Predicting the Liquid Density of Gas Condensates And LNG Mixtures from Equations of State

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(Received 5.7.85, Revised Manuscript received 1.9.86, Accepted 12.9.86)

Abstract

In this contribution, two approaches are followed to predict the saturated liquid density of liquefied natural gas (LNG) mixtures. In one approach, 12 cubic equations of state (EoSs), comprising the popular Peng-Robinson (PR) and Redlich-Kwong-Soave (RKS), are employed to predict the saturated liquid density of 20 LNG mixtures. In the other approach, these EoS are used in conjunction with a recently developed correlation to predict the liquid density of the same LNG mixtures. This correlation takes the advantages of the EoSs α functions and is remarkably accurate for LNG mixtures. The results for both approaches are presented and the best predicting methods are ranked. Also the liquid density of 3 gas condensate mixtures are predicted using 10 EoSs and the results are compared with experimental data. The method employed is discussed and the best EoSs are ranked. Our evaluation indicates that in general, the EoSs used in this study are not accurate enough for predicting the liquid density of gas condensate mixtures. The PR, Patel-Teja (PT) EoSs or one of their variant are recommended, however.

Keywords: Thermodynamics - Equation of State - Saturated liquid density - LNG - Gas condensate

Introduction

It is well known that cubic equations of state (EoSs) are not very accurate for predicting the liquid density of pure fluids and their mixtures. However, as a first approximation, it is a common practice to predict the liquid density of mixtures including liquefied natural gases (LNG) using an EoS. The widely used Peng-Robinson (PR) [1] or Redlich-Kwong-Soave (RKS) [2] are usually recommended in gas industry. These two EoSs or one of their variants are not, however, accurate enough to the same extent. Newly developed EoSs are also emerging and these EoSs look promising in calculating liquid densities. Then, a comparative study between the popular EoSs and newly developed ones is desirable. This is one of the objectives in this study.

Recently a saturated liquid density correlation was developed by Nasrifar and Moshfeghian [3] which has proven to be useful [4,5] for predicting the saturated liquid density of LNG mixtures when the correlation is used in conjunction with the α function from an EoS. At first, the α function from the PSRK EoS was used with the correlation. Then, Mchaweh et al. [5] simplified the correlation by using the α function from the RKS EoS. In this work, we attempt to use this correlation with the α function from 12 EoSs for predicting the liquid density of LNG mixtures. This is one of the objectives in this work. While it is likely to quite accurately predict the liquid density of LNG mixtures using a correlation, calculating the liquid density of gas condensate mixtures are subject to significant error. In fact, many of the EoSs are not qualified to accurately predict the retrograde behavior of natural gas mixtures because they can not predict accurately the supercritical behavior of methane [6]. Moreover, rich natural gas mixtures contain heavy ends, hence requiring characterization. Usually little information is avaible for a good characterization. It is then difficult to predict the liquid drop out accurately. In addition, the cubic EoSs are not accurate enough. Consequently, these drawbacks reduce the accuracy of EoSs in predicting the liquid density of gas condensates. The other objective of this work is to compare the accuracy of 12 EoSs for calculating the liquid density of

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Table1: PVT relations for the EoSs used in this study.

EoS	PVT relation[a]
RKS, RKT, RKS-SW	$P = \frac{RT}{v-b} - \frac{a_C\alpha(T_r)}{v(v+b)}$
PR, PRG	$P = \frac{RT}{v-b} - \frac{a_C\alpha(T_r)}{v(v+b)+b(v-b)}$
TCCNM	$P = \frac{RT}{v-b(\theta)} - \frac{a_C\alpha(\theta)}{v^2+2b(\theta)v-2b(\theta)^2}, \theta = \frac{T-T_t}{T_c-T_t}$
PT, PTV	$P = \frac{RT}{v-b} - \frac{a_C\alpha(T_r)}{v(v+b)+c(v-b)}$
SW	$P = \frac{RT}{v-b} - \frac{a_C\alpha(T_r)}{v^2+(1+3\omega)bv-3\omega b^2}$
GD	$P = \frac{RT}{v-b} - \frac{a_C\alpha(T_r)}{v(v+c)+c(v-b)}$
MMM	$P = \frac{RT}{v}\left(\frac{v+\varepsilon b}{v-b}\right) - \frac{a_C\alpha(T_r)/\sqrt{T}}{v(v+N\varepsilon b)}$
ST	$P = \frac{RT}{v-b} - \frac{a_C\alpha(T_r)}{v^2+(b+c)v-(bc+d^2)}$
ALSJ	$P = \frac{RT}{v-b_1} - \frac{a_C\alpha(T_r)}{(v-b_2)(v+b_3)}$

[a] *R* is the gas constant, *T* is the temperature, T_c is the critical temperature, T_t is the triple point temperature, T_r is the reduced temperature, θ is the reduced temperature, *P* is the pressure, *v* is the molar volume, *c*, *d*, *N* and ε are the EoSs parameters, ω is the acentric factor, *b* is the molecular co-volume, a_C is the attractive parameter at the critical point and α is the temperature dependence for attractive parameter also called α - function.

