Volume 2 Issue 1
www.westlandpublishers.com

WestLand Publishers

Digital Journal of Engineering Science and Technology (DJEST)

Research Article

Performance Evaluation of Selected Cubic Equations of State in Predicting Liquid Densities of Pure Hydrocarbon Fluids

NWANKWO Princess C*
Centre for Petroleum, Energy Economics and Law, (CPEEL, UI)

***Corresponding author:** NWANKWO Princess C Centre for Petroleum, Energy Economics and Law, (CPEEL, UI).

Received Date: **06 July, 2025** **; Published Date:** **09 September, 2025**

Keywords:
Cubic Equation of State; Liquid Density; Pure Hydrocarbon Fluids, Thermodynamic Properties; Phase Behaviour.

DOI: 10.63592/DJEST/107

Citation:
Nwankwo PC (2025) Performance Evaluation of Selected Cubic Equations of State in Predicting Liquid Densities of Pure Hydrocarbon Fluids. Digit J Eng Sci Technol 1(1): 107.

Abstract

Knowledge of the phase behaviour of hydrocarbon fluids has numerous implications in natural gas and petroleum engineering and are often predictable from Equations of State (EOSs). Equations of state methods of predicting thermodynamic properties are by far less expensive (in monetary and time terms) than laboratory or experimental forages and the results are interestingly within acceptable limits of accuracy. Several cubic EOSs have been presented in literature, however, their relative performances in predicting thermodynamic properties for pure fluids and binary mixtures under varying conditions, has not been properly established. This study aims to carry out performance evaluation of three popular Cubic Equations of State (Peng Robinson's, Patel Teja's and Adewumi-Nwankwo's) over various temperature and pressure ranges for single component hydrocarbon fluids. The results indicate that the Adewumi-Nwankwo (AN) EOS predicts the liquid densities of pure hydrocarbon components more accurately than the Peng-Robinson's (PR) and Patel-Teja's (PT) EOSs. The AN EOS predicted liquid phase densities of pure components and mixtures with a grand average percent absolute deviation (AAPD) of 1.60% as opposed to 4.32% and 11.17% for PT and PR EOSs respectively.

Introduction

Cubic Equations of State (CEOS) are a class of equations of state that may be represented by a polynomial when referencing the volume or compressibility factor, in such a way that the highest power in the polynomial is to the third degree. Cubic EOS can accurately describe the volumetric and phase behavior of pure compounds and mixtures with errors within engineering acceptance when compared to experimentally obtained values.

The states of matter of interest for which natural gas and gas condensates are handled in the industry involve only two (vapour and liquid) phases for which a cubic equation is suitable. Cubic equations of state (EOS) when solved for molar volumes (or compressibility factor) give three values; the highest value corresponds to the vapour phase property, the lowest value corresponds to the liquid phase property while the intermediate value has no known significance. The roots of cubic equations of state can be obtained analytically without the need for an iterative solution procedure, which simplifies the solution method. The popularity of cubic EOSs is further enhanced by their structural simplicity, requirement of only a few parameters for implementation and little computer resources, thus assuring low computational overhead, while providing good phase equilibrium correlations and saturated phase volumes and densities of acceptable accuracy.

Theoretical Background

All cubic equations of state equations of state have their origin from Van der Waal's equation of state which is a modification of the ideal (or perfect) gas equation of state. [1-5]

The Ideal Gas State:

The analytical expression of the PVT equation of the hypothetical perfect gas is written as:

$$PV = nRT \tag{2.0}$$

Where, V is the volume of the container containing the fluid in standard cubic feet (scf), $n = number\ of\ moles\ of\ gas$, P is the pressure of the fluid, T is the absolute temperature and R is the universal gas constant which in field units, has a value of

$$R = \frac{PV}{nT} = 10.732 \frac{psia.scf}{lb{-}mol\,^oR} \tag{2.1}$$

The deviation of real gases from ideal behaviour is captured by introducing the gas deviation factor, (or gas compressibility factor or z factor, or simply, z). Therefore, for real gases, the resulting EOS is:

$$PV = znRT \tag{2.2}$$

The value of the correction factor z generally increases with pressure and decreases with temperature. At high pressures molecules are colliding more often. This allows repulsive forces between molecules to have a noticeable effect, making the molar volume of the real gas $\bar{V}_{real} = (nV)_{real}$ $real\ gas$ greater than the molar volume of the corresponding ideal gas $\bar{V}_{ideal} = (nV)_{ideal}$, which causes z to exceed the value of 1.0.

