Road map and optimum procedures for tuning an Equation-of-State based model against reservoir oils PVT lab measurements.

By

Georgios Osama Al-Ghishan

Supervised by

Prof. Nikolaos Varotsis

Abstract

Proper tuning of EOS models to adequately match the measured PVT study values is anything but trivial. For a given compositional characterization, a developed EOS model provides in fact the mapping of each PVT property (B_o, R_s, ρ, etc) versus the ever changing during depletion overall composition and the prevailing operating conditions. These mappings, given the components selected for characterizing the fluid, can be calibrated by performing a multiple regression against several components physical properties and EOS parameters using very few matching points which are concentrated along the PVT depletion study usually at a single temperature whereas the tuned model is subsequently utilized over a fairly wide range of conditions and overall compositions. It is widely known that an inadequately tuned fluid's model can lead to poor quality of reservoir engineering calculations (material balance, reservoir simulation, etc).

Until now, an EOS model tuning is considered as an art, it relies more than anything else on the operator's instinct and expertise and no systematic guidelines appear to be available for its accomplishment.

Dedication

First of all, I thank God for helping me in every step I made. Secondly, I would like to thank my parents who are always next to me to support me and help me to fulfil my dreams. Dad and mum, I feel very proud and grateful for having you in my life, you taught me that nothing in this life comes easy, and that if I want to succeed, I have to fight and never give up no matter what life throws to us. Thank you for everything, I wouldn't have reached to this level without your support and your advices. There are not enough words to describe how grateful I am for having you in my side, thanks again for everything. I love you so much.

I would also like to thank my brother Jack, my two lovely sisters; Maria and Marina, and my friends; Ehab and John, for supporting me and standing next to me whenever I need a shoulder to lean on.

I thank my friend Gerasimos Alexopoulos (Makis), who helped me to find this course. I also want to thank him for his advices that helped me a lot.

Finally, I would like to thank someone who has a very special place in my heart, someone who helped me a lot to believe in myself and in my abilities, someone who is always here for me no matter what happens, someone who always pushes me and gives me strength every time I feel that I should stop and give up. This someone couldn't be anyone else except of you Dana. Thanks Dana for being the positive energy in my life.

Acknowledgement

First and foremost, my heartfelt gratitude goes to my supervisor Professor Nikolaos Varotsis, who made of me a proper researcher; equipping me with every knowledge and skill I might need in my future career. Massive thanks for his kindness, patience, and continuous help and support. He showed me what is like to be an idol supervisor.

I would also like to extend my gratitude to all members and staff of the mineral resources engineering department of my university. Each one of them must have contributed in my journey somehow; either by tutoring me, lending me a hand in the lab work or just enthusiastically encouraging me when i had blue days and felt sleepy.

Finally, I would like to thank Professor Nikos Pasadakis and Doctor Dimitris Marinakis for their support and for the advices they gave me.

Table of contents

List of Figures

List of Tables

Introduction

1. Equations of State Definition

The equation of state is an analytical expression that relates pressure (p) to volume (V) and temperature (T). In petroleum industry, it is used to determine the volumetric properties and the phase behavior of petroleum reservoir fluids, and it is also used to predict the performance of surface separation facilities.

Most equations of state require only the acentric factor and the critical properties of the individual components, and one of the advantages of using an equation of state is that the same equation can be used to model the behavior of all phases, but this s not always the case, for instance when gas hydrates and oil & gas are being modeled, a different equation for hydrates is needed. Having the same equation of state assures the consistency when performing phase equilibrium calculations.

The simplest and the best known equation of state is that of the ideal gas equation, which could be written as the following expression:

$$p = \frac{RT}{V}$$ Eq. (1)

where, V represents the gas molar volume with units of (ft^3/mol).

In petroleum industry Pressure-Volume-Temperature relationships (PVT) are used to describe the volumetric behavior of hydrocarbon gases at pressures close to the atmospheric pressure for which it was experimentally derived.

Several attempts have been made to derive a theoretically sound equation of state "EOS"; but, generally speaking, not much success has been achieved along that line. As a result, we use what are known as semi-empirical EOS. Most equations of state used today are semi-empirical in nature, due to the fact that they are fitted to the data that are available. Additionally, equations of state are generally developed for pure substances. In addition, to apply these equations to mixtures, composition is also required, and hence appropriate mixing rules.

A great-number of equations of state have been proposed in order to describe real gas behaviour. Only few of these equations of state are nowadays still used. The most common contemporary equations of state are the following:

1- Peng-Robinson EOS (PR EOS)
2- Soave-Redlich-Kwong EOS (SRK EOS)

Both of these EOS are cubic equations and hence they were derived from the Van der Waals equation of state (vdW).

Equations of state have a great importance in petroleum industry, as most of the petroleum engineering applications depend and rely on them. This is due to the fact that they are simple to use, and if they are properly tuned, they exhibit high accuracy. Bubble point pressure (p_b), dew point pressure (p_d), equilibrium ratios (K-value), three-phase flash calculations and simulating of PVT laboratory experiments are some of these applications.

1.1 The Van der Waals Equation of State "vdW EOS"

Van der Waal (1873)[1] attempted to eliminate the assumptions made in developing the ideal gas EOS to develop an empirical equation of state for real gases. These assumptions were as following:

> 1-The volume of the gas molecules is insignificant compared to the total volume and the distance between the molecules.
> 2-There are no attractive or repulsive forces between the molecules.

Van der Waals proposed that the volume of the gas molecules, denoted by the parameter "b" should be subtracted from the actual molar volume, because they occupy a significant fraction of the volume at higher pressures, and this led to the following term in the pressure equation:

$$p = \frac{RT}{V-b} \qquad\qquad \text{Eq. (2)}$$

where V is the actual gas molar volume and b is the volume of gas molecules.

In order to account for the attractive forces between the molecules, Van der Waals decided to introduce a corrective term denoted by "α/V^2" to the previous equation. This corrective term was subtracted from the previous equation, so the following expression was proposed:

$$p = \frac{RT}{V-b} - \frac{\alpha}{V^2} \qquad\qquad \text{Eq.(3)}$$

where, p is the system pressure "psia".
     T is the system temperature "ºR".
     R is the gas constant "10.73 psi-ft^3/ lb-mol.ºR".
     V is the molar volume "ft^3/mol".
     α is the attraction parameter.
     b is the repulsion parameter.

