Performance Evaluation of Experimental and Simulated Differential Liberation Tests on Reservoir Fluid

Ikechi Igwe, Awajiogak Anthony Ujile

Abstract— Differential Liberation (DL) test results, one of the standard experiments performed by Pressure-Volume-Temperature (PVT) laboratories on reservoir fluid samples (black oil) are presented. The laboratory DL test data was simulated using Peng-Robinson Equation of State on HYSYS. The simulated results were compared graphically and statistically to the experimental data in terms of oil formation volume factor (FVF), solution gas-oil ratio (GOR), liberated GOR, gas compressibility factor (z-factor), and gas composition, with respect to pressure, respectively. The simulation result exhibited similar trends to the experimental data in terms of oil FVF, oil liberate GOR, oil solution GOR, and gas Z-Factor. The bubble point pressure from the experimental result is 3734 psig, while that of the simulation result is 3762.9 psig. This gave an absolute deviation of 0.774 %, a satisfactory match to the laboratory (experimental) data. This show that equations of state, when sufficiently tuned can simulate the PVT properties of reservoir fluids, and can minimize the need to perform complete set of experimental PVT tests (DL) on each and every new reservoir fluid.

Index Terms— Black Oil, Bubble Point Pressure, Differential Liberation, HYSYS, Peng-Robinson Equation of State, PVT Analysis, Simulation

———————————— ◆ ————————————

1 INTRODUCTION

The hydrocarbon reservoir consists of fluids (water, oil, and gas) in varying proportions. Some may be saturated with only water and oil; water and gas; or water, oil and gas. The collection of a representative sample of these fluids and laboratory study of their phase behavior are very essential for fluid or reservoir characterization, economic evaluations (estimation of reserves), and development of reservoir management plan [1].

Differential Liberation (DL) test also known as Differential Vaporization or Differential Expansion is one of the standard experiments performed by Pressure-Volume-Temperature (PVT) laboratories on reservoir fluid samples. The DL test is designed to approximate the depletion process of an oil reservoir [1], [2] and also simulate the flowing behavior of hydrocarbon systems at conditions above the critical gas saturation, and thereby provide suitable PVT data to evaluate reservoir performance [2]. In DL process, the solution gas that is liberated from the oil during decline in pressure is continuously removed from contact with the oil, and before establishing equilibrium with the liquid phase [2]. As the saturation of these librated gas reach the critical gas saturation, the librated gas begins to flow, leaving behind the oil that originally contained it [2]. This is attributed to the fact that gases have higher mobility than oils [2]. DL process is characterized by variation in composition of the total hydrocarbon system with respect to depletion.

The relatively high cost of performing experimental PVT tests (DL test), and the uncertainty in the accuracy of such laboratory data are a major concern that needs to be addressed. Ahmed [2] recommended equations of state as an attractive approach for generating these very important data. He explained that equations of state, when adequately "tuned" are capable of simulating the PVT properties of reservoir fluids, and can consequently save significant time and expenses by eliminating the need to perform a complete

set of experimental PVT-type tests on each and every new reservoir fluid [2].

The objective of this research work is to present a laboratory DL test data, simulate the laboratory DL test data using Peng-Robinson equation of state, and then compare laboratory (experimental) and simulated results in terms of oil FVF, solution gas-oil ratio (GOR), liberated GOR, gas z-factor, and gas composition with respect to pressure, respectively.

There are three basic steps involve in developing accurate simulation model: calibration; verification; and validation. A based model should be created and calibrated so that it matches the area being studied. The calibrated model should then be verified to ensure that the model is operating as expected based on the output. Once the model has been verified, the final step is to validate the model by comparing the output to experimental data from the study area. This can be done by using statistical techniques. Unless these techniques are employed, the simulation model created will produce inaccurate result and will not be a useful prediction tool.

This research work employed HYSIS simulation package and Peng-Robinson EOS to simulate the laboratory DL test data. Peng and Robinson [3] gave examples of the use of Peng-Robinson EOS for predicting vapour pressure and volumetric behaviour of pure component and binary mixtures. Harstad *et al.* [4] reported that Peng-Robinson equation of state was superior to other EOSs, for predicting vapour-liquid equilibrium in hydrogen and nitrogen containing mixture. It was shown that Peng-Robinson EOS offers an accurate, non iterative and easy to use correlation for high pressure fluid mixture in gas turbine and pocket engines [4]. Zhao and Olesik [5] also reported that Peng-Robinson EOS is capable of representing the experimental data with an average relative deviation within 6%.