20 LNG mixtures. The accuracy of 10 EoSs is also compared with each other and experimental data in predicting the liquid density of 3 gas condensate mixtures. The results are presented and the best methods in each case are ranked.

The EoSs

The EoSs used in this study are classified as two-, three- and four-parameter EoSs. The modified Twu et al. [7] EoS by Nasrifar and Moshfeghian (TCCNM) [8] is a two-parameter EoS. The two-parameter EoSs are solely comprised by the Redlich-Kwong (RK) [9] and PR families. Of the RK family, the modifications by Soave (RKS), Twu et al. (RKT) [10] and Nasrifar and Bolland (RKS-SW) [11] are used. From the PR family, the original EoS, and a modified version by Gasem et al. (PRG) [12] are used. The three-parameter EoSs are: Schmidt and Wenzel (SW) [13], Guo and Du (GD) [14], Patel and Teja (PT) [15], a modified PT EoS by Valderrama (PTV) [16] and Mohsen-Nia et al. (MMM) [17]. The Salim, Trebble (ST) [18] and Adachi, Lu, Sue and Jensen (ALSJ) [19] EoSs are the four-parameter EoS that used in this

Table 2: The α functions for the EoSs.

EoS	α -Function[a]
RKS, PR, PT, PTV,ALSJ SW, GD, MMM	$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2$
RKS-SW	$\begin{cases} \alpha_{Subcritical} = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \\ \alpha_{Supercritical} = \dfrac{b_1}{T_r} + \dfrac{b_2}{T_r^2} + \dfrac{b_3}{T_r^3} \end{cases}$
TCCNM	$\alpha = \left[1 + m\left(1 - \sqrt{\theta}\right)\right]^2, \theta = \dfrac{T - T_t}{T_C - T_t}$
PRG	$\alpha = \exp\left[\left(A + BT_r\right)\left(1 - T_r^{C+D\omega+E\omega^2}\right)\right]$
RKT	$\alpha = \alpha^{(0)} + \omega\alpha^{(1)}, \alpha^{(i)} = T_r^{N(M-1)} e^{L(1-T_r^{NM})}$
ST	$\alpha = 1 + m\left(1 - \sqrt{T_r}\right) + p\left(\sqrt{0.7} - \sqrt{T_r}\right)\left(1 - \sqrt{T_r}\right)$

[a] T_r is the reduced temperature, ω is the acentric factor and m, a_0, a_1, a_2, a_3, A, B, C, D, E, N, M, L, p are either a constant or a function of acentric factor.

study. The pressure-volume-temperature (PVT) relationships for the above mentioned EoSs are given in Table I. In Table 2, the temperature dependences for the attractive terms of the EoSs (also called α function) are presented. The EoSs are presented briefly in the following sections, however, the details can be found in the given references.

The RKS EoS

The RK EoS successfully relates the PVT of gases, however, it poorly predicts the vapor pressure and liquid density of pure compounds. Soave [2] introduced a temperature dependence (α) for the attractive term of the RK EoS as given in Table II. This term significantly improves the accuracy of the EoS to predict vapor pressure, although the accuracy of the EoS to predict liquid density remains unchanged [20]. As a consequence of this modification, the RKS can successfully be used in fluid phase equilibria of hydrocarbon mixtures. However, the α-function causes the RKS to predict anomalous behaviors at high pressures [21].

The RKT EoS

Soave [2] correlated the α-function for the RKS EoS by matching the predicted vapor pressure of pure compounds at reduced temperature of 0.7 to the experimental value. Although it has been proven to be useful, the vapor pressure predicted by the RKS EoS usually gets worse at reduced temperatures less than 0.7. Recognizing this behavior, especially for heavy hydrocarbons, Twu et al. [10] developed an α-function that works well from the triple point to the critical point temperature. Predicting the vapor pressure of heavy hydrocarbons well, the RKT EoS could be capable of describing the vapor-liquid-equilibria (VLE) of natural gas mixtures containing heavy hydrocarbons.

The RKS-SW EoS

Nasrifar and Bolland [11] took the advantage of the square-well (SW) potential to account for the supercritical behavior of fluids in the RKS EoS. The RKS-SW is used in this paper for predicting the liquid density of gas condensate mixtures.

