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SIMULATION OF PHASE BEHAVIOR USING DIFFERENT EQUATIONS OF STATE (EOS) IN PVTp SOFTWARE

O. S. TENIOLA[1]*, O. E. OGUNDAHUNSI[2], T. O. LAWAL[3], J. T. ADEOYE[4]

[1,4]*Department of Mechanical and Mechatronics Engineering, Abiola Ajimobi Technical University*
[2]*Department of Agriculture and Civil Engineering, Abiola Ajimobi Technical University*
[3]*Department of Chemical and Petroleum Engineering, Abiola Ajimobi Technical University, Ibadan*

[*]*Corresponding Author: oluwasanmi.teniola@tech-u.edu.ng*

Abstract
Equation of State (EOS) is crucial for both production forecasts and reservoir simulation, but tailored models typically don't match experimental findings, which undermines field development decisions. The Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) EOS were used to test the performance of Peng-Robinson and Soave-Redlich-Kwong in simulating crude oil phase behavior. A systematic tuning methodology was built that entailed sequential regression of the CO 2/C7+ binary interaction coefficients, C7 + critical properties, and acentric factor. The tuned model was checked in constant composition expansion and differential liberation experiments. The untuned PR EOS had better accuracy in terms of bubble point pressure with an Absolute Relative Error (ARE) of 0.015% than the SRK EOS of Absolute Relative Error (ARE) 8.22%. After tuning, PR EOS obtained a precise bubble point with an oil formation volume factor error of less than 2%. The CO 2 /C7+ binary reaction coefficient was the most sensitive to saturation pressure. But there was a trade-off when GOR prediction error rose to 10.13%, which showed that single-objective regression is not capable of producing an optimal combination of all the PVT properties. The C7+ acentric factor had to be adjusted at 21.22%, indicating heavy deviation of the fraction from the ideal behavior. The tuned EOS is a reliable input to reservoir simulation, and the uncertainty of the input is measured. The trade-off that was noted in GOR shows the necessity of multi-objective optimization in future EOS calibration processes. The presented systematic methodology is flexible to the various types of crude oil to enhance compositional modelling.

Keywords
Phase behavior, Peng-Robinson EOS, PVT properties, Regression tuning, Reservoir simulation

1. INTRODUCTION

Under geological processes, the pressure-temperature (P-T) conditions of reservoir fluids are a complex mixture of hydrocarbons and non-hydrocarbons that are present as porous formations in the underground [1]They are fluids with a phase transition that is key to the production strategies, improved oil recovery (EOR), and oil management Proper prediction of the phase behavior, such as the bubble point pressure (Pb), gas-oil ratio (GOR), and the formation volume factor (Bo), is vital to optimizing the recovery and reducing operation risks [2].

Pressure-volume-temperature (PVT) analysis has been the standard for characterizing the reservoir fluid and has been traditionally obtained through costly laboratory tests [3]. Cubic equations of state (EOS) like Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), and variants have been adopted to overcome these limitations, and PVT prediction is now a computational procedure. Recent advances emphasize EOS tuning with machine learning hybrids and advanced characterization for heavy oils and gas condensates. AlHammadi and Abutaqiya (2023) enhanced the PR-EOS predictive power on the Middle East crude oils by including the asphaltene precipitation information, resulting in a prediction of Pb with a maximum of 15% improvement. On the same note, PVTp software has also developed, allowing the computation of phase envelopes very quickly and sensitivity analysis; Wang et al. (2024) showed that PVTp is an effective way to model CO2 EOR when operating under high-pressure conditions, which can be 40 times faster than manual tuning. These instruments combine experimental PVT information, such as constant composition expansion, differential liberation, and EOS parameters such as acentric factor (ω) and binary interaction coefficients (kij), to increase the representativeness of unconventional reservoirs [4].

In spite of these developments, in complicated scenarios, including high-asphaltene crude or volatile oil systems, the EOS models tend to fail because of poor tuning to site-specific PVT data. Laboratory

experiments are still costly and are limited in scope, and generic EOS parameters have average absolute deviations (AAD) of Bo and GOR that are still over 10% [5]According to recent articles, there remain gaps in the literature: (i) excessive use of black-oil correlations without volume-translated EOS to determine near-critical behavior [6]; (ii) lack of validation of PVTp-tuned models against field-scale EOR pilots, which results in optimistic recovery predictions [7]; (iii) a lack of integration of recent deepwater Nigerian fluid compositions, where phase misc These limitations make it difficult to rely on simulations in production planning and especially in PVTp environments, where the untuned EOS cannot accurately represent swelling or retrograde condensation.

