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## Experimental Determination and Modeling of Bottom-Hole Crude Oil Mixture Liquid Phase Density (Lpd) by Material Balance During Well Fluids Depletion Studies

**E. E. Alagoa**

Department of Science Laboratory Technology, Bayelsa State Polytechnic, Aleibiri, Nigeria  
csnbayelsa@gmail.com

**K. W. Bunonyo**

Department of Mathematics and Statistics, Federal University Otuoke, Nigeria  
wilcoxbk@fuotuo.ke.edu.ng

**B. Abovie**

Department of Electrical and Electronic Engineering Technology, Bayelsa State Polytechnic, Aleibiri, Nigeria

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**Abstract:** *The liquid-phase density behavior of petroleum reservoir fluids under prevailing reservoir conditions, methods of evaluation, and factors affecting petroleum fluid density have been examined. A high-pressure and high-temperature PVT Ruska blind cell volume was calibrated in the temperature and pressure ranges of 730F to 2500F and 15 to 6000 psia. The calibrated cell volume equation was  $(515.214 + 8.80 \times 10^{-3} T + 8.89 \times 10^{-5} P + 2.30 \times 10^{-8} PT)$ . 100.310 cm<sup>3</sup> (78.663102g) of bottom-hole oil sample was charged into the cell at 5000 psi and 73 °F, while the cell was heated to the study temperature of 1540 °F in a thermostatic silicone oil bath. A pressure density run was conducted immediately after charging the sample for study. Pump manifold compressibility was determined at 730F with a pressure range of 15 to 8000 psia to establish uniform pump manifold compressibility and to eliminate errors in pressure-volume measurements. The cell temperature was monitored using a precision type J. digital thermocouple, and the equilibrium cell temperature cycle was 154.2°F throughout the experiment. At equilibrium cell temperature, the cell opening pressure was determined at a reference pressure of 2000 psi. The open-air pressure was 274 psi at 1540F. A constant composition expansion was conducted on the fluid sample, where the bubble point pressure and volume were measured to be 2870 psi and 106.743 cm<sup>3</sup>, respectively. Differential liberation expansion was immediately performed below the bubble point. Liquid phase densities above the bubble point pressure were calculated from the relative volume data obtained from pressure volume measurement, while liquid phase densities below the bubble point pressure during differential liberation were calculated using the mass balance of the initial mass of oil in place.*

**Keywords:** *Liquid: Phase Density, Material Balance, Reservoir Fluids, Empirical Model, Bottom-Hole and Well Fluid.*

The results showed that the density of the liquid phase at pressures above the bubble point increases with pressure and decreases to a minimum as pressure falls below the bubble point during pressure depletion, and gases liberated from the liquid phase are expelled from the system. The liquid phase undergoes continuous volumetric and compositional changes with enrichment with the heavy fractions, respectively. This contributed to the increasing liquid phase densities as the oil remaining at each differentially liberated step became richer with the heavy (Heptanes plus) fractions. This result was also seen from the gas compositional analysis, as C7+ fractions increased with decreasing pressure.

## 1.0. Introduction

### 1.1. Overview

The importance of oil density data cannot be overemphasized in the oil and gas production process. Engineers rely on accurate oil density data to, among other things, determine flow characteristics, design process equipment that would produce oil well fluids from the reservoir to surface conditions, estimate oil reserves, perform material balance calculations, etc.

The properties of oil well fluids change with the volumetric changes of the fluid system due to changes in reservoir pressure and temperature as fluid is produced for surface facilities (Pedersen et al., 1984, 1989, Pedersen et al., 2007, Lyon et al., 2007). In most petroleum reservoirs, change in temperature along the oil column may be so insignificant as to be ignored, although some reservoirs have thermal gradients and a periodic temperature gradient survey is conducted to establish a predictable temperature gradient log.

The liquid-phase density of reservoir fluids is affected by temperature, pressure, gas solubility, molecular compositions, and the oil formation volume factor.

The liquid density, known as API gravity, is of interest to producers and buyers of crude oil since it determines the gasoline quality and other properties of the crude oil. Sweet crude oil such as Bonny-light has a higher API gravity or lower density compared to crude oil from Venezuela or the Iranian region, which has a lower API or higher density. The reservoir simulation process often requires predicting and optimizing oil production and recovery from oil fields. The simulation process needs input data such as the properties of the reservoir fluids as a function of pressure, temperature, and fluid compositions. The accuracy of fluid properties can drastically affect the results of the simulation. The fluid properties needed as input for reservoir simulation are liquid phase densities, liquid phase viscosities, formation volume factors, and solution gas-oil ratios. The physico-chemical properties of the reservoir fluids are a function of the fluid compositions. These compositions can be determined by experimental analysis, e.g., gas chromatography. A practical method to determine reservoir fluid densities should be to evaluate density from the molecular compositions of the fluids.

Density is a property that indicates the quality of petroleum and its products, and it is also a very useful property to estimate other physical properties such as surface tension and the viscosity of petroleum fluids (Riazi *et al.*, 2001). Petroleum fluids density evaluation required proper information on the characteristic nature, molecular compositions, and properties of petroleum fluids in the reservoirs.