The PR EoS

Another successful PVT relation among EoSs is the PR EoS. Compared to RK family EoSs, the PR family EoSs generally predicts the liquid density of compounds more accurately [20]; however, the accuracy is not good enough for industrial applications. The PR EoS takes the advantage of Soave-type α-function, hence showing similar quality with temperature. However, Peng and Robinson [3] used a reduced temperature range from 0.7 to 1 to correlate the PR α-function. The α-function was first correlated to the vapor pressure of pure compounds with acentric factor less than 0.5 and later in 1978 they extended it to compounds with larger acentric factor.

The PRG EoS

Gasem et al. [12] developed a new α-function in exponential form having recognized that the Soave-type α-function employed by the PR EoS does not decrease monotonically to zero with temperature. The PRG EoS also attempts to improve the predictive capability of the PR EoS for vapor pressure.

The TCCNM EoS

Nasrifar and Moshfeghian [8] employed a linear temperature dependence for molar covolume and a modified Soave's temperature dependence for the attractive parameter of the PVT relation proposed by Twu et al. [9] to obtain an accurate EoS for simple pure compounds and their mixtures. The TCCNM EoS [8] quite accurately predicts the liquid density of LNG mixtures.

The SW EoS

Schmidt and Wenzel [13] recognized that the RKS EoS accurately predicts the thermodynamic properties of fluids with acentric factor near zero while the PR EoS near 0.3. Knowing that, they developed a new EoS that reduces to the RK EoS at acentric factor of 0 and to the PR EoS at acentric factor of 1/3. In the SW EoS, acenteric factor is a third parameter. The SW EoS accurately predicts the liquid density and vapor pressure of light and moderate compounds.

The GD EoS

The GD EoS is a three parameter EoS, very similar in form to the PT EoS [15]. It was developed peculiarly for hydrocarbon mixtures. The α-function for the GD EoS is of Soave-type α-function, however, the parameter m is defined differently for different compounds based on acentric factor. As shown by Guo and Du, the pure and mixture properties are predicted quite accurately using the GD EoS.

The PT and PTV EoSs

The PT and PTV EoSs have the same PVT relationship and α-function. The difference is in calculating the EoSs parameters, i.e., a, b and c. In the PTV EoS, the actual compressibility factor is used while the critical compressibility factor in the PT EoS is a conventional parameter. Consequently, the PTV EoS predicts liquid densities near the critical point more accurately than the PT EoS.

THE MMM EoS

Mohsen-Nia et al. [17] did not use a van der Waals repulsive term for the MMM EoS. Instead, they employed a more accurate empirical repulsive term having considered molecular simulation data of hard spheres. The MMM EoS is accurate for predicting vapor pressure and liquid density of light and moderate pure compounds. The α-function of the MMM EoS is a Soave-type. They also used a temperature dependence term for the molecular co-volume parameter. As shown by Mohsen-Nia et al. [17], this improves the capability of the EoS for predicting liquid density, however, as pointed out by Salim and Trebble [18], may cause anomalous behaviors at high pressures.

The ST EoS

The STB is a four-parameter EoS. The PVT relationship for the ST is flexible and can be reduced to other EoSs. Although, it is accurate for predicting the thermodynamic properties of pure compounds, its extension to mixtures needs 4 mixing rules. Considering that mixing rules are in general empirical, application of 4 mixing rules may diminish the predictability of the ST EoS for mixtures.

The ALSJ EoS

Adachi et al. [19] (ALS) developed a four-parameter EoS. Jensen [22] modified the ALS EoS for application in oil and gas industries. The ALSJ EoS is quite accurate for calculating the properties of pure fluids.

Mixing Rules

The van der Waals mixing rules have proven to be useful in hydrocarbon processing. The van der Waals quadratic mixing rule with geometric combining rule is used for the attractive parameter of the EoSs:

$$a=\sum_i\sum_j x_i x_j a_{ij} \qquad (1)$$

with

$$a_{ij}=\sqrt{a_{ii}a_{jj}}\left(1-k_{ij}\right) \qquad (2)$$

where k_{ij} is the binary interaction parameter. For the second, third and fourth parameters the following mixing rule is used:

$$w=\sum_j x_j w_j \qquad (3)$$

where w stands for b, c, d and ω in different EoSs.