From the previous equation, it could be seen that at low pressures, the gas volume phase is large in comparison to the volume of the molecules, which means that parameter "b" becomes insignificant and reduces the Van der Waals equation to the

ideal gas equation. The volume "V" becomes very small at high pressures and it approaches the value of "b" parameter, and this can be expressed as the following:

$$\lim_{p \to \infty} V(p) = b$$

Eq.(4)

In general, any equation of state with respect to pressure can be expressed as the result of subtracting the attraction pressure term from the repulsion pressure term, and this is expressed as following:

$$p = p_{repulsion} - p_{attraction}$$

Eq.(5)

In order to determine the values of the two constants of the equation of state, Van der Waals observed that the critical isotherm has a horizontal slope and an inflection point at the critical point, as shown in Figure 1, and this observation was expressed mathematically as following:

$$\left[\frac{\partial p}{\partial V}\right]_{T_c, p_c} = 0$$

Eq. (6)

$$\left[\frac{\partial^2 p}{\partial V^2}\right]_{T_c, p_c} = 0$$

Eq.(7)
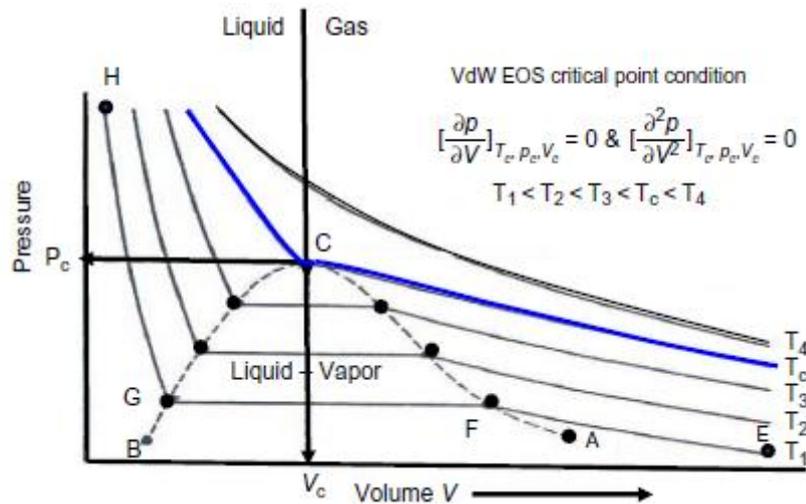
Figure 1: An idealized pressure-volume relationship for a pure component.

After differentiating the Van der Waals equation of state, the following equations were resulted:

$$\left[\frac{\partial p}{\partial V}\right]_{T_c, p_c} = \frac{-RT}{(V_c - b)^2} + \frac{2\alpha}{V_c^3} = 0$$

Eq.(8)

$$\left[\frac{\partial^2 p}{\partial V^2}\right]_{T_c, p_c} = \frac{2RT_c}{(V_c - b)^3} + \frac{6\alpha}{V_c^4} = 0 \qquad \text{Eq.(9)}$$

Solving the above equations simultaneously for the parameters α and b, the following expressions are resulted:

$$b = \frac{V_c}{3} \qquad \text{Eq.(10)}$$

$$\alpha = \frac{8RT_c V_c}{9} \qquad \text{Eq.(11)}$$

Applying the first and second derivatives of the pressure with respect to the volume at the critical point conditions which means that at temperature equal to the critical temperature ($T=T_c$) and at pressure equal to the critical pressure ($p=p_c$), the following equation is resulting:

$$p_c V_c = (0.375)RT_c \qquad \text{Eq. (12)}$$

The above equation indicates that the Van der Waals equation of state gives a universal critical gas compressibility factor "Z_c" of 0.375, regardless of the type of the substance.

Van der Waals equation of state suggests that the co-volume "b" parameter is approximately 0.333 of the critical volume "V_c" of the substance, and the critical gas compressibility factor "Z_c" has a value of 0.375, while experimental studies revealed that the co-volume "b" parameter has values in the range of 0.24 to 0.28 of the critical volume of the substance, and "Z_c" for substances ranges between 0.21 and 0.31.

By combining the above equation with the equations of "b" and "α" parameters, the two parameters of Van der Waals equation of state are calculated, which yields to the following expressions:

$$\alpha = \Omega_\alpha \frac{R^2 T_c^2}{p_c} \qquad \text{Eq.(13)}$$

$$b = \Omega_b \frac{RT_c}{p_c} \qquad \text{Eq.(14)}$$

where, $\Omega_\alpha = 0.421875$ and $\Omega_b = 0.125$.

Rearranging the Van der Waals EOS in terms of volume gives a cubic equation that could be written as following:

$$V^3 - (b + \frac{RT}{p})V^2 + (\frac{\alpha}{p})V - (\frac{\alpha b}{p}) = 0 \qquad \text{Eq.(15)}$$

Since it is a cubic equation, this means that it has three possible roots for volume, out of which at least one is a real root. This equation describes liquid-condensation phenomenon and the passage from the gas to the liquid phase as the gas is compressed. This is shown in Figure 2.
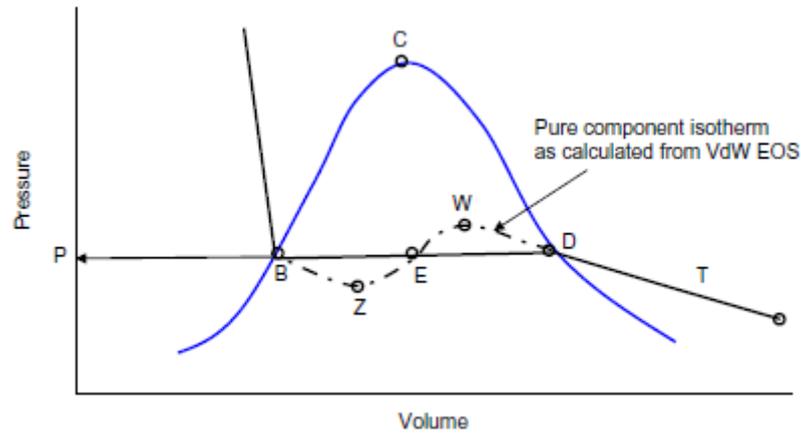
Figure 2: Pressure-volume diagram for a pure component.

From Figure 2 we can see that if we assume that the substance is kept at a constant temperature below than the critical temperature, and at a specified pressure, then this temperature line will cross the pressure-volume diagram at three points; D,E and B. These three points are the three roots of the cubic Van der Waals equation of state, and represent the three values of volume, where point D is the largest root, and it corresponds to the volume of the saturated vapor. Point B is the smallest root, and it corresponds to the volume of the saturated liquid. While the third root, point (E) doesn`t have any physical meaning.

The dashed line (DWEZB) is a typical solution of Van der Waals cubic EOS at constant temperature, and it appears to give a continuous transition from the gaseous phase to the liquid phase. The continuous straight line (DB) represents the discontinuous and abrupt transition from the gaseous phase to the liquid phase, and this is how the transition appears in reality.

Van der Waals cubic equation of state could be written in a more practical form in terms of the compressibility factor, Z, by replacing the molar volume "V" with "ZRT/p". This could be expressed by the following equation:

$$V^3 - (b + \frac{RT}{p}) \left[\frac{ZRT}{p}\right]^2 + (\frac{\alpha}{p}) \left[\frac{ZRT}{p}\right] - (\frac{\alpha b}{p}) = 0 \qquad \text{Eq.(16)}$$

Or

$$Z^3 - (1+B)\,Z^2 + AZ - AB = 0 \qquad\qquad \text{Eq.(17)}$$

where, Z = compressibility factor.

      p = system pressure, psia.