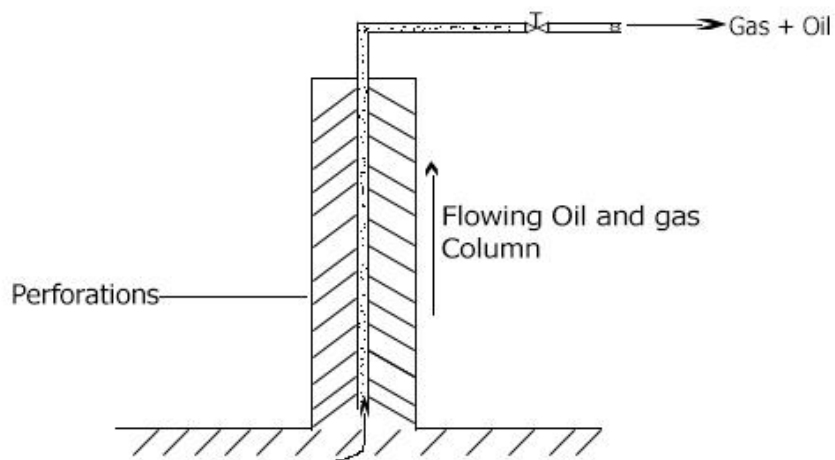
## 2.0. Literature Review

This paper outlined a brief review of methods employed by some researchers to determine density of Oil Reservoir Fluid Mixtures in recent times.

## 2.1. Methods of Determination of Density of Oil Reservoir Fluid Mixtures

### 2.1.1. Material Balance Technique

When petroleum reservoir fluid is produced to surface facilities, it undergoes significant volumetric change, which affects the liquid phase density. When other properties are measured in the laboratory, the material balance of the produced petroleum fluid (Standing, 1977, Mc Cain Jr. 1990) is performed during PVT analysis to determine the oil density.



**Figure 1. Flow of Reservoir Fluid into Well Tubing**

Mass of petroleum fluid flowing from reservoir  $M = \text{Mass of Oil} + \text{Mass of Gas}$

$M_r$  = Mass of petroleum fluid from reservoir (g).

$M_{sto}$  = Mass of stock tank oil (g) at standard condition.

$M_{gas}$  = Mass of gas (g) at standard condition.

$B_g$  = Gas volume factor

$V_R$  = Volume of flowing reservoir fluid ( $\text{cm}^3$ ) at res. conditions

$\beta_o$  = Oil Shrinkage (oil formation volume factor, FVF)

$R_s$  = Solution gas – oil ratio SCF/STB (cc/cc)

$\rho_{OR}$  = Density of oil at reservoir conditions g/cc

$\rho_{STO}$  = Density of stock tank oil at standard condition g/cc

$Y_{gas}$  = Solution gas gravity

$\rho_{air}$  = Density of air at standard condition g/cc

$T$  = Reservoir temperature ( $^{\circ}\text{F}$ )

$$M_R = M_{STO} + M_{gas} \tag{1}$$

$$V_R \rho_R = V_{STO}^{std} \rho_{STO} + V_{gas}^{std} \rho_{gas} \tag{2a}$$

$$\rho_R = \frac{V_{STO}^{std}}{V_R} \rho_{STO} + \frac{V_{gas}^{std}}{V_R} \rho_{gas} \tag{2b}$$

where  $\frac{V_{STO}^{std}}{V_R} = \frac{1}{FVF} = \frac{1}{\beta_0} = \frac{\text{Volume of oil at std conditons}}{\text{Volume of reservoir fluid at P,T}}$

$$\frac{\beta_0}{R_s} = \frac{\text{Volume of reservoir fluid at P,T}}{\text{Volume of gas at standard conditons}} = \beta_g$$

$$\Rightarrow \rho_R = \frac{\rho_{STO}^{std}}{\beta_0} + \frac{\gamma_{gas} \rho_{air}}{\beta_g} \tag{3a}$$

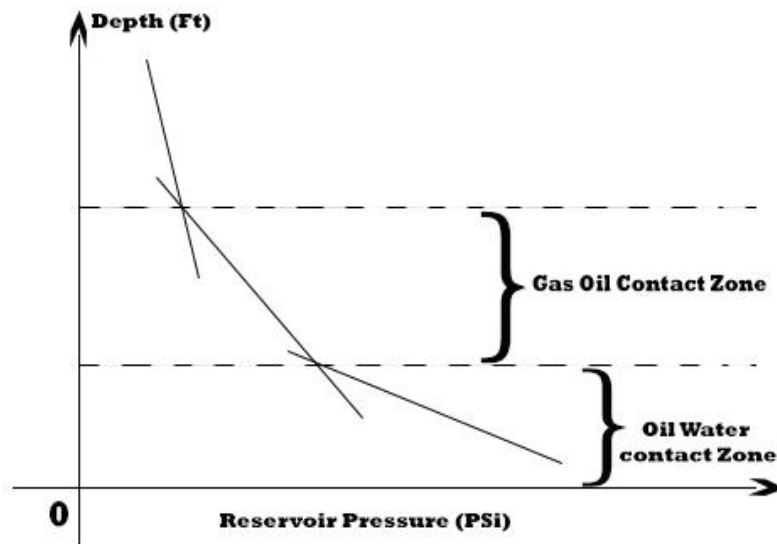
$$\rho_{R(P,T)} = \frac{\rho_{STO}^{std} + R_s \gamma_{gas} \rho_{air}}{\beta_0} \tag{3b}$$

From the above material balance equation, it is obvious that petroleum reservoir fluid density at pressure and temperature depends on accurate laboratory measurements of the density of stock tank oil, oil formation volume factor (FVF), solution gas gravity, and the solution gas/oil ratio.

**2.1.2. Pressure gradient method for formation fluid density determination**

Nathan Meehan (2011), in his formation testing report, demonstrated the practical use of pressure gradient survey, also known as bottom hole pressure (BHP) survey, to determine formation fluid density from pressure gradient data.

In a reservoir that is hydrostatic, the pressure in the continuous phases varies with depth based on the fluid density of the phases. In an oil reservoir, oil density is primarily a function of the amount of dissolved gas and the pressure if, and only if, the temperature along the oil column is fairly constant with depth. Compositional variations in the oil density and dissolved gas are common over large areas and in very thick reservoirs. Nevertheless, it is more common to have an approximately constant pressure gradient over the thickness of an oil reservoir among oil wells that are hydraulically continuous to detect variation of density or compositional gradient from a depth versus formation pressure plot using formation test data.