Heavy Ends

The heavy constituents of a natural gas are usually lumped and reported as C_{7+}. The C_{7+} fraction are commonly specified by molecular weight and specific gravity. The C_{7+} fractions may comprise of many components and different families of hydrocarbons. Although it is possible to analysis the C_{7+} fractions accurately using new techniques such as gas capillary chromatography, Pedersen et al. [23] found out that the specification of components up to C_{20} may be suffice for an accurate calculation of thermodynamic properties. Nevertheless, usually the composition up to C_6 is available with a heavy end that must be characterized. It is a common practice to split a C_{7+} fraction into a number of single carbon number (SCN) groups and then calculate the critical properties of each group using available correlations [24-27]. Katz [28] introduced a simple decay exponential function to express the distribution of SCN groups. Pedersen et al. [23] also found out that the compositional distribution of SCNs in North Sea petroleum fractions is best described by an exponential function. Starling [29] has also suggested recently an exponential decay function for splitting heavy ends. The decay functions are different in form and accuracy. However, the decay function by Pedersen et al. [23] seems to be simple but still useful [30]; hence, it will be used in this study. The decay function reads

$$Z_n=\exp\left(A+BM_n\right) \qquad (4)$$

Where Z_n is the SCN group mole fraction and M_n is the SCN group molecular weight. The unknowns A and B are determined for a C_{7+} fraction using the following constraints:

$$Z_{C_{7+}}=\sum_{C_7}^{C_N} Z_{C_n} \qquad (5)$$

and

$$M_{C_{7+}}=\frac{\sum_{C_7}^{C_N} Z_{C_n}M_{C_n}}{Z_{C_{7+}}} \qquad (6)$$

where C_N is the heaviest SCN to be considered in a C_{7+} fraction and C_n is a dummy variable. For determining A and B and hence the SCN distribution, the SCN molecular weight and volume are needed. We used the generalized SCN properties reported by Whitson [31].

The Liquid Density Correlation

Nasrifar and Moshfeghian [3] developed a saturated liquid density correlation in conjunction with EoSs. The correlation in its generalized form is expressed by:

$$\rho/\rho_C=1+d_1\Phi^{1/3}+d_2\Phi^{2/3}+d_3\Phi+d_4\Phi^{4/3} \qquad (7)$$

with

$$\Phi=1-T_r/\alpha(T_r) \qquad (8)$$

Where d_1=1.1688, d_2=1.8177, d_3=-2.6581, d_4=2.1613. The parameter T_r is the reduced temperature and α denotes the α function

Table 3: LNG mixtures studied in this work (experimental data from Refs. [32-34]).

Code	N_2	C_1	C_2	C_3	*i*-C_4	*n*-C_4	*i*-C_5	*n*-C_5
LNG1		0.8604, 0.85378	0.0460, 0.05178	0.0479, 0.0470	0.0457, 0.04741			
LNG2	0.04801	0.8094	0.04542	0.0505	0.04667			
LNG3		0.8534, 0.75442	0.07895, 0.15401	0.04729, 0.06950	0.00854, 0.00978	0.00992, 0.00978	0.00097, 0.00089	0.00089, 0.00083
LNG4	0.0484	0.8526	0.0483	0.0507				
LNG5		0.84558- 0.85892	0.05042- 0.11532	0.4038- 0.01341	0.0053- 0.02577	0.00705- 0.02901		
LNG6	0.049	0.8060	0.0468	0.0482	0.050			
LNG7	0.0554	0.7909	0.056	0.0500		0.0477		
LNG8	0.00601- 0.0425	0.8130- 0.90613	0.0475- 0.08477	0.02154- 0.0298	0.00300- 0.0241	0.00306- 0.0242		
LNG9		0.85133, 0.84566	0.05759, 0.07924	0.04808, 0.05060		0.02450, 0.04300		
LNG10	0.00599- 0.00859	0.74275- 0.90068	0.06537- 0.16505	0.02200- 0.06742	0.00291- 0.01336	0.00284- 0.01326	0.00010- 0.00223	0.00011- 0.00216
LNG11		0.85341	0.07898	0.04729	0.00854	0.00992	0.00097	0.00089
LNG12		0.86040	0.04600	0.04790	0.0457			
LNG13	0.0484	0.8094	0.04542	0.05050	0.04628			
LNG14	0.0484	0.8526	0.0453	0.0537				
LNG15		0.85443	0.05042	0.04038	0.02577	0.02900		
LNG16	0.049	0.8060	0.0468	0.0482	0.0500			
LNG17	0.0554	0.7909	0.056	0.05		0.0477		
LNG18	0.0425	0.8130	0.0475	0.0487	0.0241	0.0242		
LNG19		0.85133	0.05759	0.04808		0.0430		
LNG20	0.00599	0.74275	0.16505	0.06547	0.00843	0.00893	0.00069	0.00269

from any EoS. Equation (7) is extended to mixtures by the following mixing rules:

$$T_C = \sum_j^n x_j T_{C,j} \tag{9}$$

$$\alpha = \sum_i^n \sum_j^n x_i x_j \sqrt{\alpha_i \alpha_j} \tag{10}$$

$$\rho_C = \left[\sum_j^n x_j \rho_{C,j}^{-3/4}\right]^{-4/3} \tag{11}$$

Results and Discussion

In this section, first, the accuracy of the EoSs in predicting the saturated liquid densities of 20 LNG mixtures given in Table 3 is presented. Then, the α functions from these EoSs are used with Equations (7) and (8) and mixing rules Equations (9)-(11) to predict the saturated liquid densities of the same mixtures. Finally, the accuracy of the EoSs in predicting the liquid densities of 3 gas condensate mixtures is presented and discussed.