      T = system temperature, °R.

$$A \;=\; \frac{\alpha p}{R^2 T^2} \qquad\qquad \text{Eq.(18)}$$

$$B = \frac{bp}{RT} \qquad\qquad \text{Eq.(19)}$$

The above equation gives one real root in the single phase region and three roots in the two-phase region "where the vapor pressure of the substance equals to the systems` pressure".

One of the most important practical applications of the above equation is the density calculations.

1.2 Redlich-Kwong's Equation of State "RK EOS"

Redlich and Kwong (1949)[2] observed that the Van der Waals "a/V^2" term does not contain the system temperature to account for its impact on the intermolecular attractive forces between the molecules. Redlich and Kwong demonstrated that by a simple adjustment of the Van der Waals' "a/V^2" term, to explicitly include the system temperature, could considerably improve the predictions of the volumetric and physical properties of the vapour phase. Redlich and Kwong replaced the attraction pressure term with a generalized temperature dependence term, as given in the following form:

$$p = \frac{RT}{V-b} - \frac{\alpha}{V(V+b)\sqrt{T}} \qquad\qquad \text{Eq.(20)}$$

where, T represents the system temperature in °R.

Redlich and Kwong noted that, when the system pressure becomes very large (p→∞), then the molar volume "V" of the substance shrinks about 26% of its critical volume "V_c" regardless of the temperature of the system "b = 0.26V_c". And by imposing the critical point conditions (the first and second derivatives of pressure with respect to volume at temperature equals to T_c and pressure equals to P_c equals to zero) on RK EOS, the two parameters of the equation of state can be expressed as following:

$$\alpha = \Omega_\alpha \frac{R^2 T_c^{2.5}}{p_c} \qquad\qquad \text{Eq.(21)}$$

$$b = \Omega_b \frac{RT_c}{p_c} \qquad\qquad \text{Eq.(22)}$$

where $\Omega_\alpha = 0.42747$ & $\Omega_b = 0.08664$.

By equating the two equations for the "b" parameter of the RK EOS, and then rearranging the equation, the following expression is given:

$$p_cV_c = 0.333RT_c$$

Eq.(23)

This means that Redlich-Kwong EOS produces a universal critical compressibility factor of 0.333for all substances.

After replacing the molar volume "V" with "ZRT/P" in RK EOS, and after rearranging it, it could be written as a cubic EOS as following:

$$Z^3 - Z^2 + (A - B - B^2)\,Z - AB = 0$$

Eq.(24)

where,

$$A = \frac{\alpha p}{R^2 T^{2.5}}$$

Eq.(25)

$$B = \frac{bp}{RT}.$$

Eq.(26)

Redlich and Kwong extended the use of their equation of state to hydrocarbon liquid and gas mixtures by employing the following mixing rules:

$$\alpha_m = \left(\sum_{i=1}^{n} x_i\sqrt{\alpha_i}\right)^2$$

Eq.(27)

$$b_m = \sum_{i=1}^{n}(x_i b_i)$$

Eq.(28)

where,

α_m = parameter α for mixture.
b_m = parameter b for mixture.
n = number of components in the mixture.
α_i = Redlich-Kwong α parameter for the ith component .
b_i = Redlich-Kwong b parameter for the ith component .
x_i = mole fraction of component i in the liquid phase.

1.3 Soave-Redlich-Kwong Equation of State "SRK EOS"

Soave (1972)[3] proposed a modification on the Redlich-Kwong EOS attraction pressure term, by replacing the explicit temperature term "$\alpha/T^{0.5}$" with a more generalized temperature dependent term, denoted by "$a\alpha(T)$", and he came up with the following equation:

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

Eq.(29)

Where,

$$\alpha(T) = [1 + m(1-\sqrt{T/T_c}\,)]^2$$

Eq.(30)

Soave imposed the following conditions on the parameter "α(T)":

1- $\alpha(T) = 1$, when $T = T_c$

2- When $T \neq T_c$, Soave regressed on the vapor pressure of pure components to develop a temperature correction parameter "m" that is correlated with the acentric factor "ω" using the following equation:

$$m = 0.480 + 1.74\omega - 0,176\omega^2$$

Eq.(31)

where, ω is the acentric factor of the substance.

Soave used for any pure component the same classical Van der Waals critical point constraints to find the two parameters "α & b", and by imposing them to the SRK EOS, the two parameters were found to be as following:

$$\alpha = \Omega_\alpha \frac{R^2 T_c{}^2}{p_c}$$

Eq.(32)

$$b = \Omega_b \frac{R T_c}{p_c}$$

Eq.(33)

where, $\Omega_\alpha = 0.42747$ and $\Omega_b = 0.08664$.

Soave-Ridlich_Kwong EOS could be written in a cubic form as following:

$$V^3 - \frac{RT}{p}V^2 + \left[\frac{\alpha\alpha(T)}{p}\frac{bRT}{p} - b^2\right]V - \left[\frac{\alpha\alpha(T)*b}{p}\right] = 0$$

Eq.(34)

Edmister and Lee (1986)[4] pointed out that the following constrain satisfies the critical isotherm as given by:

$$(V-V_c)^3 = (3V_c)V^2 + (3V_c{}^2)V - (V_c{}^3) = 0$$

Eq.(35)

At the critical point, Soave-Ridlich_Kwong cubic EOS and the above equation are identical with "α=1" and this gives the following equations after equating the corresponding coefficients:

$$3V_c = \frac{RT_c}{p_c}$$

Eq.(36)

$$3V_c^2 = \frac{\alpha}{p_c} - \frac{bRT_c}{p_c} - b^2 \qquad \text{Eq.(37)}$$

$$V_c^3 = \frac{\alpha b}{p_c} \qquad \text{Eq.(38)}$$

After solving the above equations simultaneously for the two parameters "α & b" and after rearranging them, the following equation was resulted:

$$p_c Vc = RT_c / 3 \qquad \text{Eq.(39)}$$

Soave-Redlich_Kwong EOS has a universal critical gas compressibility factor of 0.333 and the expected co-volume "b-parameter" has a value of 26% of the critical volume.

Soave-Redlich_Kwong EOS could be written as a cubic equation as following:

$$Z^3 - Z^2 + (A\text{-}B\text{-}B^2)Z - AB = 0 \qquad \text{Eq.(40)}$$

with

$$A = \left[\frac{\alpha\alpha(T)*p}{(RT)^2} \right] \qquad \text{Eq.(41)}$$

$$B = \frac{bp}{RT} \qquad \text{Eq.(42)}$$

Where, p is the system pressure in "psia"

T is the system temperature "°R"

R equals to 10.730 "psia.ft^3/lb.mol. °R".