Meanwhile, the Peng-Robinson EOS is one of the most used

EOS in the petroleum industry. It is easy to use and provide accurate relationship between temperature, pressure and phase composition in binary and multi component systems. It only requires critical properties, acentric factor and little computer resources to give a good phase equilibrium correlation [4].

Whitson [6] showed that an insufficient description of the heavy fraction reduces the accuracy of PVT prediction using EOSs. Whitson [7] used gamma distribution model to describe molecular weight/mole fraction for C_{7+} fraction, which improved the accuracy of the PVT prediction. Another widely used distribution model is the exponential function [8]. Riazi [9] developed a two parameter distribution model to predict the properties of the C_{7+} fraction.

Due to errors introduced by adopted empirical correlations, it is necessary to adjust the parameter of the selected EOS to achieve a satisfactory match between the laboratory PVT data and EOS results [2]. This adjustment could be done either manually through trial and error or automatically by non linear regression approach. Coat and Smart [10] recommended that the regression variables to be adjusted should include critical temperature, critical pressure and acentric factor of the plus fractions, the constant part of the EOS plus fraction parameter (Ω) for methane, the binary interaction coefficient (BIC) between methane and the heavy fractions and non-hydrocarbon (Ω_s), and BICs for a system with significant amount of non-hydrocarbon components due to gas injection. Pedersen *et al.* [11] showed that a proper characterization of the heavy fraction will reduce the need for extensive tuning of EOS. They concluded that minimal splitting of the heavy fractions and adjusting EOS heavy fraction parameters are sufficient for getting a good match. Merrill *et al.* [12] presented a comparison of different tuning method. They concluded that the tuning process is highly dependent on the quality of the laboratory data, a major limitation.

This research work intend to present a laboratory DL data of a black oil sample from the Niger Delta (Nigeria), which when simulated using Peng-Robinson EOS will represent the experimental data with an absolute deviation within 1 %.

2 MATERIALS AND METHODS

2.1 Material
    i.   **B**lack oil (recombined surface) sample
    ii.   PVT Cell
    iii. Computer

2.2 Experimental Procedure
The reservoir fluid was physically recombined using a corrected GOR of 815 SCF/bbl. The summary of reservoir fluid data and sampling conditions are presented in Tables 1 and 2, respectively. The standard laboratory procedure of performing DL test, outlined by Ahmed [2], was rigorously followed. The black oil sample was charged into a visual (windowed) PVT cell at the saturation pressure (bubble-point pressure) and reservoir temperature. The cell pressure is reduced by increasing the cell volume. This results to

liberation of gas. The cell is then agitated until equilibrium is reached between the liquid phase and the gas phase. All the liberated gas is completely displaced from the cell through the cell flow valve, at constant pressure. The volume and specific gravity of the discharged gas are measured at standard conditions. The volume of the remaining liquid is also recorded. This procedure is repeated at decreasing pressure levels and finally at atmospheric pressure. The residual oil volume (at atmospheric pressure) is then measured at a reduced cell temperature of 60 °F [2].

TABLE 1
RESERVOIR FLUID DATA

Parameter	Value
Saturation pressure at reservoir temperature: 111 °C (323 °F)	257 bar(g) (3734 psig)
Isothermal compressibility of the reservoir fluid: T = 111 °C (232 °F)	
- at reservoir pressure: 445. 0 bar(g) (6453 psig)	1.720×10^{-4} (bar)$^{-1}$ (1.186 x 10^{-5} (psi)$^{-1}$
- at saturation pressure: 257.5 bar(g) (3734 psig)	3.170×10^{-4} (bar)$^{-1}$ (2.186 $\times 10^{-5}$ (psi)$^{-1}$
Isobaric thermal expansion of the reservoir fluid: P = 350 bar(g) (5075 psig) between 230 °C (70 °F) and 111 °C (232 °F)	1.164×10^{-3} (°C)$^{-1}$ (0.647 $\times 10^{-3}$ (°F)$^{-1}$
One stage separation of the reservoir fluid - solution gas oil ratio:	227 sm³/m³ (1275 SCF/STB)
- oil formation volume factor at saturation pressure:	1.768
- stock tank oil density at 15 °C:	836.2 kg/m³ (37.7 °API)
Viscosity of the reservoir fluid: - at saturation pressure and reservoir temperature:	0.269×10^{-3} Pa.s

2.3 Computer Simulation of Differential Liberation Test
HYSYS computer program was used to execute the simulation of the DL test using Peng-Robinson EOS. The simulation procedure proposed by Ahmed [2], [8] was meticulously followed. The algorithm for simulating the DL test by Peng-Robinson EOS is presented in Fig. 1.