In Table 3, one can also find the compositions for LNG mixtures, code names. The LNG compositions cover a range of compositions for methane from 74.2% to 90.6%. The temperature of LNG mixtures, given in Table IV, ranges from 105 K to 135 K. Given in Table IV are also the number of points used in calculations and average absolute deviations obtained in predicting the saturated liquid densities of 20 LNG mixtures. The procedure for calculating saturated liquid densities is as follow. After having calculated the bubble point pressure of each mixture at the given temperature, the liquid densities of LNG mixtures are calculated using the bubble point pressure and the compressibility factor of the liquid phase. As can be seen, the SW, TCCNM and ALSJ EoSs are the most accurate EoSs in predicting the liquid densities of the LNG mixtures,

Table 4: Accuracy[a] of the EoS in predicting the saturated liquid density of LNG mixtures.

Code	n	T-range(K)	RKS	RKT	PR	PRG	TCCNM	SW	GD	MMM	PT	PTV	ST	ALSJ
LNG1	9	115-135	1.98	1.96	10.55	10.74	0.54	0.12	2.1	3.70	1.36	5.27	2.32	0.90
LNG2	4	115-130	1.70	1.68	10.86	11.06	0.79	0.22	2.87	3.30	1.70	5.49	2.13	0.57
LNG3	9	110-130	1.89	1.90	10.56	10.75	0.58	0.08	2.06	4.70	1.48	5.56	2.54	0.98
LNG4	4	105-120	0.84	0.91	11.80	11.97	0.40	0.37	2.94	3.49	2.07	6.43	1.68	0.32
LNG5	12	105-130	1.75	1.76	10.77	10.95	0.47	0.13	2.12	4.08	1.45	5.61	2.28	0.91
LNG6	4	105-120	1.64	1.62	10.78	10.99	0.43	0.26	2.48	5.65	1.77	5.47	3.06	0.80
LNG7	6	105-130	1.67	1.64	10.82	11.02	0.51	0.22	2.52	4.26	1.73	5.78	2.27	0.71
LNG8	15	105-130	1.45	1.48	11.17	11.34	0.46	0.17	2.46	3.05	1.58	5.88	1.75	0.66
LNG9	9	115-135	1.95	1.93	10.59	10.77	0.53	0.12	2.13	3.32	1.40	5.56	1.98	0.88
LNG10	13	110-130	1.89	1.91	10.58	10.76	0.59	0.11	2.13	4.31	1.46	5.56	2.41	0.95
LNG11	5	110-130	1.67	1.68	10.87	11.05	0.47	0.09	2.21	3.76	1.52	5.73	2.08	0.82
LNG12	5	115-135	2.00	1.97	10.55	10.74	0.61	0.15	2.10	3.45	1.33	5.25	2.22	0.89
LNG13	4	115-130	1.70	1.68	10.86	11.07	0.79	0.22	2.87	3.30	1.70	5.49	2.13	0.57
LNG14	4	105-120	0.84	0.91	11.80	11.97	0.40	0.37	2.94	3.49	2.06	6.43	1.68	0.32
LNG15	4	105-120	2.05	2.01	10.30	10.51	0.61	0.15	1.83	6.41	1.36	5.24	3.33	1.26
LNG16	4	105-120	1.64	1.62	10.78	10.99	0.43	0.26	2.48	5.65	1.77	5.47	3.06	0.80
LNG17	2	105-110	1.65	1.60	10.69	10.92	0.42	0.35	2.32	6.63	1.85	5.72	3.18	0.88
LNG18	4	105-120	1.73	1.70	10.68	10.90	0.43	0.20	2.38	5.63	1.70	5.53	2.96	0.88
LNG19	5	115-135	2.06	2.02	10.46	10.65	0.64	0.13	2.09	3.29	1.34	5.45	1.99	0.91
LNG20	4	110-125	2.33	2.33	9.99	10.18	0.911	0.24	1.74	5.97	1.27	5.17	3.28	1.34
AVE			1.74	1.74	10.77	10.96	0.54	0.17	2.29	4.12	1.55	5.61	2.31	0.83

[a] $\%AAD = (100/n)\sum_j \left|\rho_{cald,j} - \rho_{expl,j}\right| / \rho_{expl,j}$

whilst the PR and PRG EoSs are the least. Among the popular two-constant RKS and PR EoSs, clearly, the RKS EoS is more accurate and must be preferred.