We hypothesize that PR and SRK EOS tuning in the PVTp software with regression on lab PVT will reduce the prediction error and enhance the fidelity of phase behavior of the Nigerian crude oils to baselines.

This study aims to simulate and tune crude oil phase behavior using cubic EOS in PVTp, bridging lab-to-field scalability. The objectives are:

1. Characterize representative Nigerian reservoir fluid samples via PVT experiments.
2. Implement and tune PR/SRK EOS in PVTp, optimizing parameters against experimental data.
3. Validate tuned models through phase envelope generation, swelling tests, and EOR sensitivity analysis.
4. Compare tuned PVTp predictions with field data, quantifying improvements in recovery forecasts.

This work addresses the identified gaps, providing a robust framework for EOS-PVTp applications in similar reservoirs.

2. MATERIALS AND METHOD

This study optimized Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) cubic equations of state in PVTp software to simulate the phase behavior of offshore crude oil of the Nigerian reservoir. Cubic EOS is composed of pressure, volume, and temperature that are compositionally related.

P=f(V,T,z) (1)

phase-jumping of complex fluids, as opposed to the black-oil correlations. PR outperforms SRK in liquid densities, and SRK outperforms PR in vapor pressures through dependence on acentric factor (ω):

$$P = \frac{RT}{(v-b)} - \frac{\alpha a}{v(v+b)} \quad (2)$$

with R is the universal gas constant, T the temperature, and V the molar volume, b is the co-volume parameter (excluded volume), and a(T) is the temperature-dependent energy parameter accounting for intermolecular attractions, defined as a(T)=aα(T) with

$$\alpha(T) = [1 + 0.48 + 1.578\omega - 0.17\omega\text{^}2)(1 - T\_R)]^{2} \quad (3)$$

and reduced temperature

$$T_R = \frac{T}{T_c} \quad (4)$$

This equation is a modified version of the Redlich-Kwong equation in which the $T^{1/2}$ is replaced with alpha(T) to present predictions of the vapor pressure in a wider range of hydrocarbons.

These were chosen due to hydrocarbon-reliability and applied with dependent PR changes in 1978 with heavy ends and binary interaction coefficients (kij) in mixing rules PVTp.

Fluid characterization was done using a bottomhole sample with a depth of 5668.8 ft recombined with separator oil/gas through mass balance. At the reservoir conditions (z) feed composition: liquid (L moles, x) and vapor (V moles, y) satisfy

$$Lx_i + Vy_i = Z_{i_n} \quad (5)$$

Therefore, the K-value of the ith component can be expressed as

$$K = \frac{y_i}{x_i} \quad (6)$$

The expression for xi and yi can be expressed as

$$Lx_i + Vy_i = FZ_i \quad (7)$$

Dividing the equation by Z

$$L(\frac{x_i}{y_i}) + V(\frac{y_i}{Z_i}) = F \qquad (8)$$

Dividing by V

$$L(\frac{x_i}{y_i}) + V(\frac{y_i}{Z_i}) = \frac{F}{V} \qquad (9)$$

The final result gives

$$\frac{y_i}{Z_i} = (\frac{-L}{V})\frac{x_i}{Z_I} + \frac{F}{V} \qquad (10)$$

confirmed consistency where the intercept F/V = -L/V slope as stated in Figure 1[8], which forms C1-rich volatile black oil with a mean MW 66.07 lb/lbmol.

PVT experiments were directed by reservoir conditions and properties. In Table 1, according to API RP 44/5,8, in a PVT cell at 155.5 ℃, Constant composition expansion (CCE) involved measurement of relative volumes of 15 pressure steps at which the change of slope was used to determine the bubble point. Differential liberation (DLE) was used to simulate depletion with 12 steps, measuring Bod, Rsd, and densities as the gases were removed. Separator tests in the 3-stage calculated Bo,