2.4 Model Equations
It is important to select an EOS that is able to achieve a satisfactory match between EOS result and all available PVT laboratory data [2], [8]. In this work, Peng-Robinson EOS is used for estimation of the volumetric properties and phase behavior description of reservoir fluid sample by simulating the DL test. It is used alongside with flash calculation to

account for continuous compositional changes and proper volumetric property determination when simulating differential liberation test.

TABLE 2
SAMPLING CONDITIONS

Parameter	Value
Reservoir and well characteristics:	
- production zone:	sandstone
- reservoir static pressure:	445 bar(g) (6453 psig)
- reservoir temperature:	111 °C (232 °F)
- bottom hole flowing pressure:	428.8 bar(g) (6218 psig) at 3880 m RKB
- bottom hole flowing temperature:	110.5 °C (231 °F) at 3880 m RKB
Surface sampling conditions:	
- choke size:	28/64''
- well head pressure:	226.6 bar(g) (3286 psig)
- well head temperature:	52 °C (126 °F)
- first stage separator pressure:	31.7 bar(g) (469 psig)
- first stage separator temperature:	51.5 °C (125 °F)
- stock tank temperature:	15.6 °C (60 °F)
- atmospheric pressure:	1.013 bar (a)
- stock tank oil rate:	670.5 m³/d (4218 STB/D)
- first stage separator oil rate:	739.3 m³/d (4650 BBL/D)
- first stage separator gas rate:	107220 m³/d (3.786 MMSCF/D)
At 0.0 bar(g) and 15 °C:	
- relative gas density (air = 1)	0.732
- gas compressibility factor:	0.919
- density of stock tank oil at 15.6°C:	830 kg/m³ (39 °API)
- B.S.W.:	0 %
- shrinkage:	0.907
- separator gas-stock tank oil ratio:	159.9 Sm³/m³ (898 SCF/STB)

Peng-Robinson [13] proposed a two-constant equation of state:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)} \qquad (1)$$

Where;
P = pressure
V = volume
a = parameter that measure attractive force between molecules
b = effective volume of the molecules
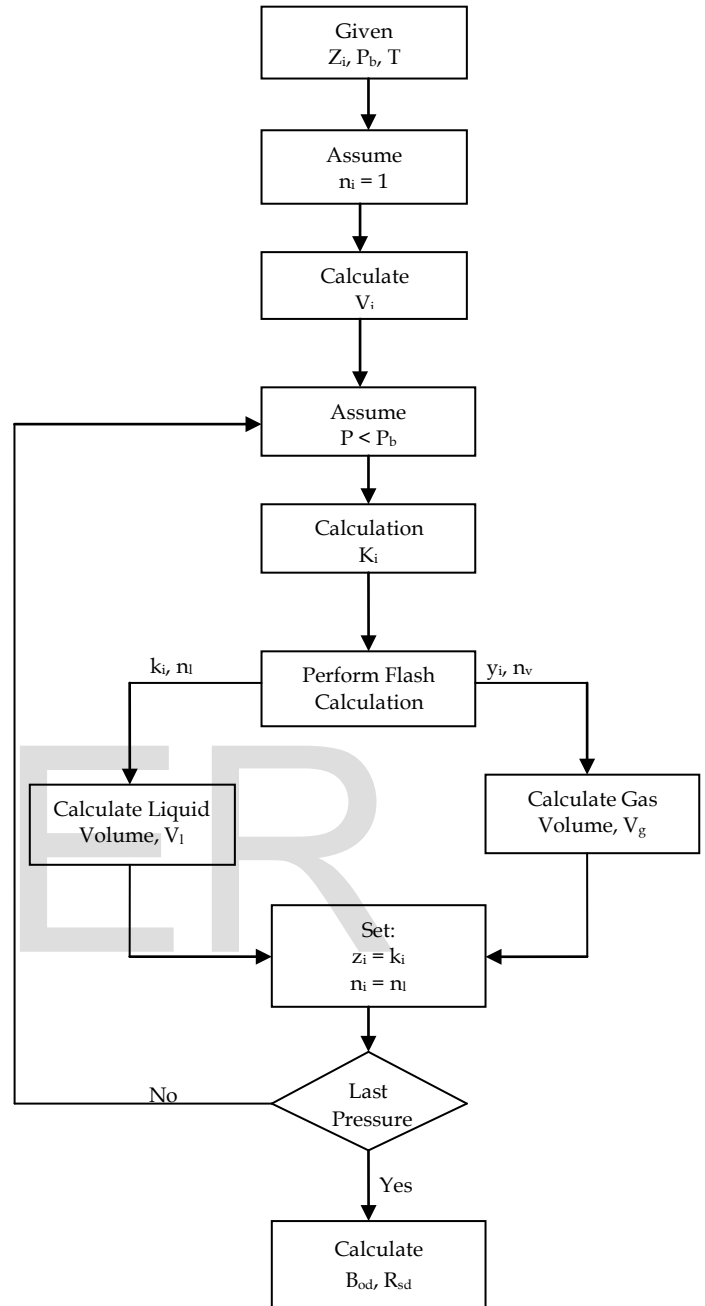α = temperature-dependent parameter
R = universal gas constant