The poor accuracy of cubic EoSs in predicting liquid densities is attributed to the weak representation of repulsive forces by the van der Waals repulsive term ($RT/(v-b)$). This inaccuracy could partly be compensated by adapting a too strong attractive term and partly by using a temperature dependence for molecular co-volume, e.g. as in TCCNM EoS.

Table 4 indicates the accuracy of the saturated liquid density correlation, Equation (7), when it is coupled with the α function from different EoSs. Table 4 clarifies that the coupling of the correlation with the PR or PRG EoSs gives the best results and with the TCCNM EoS the worst. However, even in the worst case, the average deviation is better than 1.6%. In other words, if the correlation is coupled with the α function of different EoSs, good agreement with experimental data is obtained no matter which EoS α function is used. In general, the coupling of the correlation with the PR, PRG, ALSJ and GD give the best results, respectively.

It is worth stressing that the EoS α functions are independent of the behavior of the EoSs in predicting liquid density. It is normally used to fit the EoS to the vapor pressure of pure compounds and indicates the interaction of molecules due to the attraction forces. While liquid density mostly represents the repulsive behavior of molecules.

In Table 5, the accuracy of 10 EoSs in predicting the liquid densities of 3 gas condensate mixtures, namely GC1, GC2 and GC3 is presented. Given in Table 5 are also the compositions, number of points, temperature ranges and pressure ranges of the systems under study. The mixtures GC2 and GC3 are synthetic mixtures with known compositions; hence, calculations are straight forward, i.e., using the isothermal-isobaric flash calculation, the compositions of the liquid formed by retrograde condensation are predicted. Then, using the predicted compositions and compressibility factor for the liquid phase and the given temperature, pressure, the liquid density of the condensate is predicted. The mixture GC1 is, however, a rich natural gas containing a heavy end. Before performing the calculations, the heavy end of the mixture should be characterized as explained in the section entitled ‘heavy ends.’ For the mixture GC1, the distribution given in Figure 1 was obtained for the heavy end. Then a series of calculations at two temperatures were performed to locate the optimum number of splitting the heavy ends. As it is seen in Figure 2, the more the number of SCN groups, the more accurate prediction is obtained. After 12 SCN, however, the deviations do not change appreciably. Hence, we split the heavy end into 12 SCN groups. After characterizing, the calculation procedure is similar to that mentioned above.

Table 5: Accuracy[a] of the saturated liquid density correlation together with the α function of different EoS in predicting the saturated liquid density of LNG mixtures.

Code	n	T-range(K)	RKS	RKT	PR	PRG	TCCNM	SW	GD	MMM	PT	PTV	ST	ALSJ
LNG1	9	115-135	1.16	1.14	0.26	0.24	1.93	0.99	0.29	1.45	0.67	0.69	1.59	0.25
LNG2	4	115-130	1.27	1.25	0.20	0.21	1.78	1.09	0.35	1.34	0.77	0.79	1.44	0.28
LNG3	9	110-130	1.49	1.44	0.24	0.34	1.54	1.29	0.58	1.10	1.00	1.01	1.21	0.47
LNG4	4	105-120	1.96	1.86	0.59	0.73	1.06	1.77	1.01	0.54	1.51	1.55	0.79	0.95
LNG5	12	105-130	1.45	1.40	0.22	0.28	1.62	1.26	0.52	1.12	0.97	0.99	1.30	0.44
LNG6	4	105-120	1.59	1.54	0.30	0.45	1.30	1.39	0.71	0.94	1.11	1.14	0.99	0.60
LNG7	6	105-130	1.63	1.59	0.36	0.47	1.40	1.43	0.72	0.96	1.13	1.15	1.06	0.61
LNG8	15	105-130	1.54	1.48	0.25	0.33	1.57	1.36	0.58	1.01	1.07	1.11	1.27	0.52
LNG9	9	115-135	1.30	1.28	0.25	0.27	1.82	1.12	0.40	1.32	0.80	0.82	1.48	0.33
LNG10	13	110-130	1.46	1.41	0.23	0.31	1.59	1.26	0.54	1.13	0.97	0.98	1.25	0.46
LNG11	5	110-130	1.49	1.44	0.26	0.33	1.60	1.30	0.55	1.09	1.01	1.03	1.28	0.47
LNG12	5	115-135	1.12	1.10	0.31	0.27	1.99	0.94	0.28	1.51	0.62	0.64	1.65	0.25
LNG13	4	115-130	1.27	1.25	0.20	0.21	1.78	1.09	0.35	1.34	0.77	0.79	1.44	0.28
LNG14	4	105-120	1.96	1.86	0.59	0.73	1.06	1.77	1.00	0.54	1.51	1.55	0.79	0.95
LNG15	4	105-120	1.48	1.43	0.23	0.34	1.44	1.28	0.60	1.05	1.00	1.02	1.11	0.49
LNG16	4	105-120	1.59	1.54	0.30	0.45	1.30	1.39	0.71	0.94	1.11	1.14	0.99	0.60
LNG17	2	105-110	1.94	1.90	0.67	0.85	0.90	1.74	1.10	0.56	1.47	1.49	0.58	0.97
LNG18	4	105-120	1.62	1.58	0.33	0.48	1.30	1.43	0.75	0.91	1.14	1.16	0.97	0.63
LNG19	5	115-135	1.23	1.22	0.28	0.28	1.85	1.05	0.36	1.41	0.72	0.74	1.56	0.31
LNG20	4	110-125	1.30	1.25	0.13	0.20	1.66	1.08	0.43	1.30	0.80	0.79	1.30	0.30
AVE			1.46	1.42	0.28	0.35	1.58	1.27	0.55	1.12	0.98	1.00	1.26	0.47