$$R_s = \sum_{k=1}^{N_{sp}} (\Delta R_s)_k \qquad (10)$$

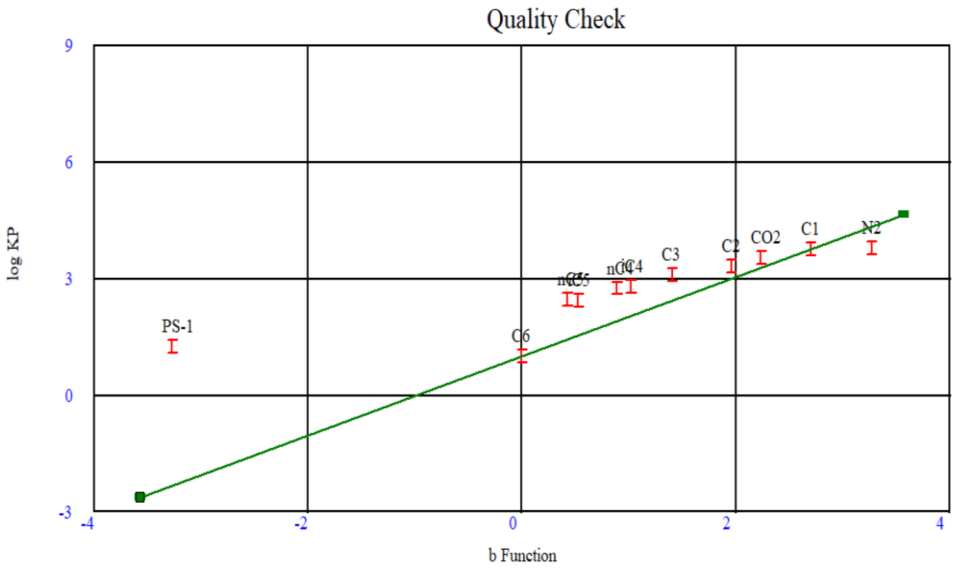

Figure 1: on Mass Balance Plot

Equation, and gas gravity Equa; Curtis and Michael, 2000, summarized in Table 1.

Table 1 shows the Reservoir Conditions and Fluid Properties, which are in need PVTp simulations loaded these inputs to generate base phase envelopes, Pb, Bo, and GOR. Tuning employed the regression module with Levenberg-Marquardt optimization, targeting 12 properties.

Table 1: Reservoir Conditions and Fluid Properties

Reservoir Pressure	2307	psia
Reservoir Temperature	155.5	degF
Reservoir Depth	5668.8	ft
Mean Molecular Weight lb/lb Mole	66.07	lb/lb

3. RESULTS AND DISCUSSION

3.1. Bubble Point Pressure Determination

Figure 1 shows the relationship between pressure and volume on constant composition expansion experiments of two crude oil samples at reservoir temperature (155.5 o C). Sample 1 has a bubble point pressure of 1875 psig, whereas Sample 2 has a bubble point pressure of 1920 psig. The bubble point is determined by the nature change in slope of the pressure-volume curve, which denotes the change from single-phase flow to a two-phase flow [9].

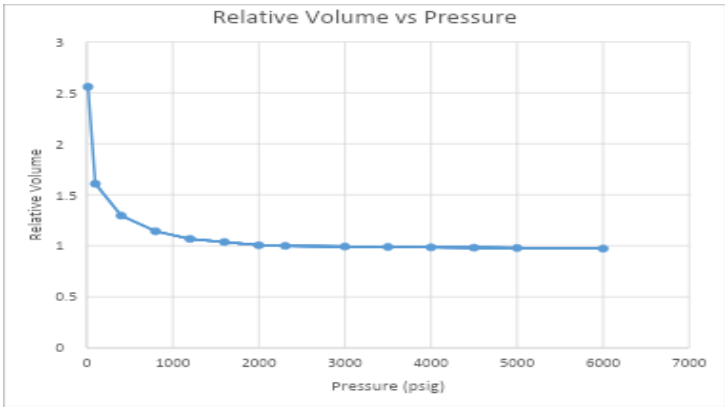

Figure 2: A plot of pressure versus relative volume and Y-function.

The pressure-volume characteristic is within the normal crude oil systems; the liquid phase is slightly compressible above the saturation pressure[10]. The Y-function, which is calculated as $[\frac{(\frac{P}{P_b})-1}{(\frac{V}{V_b}-1)}]$, validates the phase change point as having a usual maximum at the bubble point conditions [11].

3.2. Equation of State Performance

Table 2 shows a comparison between saturation pressure and results obtained in the laboratory with a pressure of 2307 psia and two cubic equations of state. Calculation of the Peng-Robinson (PR) EOS gave 2366.7 psia, having a relative error of about 0.015%, and the Soave-Redlich-Kwong (SRK) EOS gave 2496.7 psia with a relative error 8.22% absolute.