**Figure 2. Pressure Depth Gradients for Fluid Density Measurement**

Thus, formation fluid density can be evaluated from the relation below:

The pressure gradient is equal to the fluid density multiplied by the conversion factor (4).

Jackson *et al.* (2007) presented a paper on the application of the pressure gradient technique to determine, among others, formation fluid characteristics such as fluid density, pressure, temperature, etc.

Pressure-depth plots have been used for over thirty (30) years to evaluate fluid density and other formation characteristics using formation testers. They identified in their paper that there are emerging challenges in the use of the pressure-gradient technique, especially in the Niger Delta region and other offshore deepwater environments where many reservoirs are multi-layered and highly variable in terms of connectivity, permeability, and fluid properties.

### **2.1.3. Situ Fluid Density Measurement Techniques**

#### **2.1.3.1. Bottom Hole Optical Spectroscopic Techniques**

Schlumberger's down hole fluids laboratory reported the success of deploying an optical spectrometer in down hole to measure the optical densities (refractive indices) of reservoir fluids ([www.slb.com](http://www.slb.com), [www.onepetro.org/spe/paperno114648](http://www.onepetro.org/spe/paperno114648)). The optical density measurement is correlated to the density of petroleum fluid.

The spectrometer is attached to the down hole tool string and deployed into the down hole, where continuous fluid analysis of fluid compositions and changes in optical densities with fluid compositions are measured.

The principle of the optical spectroscopic method of measurement of fluid density is that a change in the optical density of reservoir fluid is related to the density of the reservoir fluid based on Lambert's law. The measurement of refractive indices or optical densities of various gaseous and liquid systems is used to determine the densities of such fluid systems.

#### **2.1.3.2. Fluid Density Sensor Probe**

Schlumberger (2014) has currently deployed its latest in situ density sensor device that measures formation fluid density down hole in real time.

The Schlumberger case study on the down hole fluid analysis of channel sands in a Nigerian deep water appraisal well presented a technical report stating that the in situ density sensor measurements identify fluid composition and contacts.

It was designed to overcome the challenge of dynamically investigating the formation fluid densities at reservoir conditions in an appraisal well drilled with oil-base mud.

The report claimed a solution combining an in situ density reservoir with quicksilver probe focused extraction to obtain accurate density measurements under flowing conditions while other down hole fluid analysis is being conducted.

#### **Principles of Operation**

The in situ density sensor was deployed with an innovative quicksilver probe that focused extraction and diverted filtrate-contaminated fluids to the perimeter of the probe to collect pure reservoir fluid into the extraction flow line. The separation of pure reservoir fluid makes it possible to accurately conduct down-hole fluid analysis even in an oil-base mud environment. Under flowing conditions, the in situ density sensor employs dual resonance modes to directly compute density from resonator-fluid interaction, with measurement quality evaluated in relation to standard fluid characterization parameters.

The composition of the oil was also determined in real time through down-hole fluid analysis of the fluid density measurements and optical spectrometry data.

### 2.1.4. High Pressure Densitometer Technique

The most recently used high-pressure densitometer or density meter is the Anton Paar DMA HPM density meter cell. It is an in-line cell with a built-in temperature sensor that determines the equilibrium fluid temperature. The cell is versatile and has a wide range of operating pressure and temperature (0–70 kPa and up to 200 °C).

The cell is normally connected by an interface module to an Anton Paar MPDS 2000 V3 evaluation unit, which displays the meter oscillation period and the temperature. The oscillation period has a precision range of 0.001–0.005 microseconds, and the temperature has a precision of 0.01<sup>0</sup>C. Both are required to obtain an accurate density from the density meter.

The Anton Paar density meter is based on the harmonic oscillation period of a quartz U-tube. The fluid sample is injected into the U-tube at a given temperature and pressure, and its density changes the period of oscillation. The U-tube is regarded as an undamaged oscillating mass suspended from a spring (Lagourette *et al.* 1992).

The period of vibration of an oscillating mass M is given by

$$T = 2\pi \frac{\sqrt{E}}{\sqrt{M}} \quad (5)$$

where T = period of oscillation in sel.

M = total oscillating mass (sum of U-tube mass and sample fluid mass)

M = M<sub>0</sub> + ρV<sub>0</sub>

M<sub>0</sub> = mass of U-tube

V<sub>0</sub> = volume of sample fluid

ρ = fluid density at the prevailing pressure and temperature conditions of the cell.

E = Elastic constant of the spring.

$$\rho = \frac{ET^2}{4\pi^2V_0} - \frac{M_0}{V_0} \quad (6)$$

$$A = \frac{E}{4\pi^2V_0} \text{ and } B = \frac{M_0}{V_0}$$

$$\rho = AT^2 - B \quad (7)$$

A and B are pressure- and temperature-dependent constants that are determined at any given pressure and temperature from a calibration of two fluids of known densities. Standard fluids like n-decane and n-hexane are used to establish calibration data. Once the constants are known, the density of the fluid sample under investigation can be determined with an accuracy of 0.0001 g/cm<sup>3</sup>, depending on the resolution.

### 2.1.5. High Pressure, High Temperature (HP-HT) Cell Techniques

#### 2.1.5.1. High Pressure and High Temperature Cylinder

The High pressure, high temperature cylinder is used to measure the density of petroleum reservoir fluids at pressure up to 10,000 psi and temperature up to 175<sup>0</sup>C, typical reservoir conditions.

The principle consists of transferring the oil sample into the cell at reservoir conditions and weighing the cell filled up with the sample using a high resolution analytical balance. The density of the sample is evaluated by simply dividing the mass of the sample (i.e. mass of the filled cell minus mass of the

evacuated cell.), by the known volume of the cell, this method provides reliable, correct and repeatable measuring results under extreme conditions of temperature and pressure. The resolution of the density measurement mainly depends on the balance used. With a weighing accuracy of  $\pm 1\text{mg}$ , maximum resolution of  $\pm 0.0006\text{g/cc}$  is attainable using this technique.