Fig. 1. Flow Diagram for Simulating Differential Liberation Test by Peng-Robinson EOS [2], [8]

Imposing the classical critical point conditions:
$\left(\frac{\partial P}{\partial V}\right)_{T_C} = 0$, and $\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0$ on (1) and solving for parameters a, and b, gives:

$$a = \Omega_a \frac{R^2 T_C^{\,2}}{P_C} \qquad (2)$$

$$b = \Omega_b \frac{R\,T_C}{P_C} \tag{3}$$

Where;

$$\Omega_a = 0.45724$$

$$\Omega_b = 0.07780$$

Equation (1) predicts a universal critical gas compressibility factor ($Z_c = 0.307$). Peng and Robinson [13] adopted Soave's approach for calculating temperature-dependent parameter, α :

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \tag{4}$$

Where;

$$T_r = reduced\ temperature = \frac{T}{T_C}$$

$$m = 0.37646 + 1.54227\omega - 0.26992\omega^2 \tag{5}$$

Where;

ω = acentric factor

For ω greater than 0.49,

$$m = 0.37646 + 1.48503\omega - 0.1644\omega^2 + 0.016666\omega^3 \tag{6}$$

Equation (1) can also be expressed in cubic form in terms of compressibility factor:

$$Z^3 - Z^2(1 - B) + Z(A - 3B^2 - 2B) - (AB - B^2 - B^3) = 0 \tag{7}$$

For pure component;

$$A = \frac{a\alpha P}{R^2 T^2} \tag{8}$$

$$B = \frac{bP}{R\,T} \tag{9}$$

Where a, b, and a, are as defined in (2), (3), and (4), respectively.

For mixtures:

$$A = \frac{(a\alpha)_m P}{R^2 T^2} \tag{10}$$

$$B = \frac{b_m P}{R\,T} \tag{11}$$

Where;

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_i \alpha_j}(1 - k_i)\right]^2 \tag{12}$$

$$b_m = \sum_i [x_i b_i] \tag{13}$$

k_i = binary interaction coefficient

Binary interaction coefficient is not required for hydrocarbon systems (i.e, $k_i = 0$). In the presence of non-hydrocarbon compounds, its value is obtained from correlations. The solution of (7) generates three real roots. The largest root is considered the vapour phase compressibility factor (Z^v) while the smallest is regarded as the liquid phase compressibility factor (Z^L) [13].