When pressures are lower, the molecules are freer to move. In this case attractive forces dominate, making $z < 1.0$. The closer the gas is to its critical or boiling points, the more the gas deviation factor or z factor deviates from the ideal case. If the gas deviation factor is accurately determined, the actual gas law can give tolerable estimates of gas thermodynamic behavior, but like the perfect gas law, it too, fails to predict the condensation of liquid from gas. This was one of the motivating factors in early equations of state research.

A plot of Z versus pressure, (figure 1.0) [6-7] distinguishes three categories of real gases: first, those for which Z =1 $(\ that\ is, PVM = RT)$for all temperatures and pressure, which is an ideality behaviour, second, those for which $Z > 1$,$(\ that\ is, PVM > RT)$ and thirdly, those for which $Z < 1(\ that\ is, PVM < RT)$.

Figure 1:

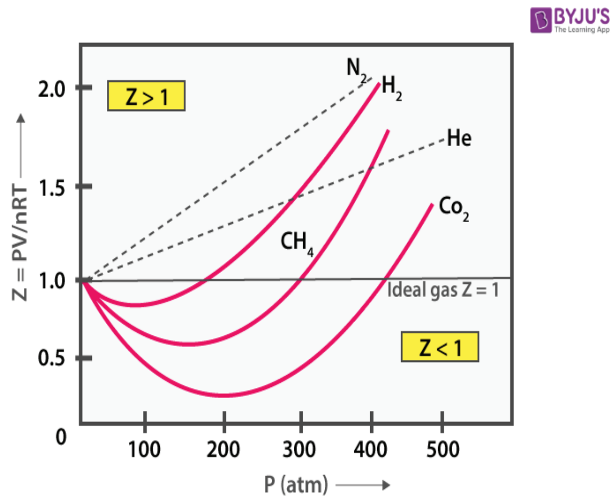

Figure 1 Plot of $Z = \frac{P\bar{V}}{RT}$ against Pressure [7]

Van der Waals (1873) EOS: Van der Waals is credited for being the pioneer of Cubic EOSs. His research in 873, corrected for the departure of real gases from ideal gas behaviour and extended the use of the ideal gas EOS to account for vapor-liquid co-existence, for which he won a Nobel Price in 1910. Van der Waal's (vdW) EOS is written as:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{2.3}$$

Where, $P, V, T\ and\ n$ are Pressure, Volume, Temperature and number of moles of gas, respectively. The parameters $'a'\ and\ 'b'$ are constants specific to each gas and represent the "attraction" and "repulsion" parameters, respectively.

In pressure explicit and molar volume terms, Equation (2.3) is written as

$$P = \frac{RT}{(\bar{V} - b)} - \frac{a}{\bar{V}^2} \tag{2.4}$$

Where, $\bar{V}$ is molar volume given as:

$$\bar{V} = \frac{V}{n} \tag{2.5}$$

The work of vdW also provided the criteria that are used to define the parameters "a" and "b", namely, that the first and second derivative of pressure with respect to volume equal zeroat the critical point of a pure compound. This implies that for a pure compound,

$$\left(\frac{\partial P}{\partial V}\right)_{P_c,T_c,V_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{P_c,T_c,V_c} \tag{2.6}$$

Equation (2.6) is called the criticality criteria. On imposing the conditions of Equation (2.6) on Equation (2.4) and specifying the critical propertiesP_c and T_c, the parameters "a" and "b" are obtained as:

$$a = \frac{27}{64}\,\frac{R^2 {T_c}^2}{P_c} \tag{2.7a}$$

and $b = \frac{1}{8}\,\frac{RT_c}{P_c}$ (2.8a)