### 2.1.5.2. High Pressure High Temperature Pycnometer Technique

High pressure pycnometer functions in a similar way with high pressure and high temperature cylinder. It is fabricated from corrosion resistant alloy material. It has the following excellent features.

1. It is spherical in shape for uniform pressure distribution in trapped fluid body for easy measurement of density.
2. Maximum volume to mass ratio
3. Maximum operating pressure of 18,500psi at room temperature and working temperature up to 350<sup>0</sup>F.
4. Possesses a positive shut off valve system to trap accurate sample volume.
5. Total weight is under 1000g when completely filled with any liquid so that a highly sensitive metler gravimetric balance which has a limit of 1000gram can be used for mass measurement.
6. Made from corrosion resistant steel.
7. Highly polished surface to eliminate the clinging of oil or any calibration liquid or foreign material on the outside while weighing.

### 2.1.6. Vibrating Element Technique for Petroleum Fluid Density Measurement

As reported by Sherri Harris et al., an online fluid densitometer based on a vibrating element is receiving commercial application. It is a device that measures the density of crude oil in pipe lines and transmits the measured density data in the pipe lines in real time via a distributed control system (DCS). One version of such a vibrating element densitometer is used to measure the density of West Texas crude oil in pipelines. Micro Motion Coriolis Meter with a model number of CMFO50 is the hardware interfaced with flow sensor, with an analog output configured as density output, and communicates or transmits density output to an existing DCS system (a PC window as a data logger). According to the reporters, such a device has an accuracy of 0.0005 g/cc and a precision of 0.00002 g/cc and is less sensitive to vibration.

William *et al.* (2008) reviewed vibrating objects for the measurement of density and viscosity of crude oil in oilfields. The reviewers claimed that the vibrating object is a micro-electromechanical system (MEMS) designed to operate in oilfield conditions, particularly to measure both density and viscosity of hydrocarbon reservoir fluids in bottom-hole conditions. The measurement errors for density and viscosity are 1% and 10%, respectively, and are considered adequate for the evaluation of reservoir fluid properties.

The vibrating object based on a micro-electro-mechanical system (MEMS) consists of a metallic wire, usually made from tungsten or stainless steel, that is tensioned either by a mass suspended from its lower end or by being clamped between two rigid supports. An electric current is passed through the tensioned wire, which is in a permanent magnetic field perpendicular to its length, forcing it to move. A continuous alternating current can be used as a source of forced vibrations, or a direct current may be applied to displace the wire from its rest position, with the decay of amplitude measured after release. The measurement of the current induced in the wire due to its motion in the magnetic field provides the resonance in the forced oscillation mode or the logarithmic decrement of frequency in the transient decay mode. From this method of measurement, it is possible to determine the viscosity when a mass is suspended from one end, and it is also possible to obtain the density of fluids using other variant models

as reported elsewhere (Sherri Harri et al., Retsina et al., 1986, 1987, Goodwin *et al.*, 2006), and William et al., 2008).

The working equation based on the vibrating object for fluid density determination is given by;

$$\rho = \left[ \frac{c_1 E V_n^5 d^5}{24(1-\sigma^2) a^5 (2\pi f)^2} \right] - \frac{c_2 \rho_s d v_n}{2a} \quad (8)$$

$\rho$  = Fluid density in g/cc

$\rho_s$  = Density of plate material

f = Resonance frequency – of the plate immersed in the fluid

E = Young's modulus

$\sigma$  = Poisson's ratio for the plate material

d = Plate thickness

Vn = Eigenvalue (n = 1, 2, 3, -----) usually, n = 1

$c_1$  and  $c_2$  = calibration constants

a = length of the oscillating plate

### 2.1.7. Acoustic Wave Technique of Fluid Density Measurement

Acoustic measurements can give very useful clues or information on the in-situ characterization of reservoir fluids. The possibilities of obtaining the density and/or the viscosity of oil from acoustic measurements were studied by Ball *et al.* (2002). Batzle and Wang (1992) examined the seismic properties of different fluids in pores; including hydrocarbon gases, liquids, and brines (formation water). They calculated the density, velocity, and bulk modulus of gases based on Thomas et al. (1970). The approximation is adequate as long as Ppr and Tpr are 0.9. They used the Dodson and Standing (1943) equation to calculate the density of dead oil and Wang (1988) and Wang et al. (1988) empirical relations to calculate the velocity. They estimated the seismic properties of live oils by considering them to be a mixture of the original gas-free oil and a light liquid representing the gas component. Velocities can still be calculated using the Wang (1988) empirical model by substituting a pseudo-density based on the expansion caused by the gas intake. True densities of live oils are also calculated using a volume factor from standing correlation (1962), but the mass of the dissolved gas must be included.

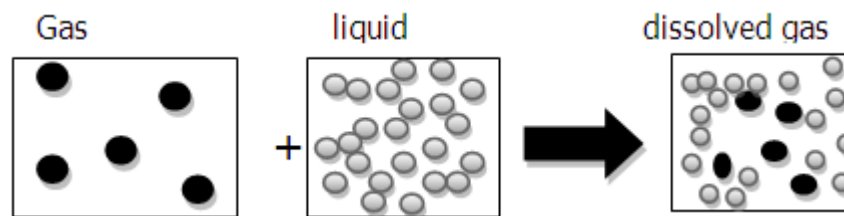
Han and Batzle (2000) improved on the velocity and density models of Batzle and Wang (1992) based on a series of new data. These new data suggest that the velocity-density model developed by Batzle and Wang (1992) overestimated the gas-oil ratio effect on the velocity of hydrocarbon liquids. They used two techniques to fit the data: a model based on engineering concepts of ideal liquids and one on purely empirical forms.