Peng and Robinson [13] defined the fugacity coefficient for component i in the liquid phase as:

$$\ln \frac{f^v}{x_i p} = \ln(\Phi_i^L) = \frac{b_i(Z^L - 1)}{b_m} - \ln(Z^v - 1) - \frac{A}{2\sqrt{2}B}$$

$$\left[\frac{2\Psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right] \ln \left[\frac{Z^v + (1 + \sqrt{2})B}{Z^v - (1 - \sqrt{2})B}\right] \tag{14}$$

Where;

A, B, $(a\alpha)_m$, b_m, b_i, Z^L are as defined previously, and

$$\Psi_i = \sum_j \left[x_i \sqrt{a_i a_j \alpha_i \alpha_j}(1 - k_{ij})\right] \tag{15}$$

The fugacity coefficient for any component in the gaseous phase is determined by substituting the composition of the liquid phase in (14) with that of the vapour phase:

$$\ln \frac{f^v}{y_i p} = \ln(\Phi_i^v) = \frac{b_i(Z^v - 1)}{b_m} - \ln(Z^v - 1) - \frac{A}{2\sqrt{2}B}$$

$$\left[\frac{2\Psi_i}{(a\alpha)_m} - \frac{b_i}{b_m}\right] \ln \left[\frac{Z^v + (1 + \sqrt{2})B}{Z^v - (1 - \sqrt{2})B}\right] \tag{16}$$

The material balance of components in a two-phase mixture consisting of liquid and vapour phases is given thus [2], [8]:

$$n = n_L + n_V \tag{17}$$

$$z_i n = y_i n_V + x_i n_L \tag{18}$$

Where;

n = total number of mole in the mixture

n_L = number of mole in the liquid phase

n_V = number of mole in the vapour phase

z_i = mole fraction of component i in the mixture

y_i = mole fraction of component i in the vapour phase

x_i = mole fraction of component i in the liquid phase

$z_i n$ = total number of moles of ith component in the mixture

$x_i n_L$ = total number of moles of ith component in the liquid phase

$y_i n_V$ = total number of moles of ith component in the vapour phase

Also, the total number of mole fraction in a hydrocarbon system is given thus:

$$\sum_{i=1}^{N} z_i = 1 \tag{19}$$

$$\sum_{i=1}^{N} x_i = 1 \tag{20}$$

$$\sum_{i=1}^{N} y_i = 1 \tag{21}$$

Phase equilibra calculation is done on the basis of one (1) mole of hydrocarbon mixture ($n = 1$). This reduces (17) and (18) to (22) and (23), respectively:

$$1 = n_L + n_V \tag{22}$$

$$z_i = y_i n_V + x_i n_L \tag{23}$$

For a system in equilibrium, the equilibrium constant, k_i, of a component, i, is the ratio of the mole fraction in the vapour phase to its mole fraction in the liquid phase. Thus [8]:

$$k_i = \frac{y_i}{x_i} \tag{24}$$

Therefore,

$$y_i = x_i k_i \tag{25}$$

Substituting (25) into (23) gives:

$$x_i = \frac{z_i}{n_L + n_V k_i} \tag{26}$$

Substituting for n_L in (26) with (22) gives:

$$x_i = \frac{z_i}{n_V(k_i - 1) + 1} \tag{27}$$

Similarly,

$$y_i = x_i k_i = \frac{z_i k_i}{n_V(k_i - 1) + 1} \tag{28}$$

It can be shown from (20) and (21) that:

$$\sum_{i=1}^{N} y_i - \sum_{i=1}^{N} x_i = 0 \tag{29}$$

Substituting (27) and (28) into (29) yields:

$$f(n_V) = \sum_{i=1}^{N} \frac{z_i(k_i - 1)}{1 + n_V(k_i - 1)} = 0 \tag{30}$$

Equation (30) can be solved by successive substitution or Newton Raphson method. The equilibrium ratio, for real solution, is not only a function of pressure and temperature, but also a function of the composition of the hydrocarbon mixture. Ahmed [2], [8], presented a step-by-step procedure for the determination of the equilibrium constant, k_i.

3 RESULTS AND DISCUSSION

3.1 Experimental Results

The results of the compositional analysis of the separator fluids (one stage separation of the reservoir fluid) and calculated reservoir fluid are presented in Table 3. Table 3 shows the composition (mole %) of each component in the separator gas and oil, respectively, and the reservoir oil. The separator gas contains more intermediate components (ethane–n-butane) than the separator oil. The DL test data obtained from laboratory experiment are presented in Table 4. Table 4 indicates that during decline in reservoir pressure as a result of depletion of the reservoir fluid (black oil), the bubble point or liquid saturation pressure (the pressure at which the first bubble of solution gas evolves from the oil) is 3734 psig. The oil FVF, also known as oil shrinkage factor or relative volume, is the ratio of the volume of oil at reservoir conditions to the volume of oil at stock tank conditions. Table 4 also shows that at the start of the experiment (above bubble point pressure), the oil FVF increased gradually up to the bubble point pressure, with decreasing pressure. The oil FVF starts decreasing immediately after the bubble point pressure. The oil volume shrinks gradually. This is due to liberation of dissolved gas and immediate removal of same from contact with the oil. This is a typical phase behavior of a black oil reservoir fluid undergoing DL.