The critical molar volume, that is, molar volume at the critical point is given by the expression:

$$\bar{V}_c = \frac{3}{8}\,\frac{RT_c}{P_c} \tag{2.9}$$

So that the parameters 'a' and 'b' can be expressed as follows:

$a = 3P_c\bar{V}_c^{\,2}$, and (2.7b)

$$b = \frac{\bar{V}_c}{3} \tag{2.8b}$$

The EOS of vdW can be arranged in a cubic in molar volume terms as shown below:

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{p}\bar{V} - \frac{ab}{P} = 0 \tag{2.10}$$

Given that the compressibility factor Z, is defined as:

$$Z = \frac{P\bar{V}}{RT} \tag{2.11}$$

The vdW EOS can thus, be expressed in terms of compressibility factor as follows:

$$Z^3 - (B+1)Z^2 + AZ - AB = 0 \tag{2.12}$$

Where,

$$A = a\,\frac{P}{(RT)^2} \tag{2.13}$$

and $B = b\frac{P}{RT}$ (2.14)

The vdW's EOS as expressed in pressure-explicit form in Eq. (2.4), has the repulsive term as $\frac{RT}{(V-b)}$ and the attractive term as $\frac{a}{V^2}$, (also known as the hard sphere term). This therefore, indicates that pressure can be regarded as the sum of two terms: an attractive term and a repulsive term, that is:

$$P = P^{repulsion} + P^{attraction} \tag{2.15}$$

Which by implication, means that compressibility factor can be expressed as:

$$z = z^{repulsion} + z^{attraction} \tag{2.16}$$

The phase diagrams using the vdW EOS to model hydrocarbon fluid behaviour reveals that, at temperatures equal to or greater than the critical temperature (T_c), only single roots exist. However, at temperatures below T_c, three roots exist. The smallest root represents liquid-like volume, the intermediate root has no known significance and the largest root represents the vapour-like volume. The vdW EOS has limitations which include the facts that it provides inaccurate vapour pressure predictions because the attraction term parameter, a, is not optimized to fit vapour pressure. Also, it provides inaccurate critical point predictions.

The critical compressibility factor, z_c from the vdW EOS has a fixed value of

$$Z_c = \frac{P_c\bar{V}_c}{RT_c} = \frac{3}{8} = 0.375 \tag{2.17}$$

This value is a lot greater than that obtained for real hydrocarbon fluids (0.24 to 0.29). The vdW's EOS however, has significant historical relevance since it provides the basic foundation over which most other researchers have built their framework by either modifying the attractive term or repulsive term of the original van der Waals Equation or both.

Equations of state based on modifications of the attraction term of the original vdW's EOS are called van der Waal's family of EOSs and usually can be shown to be cubic polynomials when expressed in terms of either molar volume or compressibility factors.

Peng and Robinson (PR) EOS: Ding-yu Peng and Donald Robinson (1976) developed another two-parameter equation of state with the goal of improving on the accuracy of especially, liquid density and equilibria ratios using cubic EOS.

Peng and Robinson's (PR) EOS has the form:

$$P = \frac{RT}{(V-b)} - \frac{a\alpha(T)}{V(V+b)+b(V-b)} \tag{2.18}$$

With the parameters given as:

$$a = \Omega_a \frac{R^2 {T_c}^2}{P_c} \approx 0.45724 \frac{R^2 {T_c}^2}{P_c} \tag{2.19}$$

$$b = \Omega_b \frac{RT_c}{P_c} \approx 0.07780 \frac{RT_c}{P_c} \tag{2.20}$$

Expressed in terms of gas compressibility factor, the PR EOS has the form:

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \tag{2.21}$$

Where,

$$A = \frac{a\alpha(T)\,P}{R^2T^2} \tag{2.22}$$

$$B = \frac{bP}{RT} \tag{2.23}$$

$$\alpha(T) = \left[1 + (m\left(1 - \sqrt{T_r}\right)\right]^2 \tag{2.24}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{2.25}$$