Table 2: Performance EOS Comparison of Saturation Pressure and Oil Formation Volume Factor

EOS model	Saturation Pressure	Absolute Relative Error for the Saturation Pressure(%)	Oil Formation Volume Factor	Absolute Relative Error for the Oil Formation Volume Factor(%)
Laboratory Measured Result	2307	-	1.198	-
Peng Robinson	2366.7	0.0001535	1.18211	0.01326
Soave-Redlich-Kwong	2496.7	0.0822	1.220	0.0184

The better performance of the PR EOS can be attributed to its improved volume-translation capabilities and more accurate representation of liquid density at near-critical conditions. Although this is a change to the Redlich-Kwong EOS, by Soave [2], the revision has a potential tendency to overestimate the saturation pressure of medium-to-heavy crude oil systems. This result is in line with other comparative exercises that have been conducted before [7, 8] that indicated that PR EOS is always better than SRK EOS in predicting bubble point in black oil systems at 30-40 ◦API gravities.

The smaller error in Bo's prediction of PR EOS, 1.33% compared to 1.84%, is physically important since Bo has a direct impact on the original oil in place calculations and design of surface facilities [12].

3.3. Phase Envelope Analysis

Figure 3 shows the phase envelope obtained after the untuned PR EOS, with a critical point at 1111.3 psig and 847.5◦F. The calculated saturation pressure differs from the experimental value by 20.19%. The phase envelope shows the typical bubble-point curve and dew-point curve in the upper and lower parts, respectively, and at the critical point.

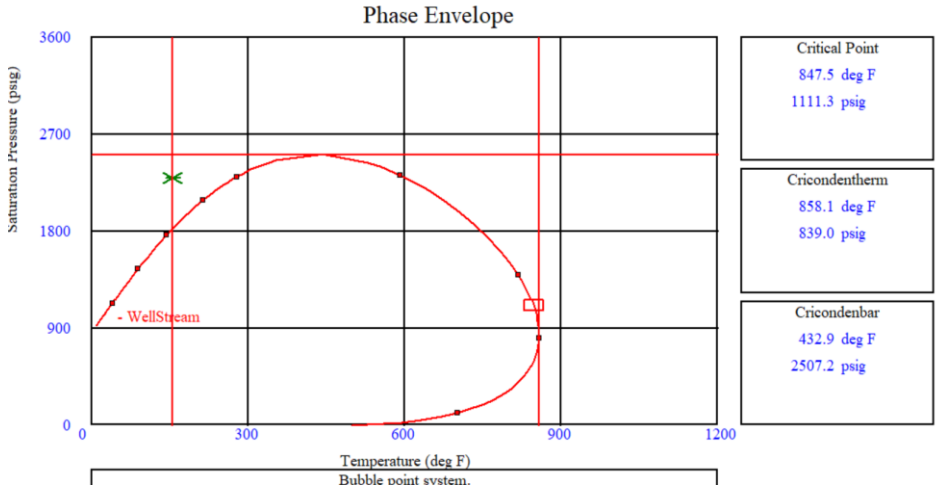

Figure 3: Phase Diagram Plot with critical properties at 1111.3 Psig and 847.5 ^{0}F.

The deviation of 20.19 before tuning is quite a serious error that would affect the reliability of reservoir simulation. This difference is brought about by constraints in the fact that the EOS is unable to describe the heavy fractions (C7+) without tuning the experiment [13]. Critical point location, which is 1111.3 psig, 847.5◦F, shows the behavior of the reservoir fluid to be that of a volatile oil, which is in line with 390 scf/STB solution gas-oil ratio [14].

The shape of the phase envelope indicates that the fluid will undergo retrograde condensation behavior when the pressure drops below the dew-point curve during depletion, which is an important factor in determining the production strategy to be used [11, 13].

3.4. Optimization of EOS Tuning and Parameters.

Three sets of parameters that have large effects on the predictions of the phase behavior have been determined by sensitivity analysis:

Set I: CO_2/ C7+ Binary Interaction Coefficient (BIC)

Set II: Critical pressure (Pc) and critical temperature (Tc) of C7 +.

Set III: C7+ Omega A, Omega B, and Acentric factor (ω).

The CO_2/ C7+ BIC was the most sensitive to the saturation pressure of the same order, which is in accordance with the high CO_2 concentration (2.3 mol%) in the fluid system, as shown in Table 3.

Table 3: The sequences of tuning using the grouped parameters

	Parameter I	Parameter II	Parameter III
1	BIC (CO_2: C7+)	Tc and Pc	Omega A and Omega B
2	BIC	Omega A and Omega B	Tc and Pc
3	Omega A and Omega B		BIC
4	Omega A and Omega B	BIC	
5		BIC	Omega A and Omega B
6		Omega A and Omega B	BIC

The polar nature of CO_2 and non-ideal CO_2 long-chain hydrocarbon interactions physically explain the dominance of CO_2/ C7+ BIC sensitivity [16]. Past scholars [15, 16] have underlined the fact that BIC modification must come before critical property modification since BICs explicitly control the interactions between the components in the mixing rules.