TABLE 3
COMPOSITIONAL ANALYSIS OF THE SEPARATOR FLUIDS
(ONE STAGE SEPARATION OF THE RESERVOIR FLUID) AND
CALCULATED RESERVOIR FLUID

Components	Separator Gas (mol. %)	Separator Oil (mol. %)	Reservoir oil (mol. %)
Hydrogen Sulfide	0.00	0.00	0.00
Nitrogen	0.92	0.00	0.64
Carbon Dioxide	1.62	0.00	1.14
Methane	66.56	0.00	46.55
Ethane	10.42	0.20	7.34
Propane	10.17	1.15	7.45
i-Butane	1.34	0.42	1.06
n-Butane	4.35	2.44	3.77
i-Pentane	1.16	1.49	1.26
n-Pentane	1.51	3.17	2.01
Hexanes	1.04	5.93	2.51
Heptanes	0.70	10.15	3.54
Octane	0.20	10.60	3.33
Nonanes	0.01	8.65	2.61
Decanes	0.00	5.15	1.55
Undecane-plus	0.00	50.65	15.24
Total	**100.00**	**100.00**	**100.00**
Molecular weight	26.3	202.5	79.3
Gas relative density (Air = 1000)	0.907		

TABLE 4
EXPERIMENTAL DIFFERENTIAL LIBERATION TEST DATA
AT 111 ^{O}C (232 ^{O}F)

Pressure (psig)	Oil FVF (bbL/STB)	GOR: dissolved gas (Sm³/m³)	GOR: liberated gas (SCF/STB)	Z factor
6453	1.841			
6090	1.849			
5807	1.857			
5467	1.866			
5082	1.878			
4502	1.898			
3850	1.923			
3734	1.928	1486	0	
3052	1.744	1152	334	0.873
2443	1.623	921	565	0.862
1842	1.523	724	762	0.863
1240	1.439	548	938	0.880
609	1.347	366	1120	0.920
0	1.089	0	1486	

Table 4 also shows that, below the bubble point pressure, the GOR of the dissolved gas decreases while that of the liberated gas increases.

3.2 Simulation Results

The experimental DL data were simulated using Peng-Robinson EOS on HYSYS. The simulation results are presented in Table 5. The phase behaviour of black oil and volatile oil at, and below bubble point is critical to the prediction of the behaviour of the reservoir systems under production. This is because, above the bubble point, black oil is under-saturated and exists as liquid only. Below the bubble point, gases evolve from the oil and two phases (gas and liquid) exist in the system. The simulation result presented in Table 5, is the phase behaviour of the black oil system at bubble point pressure and below the bubble point pressure. The simulated result follows the same trend as the experimental DL test data presented in Table 4.

TABLE 5
SIMULATED DIFFERENTIAL LIBERATION TEST DATA
AT 111 ^{O}C (232 ^{O}F)

Pressure (psig)	Oil FVF (bbL/STB)	GOR: dissolved gas (Sm³/m³)	GOR: liberated gas (SCF/STB)	Z factor
3762.9	1.959	1511	0	0.9119
3052.0	1.789	1178	333.2	0.8778
2443.0	1.670	943	568.1	0.8631
1842.0	1.567	742	769.1	0.8636
1240.0	1.473	561	950.4	0.8792
609.0	1.347	380	1131.4	0.9110
0.0	1.046	0	1511.4	0.9873

Residual oil density at standard conditions = 46.3 Ib/ft³
Bubble point pressure = 3762.9 psig

3.3 Comparison of Experimental and Simulated Data

The comparisons of the experimental and simulated DL data are presented graphically in Fig. 2, Fig. 3, Fig. 4, and Fig. 5. The results of the experimental and simulated oil FVF with respect to pressure are compared in Fig. 2. The comparison of the experimental and simulated oil liberated GOR is presented in Fig. 3. Fig. 4 shows the comparison of the experimental and simulated oil solution GOR with respect to pressure. The comparison of the experimental and simulated gas z-factor is presented in Fig. 5. The results presented in Fig. 2, Fig. 3, Fig. 4, and Fig. 5, shows that the simulated data, represented by the solid line curves (—) followed the same trend with the experimental data, represented by the dotted line curves (•). An indication that the simulated results are very good approximation of the experimental data (the data points are closely matched).