1.4 Modifications of the SRK EOS

Groboski and Daubert (1978)[5] proposed a new expression to calculate the parameter "m" that was used with the SRK EOS in order to improve the predictions of the pure component vapour pressure. The expression is as following:

$$m = 0.48508 + 1.55171\omega - 0,15613\omega^2 \qquad \text{Eq.(43)}$$

Sim and Daubert (1980)[6] proposed the following equations in order to determine the parameter "m" based on the type of equation that is used in determining the acentric factor "ω":

1. If Edmister correlation is used to determine the acentric factor, then the following expression should be used:

$$m = 0.431 + 1.57\omega_i - 0.161\ \omega_i^2$$
Eq.(44)

2. If Lee and Kesler correlation is used to determine the acentric factor, then "m" should be found using the following expression:

$$m = 0.315 + 1.60\ \omega_i - 0.166\ \omega_i^2$$
Eq.(45)

Elliot and Daubert (1985)[7] stated that the optimal binary interaction coefficient, k_{ij}, would minimize the error in the representation of all the thermodynamic properties of a mixture. Properties of particular interest in phase equilibrium calculations include bubble point pressure, dew point pressure, and equilibrium ratios. They proposed a set of relationships for determining the interaction coefficients for asymmetric mixtures that contain methane, N_2, CO_2, and H_2S. Referring to the principal component as *i* and other fractions as *j*, Elliot and Daubert proposed the following expressions:

Binary Interaction between N_2 – Components:

$$k_{ij} = 0.107089 + 2.9776\ k_{ij}\infty$$
Eq.(46)

Binary Interaction between CO_2 – Components:

$$k_{ij} = 0.08058 - 0.77215\ k_{ij}\infty - 1.8404\ k_{ij}\infty$$
Eq.(47)

Binary Interaction between H_2S – Components:

$$k_{ij} = 0.07654 + 0.017921\ k_{ij}\infty$$
Eq.(48)

Methane with components> C_9 (Nonane):

$$k_{ij} = 0.17985 + 2.6958\ k_{ij}\infty + 10.853\ (k_{ij}\infty)^2$$
Eq.(49)

where,

$$k_{ij}\infty = \frac{-(\varepsilon_i - \varepsilon_j)^2}{2\varepsilon_i\varepsilon_j}$$
Eq.(50)

$$\varepsilon_i = \frac{0.480453\ \sqrt{\alpha_\iota}}{b_i}$$
Eq.(51)

$$\alpha_i = \Omega_\alpha \frac{R^2 T_c^2}{p_c}$$
Eq.(52)

$$b_i = \Omega_b \frac{RT_c}{p_c}$$
Eq.(53)

1.5 The Peng-Robinson Equation of State "PR EOS"

Peng and Robinson (1976a)[8] pointed on the need of an improved equation of state that has the ability to predict liquid densities. Based on the comprehensive study they did on the use of SRK EOS for predicting the behaviour of naturally occurring hydrocarbon systems, they proposed the following equation:

$$p = \frac{RT}{V-b} - \frac{a\alpha(T)}{(V+b)^2 - cb^2} \qquad \text{Eq.(54)}$$

Where "aα(T)" and "b" have the same significance as they have in the Soave-Redlich_Kwong model, and the parameter "c" is a number that is optimized by analyzing the values of terms "Z_c" and "b/V_c". Z_c should have a value close to 0.28 while "b/V_c" should be approximately 0.26.

Based on an optimized value of "c" that is equal to two" which will give a value of 0.253 for" b/V_c" ", Peng and Robinson proposed the following equation:

$$p = \frac{RT}{V-b} - \frac{a\alpha(T)}{V(V+b)+b(V-b)} \qquad \text{Eq.(55)}$$

Using the classical critical point conditions with Peng-Robinson (PR) EOS and solving for parameters "α" and "b", the following expressions was yielded:

$$a = \Omega_a \frac{R^2 T_c^2}{p_c} \qquad \text{Eq.(56)}$$

$$b = \Omega_b \frac{RT_c}{p_c} \qquad \text{Eq.(57)}$$

where $\Omega_a = 0.45724$ and $\Omega_b = 0.07880$.

Peng-Robinson EOS predicts a universal critical gas compressibility factor of 0.307.

Peng and Robinson adopted Soave's approach for calculating parameter "α":

$$\alpha(T) = [1 + m(1 - \sqrt{T/T_c})]^2 \qquad \text{Eq.(58)}$$

Where,

$$m = 0.3796 + 1.5422\omega - 0,2699\omega^2 \qquad \text{Eq.(59)}$$

Peng-Robinson (1978)[9] proposed the following modified expression for calculating "*m*" that is recommended for heavier components with acentric values greater than 0.49:

$$m = 0.379642 + 1.48503\omega - 0.1644\omega^2 + 0.016667\omega^3 \qquad \text{Eq.(60)}$$

Peng-Robinson EOS can be written as a cubic equation as following:

$$Z^3 + (B-1)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0 \qquad \text{Eq.(61)}$$

$$A = \frac{(\alpha\alpha)_m p}{(RT)^2} \qquad \text{Eq.(62)}$$

$$B = \frac{b_m p}{RT} \qquad \text{Eq.(63)}$$

$$\alpha\alpha(T)_m = \sum_i \sum_j \left(x_i x_j \sqrt{\alpha_i \alpha_j \alpha_i \alpha_j} (1 - k_{ij}) \right) \qquad \text{Eq.(64)}$$

$$b_m = \sum_i (x_i b_i) \qquad \text{Eq.(65)}$$

The sets of binary interaction coefficient, k_{ij}, traditionally used when predicting the volumetric behaviour of hydrocarbon mixture with the Peng-Robinson EOS are shown in Table 1[10].

Table 1: Binary Interaction Coefficients of hydrocarbon mixture used with the PR EOS.

component	N_2	H_2S	C_1	C_2	C_3	i- C_4	n- C_4	i- C_5	n- C_5	C_6	C_7	C_8	C_9	C_{10}
CO_2	0	0.135	0.105	0.130	0.125	0.120	0.115	0.115	0.115	0.115	0.115	0.115	0.115	0.115
N_2		0.130	0.025	0.010	0.090	0.095	0.095	0.100	0.100	0.110	0.115	0.120	0.120	0.125
H_2S		0	0.070	0.085	0.080	0.075	0.075	0.070	0.070	0.070	0.060	0.060	0.060	0.055
C_1			0	0.005	0.010	0.035	0.025	0.050	0.030	0.030	0.035	0.040	0.040	0.045
C_2				0	0.005	0.005	0.010	0.020	0.020	0.020	0.020	0.020	0.020	0.020
C_3					0	0.000	0.000	0.015	0.015	0.010	0.005	0.005	0.005	0.005
i-C_4						0	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
n- C_4							0	0.005	0.005	0.005	0.005	0.005	0.005	0.005
i-C_5								0	0.000	0.000	0.000	0.000	0.000	0.000
n- C_5									0	0.000	0.000	0.000	0.000	0.000
C_6										0	0.000	0.000	0.000	0.000
C_7											0	0.000	0.000	0.000
C_8												0	0.000	0.000
C_9													0	0.00
C_{10}														0
Note that $k_{ij} = k_{ji}$														