A modified expression form was presented in 1979 by Robinson et al and Robinson and Peng for heavy components with acentric factor greater than 0.49 ($\omega > 0.49$) as follows:

$$m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 \tag{2.26}$$

Patel and Teja (1982) EOS: Patel and Teja presented a 3-parameter EOS in 1982, which showed great promise in prediction of phase equilibria and volumetric properties of single hydrocarbon fluids and mixtures. The EOS has the form:

$$P = \frac{RT}{(\bar{V}-b)} - \frac{a\alpha(T)}{V(V+b)+c(V-b)} \tag{2.27}$$

With the three parameters given as:

$$a = \Omega_a \frac{R^2 {T_c}^2}{P_c} \approx \qquad \frac{R^2 {T_c}^2}{P_c} \tag{2.28}$$

$$b = \Omega_b \frac{RT_c}{P_c} \approx \qquad \frac{RT_c}{P_c} \tag{2.29}$$

$$c = \Omega_c \frac{RT_c}{P_c} \approx \qquad \frac{RT_c}{P_c} \tag{2.30}$$

Adewumi-Nwankwo (2017) EOS. Adewumi and Nwankwo developed a semi empirical 3-parameter EOS of the form:

$$P = \frac{RT}{V-b} - \frac{a_c\alpha(T)}{V(V+b)+c(V-b)+c(c-b)} \tag{2.31}$$

Which when expressed in terms of compressibility factor has the form:

$$Z^3 + (C-1)Z^2 + (A - B - C - 3BC - B^2 + C^2)Z + (2BC + 2B^2C - BC^2 - C^2 - AB) = 0 \tag{3.32}$$

The terms $A, B\ and\ CA, B\ and\ C$ have the usual meanings as in other three-parameter EOS such as PT EOS, for example. Therefore,

$$A = \frac{aP}{(RT)^2} \tag{3.33}$$

$$B = \frac{bP}{RT} \tag{3.34}$$

$$C = \frac{cP}{RT} \quad (3.35)$$

$$a = \frac{\Omega_a R^2 T_c^{\,2}}{P_c}, \quad (3.36)$$

$$b = \frac{\Omega_b R T_c}{P_c}, \quad (3.37)$$

and $c = \frac{\Omega_c R T_c}{P_c}$. (3.38)

$$m(I) = 0.359 + 0.288 * \omega(I) + 1.846\omega(I)^2 \quad (3.39)$$

Further, $\Omega_b$is smallest root of the equation:

$$\Omega_b^{\,3} + (2 - 3\xi_c)\Omega_b^{\,2} + 3\xi_c^{\,2}\Omega_b - \xi_c^{\,3} = 0. \quad (3.40)$$

$\Omega_c = 1 - 3\xi_c$ and (3.41)

$$\Omega_a = 3\xi_c^{\,2} + 3(1 - 2\xi_c)\Omega_b + \Omega_b^{\,2} + (1 - 3\xi_c) \quad (3.42)$$

$$\xi_c = 0.329032 - 0.0767992\omega + 0.0211947\omega^2 \quad (3.43)$$

Methodology

Most CEOS provide fairly accurate predictions of vapor molar volumes but fail significantly in predicting liquid densities to a good degree of accuracy. Therefore, liquid densities have become an acid test for measuring equation of state capabilities. The prediction evaluation was based on the ability to predict liquid densities with errors compared against values of liquid densities measured in the laboratories, obtained from literature, for single component fluids. The PR EOS has shown capacity in predicting liquid densities more accurately than other popular 2-parameter EOSs, so it is chosen as the 2-parameter EOS to be evaluated against the 3-parameter PT and AN EOSs. A FORTRAN 95 program was written and implemented to facilitate computation and comparisons.