### 2.2. Models for Prediction of Density of Petroleum Fluid Mixtures with Dissolved Gases

The density of mixtures with dissolved gases can be modeled directly, although not necessarily accurately, with the equations of state or corresponding states method. However, when mixture densities are modeled using mixing rules, a liquid mixture with a dissolved gas is a special case. The density of the gas dissolved in the liquid is not the same as the density of the pure gas, as shown in figure 3 below. What then is the correct density to use in a regular solution mixing rule?

One solution is to determine the density of the gas in a hypothetical liquid state; that is, its effective density when part of a liquid mixture.





**Figure 3. Process of Dissolving a Gas Component in a Liquid Mixture**

Standing and Katz (1942) presented an empirical correlation based on this method to determine the density of liquid hydrocarbon mixtures containing dissolved 15.70 °C. methane and ethane. Using compressibility and thermal expansion coefficients, they extrapolated measured mixture densities to an atmospheric condition of 101.325 kPa and 15.7<sup>0</sup>C. They calculated the densities of methane and ethane from the mixture densities by applying the regular solution mixing rule. It was assumed that propane and any higher carbon number components would behave normally.

The method was originally designed to determine live oil densities. Since the solution gas composition is usually unknown, Standing and Katz (1942) developed an applicable correlation for calculating the density when only the oil API gravity, the gas gravity, and the solution GOR are known. The method is graphical and not suitable for computer modeling.

Tharanivasan *et al.* (2011) developed empirical correlations to predict the effective density of the dissolved gas component in petroleum. His correlations were divided into two separate groups: one for n-pentane and higher n-alkane, and the other for light n-alkane from methane up to n-butane and i-butane. The density data for the higher n-alkanes were fit at a given temperature using a pressure-dependent compressibility as follows:

$$\rho = P_0 \exp\{\alpha_1 P + \alpha_2(1 - \exp(-\beta P))\} \quad (9)$$

where  $\rho_0$  is the density in kg/m<sup>3</sup> at 101kPa,  $\alpha_1$  is the compressibility at high pressure, and  $\alpha_2 = \Delta \alpha / \beta$ , where  $(\alpha_1 + \Delta \alpha)$  is the compressibility at low pressure,  $\beta$  is the decay rate from the low to high pressure compressibility, and P is the pressure in kPa. The correlation parameters were then related to temperature as follows:

$$\rho_0 = a_0 + b_0 T + c_0 T^2 \quad (10)$$

$$\alpha_2 = \alpha_1 T^n \quad (11)$$

where  $a_0$ ,  $a_1$ ,  $b_0$ ,  $c_0$  and  $n$  are fitting parameters and T is temperature in Kelvin. For methane, ethane, propane, n-butane, and i-butane the molar volume of the higher n-alkanes were plotted versus their molar mass and fit with a quadratic equation. The plot was extrapolated for lighter n-alkane to estimate the molar volume (and therefore density). The extrapolated densities were fitted in the same procedure as for higher carbon number components with Equation 6 but the temperature dependent parameters were modified as follows:

$$\alpha_1 = a_1 + b_1 T \quad (12a)$$

$$\alpha_2 = a_2 + b_2 T + c_2 T^2 \quad (12b)$$

Han and Batzle (2000) developed a density model for the determination of undersaturated oil with dissolved gas based on the engineering concepts of McCain (1973, 1990). De-hua Han et al. (2002) made improvements to the model with new corrections to cover pressures higher than 10,000 psi (69 MPa).

In their investigation, they derived apparent liquid densities through a study of an oil-gas system in which gases (methane and ethane) dissolved in oil phase with different API gravities (Standing and Katz, 1942),

experimentally determined the density of an oil-gas system at various elevated pressures and temperatures, and then adjusted the density to standard conditions using fluid compressibility and coefficient of thermal expansion factors.

The mass and volume contributed by the oil were subtracted. This left the contribution due to methane or ethane as the apparent liquid density. They used the method proposed by Katz (1942), the apparent liquid density of natural gas, to develop the following model for oil density calculation under reservoir conditions:

$$\rho_a = 0.61703 \times 10^{-0.0032API} + [1.51775 - 0.54351 \log API] \log \quad (13a)$$

$$API = \frac{141.5}{\rho_o} - 131.5 \quad (13b)$$

$\rho_a$  = apparent liquid density

$\rho_0$  = Density of dead oil at standard conditions

G = Solution gas gravity

API = Tank oil API gravity

Pseudo-liquid density  $\rho_o$  of Oil with gas dissolved in it is calculated from the expression below; assume ideal solution principle

$$\rho_{po} = \frac{W_{oil}}{V_{oil}} + \frac{W_{gas}}{V_{gas}} = \frac{\rho_o \times 1 + W_{gas}}{1 + \frac{W_{gas}}{\rho_a}} \quad (14)$$

$\rho_o$  = g/cc of oil.

$W_{gas}$  = weight of gas in gram dissolved in 1cc of oil.

$\rho_{p0}$  = Pseudo density of liquid of standard condition.

$W_{gas}$  = 0.001223 RsG

Rs is GOR, Soln – gas – oil ratio in (litre/litre)

G = Solution gas gravity (Air = 1)

The pseudo liquid density is corrected to account for the dissolved gas at the prevailing conditions of temperature and pressure of the system. The model for pressure correction at standard temperature is given by the expression.

$$\Delta\rho_p = AP \exp\left(-\frac{BP}{A}\right) \quad (15)$$

where

A =  $0.00038794 + 0.0375885 \times 10^{-2.653} P_{po}$

B =  $1.00763 \times 10^{-6} + 0.00088631 \times 10^{-3.7645} P_{po}$

Oil density corrected to reservoir pressure and standard temperature is:

$$\rho_{RS} = P_{p0} + \Delta\rho_p \quad (16)$$

Witte (1987) developed a model for temperature correction on density based on statistical analysis on measured data.