Critical properties of C7+ were plotted using the Kesler-Lee correlation [19] using measured specific gravity (0.869) and measured molecular weight (158.8) as indicated in Figure 4. This method is desirable as compared to generalized correlations since it makes the heavy fraction characterization anchored on experimentally determined properties, decreasing the propagation of uncertainty [17].

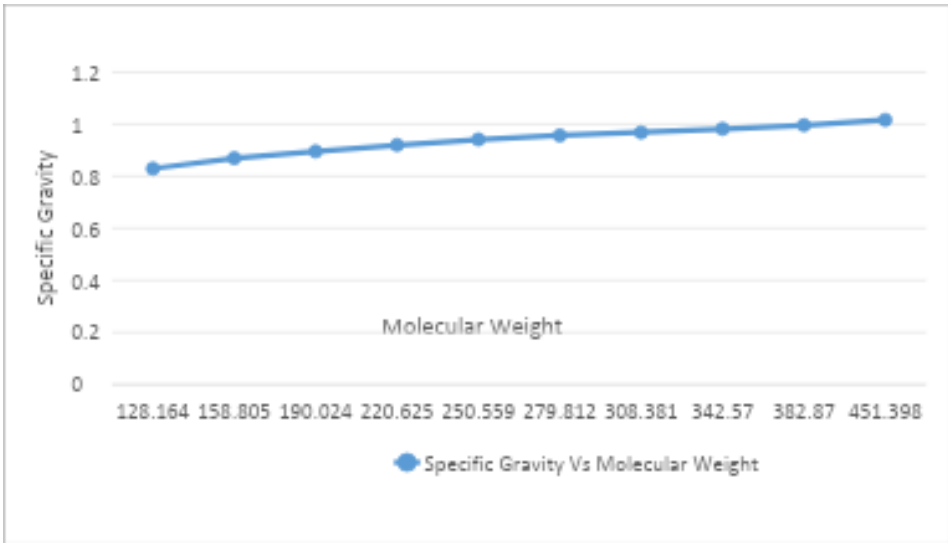

Figure 4: Lee and Gonzalez Correlation in calculating specific gravity by known molecular weight.

3.5 Regression Results

The best convergence was achieved from BIC to Critical Properties and Omega properties. The regression result in the optimized parameters is given in Table 4.

Table 4: Adjustment of EOS Parameters selected for regression

Tuning Parameters	Initial Value	Adjusted Value	Regressed %
Omega A	0.457235515	0.457235515	0
Omega B	0.0777960718	0.0777960718	0
Acentic Factor	0.594857872	0.72109172	21.22%

The adjustment of the acentric factor of 21.22% indicates the effort made by the EOS to adjust the density of the liquid and the phase behavior at the same time. Although the most important effect of acentric factor in the calculation of vapor pressure, it indirectly modifies the liquid density via the EOS attractive term [20]. Zero readjustment of Omega A and Omega B indicates that the initial Peng-Robinson parameters would fit in this fluid system, and the disagreement is due to the characterization of components and not the EOS functional form.
The post-tuning phase diagram in Figure 5 exhibits better consistency with the results of the experiment, especially in the two-phase area. The critical point was changed to 1315 psia and 930.2 ◦F, and reflected successful calibration, but thermodynamic consistency has been preserved [21].