The bubble point pressure from the experimental result presented in Table 4 is 3734 psig, while that of the simulated result from Table 5 is 3762.9 psig. This resulted to an absolute deviation of 0.774 %, a satisfactory match with the laboratory (experimental) data.
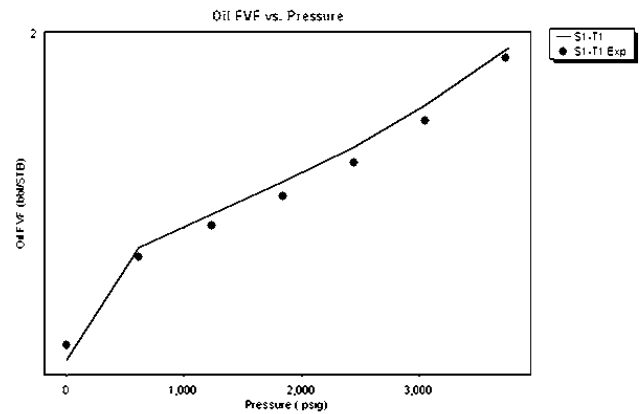

Fig. 2. Comparison of Experimental and Simulated Oil Formation Volume Factor (FVF) with Respect to Pressure. The solid line curve (—) represents the simulated data, while the dotted line curve (•) represents the experimental data.
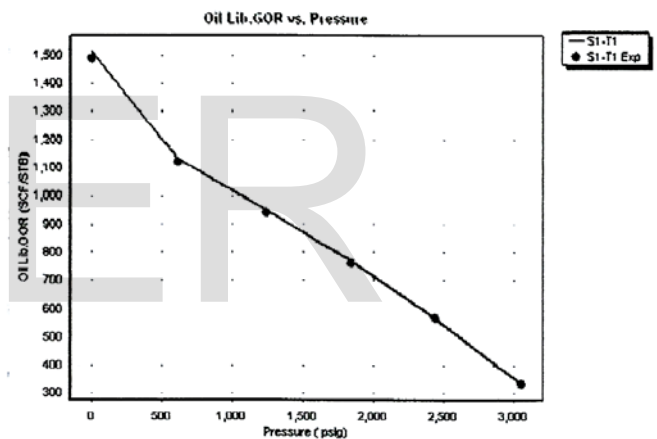

Fig. 3. Comparison of Experimental and Simulated Oil Liberated GOR with Respect to Pressure. The solid line curve (—) represents the simulated data, while the dotted line curve (•) represents the experimental data.
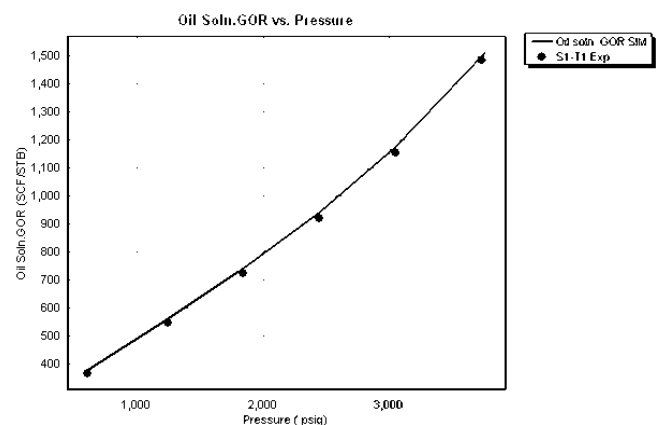
Fig. 4. Comparison of Experimental and Simulated Oil Solution GOR with Respect to Pressure. The solid line curve (—) represents the simulated data, while the dotted line curve (•) represents the experimental data.
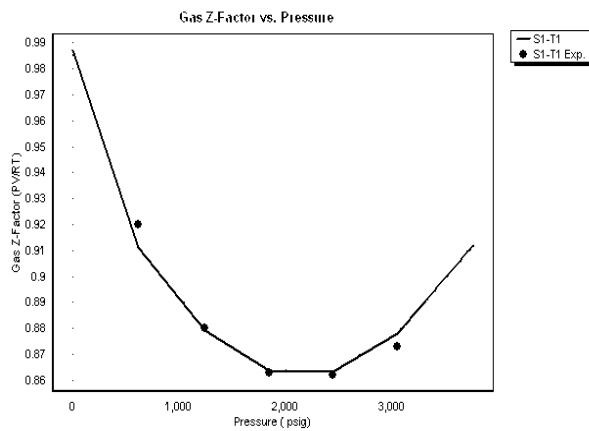