The model expressions with correction for temperature of pressure as given by;

$$\Delta\rho_T = 0.01602\{0.00302 + 0.02952\rho^{-0.951}\} \quad (17)$$

The Batzle and Wang (1992) model has been used for years for the prediction of crude oil densities with good results at low GOR and temperature. At high GOR, temperature, and pressure, the model could not predict with high accuracy. Further investigation by Han and Batzle revealed that the model overpredicts crude oil densities at high GOR, temperature, and pressure. Jiajin and Liu (2010) developed a new model for densities at high GOR, temperature, and pressure. They made further adjustments on temperature and GOR, which significantly improved the prediction of crude oil densities at high GOR for live oil at high temperature and pressure.

The new, improved model after temperature adjustment is given by:

$$\Delta\rho_T = C \exp(-d\Delta\rho_T) \quad (18)$$

$$C = C_0 + C_1(T - 15.56) + C_2(T - 15.56)^2 \quad (19a)$$

$$d = d_0 + d_1(T - 15.56) + d_2(T - 15.56)^2 \quad (19b)$$

$$C_0 = 0.000169756, C_1 = 0.000933538, C_2 = -0.00000153832$$

$$d_0 = 12.9686, d_1 = 0.00401368 \text{ and } d_2 = -0.00011863$$

The effective pseudo liquid density  $\rho_{p0}$  after correction/adjustments for GOR, high temperature and pressure is given by the expression:

$$\rho_{e0} = \{ \rho_{p0} \text{ dead crude oil } \} \text{ at } R_s = 0$$

$$\{ \rho_{p0}(m + n \ln(P/T)) \} \text{ at } R_s > 0 \quad (20)$$

$$m = m_0 + m_1(\rho_{p0}/\rho_0) + m_2(\rho_{p0}/\rho_0)^2 \quad (21a)$$

$$n = n_0 + n_1(\rho_{p0}/\rho_0) + n_2(\rho_{p0}/\rho_0)^2 \quad (21b)$$

where  $m_0$ ,  $m_1$ ,  $n_0$ ,  $n_1$  and  $n_2$  are numerical coefficient given by;  $m_0 = -1.2818$ ,  $m_1 = 4.8303$ ,  $m_2 = -2.5485$ ,  $n_0 = 0.6827$ ,  $n_1 = -1.3039$  and  $n_2 = 0.6212$ .

De hua Han et al. claimed that their new model based on the current model shows a significant improvement especially for live oils with high GOR, at high temperature condition.

### 3.0. Materials and method

#### 3.1. Materials to be used

This section describes the materials and methods that were used to determine liquid phase density by conducting PVT analysis on a crude oil sample.

Materials used for the experiment include normal hexane, acetone, and toluene, all of which are technical grade solvents used for cleaning equipment; compressed air; helium gas; liquid nitrogen; standard analytical grade gas for GC analysis; mercury as displacement or pressing fluid; complete PVT laboratory equipment with accessories; a gas chromatograph; and a desktop or laptop computer, etc.

#### 3.2. Experimental Procedure

##### 3.2.1. Pump Calibration

- Pump movement was calibrated for actual volume of mercury injected or withdrawn from cell. Pump volume correction factor was  $b$  determined from calibration. Factory Pump factor was 0.9997.

### 3.2.2. Ruska Cell Preparation for Volume Calibration

- The high pressure and temperature PVT blind cell in an oil bath would be cleaned with n-hexane and acetone and evacuated at high vacuum for 8 hours.
- The cell volume was calibrated at temperature and pressure range of 73<sup>0</sup>F to 250<sup>0</sup>F and 1 atmospheric pressure to 6000psia. Pump and temperature reading were plotted to obtain V –T chart and V – P isotherm charts, from where the cell volume equation was determined as follows;
- $V_{cell} = 515.214 + AT + BPT + CP$
- Where A, B and C are Temperature and pressure coefficients obtained from the calibration curves. For this study,  $A = 8.80 \times 10^{-3}$ ,  $B = 8.89 \times 10^{-5}$  and  $C = 2.30 \times 10^{-8}$ .

#### 3.2.2.3. Pump Manifold Compressibility Test for Accurate P-V Measurement

- The entire pump and its manifold were cleaned with solvent, evacuated for 4 – 6 hours. 250cm<sup>3</sup> of fresh mercury was dispensed from the Hg reservoir to fill the pump barrel. Compressibility was performed at 73<sup>0</sup>F and pressure range 15 – 8000 psi.
- A good pump manifold compressibility with mercury at room temperature should be a straight line when the pump volume reading is plotted against test pressure. This was done to eliminate errors in pressure-volume measurements.

#### 3.2.2.4. Bottom Hole Crude Oil Sample Transfer for CCE/DL Tests

- 100.310cm<sup>3</sup>(78.663102g) of the crude oil sample was transferred at 5000Psia and 73<sup>0</sup>F in single phase to the PVT cell installed in silicone heating oil bath maintained at constant temperature of 154<sup>0</sup>F.
- Equilibrium cell temperature was monitored with J-type digital thermocouple.
- Room temperature fluid pressure – density of the oil sample was determined at 5000psia and 73<sup>0</sup>F immediately after the sample was transferred into the cell.

#### Two types of experiments were conducted on the crude oil mixture, namely:

- Constant composition expansion (flash liberation) CCE.
- Differential liberation expansion DLE.

103.310cm<sup>3</sup> Bottom Hole Crude Oil sample was subjected to gradual pressure depletion from 5000 psi in steps of 500. Pressure- Volume measurements/ readings were taken and confirmed the bubble point Pressure to be 2870 psi. The bubble point fluid volume was read from the Pump Venier scale to be 106.743cm<sup>3</sup> with a bubble point density of 0.7369g/cm<sup>3</sup> respectively.