Nikos Varotsis (1986)[11] proposed a correlation for generating the binary interaction coefficients, to improve the predictive capability of Peng-Robinson equation of state when it is applied for mixtures that contain non-hydrocarbon components, like (N2 and CO2). He correlated the binary interaction coefficients with the system pressure, temperature and acentric factor. This correlation has the following expression:

$$k_{ij} = \lambda_2 T_{rj}^{\,2} + \lambda_1 T_{rj} + \lambda_0 \qquad \text{Eq.(66)}$$

where,

$T_r = T/T_c$ is the reduced temperature.
i refers to the principal components (N2,CO2 or CH4).
j refers to the other hydrocarbon component of the binary system.

λ_0, λ_1 and λ_2 are parameters that depend on the acentric factor and on the type of the binary system, which can be classified as following:

1- BIC between nitrogen- hydrocarbon:

$$\lambda_0 = 0.1751787 - 0.7043 \log(\omega_j) - 0.862066 \, [\log(\omega_i)]^2 \qquad \text{Eq.(67)}$$

$$\lambda_1 = -0.584474 - 1.328 \log(\omega_j) + 2.035767 \, [\log(\omega_j)]^2 \qquad \text{Eq.(68)}$$

$$\lambda_2 = 2.257079 + 7.869765 \log(\omega_j) + 13.50466 \\ [\log(\omega_j)]^2 + 8.3864[\log(\omega)]^3 \qquad \text{Eq.(69)}$$

Varotsis also suggested the following pressure correlation:

$$k`_{ij} = k_{ij} \, (1.04 - 4.2*10^{-5}P) \qquad \text{Eq.(70)}$$

Where, P is the pressure in psi.

2- BIC between methane-hydrocarbons:

$$\lambda_0 = -0.01664 - 0.37283 \log(\omega_j) + 1.31757 \, [\log(\omega_i)]^2 \qquad \text{Eq.(71)}$$

$$\lambda_1 = 0.48147 + 3.35342 \log(\omega_i) - 1.0783 \, [\log(\omega_i)]^2 \qquad \text{Eq.(72)}$$

$$\lambda_2 = -0.4114 - 3.5072 \log(\omega_i) - 0.78798 \, [\log(\omega_i)]^2 \qquad \text{Eq.(73)}$$

3- BIC between CO2-hydrocarbons:

$$\lambda_0 = -0.4025636 + 0.1748927 \log(\omega_j) \qquad \text{Eq.(74)}$$

$$\lambda_1 = -0.94812 - 0.6009864 \log(\omega_j) \qquad \text{Eq.(75)}$$

$$\lambda_2 = 0.741843368 + 0.441775 \log(\omega_i) \qquad \text{Eq.(76)}$$

The following pressure correlation is suggested for CO2 BIC:

$$k`_{ij} = k_{ij} \, (1.044269 - 4.375*10^{-5}p) \qquad \text{Eq.(77)}$$

Peng and Robinson (1978) proposed the following expression to calculate "m" parameter for the heavier components with acentric factor lower than 0.49:

$$m = 0.379642 + 1.48503\omega - 0{,}1644\omega^2 + 0{,}016667\omega^3 \qquad \text{Eq.(78)}$$

Stryjek and Vera (1986)[12] proposed an improvement in the reproduction of vapour pressures of a pure component by the PR EOS in the reduced temperature range from 0.7 to 1.0, by replacing the *"m"* term used in Eq. (66) with the following expression:

$$m_0 = 0.378893 + 1.4897153 - 0.17131848\omega^2 + 0,01965543\omega^3 \qquad \text{Eq.(79)}$$

To reproduce vapor pressures at reduced temperatures below 0.7, Stryjek and Vera modified the "m" parameter in the Peng-Robinson equation by introducing an adjustable parameter "m" characteristic of each compound to Eq. (66). They proposed the following generalized relationship for the parameter "m":

$$m = m_0 + [m_1(1 + \sqrt{T_c})(0.7 - T_c)] \qquad \text{Eq.(80)}$$

Where,

T_c is the reduced temperature of the pure component.

m_0 is defined Eq. (87).

m_1 is adjustable parameter.

Stryjek and Vera recommended setting $m_1 = 0$ for all components with a reduced temperature above 0.7. Table 2 shows the optimum values of m_1 for compounds of industrial interest with a reduced temperature greater than 0.7.

Table 2: Optimum values of m1 for compounds of industrial interest.

Component	m_1
Nitrogen	0.01996
Carbon dioxide	0.04285
Water	-0.0664
Methane	-0.0016
Ethane	0.02669
Propane	0.03136
Butane	0.03443
Pentane	0.03946
Hexane	0.05104
Heptane	0.04648
Octane	0.04464
Nonane	0.04104
Decane	0.0451
Undecane	0.02919
Dodecane	0.05426
Tridecane	0.04157
Tetradecane	0.02686
Pentadecane	0.01892
Hexadecane	0.02665

Stryjek and Vera could not find a generalized correlation for m_1 in terms of pure component parameters due to the totally empirical nature of the parameter m_1. They pointed out that these values of m_1 should be used without changes.

Jhaveri and Youngren (1984)[13] pointed out that, when applying the Peng-Robinson equation of state to reservoir fluids, the error associated with the equation in the prediction of gas-phase Z-factors ranged from 3% to 5% and the error in the liquid density predictions ranged from 6% to 12%. Following the

procedure proposed by Peneloux, Jhaveri and Youngren introduced the volume correction parameter, "c_i" to the PR EOS. This third parameter has the same units as the second parameter, "b_i" of the unmodified PR equation and is defined by the following relationship:

$$c_i = S_i b_i \qquad \text{Eq.(81)}$$

where,

S_i is a dimensionless parameter known as "Shift Parameter".

b_i is the Peng-Robinson co-volume.

Whitson and Brule (2000)[14] pointed out that the volume translation concept can be applied to any two-constant cubic equation, thereby eliminating the volumetric deficiency associated with the application of EOS. Whitson and Brule extended the work of Jhaveri and Youngren and tabulated the shift parameters, S_i, for a selected number of pure components. These tabulated values, are used in Eq. (88) to calculate the volume correction parameter, c_i, for the Peng-Robinson and SRK equations of state.

Table 3: Values of the shift parameters "S_i" proposed by Whitson and Brule (2000).