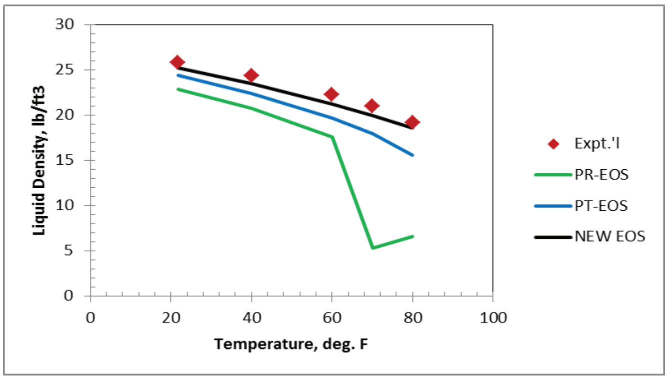

Figure 2: Plot of Liquid Density versus Temperature for Ethane at Various Pressures

The Average Absolute Percent Deviations (AAPD) and Root Mean Square Errors (RMSE) are summarized in Table 4.1b below:

Table 1: Error Analysis for Liquid Densities Prediction for Ethane

EOS	AAPD	RMSE
PR	1.0882	1.5842
PT	0.1338	0.1470
AN	0.0385	0.0397

4.2 Propane

The results for the testing for propane are as shown in the table below. At the ranges of temperature and pressure for which the propane is being tested, $40.0\ to\ 130.0^o F$ and $79.5\ to\ 272.0\ psia$ respectively, had all the equations of state predicting acceptably accurately. The New equation of state, however gave best average results for all the estimates made.

Table 2: Calculated and Experimental Liquid Density of Propane

Temperature (°F)	Pressure (Psia)	Experimental *ρ(lb/ft³)*	PR-EOS *ρ(lb/ft³)*	PT-EOS *ρ(lb/ft³)*	AN-EOS *ρ(lb/ft³)*
40.0	79.5	**32.61024**	30.3642	32.6758	32.6007
60.0	108.0	**31.62432**	29.0666	31.4496	31.4686
80.0	143.0	**30.56352**	27.6523	30.1002	30.2350
100.0	188.0	**29.43408**	26.1071	28.6078	28.8879
130.0	272.0	**27.35616**	23.4098	26.0014	26.5852

The predictions by the PR EOS are fairly accurate with an average absolute deviation of 11.27%. Those of the PT EOS were better than that of PR EOS with an Average Absolute Percent Deviation of 2.08%.The performance of the AN EOS gave the predictions with least error when compared to the measured values. The average absolute deviation for estimates using the AN EOS was 1.28%. The summary of error analysis for propane, showing values of AAPD and RMSE are as shown in table4.2 b below:

Table 3: Error Analysis for Liquid Densities Prediction for Propane

EOS	AAPD	RMS
PR	0.1127	0.1174
PT	0.0208	0.0276
AN	0.0128	0.0164

The results from the error analysis for propane shown above can be pictorially shown using, for consistency, bar charts for RMSE and AAPD as shown below.

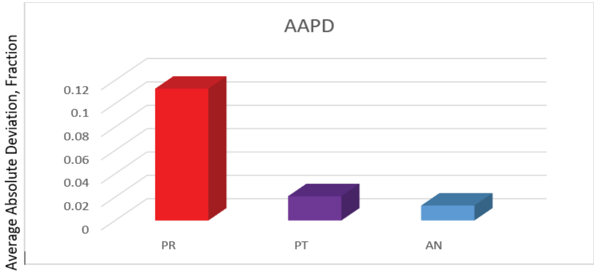

Figure 3: Bar Chart showing Average Absolute Percent Deviation (AAPD) for Liquid Densities of Propane Predicted with PR, PT and AN EOSs.

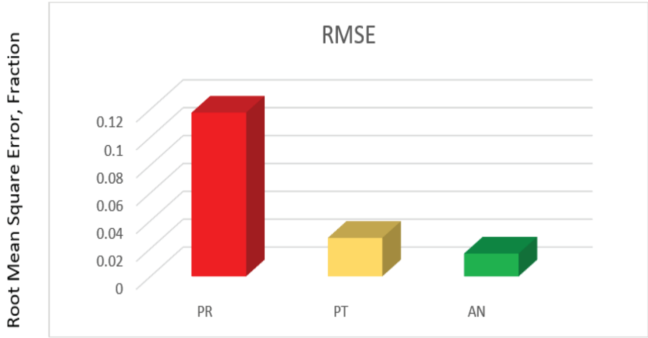

Figure 4: Bar Chart showing Root Mean Square Errors (RMS) from Propane Liquid densities Prediction Using PR, PT and AN EOS.