Differential liberation was followed below the bubble point. The first pressure point was 2300 psi in 7 depletion steps down to atmospheric pressure. The liquid properties were determined. The components gases from the vaporization process were analyzed using a 500 series SHIMAZU Digital Gas Chromatograph. The experimental results are shown in table 1 and 2.

### 4.0. Discussion of Experimental Results

The observed trends during CCE and DLE are as follows:

At a monophasic region, i.e., P<sub>b</sub>P at a constant temperature of 154 °F, liquid phase density decreases linearly as reservoir pressure decreases from 5000 psi down to bubble point pressure of 2870 psi. As cell pressure decreased toward the bubble point pressure, fluid volume underwent continuous expansion at a

constant temperature (isothermal fluid expansion) and constant mass or composition of the hydrocarbon fluid system. The liquid-phase density was calculated from the relative volume at each pressure point.

At the bubble point pressure  $P_b$ , the first bubble of gas evolution was observed through an optical device. Maximum volume expansion occurred at the bubble point at constant mass, the liquid phase density at the bubble point pressure  $P_b$  was at a minimum.

The relative volume of the hydrocarbon fluid system is a rectangular hyperbolic function of reservoir pressure at a constant temperature of 1540 °F.

There was a sudden change in the slope of the P-V curve as experienced in the experiment (pressure volume measurements). The Y-function of the hydrocarbon fluid system in the two-phase region is a straight line.

At pressures below the bubble point, during the differential vaporization process, the liquid phase undergoes continuous volumetric and compositional change as pressure falls below the bubble point, and the solution gas evolved from the liquid phase is expelled from the cell. The liquid-phase density increased monotonically down to the atmospheric pressure of 15 psi.

**Table 1 – 2 shows the experimental results of the depletion study at 154<sup>0</sup>F**

Pressure (Psia)	Relative Volume *(V/V <sub>b</sub> )	Liquid phase density (g/cm <sup>3</sup> )	Y-Function = $\frac{P_b - P}{P \left( \frac{V}{V_b} - 1 \right)}$
5000	0.9782	0.7533	
4500	0.9826	0.75	
4000	0.9874	0.7463	
3500	0.9926	0.7424	
3000	0.9984	0.7381	
2870	1.0000	0.7369	-
2552	1.0321		3.8875
2243	1.0764		3.6589
1835	1.1693		3.3316
1573	1.2628		3.1375
1238	1.4503		2.9275
880	1.8574		2.6375
596	2.5774		2.4188

Table 2: Differential Liberation of Oil Reservoir Fluid Sample at 154°F

Pressure (Psia)	Formation Volume Factor (Bo)	Solution gas	Liberated	Specific gravity of liberated gas (Air=1.0000)	Liquid Phase Density (g/cm3)	Liquid phase volume (cm3)	Solution Gas	Gas Volume in cell (cm3)	Volume of gas std liberated (cm3)
		-oil ratio	gas-oil ratio				Gas volume		
		SCF/STB (Rs)	SCF/STB				std Condition		
2870	1.26	552	0	-	0.7369	106.743	8349	-	0
2300	1.214	438	114	0.6411	0.752	102.862	6631	10.891	1718
1800	1.18	342	96	0.6387	0.763	99.934	5179	11.823	1452
1300	1.147	249	93	0.6388	0.7741	97.116	3773	16.196	1406
800	1.113	158	91	0.6483	0.7858	94.319	2395	26.417	1378
300	1.08	67	91	0.6897	0.7977	91.494	1023	70.581	1372
100	1.065	29	38	0.7826	0.8033	90.179	443	85.06	580
15	1.041	0	29	1.0692	0.8152	88.169	0		443
Residual oil data at standard conditions					SG=0.8486 oAPI=35.10 MOLWt C7+= 212				
			552			84.699			8349
60°F and 14.7Psia									

**5.0. Determination of Liquid Phase Density by Material Balance Computational Technique**

**5.1. Computational Model Development**

**5.1.1. Mass Balance of the Fluid Sample for Liquid Phase Density Calculation Definition of Variables**

$M_i$  = Initial mass of reservoir fluid in place at reservoir pressure and temperature (P,T).

$V_i$  = Initial volume of reservoir fluid in place at (P,T).

$\rho_L$  = Single phase fluid density at (P,T)

$P_b$  = bubble point pressure

$V_b$  = Volume of fluid at bubble point pressure

$\rho_b$  = Density of fluid at bubble point pressure

$V_i$  = Volume of saturated liquid phase after degassing at pressure point  $P_i$

$\rho_{Li}$  = liquid phase density at pressure point  $P_i$

$M_{oi}$  = mass of saturated liquid phase after degassing at pressure  $P_i$

$P_i$  =  $i^{th}$  pressure point below bubble point

$M_{gi}$  = mass of gas evolved from reservoir fluid (solution) at pressure  $P_i$

$V_r$  = Relative volume

Let  $M_i = V_i \rho$  (23)

At  $P_i > P_b$  (single phase fluid system)

From (CCE),/ PV;

$$\text{Relative VOL}(V_r) = \frac{\text{Volume of reservoir fluid at } (P,T)}{\text{Volume of reservoir fluid at bubble point}} \tag{24}$$

Liquid phase density of reservoir fluid at  $P > P_b$  is given by

$$\rho_L(P_1 > P_b) = \rho_b / V_r = M_1 / V_1(P \geq P_b) \tag{25}$$

At  $P_1 < P_b$  is solution gas evolved from liquid which is extracted or pushed out of cell at constant pressure  $P_1$ .

Let the mass of gas evolved from liquid phase at pressure  $P_1 = M_{g1}$ .