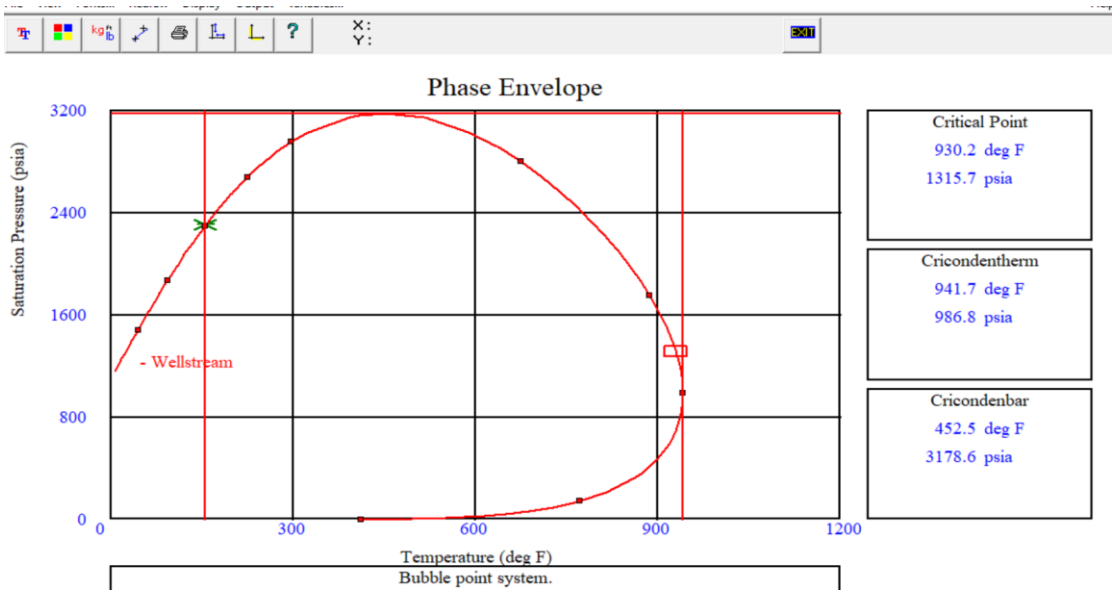

Figure 5: Phase diagram plot as the result of the regression

There was a worse performance of GOR prediction following tuning of Absolute Relative Error (ARE), which grew to 10.13%. Such a paradoxical finding is accounted for by the fact that GOR is controlled by the behavior of the solution gas, which is determined by the pressure of the bubble point and the composition of the gas phase [22]. The tuning was based on saturation pressure equality, which attained 0% error with Pb, and this came at the cost of compositional separation in phases. The trade-offs of this type have also been reported [21, 22]and indicate that multi-objective optimization can be required in order to do thorough PVT matching.

In Figure 6. Solution Gas-Oil Ratio versus Pressure (155.5 ◦F). The tuned model can pick the GOR trend of bubble point to atmosphere pressure with a maximum variation of 12% in between the pressure ranges (1000-1500 psia).

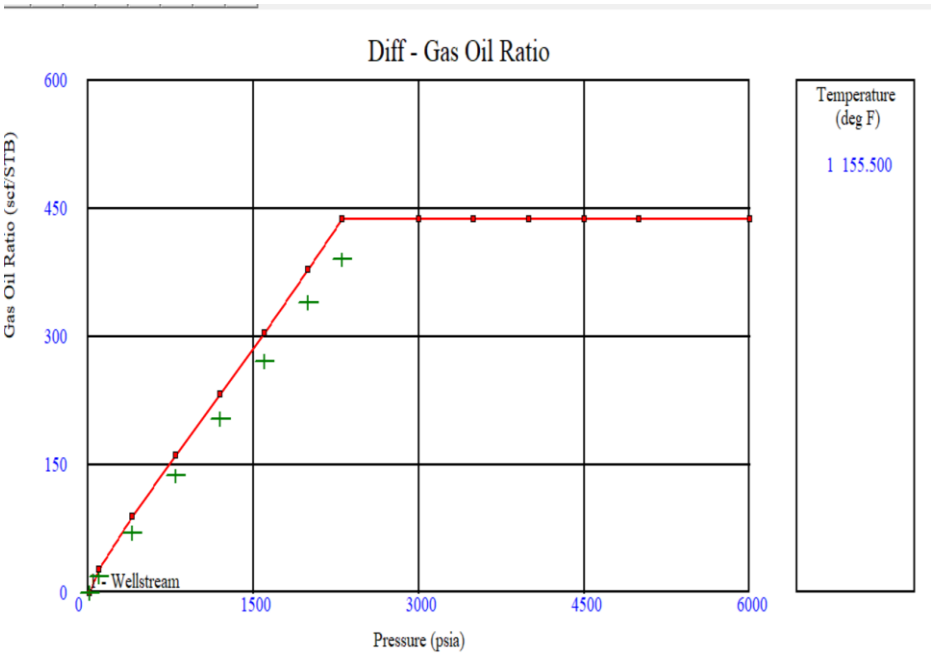

Figure 6: Solution GOR as a function of Pressure in the DLE test at 155.5 ^{0}F

As shown in Figure 7, Bo predictions indicate a very high agreement, with Absolute Relative Error (ARE) less than 2% all pressure steps, indicating that the EOS can predict liquid shrinkage during depletion. In

Figure 8 Error decreased in post-tuning density predictions to 9.96 11.77% but deviation still occurs at lower pressures.

