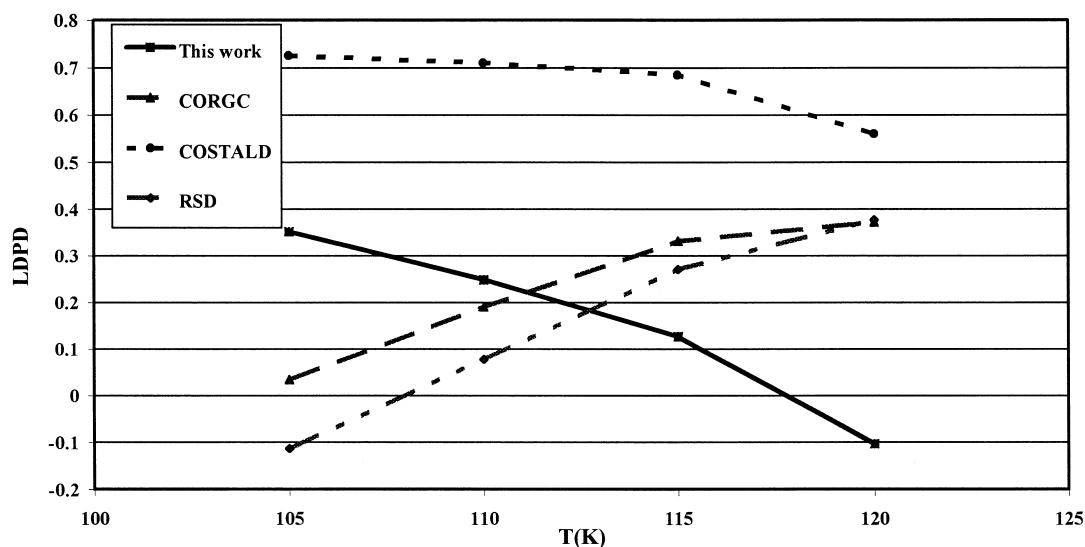


Fig. 3. Ability of different methods for the prediction of liquid density of 0.0425 N<sub>2</sub> + 0.8130 CH<sub>4</sub> + 0.0475 C<sub>2</sub>H<sub>6</sub> + 0.0487 C<sub>3</sub>H<sub>8</sub> + 0.0241 *n*-C<sub>4</sub>H<sub>10</sub> + 0.0242 *i*-C<sub>4</sub>H<sub>10</sub> system (experimental data from Ref. [25]).

The AAPDs are 0.33, 0.43, 0.55 and 0.81 for the model in this work, the CORGC EOS, COSTALD and RSD, respectively. The total number of points for these comparisons was 132. These data points were consisted of 2, 3, 4, 5 and 6 component LNG systems. It should be noted that no adjustable parameter or curve fitting was performed in predicting the liquid densities of these mixtures.

Fig. 3 presents a deviation plot for liquid density of N<sub>2</sub> + CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub> + *n*-C<sub>4</sub>H<sub>10</sub> + *i*-C<sub>4</sub>H<sub>14</sub> multicomponent system. Although with opposite trends, the model introduced here and the CORGC EOS and RSD show merely the same ability for this system and they predict better than COSTALD. However, as indicated by Table 6, the COSTALD generally predicts the liquid density of LNG mixture better than RSD.

## 6. Conclusion

Using the PSRK EOS [2], the vapor pressure of 28 refrigerants have been calculated. In this respect  $c_1$ ,  $c_2$  and  $c_3$ , the parameters of Mathias and Copeman [1] temperature dependent term for relevant refrigerants have been optimized and reported. Of course some of them including the parameters of the hydrocarbon refrigerants have been reported before [2] and what are reported in this work are the revised parameters. Nevertheless, the use of the revised parameters with Eq. (6) are not essential inasmuch as they depend on vapor pressure and so any  $c_1$ ,  $c_2$  and  $c_3$  by any worker could be used.

A correlation and a set of mixing rules for the calculation of saturated liquid density of pure refrigerants and LNG multicomponent systems have been developed. The correlation uses a characteristic parameter for each refrigerant; however, if the parameter is not available, a value of zero could be used. Except for He and H<sub>2</sub> an AAPD of less than 1.49 could be supposed if  $\delta$  is taken equal to 0. Moreover, use of the characteristic parameter,  $\delta$ , improves the prediction of liquid density for pure

refrigerants and multicomponent LNG systems to within 0.42% of experimental data. In a word, a saturated liquid density model has been developed that can be used in conjunction with the PSRK EOS and still not more than one fitting parameter for each component in excess of those required for the calculation of other properties by the PSRK EOS will be necessary. Even with  $\delta$  equal to zero a saturated liquid density with a deviation less than 1.49% for pure refrigerants could be expected.

## 7. Nomenclature

$a$	attraction parameter in the PSRK EOS, Pa m <sup>6</sup> /kmol <sup>2</sup>
$b$	excluded molar volume in the PSRK EOS, m <sup>3</sup> /kmol
$c_1, c_2, c_3$	parameters of Mathias and Copeman equation, Eq. (4)
$d_1, d_2, d_3, d_4$	global constants in Eq. (7)
$f$	temperature dependent function given by Eq. (4)
$P$	pressure, Pa
$R$	universal gas constant, 8314 Pa m <sup>3</sup> /kmol K
$T$	temperature, K
$v$	molar volume, m <sup>3</sup> /kmol
$X$	mole fraction
<i>Greek letters</i>	
$\delta$	characteristic parameter for each component
$\rho$	molar liquid density, kmol/m <sup>3</sup>
$\Omega$	objective function
<i>Subscript</i>	
c	critical
m	mixture
r	reduced

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