Mass of saturated liquid phase (oil) left after degassing at pressure  $P_1$  will be given by:

$$M_{o1} = M_1 - m_{g1} \tag{26}$$

At the next pressure point  $P_2$  below  $P_1$  and  $P_d$ , i.e.  $P_2 < P_1 < P_b$ , more solution gas evolves from liquid phase with mass  $m_{g2}$  so that:

$$M_{o2} = M_1 - m_{g1} - m_{g2} \tag{27}$$

$$\text{OR } M_{o2} = M_{o1} - m_{g2} \tag{28}$$

At the next pressure point  $P_3$  below  $P_2$  i.e.  $P_3 < P_2 < P_1 < P_b$ ,

Let the mass of solution gas evolved =  $m_{g3}$

$$M_{o3} = M_1 - m_{g1} - m_{g2} - m_{g3} - m_{g4} - \dots - m_{gi} \tag{29}$$

If the process continues up to  $i^{\text{th}}$  pressure point  $P_i$ , then equation (27) gives the mass of the saturated liquid phase at any pressure point  $P_i$ .

Let  $V_i =$  Volume of the saturated liquid phase (oil) after degassing at pressure point  $P_i$

Therefore, the liquid phase density  $\rho_{Li}$  at any pressure point below  $P_b$  during depletion by differential liberation at reservoir temperature  $T$  is given by:

$$\rho_{Li}(P,T) = \frac{M_i - \sum_{i=1}^n m_{gi}}{V_i(P,T)} \tag{30}$$

where  $i = (1,2,3,4, \dots, n)$  pressure depletion steps

The above empirical model gives the liquid phase density of petroleum reservoir fluid mixture during well fluid depletion by differential liberation for black oil system.

The above model/ equation 30 was applied in the computation of liquid phase density for single phase fluid during constant composition expansion (CCE) where the mass or composition does not change, so that, the term  $\sum m_{gi}$  in the model will be practically zero since no material was removed from the system.

For computational purpose, PV/DV data provide for  $M_1, M_{oi}, M_{gi}, V_i, \rho_s, P_b, V_b, \rho_b, V_r$  and molecular compositions of liberated gases at different pressure point  $P_i$  respectively.

Computer program was developed for the empirical model for iterative speedy computation using input data from PV/DV during well depletion i.e., differential and flash liberation processes.

How the empirical model is used to compute liquid phase density?

Data obtained from differential liberation of this experiment on the fluid sample are given below:

Initial mass of reservoir fluid  $M_I = 78.6631g$

Volume of liquid phase at 2300psia =  $102.862\text{ cm}^3$

Pressure  $P_1 < P_b = 2300\text{psia}$

Reservoir temperature =  $154^\circ\text{F}$

Volume of gas liberated at 2300psia and  $154^\circ\text{F} = 1669\text{cm}^3$  corrected to std. condition

Molecular weight of librated solution gas =  $18.57218\text{g/mole}$ .

To calculate the liquid phase (oil) density at 2300psia and  $154^\circ\text{F}$ :

Required:  $M_i = 78.6631g$ ,  $V_i = 102.862\text{cm}^3$  standard volume of liberated gas  $V_{\text{std}} = 1669\text{cm}^3$

Mwt gas =  $18.57218$

Molar volume of gas at stp =  $23613\text{cm}^3$  at 14.7psia and  $60^\circ\text{F}$   $15^\circ\text{C}$  (standard conditions for oil industry).

$$m_{g_i} = \frac{V_{\text{std gas}} \times \text{Mwt}_{\text{gas}}}{23613} = \frac{(1669 \times 18.57218)}{23613} g = 1.3127g$$

$$\text{moi} = M_I - m_{g_i} = (78.6631 - 1.31127)g = 77.3504g$$

$$\therefore \rho_L (@ 2300\text{psia} \ \& \ 154^\circ\text{F}) = \frac{77.3504\text{g/cc}}{102.862} = 0.7520\text{g/cc}$$

The computer programme used for the calculation of liquid phase density is known as the “liquid phase density calculator” was developed in the cause of this study.

The experimental data used for computation of liquid phase density are shown in table 1 – 2

### 5.2. Empirical Model Computational Results

**Reservoir Data**

Reservoir Pressure (psia):

Reservoir Temperature  
 °Celsius:  °C      Fahrenheit:  F

Reservoir Initial Mass (g):

Number of De-gassing Points:

Pressure Point	Pressure at Point (psia)	Volume (Standardized) of Liberated Gas (cc)	Volume of Liquid Phase(cc)	Molar Weight of Gas (g/mol)	Mass of Liberated Gas (g)	Mass of Liquid Phase (g)	Density of Liquid Phase (g/cc)
1	5000	0	104.418	0	0.00000	78.66310	0.75335
2	4500	0	104.883	0	0.00000	78.66310	0.75001
3	4000	0	105.396	0	0.00000	78.66310	0.74636
4	3500	0	105.953	0	0.00000	78.66310	0.74243
5	3000	0	106.573	0	0.00000	78.66310	0.73811
6	2870	0	106.743	0	0.00000	78.66310	0.73694
7	2300	1669	102.862	18.57218	1.31271	77.35039	0.75198
8	1800	1408	99.934	18.52048	1.10434	76.24605	0.76296
9	1300	1363	97.116	18.52579	1.06935	75.17670	0.77409
10	800	1337	94.319	18.80138	1.06456	74.11214	0.78576
11	300	1333	91.494	19.9981	1.12893	72.98321	0.79768
12	100	563	90.179	22.69274	0.54106	72.44215	0.80332
13	15	432	88.169	31.0035	0.56721	71.87494	0.81520



## 6.0. Conclusion

Empirical model was developed by material balance technique to calculate the liquid phase density of petroleum reservoir fluid mixture. This research work was primarily developed to enhance computation of liquid phase density both online and offline application in laboratory and in oil field. It is a user friendly programme calculator as shown in figure five above.

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