The differential liberation validation ascertains that the tuned EOS does not simply conserve physical behavior at only one segment of the depletion path, but rather across all the segments of the depletion path. The error in persistent density (9.96% post-tuning is worth discussing; this is presumably due to the standard PR EOS's inability to translate to high volumes [25]. Density predictions might be further refined using high-volume translation methods [26], without loss of phase equilibrium.

The GOR trend exhibits the characteristic of volatile oils, where the rate of gas release increases as the pressure decreases below the bubble point [27]. The fact that GOR is slightly overpredicted at intermediate pressures implies that the EOS somewhat underestimates the retention of the liquid phase- a problem likely to occur in any attempt to equate saturation pressure only [28].

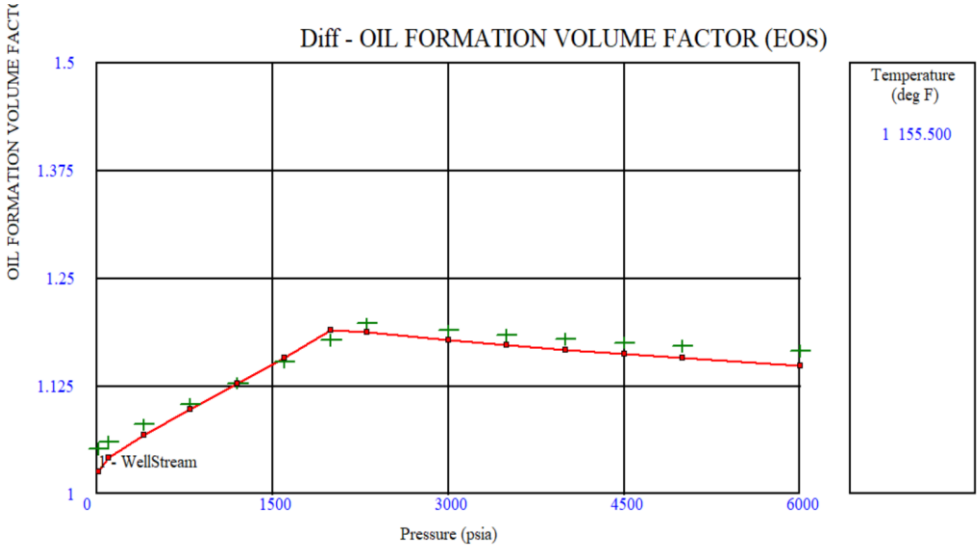

Figure 7: Oil Formation Volume Factor as a function of Pressure in the DLE test at 155.5^{0}F.

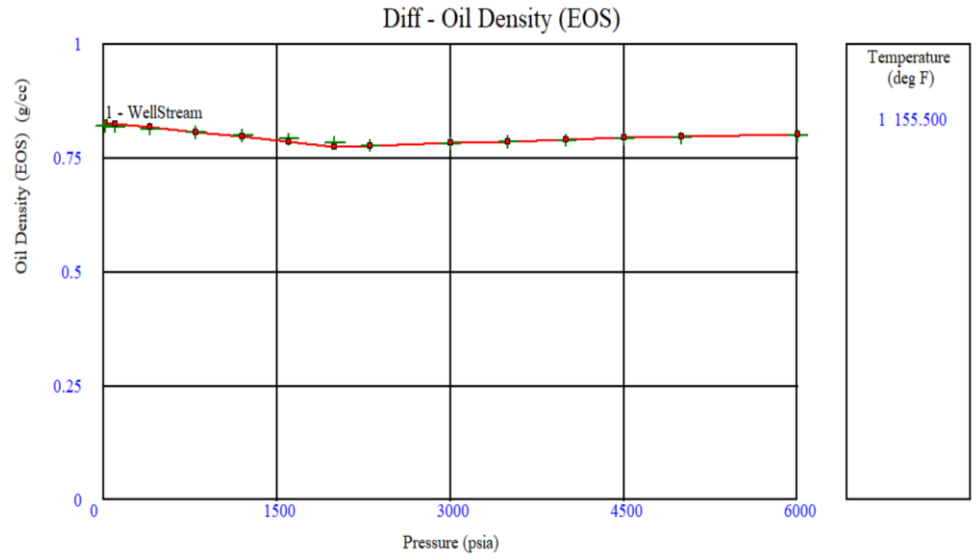

Figure 8: Liquid Density as a function of Pressure in the DLE test at 155.5 ^{0}F.