Component	PR EOS	SRK EOS
N_2	-0.1927	-0.0079
CO_2	-0.0817	0.0833
H_2S	-0.1288	0.0466
C_1	-0.1595	0.0234
C_2	-0.1134	0.0605
C_3	-0.0863	0.0825
$i\text{-}C_4$	-0.0844	0.0830
$n\text{-}C_4$	-0.0675	0.0975
$i\text{-}C_5$	-0.0608	0.1022
$n\text{-}C_5$	-0.0390	0.1209
$n\text{-}C_6$	-0.0080	0.1467
$n\text{-}C_7$	0.0033	0.1554
$n\text{-}C_8$	0.0314	0.1794
$n\text{-}C_9$	0.0408	0.1868
$n\text{-}C_{10}$	0.0655	0.2080

Jhaveri and Youngren proposed the following expression for calculating the shift parameter for the C_{7+}:

$$S_{C7+} = 1 - \frac{d}{(M)^c} \qquad \text{Eq.(82)}$$

Where, M is the molecular weight of the heptanes-plus fraction.

   d and e are positive correlation coefficients.

Jhaveri and Youngren proposed that, in the absence of the experimental information

needed for calculating *e* and *d*, the power coefficient *e* could be set equal to 0.2051 and the coefficient *d* adjusted to match the C_{7+} density with the values of *d* ranging from 2.2 to 3.2. Table 4[10] shows the values that may be used for C_{7+} fractions, by hydrocarbon family:

Table 4: Values of the positive correlation coefficients used for C_{7+} fractions proposed by Jhaveri and Youngren.

Hydrocarbon family	*d*	*e*
Paraffins	2.258	0.1823
Naphthenes	3.044	0.2324
Aromatics	2.516	0.2008

To use the PR EOS to predict the phase and volumetric behavior of mixtures, the critical pressure, the critical temperature, and the acentric factor for each component in the mixture should be provided. For pure compounds, these properties are well-defined and known. Almost all the naturally occurring petroleum fluids contain a quantity of heavy fractions that are not well defined. These heavy fractions often are lumped together as a plus fraction "C_{7+}". Characterizing the plus fractions in terms of their critical properties and acentric factors has always been a problem. Changing the characterization of the plus fractions, even if they are present in small amounts, can have a profound effect on the pressure-temperature-volume "PVT" properties and on the phase equilibria of a hydrocarbon system as predicted by the Peng-Robinson equation of state.

The usual approach for such situations is to "tune" the parameters in the EOS in an attempt that will improve the accuracy of predictions. During the tuning process, the critical properties of the plus fraction and the binary interaction coefficients are adjusted to obtain a reasonable match with the experimental data that are available on the hydrocarbon mixture.

Recognizing that the inadequacy of the predictive capability of the PR EOS lies with the inproper procedure for calculating the parameters *a*, *b*, and α of the equation for the C_{7+} fraction, Ahmed (1991)[15] devised an approach for determining these parameters from the following two readily measured physical properties of C_{7+}: the molecular weight, M_{7+}, and the specific gravity, γ_{7+}.

The approach is based on generating 49 density values for the C_{7+} by applying the Riazi and Daubert correlation. These values were subsequently subjected to ten temperature and ten pressure values in the range of 60–300°F and 14.7–7000 psia, respectively. The Peng-Robinson EOS was then applied to match the 4900 generated density values by optimizing the parameters *a*, *b*, and α using a nonlinear regression model. The optimized parameters for the heptanes-plus fraction are given by the following expressions:

1- For the parameter "α" of C_{7+}:

$$\alpha(T) = [1 + m(1 - \sqrt{\tfrac{520}{T}})]^2 \qquad\qquad Eq.(83)$$

Where "m" defined by the following equation:

$$m = \frac{D}{A_0 A_1 D} + A_2 M_{7+} + A_3 M_{7+}^2 + \frac{A_4}{M_{7+}} + A_5 \gamma_{7+}^2 + \frac{A_7}{\gamma_{7+}} \qquad \text{Eq.(84)}$$

Where,
D is the ratio of the molecular weight of the heptanes-plus fraction to its specific gravity:

$$D = M_{7+} / \gamma_{7+} \qquad \text{Eq.(85)}$$

M_{7+} is the molecular weight of the heptanes-plus fraction.
γ_{7+} is the specific gravity of the heptanes-plus fraction.
A_0-A_7 are the coefficients as given in Table 5[10].

Table 5: Values of A_0-A_7 coefficients.

Coefficient	A	B	m
A_0	-2.433525×10^7	-6.8453198	-36.91776
A_1	8.3201587×10^3	1.730243×10^{-2}	$-5.2393763 \times 10^{-2}$
A_2	-0.18444102×10^2	$-6.2055064 \times 10^{-6}$	1.7316235×10^{-2}
A_3	3.6003101×10^{-2}	9.0910383×10^{-9}	$-1.3743308 \times 10^{-5}$
A_4	3.4992796×10^7	13.378898	12.718844
A_5	2.838756×10^7	7.9492922	10.246122
A_6	-1.1325365×10^7	-3.1779077	-7.6697942
A_7	6.418828×10^6	1.7190311	-2.6078099

For "*a*" and "*b*" parameters of C_{7+}, the following generalized correlation is proposed:

$$\alpha \text{ or } b = \sum_{i=0}^{3}(A_i D^i) + \frac{A_4}{D} + \sum_{i=5}^{6}(A_i \gamma_{7+}^{i-4}) + \frac{A_7}{\gamma_{7+}} \qquad \text{Eq.(86)}$$

The coefficients A_0–A_7 are included in Table 5.

Ahmed (1991) optimized α,b and m coefficients for nitrogen, CO_2, and methane, to improve the predictive capability of the Peng-Robinson EOS, by matching one hundred Z-factor values for each of these components.

The optimized values in Table 6 are recommended while using a nonlinear regression model.

Table 6: Optimized values of a, b and m coefficients as proposed by Ahmed (1991).

Component	a	b	m (eq. 56)
CO_2	$1.499914 * 10^4$	0.41503575	-0.73605717
N_2	$4.5693589 * 10^3$	0.4682582	-0.97962859
C_1	$7.709708 * 10^3$	0.46749727	-0.549765

The following steps are proposed to provide the modified Peng-Robinson EOS with a consistent procedure for determining the

binary interaction coefficient "k_{ij}":

1- Binary interaction coefficients between methane and the heptanes-plus fraction is found by using the following equation:

$$k_{C_1-C_{7+}} = 0.00189*T - 1.167059 \qquad \text{Eq.(87)}$$

Where, T is the temperature in °R.

2- Set the following values to each parameter as shown below:

$$k_{CO_2-N_2} = 0.12$$
$$k_{CO2-hydrocarbon} = 0.10$$
$$k_{N2-hydrocarbon} = 0.10 \qquad \text{Eq.(88)}$$

3- Adopting the procedure recommended by Pedersen, Thomassen and Fredenslund(1989)[16] to calculate the binary interaction coefficients between components heavier than methane (i.e., C_2, C_3, etc.) and the heptanes-plus fraction using the following equation:

$$k_{Cn-C7+} = 0.8 \, k_{C(n-1)-C7+} \qquad \text{Eq.(89)}$$

Where n is the number of carbon atoms of component C_n.