Iso-Butane

For the liquid density prediction of iso-butane, the fluid temperatures ranged from $40.0^oF\ to\ 130.0^oF$ and pressures ranged from $27.0\ to\ 110.0\ psia$. The predicted and experimental liquid densities over these temperature and pressure ranges are as shown in the table below:

Table 4: Calculated and Experimental Liquid Density of Iso-Butane [7]:

Temperature (°F)	Pressure (Psia)	Experimental ρ(lb/ft3)	PR-EOS ρ(lb/ft3)	PT-EOS ρ(lb/ft3)	AN-EOS ρ(lb/ft3)
40.0	27.0	35.9112	33.8447	36.6524	36.1064
60.0	38.0	35.11248	32.8196	35.7135	35.2102
80.0	52.5	34.23888	31.7305	34.7013	34.2526
100.0	71.5	33.34032	30.5702	33.6070	33.2264
130.0	110.0	31.83024	28.6689	31.7832	31.5366

Over these ranges of temperatures and pressures, the PR EOS gave an average absolute deviation (AAPD) of 8.23% and a root mean square (RMS) error of 8.39%. PT EOS's predictions were better than those by PR with average absolute deviation of 1.19% and root mean square error of 1.36%. The AAPD and RMSE calculated for the AN EOS were 0.004% and 0.005% respectively. The minimum absolute deviation of $4.01E-04$ was obtained for predictions made with the AN EOS. The maximum absolute deviation of 11.03% was obtained with the PR EOS. The summary of errors is as shown in the table 4.3b below:

Table 5: Error Analysis for Liquid Densities Prediction for Iso-Butane

EOS	AAPD	RMSE
PR	0.0823	0.0839
PT	0.0119	0.0137
AN	0.0043	0.0052

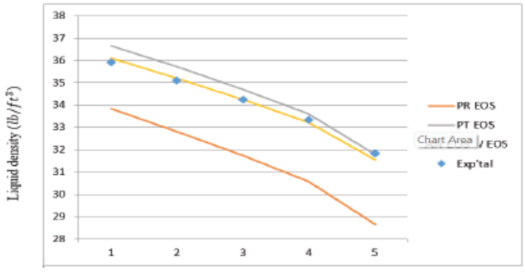

Figure 5: Calculated liquid densities with EOSs compared to Measured Liquid densities for Iso-Butane

Normal-Butane:

The equations of state were used to predict liquid densities for normal butane at $60^o\ and\ 130^oF$. The pressures corresponding to these temperatures are $26.0\ and\ 79.0\ psia$, respectively. The results obtained are compared to experimentally measured results as shown in table 4.4a below:

TABLE 6: Calculated and Experimental Liquid Density of n-Butane

Temperature (°F)	Pressure (Psia)	Experimental ρ(lb/ft3)	PR-EOS ρ(lb/ft3)	PT-EOS ρ(lb/ft3)	BNA-EOS ρ(lb/ft3)
60.0	26.0	36.46656	33.9177	37.0017	36.2923
130.0	79.0	33.50256	30.2129	33.5439	33.0044

Analyzing the error from the predictions from the various EOSs reveals that the AAPD for PR, PT and AN EOSs are, respectively, 9.20%, 0.79% and 0.995%. The root mean square error, (RMSE) is for PR EOS, 9.36%, for PT EOS, 1.03% and for AN EOS, 1.12%. as seen in the table 4.4b below:

Table 7: Error Analysis for Liquid Densities Prediction for n-Butane

EOS	AAPD	RMSE
PR	0.09202	0.0936
PT	0.00787	0.0103
AN	0.00995	0.0112

All the results considered for ethane, propane, n-butane and i-butane are summarized in table 4.5 below. These summarized result of error analyzed for all the single component systems considered reveals that the AN EOS gave the smallest average absolute percentage error (1.75%) and smallest root mean square error (2.38%). The Peng Robinson equation of state had the highest average absolute error of 38.82% and highest root mean square error of 86.33%. The extremely high error values measured for the Peng-Robinson's equation of state are due to the effect of the near critical point predictions for which the Peng Robinson's equation shows immense weakness. The AAPD and RMSE recorded were 4.99% and 8.15% for the PT EOS. Plots of the errors (AAPD and RMSE) are included for quick comparison of EOS's performances.