3.6 Literature Comparative Analysis.

The tuning approach which was used in this paper is the same as the one suggested by Ali and McCain [29], who have shown that sequential tuning of BIC Critical Properties Volume Translation is the most efficient in the case of black oil systems. Nonetheless, we had to adjust acentric factors (21.22), which is not the same as the suggestion by them to adjust acentric factors upon regression. This could be due to the increased

molecular weight (158.8) of our C7+ fraction in comparison with the typical Gulf of Mexico oils (MW 250) that Ali and McCain investigated.

This is confirmed by the better performance of PR EOS as compared to SRK EOS, as reported by Coats and Smart [30], that PR EOS gives better estimates of the density of liquid in the reservoir fluids in situations where the API gravity exceeds 30 degrees. More current investigations by Epelle et al. [31] based on machine learning-aided EOS tuning likewise found that PR EOS provides a worse bubble point pressure of light-to-medium crude oil.

It has been reported that the trade-off between GOR and Pb equalizes in the compositional simulation studies [18], where the single-objective regression fails to encompass the entire spectrum of the PVT behavior. This limitation could be overcome with the use of multi-objective optimization algorithms [15] or weighted regression using suitable objective functions.

The initial estimation of the critical property based on Kesler-Lee correlation [32] resulted in consistent values that are consistent with what is done in the industry [33]. The acentric factor adjustment of 21.22% is, however, an indication that the generalized correlations might not be able to adequately reflect the unique properties of this reservoir fluid, especially in the event of the presence of asphaltenic or waxy constituents [3].

3.7 Tuning parameter physical implications.

There is a significant physical implication of the dominance of CO_2/C7+ BIC sensitivity. Quadrupolar gas CO_2 cannot be mixed ideally with hydrocarbons, which cannot be mixed using van der Waals mixing rules, unless they are adjusted with empirical BIC [6]. The optimized BIC is effective in explaining:

1. Polar-nonpolar forces are not contained in the original EOS.
2. The size effect of an asymmetric effect between CO_2 long-chain hydrocarbons.
3. The possible CO_2 -hydrogen bonding of aromatic components in the C7+ fraction [22].

The acentric factor adjustment is a physical measure simply denoting the difference between the C7+ fraction and the simple fluid behavior[10]. The original correlation-based value was that of a hypothetical normal alkane with the same boiling point, whereas the adjusted value is 72% closer to the true mixture of branched, aromatic, and naphthenic compounds in the reservoir fluid[34].

The fact that the zero adjustment to Omega A and Omega B is satisfactory proves that the Peng-Robinson EOS functional form is theoretically viable to use in this application. These are parameters, obtained by the van der Waals repulsive term and critical point conditions [4], that are independent of fluids and do not need to be adjusted when changing reservoir fluids [9].

The phase envelope with a critical point at 1315 psia suggests that miscible gas injection could be possible above 1500 psia, which will be used to inform the choice of EOR methods [18].

4. CONCLUSION

The paper assessed equation of state performance in the context of crude oil phase behavior modeling and a systematic tuning strategy. The prediction of bubble point pressure of the analyzed crude oil system with API gravity of 31.2° and GOR of 390 scf/STB was better in the Peng-Robinson EOS with Absolute Relative Error (ARE) of 0.015 than in the Soave-Redlich-Kwong EOS with ARE: 8.22. By this difference in performance, it is established that PR EOS is the cubic EOS of choice in black oil systems of a similar nature.

Sequential regression targeting of CO_2/ C7 binary interaction coefficient, C7+ critical properties, and C7+ acentric factor achieved zero error experimental saturation pressure. Nevertheless, this univariate strategy actually led to the fact that GOR error became not only 4.92 but 10.13, which is a significant trade-off between the similarity of various PVT properties.

CO_2/C7+ binary interaction coefficient had the most significant effect on the determination of saturation pressure, followed by the C7+ acentric factor. Omega A and Omega B did not need to be changed, which confirmed the use of the Peng-Robinson EOS functional form here.

These accuracies allow pool reservoir simulation and OOIP estimation as well as surface facility design with a high level of confidence, but GOR uncertainty must be factored in sensitivity tests.

Future Research Recommendations.

Future research should explore machine learning for rapid estimation of EOS parameters, validate tuning across different crude oils, enhance volume translation for accurate density prediction, use multi-objective optimization to align multiple PVT properties, and assess input uncertainty to boost reliability and support risk-informed compositional reservoir simulation decisions.

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