4- Determine the remaining k_{ij} using the following equation:

$$k_{ij} = \ k_{i-C7+} * \left[\frac{M_j^5 - M_i^5}{M_{C7+}^5 - M_j^5} \right] \qquad \text{Eq.(90)}$$

2. Volume Translation Parameter (volume shift)

Peneloux et al (1982)[17] developed a procedure to improve the volumetric predictions of the SRK-EOS by introducing a volume correction parameter "c_i". This third parameter does not change the vapour-to-liquid equilibrium conditions which were determined by the unmodified SRK equation, in other words, the equilibrium ratio K_i, but it modifies the liquid and gas volumes. This method is known as the volume translation method, and it uses the following expressions:

$$V^L_{corr} = V^L - \Sigma_i(x_i c_i) \qquad \text{Eq.(91)}$$

$$V^v_{\ corr} = V^v - \Sigma_i(y_i c_i) \qquad \text{Eq.(92)}$$

Where

V^L_{corr} is the corrected liquid molar volume in "ft^3/mol"

V^V_{corr} is the corrected gas molar volume in "ft^3/mol".

V^L is the uncorrected liquid molar volume in" ft^3/mol".

$$V^L = Z^V RT/p$$

V^v is the uncorrected gas molar volume in" ft^3/mol".

$$V^V = Z^V RT/p.$$

x_i is the mole fraction of component "i" in the liquid phase.

y_j is the mole fraction of component "i" in the gas phase.

Peneloux et al proposed six schemes for calculating the correction factor, c_i, for each component. For petroleum fluids and heavy hydrocarbons, they suggested that the best correlating parameter for the volume correction factor "c_i" is the Rackett compressibility factor"Z_{RA}". The correction factor then is defined mathematically by the following relationship:

$$c_i = 4.437978 \ (0.29441 - Z_{RA}) \ T_{ci}/p_{ci} \qquad \text{Eq.(93)}$$

where,

c_i is the volume shift coefficient for component i "ft^3/lb.mol".

T_{ci} is the critical temperature of component i, ºR.

p_{ci} is the critical pressure of component i, psia.

The Rackett compressibility factor "Z_{RA}" is a unique constant for each compound. In general the values of Z_{RA}, are not much different from those of the critical compressibility factors Z_c. If their values are not available, Peneloux et al. proposed the following correlation for calculating c_i:

$$c_i = (0.0115831168 + 0.411844152\omega_i)(T_{ci}/p_{ci}) \qquad \text{Eq.(94)}$$

Where ω_i is the acentric factor of component i.

3. Reservoir Fluids Components Description

Reservoir fluids are mixtures of hydrocarbon and non-hydrocarbon components. Hydrocarbons are mixtures of hydrogen and carbon atoms. N2, H2S and CO2 are the non-hydrocarbon components that could be present in the reservoir fluids. The hydrocarbon components of a compositional analysis are divided into three main categories:

1- Pure components, with physical properties that were measured and compiled over the years, and they are well-defined properties, like: critical properties (p_c & T_c) and acentric factor (ω).
2- Single Carbon Number components (SCN) or known as true boiling point components (TBP) or as pseudo-components: with measured or estimated specific gravity, molecular weight and critical properties that are difficult to obtain experimentally. (between two normal alkanes).
3- Plus fraction components known also as heavy-ends, with a measured mole fraction, specific gravity and molecular weight.

Katz and Firoozabadi (1978)[18] presented a generalized set of physical properties for the hydrocarbon groups C_6 through C_{45} that are expressed as a SCN, such as the C_6-group, C_7-group, C_8-group, and so on. These properties were generated by analysing the physical properties of 26 condensates and crude oil systems. These properties are tabulated in Table 7.

Table 7: Generalized Physical Properties

Group SCN	T_b (°R)	γ	K_w	M	T_c (°R)	p_c (psia)	ω	V_c (ft³/lb)
C_6	607	0.69	12.27	84	914	476	0.271	5.6
C_7	658	0.727	11.96	96	976	457	0.310	6.2
C_8	702	0.749	11.87	107	1027	428	0.349	6.9
C_9	748	0.768	11.82	121	1077	397	0.392	7.7
C_{10}	791	0.782	11.83	134	1120	367	0.437	8.6
C_{11}	829	0.793	11.85	147	1158	341	0.479	9.4
C_{12}	867	0.804	11.86	161	1195	318	0.523	10.2
C_{13}	901	0.815	11.85	175	1228	301	0.561	10.9
C_{14}	936	0.826	11.84	190	1261	284	0.601	11.7
C_{15}	971	0.836	11.84	206	1294	268	0.644	12.5
C_{16}	1002	0.843	11.87	222	1321	253	0.684	13.3
C_{17}	1032	0.851	11.87	237	1349	240	0.723	14
C_{18}	1055	0.856	11.89	251	1369	230	0.754	14.6
C_{19}	1077	0.861	11.91	263	1388	221	0.784	15.2
C_{20}	1101	0.866	11.92	275	1408	212	0.816	15.9
C_{21}	1124	0.871	11.94	291	1428	203	0.849	16.5
C_{22}	1146	0.876	11.95	300	1447	195	0.879	17.1
C_{23}	1167	0.881	11.95	312	1466	188	0.909	17.7
C_{24}	1187	0.885	11.96	324	1482	182	0.936	18.3
C_{25}	1207	0.888	11.99	337	1498	175	0.965	18.9
C_{26}	1226	0.892	12.00	349	1515	168	0.992	19.5
C_{27}	1244	0.896	12.00	360	1531	163	1.019	20.1
C_{28}	1262	0.899	12.02	372	1545	157	1.044	20.7
C_{29}	1277	0.902	12.03	382	1559	152	1.065	21.3
C_{30}	1294	0.905	12.04	394	1571	149	1.084	21.7
C_{31}	1310	0.909	12.04	404	1584	145	1.104	22.2
C_{30}	1326	0.912	12.05	415	1596	141	1.122	22.7
C_{33}	1341	0.915	12.05	426	1608	138	1.141	23.1
C_{34}	1355	0.917	12.07	437	1618	135	1.157	23.5

C35	1368	0.92	12.07	445	1630	131	1.175	24
C36	1382	0.922	12.08	456	1640	128	1.192	24.5
C37	1394	0.925	12.08	464	1650	126	1.207	24.9
C38	1407	0.927	12.09	475	1661	122	1.226	25.4
C39	1419	0.929	12.10	484	1671	119	1.242	25.8
C40	1432	0.931	12.11	495	1681	116	1.258	26.3
C41	1442	0.933	12.11	502	1690	114	1.272	26.7
C42	1453	0.934	12.13	512	1697	112	1.287	27.1
C43	1464	0.936	12.13	521	1706	109	1.300	27.5
C44	1477	0.938	12.14	531	1716	107	1.316	27.9

Ahmed (1985)[19] by using a regression model, conveniently correlated Katz and Firoozabadi's tabulated physical properties with single carbon number as represented by the number of carbon atoms "n". The generalized equation is of the following expression:

$$\theta = \alpha_1 + \alpha_2 n + \alpha_3 n^2 + \alpha_4 n^3 + \frac{\alpha_5}{n} \qquad \text{Eq.(95)}$$

Where,

θ represents any physical property, such as p_c, T_c or V_c.

n represents the effective number of carbon atoms of the single carbon number group, eg, 6,..etc.