Fig. 5. Comparison of Experimental and Simulated Gas Compressibility Factor (Z-Factor) with Respect to Pressure. The solid line curve (—) represents the simulated data, while the dotted line curve (•) represents the experimental data.

4.0 CONCLUSION

Laboratory Differential Liberation test data were simulated using Peng-Robinson EOS on HYSYS computer software. The simulation result exhibited similar trends with the experimental date in terms of oil FVF, oil liberate GOR, oil solution GOR, and gas Z-Factor. The bubble point pressure from the experimental result is 3734 psig, while that of the simulated result is 3762.9 psig. This gave an absolute deviation of 0.774 %, a satisfactory match with the laboratory (experimental) data. Hence, equations of state, when sufficiently tuned can simulate the PVT properties of reservoir fluids, and minimize the need to perform complete set of experimental PVT tests (DL) on each and every new reservoir fluid.

5.0 ACKNOWLEDGMENTS

6.0 REFERENCES

[1] N. Ezekwe, *Petroleum Reservoir Engineering Practice.* Pearson Education, Inc.: Boston, pp. 53-54, 2007.

[2] T. Ahmed, *Equations of State and PVT Analysis.* Gulf Publishing Company, Houston, pp. 410-445, 2007.

[3] D.Y. Peng and D.B. Robinson. "A Rigorous Method for Predicting the Critical Properties of Multi-component Systems from an Equation of State." *AIChE J.* vol. 23, issue 2, pp. 137-213, March 1977.

[4] R.G. Harstad, R.S. Miller, and J. Bellan, "Efficient High Pressure Equation of State." *AIChE J.* vol. 43, issue 6, pp. 1605-1610, June 1997.

[5] J. Zho and S.V. Olesik, "Phase Diagram Studies of Ethanol-CHF$_3$ and Methanol-H$_2$O-CHF$_3$ Mixtures." *Fluid Phase Equilibrium,* vol. 154, no. 2, pp. 261-284, January 1999.

[6] C.H. Whitson, "Characterizing Hydrocarbon Plus Fractions. " *Society of Petroleum Engineers Journal,* vol. 23, issue 4 pp. 683-694, 1983.

[7] C.H. Whitson, "Effect of C$_{7+}$ Characterization on Equation of State Prediction." *Society of Petroleum Engineers Journal,* vol. 24, issue 6 pp. 685 694, December 1984.

[8] T. Ahmed, *Hydrocarbon Phase Behavior.* Gulf Publishing Company, Houston, pp. 379-405, 1989.

[9] M.R. Riazi, "A continuous Model for C$_{7+}$ Fraction Characterization of Petroleum Fluids." *Ind. Eng. Chem. Res.,* vol. 36, no. 10 pp. 4299-4307, October 1997.

[10] K.H. Coat and G.T. Smart, "Application of Regression Based Equation of State PVT Program to Laboratory Data." *SPE Reservoir Eng.* vol. 1. Issue 3, pp. 277 299, May 1986.

[11] K.S. Pederson, P. Thomassen, and A. Fredenslund, *The Properties of Oils and Natural Gases.* Gulf Publishing Company, Houston: Texas, pp.114-133, 1989.

[12] R.C. Merill, K.G. Hartman, and J.L. Greek, "A Comparison of Equation of State Tuning Methods." Technical Report SPE 28589-MS, Presented at the SPE Annual Technical Conference and Exhibition, New Orlean, Louisiana, 25-28 Septembe 1994.

[13] D.Y. Peng and D.B. Robinson, "A New Two-Constant Equation of State." *Ind. Eng. Chem. Fundamen.,* vol. 15, no. 1, pp 59-64, February 1976.