[a] $\%AAD = (100/n)\sum_j \left|\rho_{cald,j} - \rho_{\exp l,j}\right| / \rho_{\exp l,j}$

Table 6: Average absolute deviation[a] in predicting the liquid density of gas condensate mixtures.

Code	n	T (K)	P range (MPa)	RKS	RKS-SW	RKT	PR	PRG	GD	MMM	PT	PTV	ST
GC1[b]	24	333.2, 371.6, 410.1	4.48-39.01	14.04	14.96	12.67	5.56	3.92	7.88	16.66	7.65	11.19	18.87
GC2[c]	6	303.15	19.41-30.44	33.34	33.81	29.67	28.09	26.12	15.82	8.91	15.43	7.49	10.71
GC3[d]	3	353.15	27.68-30.44	25.87	30.12	21.27	25.40	21.52	2.42	26.12	2.23	4.17	23.27
AVE				18.62	19.77	16.54	11.46	9.56	8.83	16.11	8.57	9.88	17.79

[a] $\%AAD = (100/n)\sum_j \left|\rho_{cald,j} - \rho_{\exp l,j}\right| / \rho_{\exp l,j}$

[b] Composition: N_2, 3.912%; CO_2, 0.750%; C_1, 70.203; C_2, 9.220; C_3, 2.759; *i*-C_4, 0.662; *n*-C_4, 0.981; *i*-C_5, 0.402; *n*-C_5, 0.422; C_6, 0.816; C_{7+}, 9.873%. The C7+ specification: MW=192.8, Sp.Gr=0.803 (Ref. [35])

[c] Composition: C_1, 82.32%; C_3, 8.71%; *n*-C_5, 5.05%; *n*-C_{10}, 1.98%; *n*-C_{16}, 1.94% (Ref. [36]).

[d] Composition: C_1, 82.05%; C_3, 8.95%; *n*-C_5, 5.00%; *n*-C_{10}, 1.99%; *n*-C_{16}, 2.01% (Ref. [36]).

The results for predicting the liquid densities of gas condensate mixtures are also given in Table 5 in terms of average absolute deviation. As it is clear, in general, the PT, GD and PRG EoSs are more accurate than the others, whilst the RKS-SW is the least. Figure 3 shows a deviation plot indicating the distribution of errors in predicting the saturated liquid density of GC1 mixtures with pressure at three different temperatures. The deviations are well behave and nearly constant with pressure, while the deviations at low temperatures are larger than that at higher temperature.

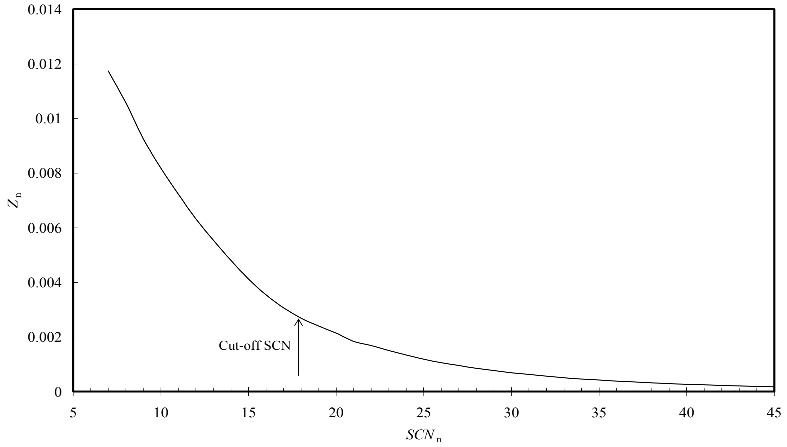

Figure 1: Distribution of SCN groups for the mixture GC1.