Table 8: Summarized Results for All Single Component Hydrocarbon Systems Considered

EOS	AAPD	RMSE
PR	0.3882	0.8633
PT	0.0499	0.0815
AN	0.0175	0.0238

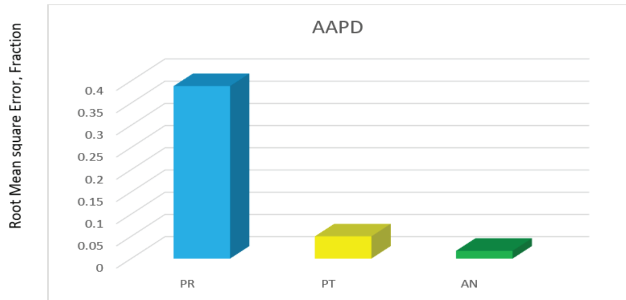

Figure 6: Bar Chart Representation of Average Absolute Percentage Deviation (AAPD) for Liquid Density Predictions Using: PR, PT and AN EOSs for all Single Component Systems Analyzed.

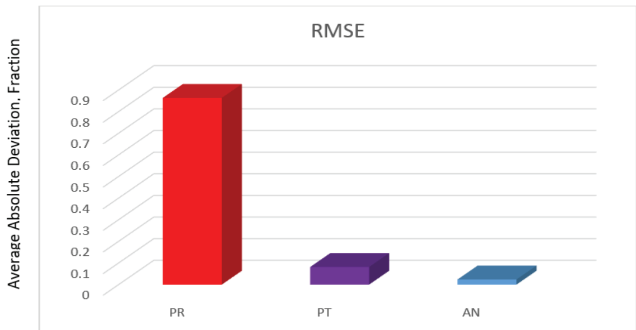

Figure 7: Column Chart showing Average Absolute Deviation (AAD) for PR, PT and New Equations of State for all Single Component Systems Analyzed.

Conclusions and Recommendations

The evaluation study has shown that the AN EOS is more accurate in predicting liquid densities of single component hydrocarbon fluids, with predictions that are consistent with minimal errors when compared to experimentally measured values. It is noteworthy to point out that the AN equation EOS maintains predictive superiority, where other faltered such as at conditions close to critical point. The AN EOS gives better hydrocarbon liquid and vapor property predictions than Peng Robinson's and Patel-Teja's EOSs. It is recommended that the evaluation should be extended in future work, to multicomponent systems including, complex systems containing acid gases and heavy hydrocarbon fractions, also called Heptanes plus (C_{7+}), and for testing other volumetric phase behaviour properties. More cubic equations should also be tested for a more robust conclusion on predictive abilities of several more EOSs.

Conflicts of interest: None

Funding: None

References

1. Ayala LF (2006) Lecture Notes on PNG 520: Phase Behavior of Hydrocarbon Fluids. The Pennsylvania State University.
2. Nwankwo PC, Adewumi MA, Ityokunbol MT (2017) A New Cubic Equation of State for Improved Liquid Density Prediction. Petroleum & Petrochemical Engineering Journal Vol 1(5): 000128.
3. Patel NC and Teja AS (1982) A New Cubic Equation of State for Fluids and Fluid Mixtures. Chem Eng Sci 37: 463-473.
4. Peng DY and Robinson DB (1976) A New Two-Constant Equation of State. Ind Eng Chem Fundam 15(1): 59-64.
5. Van Der Waals JD (1873) On the Continuity of the Gaseous and Liquid States (doctoral dissertation). Leiden, Holland.
6. Schimdt G, Wenzel H (1980) A modified van der Waals type equation of state. Chem Eng Sc 35 (7): 1503 -1512.
7. Weast RC (1972) Handbook of Chemistry and Physics, (53rd Edition) Chemical Rubber Publishers.