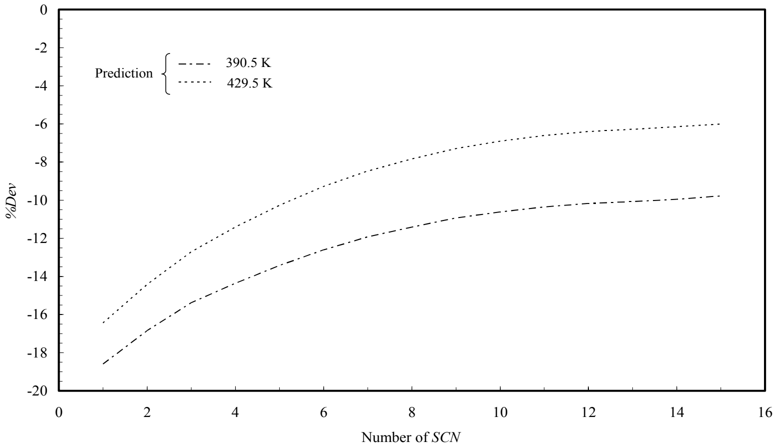

Figure 2: Percent deviations in predicting the dew points of the mixture GC1 using the PRG EoS.

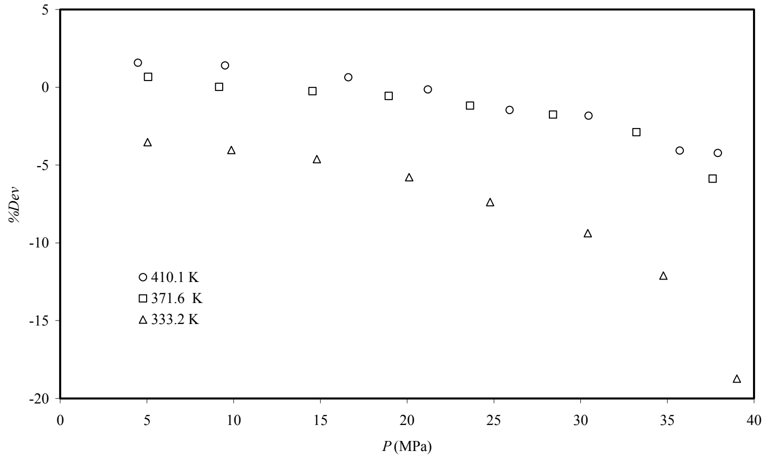

Figure 3: Percent deviations in predicting the saturated liquid density of liquid dropout produced from mixture GC1 using the PRG EoS.

Conclusions

The liquid densities of 20 LNG mixtures have been predicted using 12 EoSs. In these predictions, the SW EoS has been ranked number 1, the TCCNM number 2 and ALSJ number 3, respectively. A saturated liquid density correlation has successfully been used with the α function from the 12 EoSs for predicting the liquid densities of the same LNG mixtures. It has been found that the coupling of the correlation with the PR, PRG and ALSJ EoSs give the best results, respectively. The coupling of the correlation with the TCCNM EoS gives the worst results with an average absolute deviation equal to 1.58%. The liquid densities of 3 gas condensate mixtures have been predicted using 10 EoSs. It was found out that the PT, GD, PRG and PTV EoSs are the most accurate, respectively.

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پیش بيني چگالی مایعات معیانی و مخلوط های LNG با استفاده از معادلات حالت

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در این مقاله دو روش برای پیش بینی چگالی مخلوط گاز های طبیعی مایع شده در نظر گرفته می شود. در یکی از این دو روش ۱۲ معادله ی حالت شامل معادله های پنگ –رابینسون و ردلیک – کانگ – ساوه برای پیش بینی چگالی ۲۰ مخلوط گازی مایع شده بکار گرفته می شود. در روش دیگر این معادله های حالت به همراه یک رابطه نسبتاًجدید برای پیش بینی چگالی مایع های گازی بکار می روند. لازم به توضیح است که این رابطه چگالی از تابع دمایی معادله های حالت استفاده کرده و جواب دقیقی ارئه می دهد. علاوه بر پیش بینی چگالی گازهای طبیعی مایع شده، با استفاده از ۱۰ معادله حالت چگالی سه مخلوط میعانی نیز پیش بینی می شود. بررسی های بکار گرفته شده نشان می دهد که به طور کلی معادله های حالت بکار گرفته شده دارای دقت کافی برای پیش بینی چگالی مایعات میعانی نیستند. با این حال معادله های پنگ-رابینسون، پتیل-تجا یا یکی از مشتقات آنها توصیه می شود.

واژه هاي کليدي: ترمودینامیک - معادله ی حالت - چگالی اشباع مایعات - گازطبیعی مایع شده - مایع میعانی