α_1- α_5 are the coefficients of the equation, with values found in Table 8.

Table 8: Coefficient values of Ahmed's (1985) equation based on physical properties.

θ	M	T_c (°R)	p_c (psia)	T_b (°R)	ω	γ	$V_c(ft^3/lb$ m.mol)
a_1	-131.11375	926.602244514	311.2361908	427.2959078	-0.31428163	0.86714949	-0.232837085
a_2	24.96156000	39.729362915	-14.6869301	50.08577848	7.80028E-02	3.4143E-03	0.974111699
a_3	-0.34079022	0.722461850	0.3287671	0.88693418	-1.39205E-03	-2.8396E-05	-0.009226997
a_4	2.49411840E-03	0.005519083	-0.0027346	6.75667E-03	1.02147E-05	2.4943E-08	3.63611E-05
a_5	468.32575000	-1366.431748654	1690.9001135	-551.2778516	0.991028867	1.1627984	0.111351508

4. The plus fraction "heavy-end" compound of reservoir fluid

4.1 Characterization of the plus fraction

Characterization of the plus fraction (heavy-ends) means that the plus fraction should be split into single carbon number (SCN) groups, and the critical properties (p_c and T_c) and the acentric factor (ω) for each SCN should be assigned. After that, grouping the SCN into multiple-carbon number (MCN) groups should be done. This is done because direct measurements of the critical properties of the plus fraction component

are not practical. One more reason for characterizing the plus fraction is that if the plus fraction was used as one component, the equation of state "EOS" calculations could predict bubble point pressure instead of dew point pressure at reservoir temperature for gas condensate samples.

"Riazi and Daubert, Cavett, Kesler-Lee, Edmister, Standing, Hall-Yarborough and Twu" are some of the correlations that have been found for estimating the physical properties of the petroleum fractions, and most of these correlations use the boiling point T_b and the specific gravity (γ).

4.2 Riazi and Daubert correlation

Riazi and Daubert (1980)[20] developed a two-parameter equation to predict the physical properties of pure compounds and undefined hydrocarbon mixtures. This equation was based on the use of normal boiling point and specific gravity and has the following expression:

$$\theta = \alpha T_b^b \gamma^c \qquad \text{Eq.(96)}$$

Where,
θ corresponds to any physical property (T_c, p_c, V_c or M).
T_b is the normal boiling point temperature ºR.
M is the molecular weight.
α,b and c are correlation constants given in Table 9 [10].

Table 9: Correlation Constants for Riazi and Daubert equation.

θ	a	b	C	Deviation (%)	
				Average	Maximum
M	4.56730×10^{-5}	2.19620	-1.0164	2.6	11.8
T_c (ºR)	24.27870	0.58848	0.3596	1.3	10.6
P_c (psia)	-3.12281×10^9	-2.31250	2.3201	3.1	-9.3
V_c (ft³/lb)	-7.52140×10^{-3}	0.28960	-0.7666	2.3	-9.1

In Table 9, the deviation percent corresponds to the average errors for estimating each property.

Riazi and Daubert (1987)[21] improved their correlation for predicting the physical properties of petroleum by taking into account the following factors: accuracy, simplicity, generality and availability of input parameters like the ability to extrapolate. Taking these factors into consideration, they proposed the following equation:

$$\theta = \alpha \theta_1^b \theta_2^c \exp[d\theta_1 + e\theta_2 + f\theta_1\theta_2] \qquad \text{Eq.(97)}$$

Where,
θ is any physical property.

α-*f* are constants for each property.

Riazi and Daubert stated that θ_1 and θ_2 can be any two parameters capable of characterizing the molecular forces and molecular size of compound. They identified (T_b, γ) and (M, γ) as appropriate pairs of input parameters in the equation. So, they proposed the following two forms of generalized correlations:

1- If the boiling point (T_b) and the specific gravity (γ) are the correlating parameters that are going to be used, then the following correlation is applied:

$$\theta = \alpha T_b^b \gamma^c \exp[dT_b + e\,\gamma + fT_b\,\gamma] \qquad \text{Eq.(98)}$$

Where α-*f* are constants for each property, with values given in Table 10 [10].

Table 10: Constants values used for modified Riazi and Daubert (1987) equation.

Θ	a	b	C	d	e	f
M	581.96000	-0.97476	6.51274	5.43076×10^{-4}	9.53384	1.11056×10^{-3}
T_c (ºR)	10.6443	0.81067	0.53691	5.17470×10^{-4}	-0.54444	3.59950×10^{-4}
p_c (psia)	6.16200×10^6	-0.48440	4.08460	4.72500×10^{-3}	-4.80140	3.19390×10^{-3}
V_c (ft^3/lb)	6.23300×10^{-4}	0.75060	-1.20280	-1.46790×10^{-3}	-0.26404	1.09500×10^{-3}

2- If the molecular weight (M) and the specific gravity (γ) are correlating parameters that are going to be used, then the following correlation is applied:

$$\theta = \alpha(M)^b \gamma^c \exp[dM + e\gamma + f\gamma M] \qquad \text{Eq.(99)}$$

Where α-*f* are constants for each property, with values given in Table 11.

Table 11: Constants values for modified Riazi and Daubert (1987) equation.

θ	α	b	C	d	e	f
T_c (ºR)	544.40000	0.299800	1.05550	-1.34780×10^{-4}	-0.616410	0.00000
p_c (psia)	4.52030×10^4	-0.806300	1.60150	-1.80780×10^{-3}	-0.308400	0.00000
V_c (ft^3/lb)	1.20600×10^{-2}	0.203780	-1.30360	-2.65700×10^{-3}	0.528700	2.60120×10^{-3}
T_b (ºR)	6.77857	0.401673	-1.58262	3.77409×10^{-3}	2.984036	-4.25288×10^{-3}

4.3 Cavett's Correlations

Cavett (1962)[22] proposed correlations to estimate the critical temperature and the critical pressure of hydrocarbon fractions. The correlations were expressed as functions of normal boiling pint (T_{bF}) in ºF and API gravity. These correlations are expressed in the following equations:

$$T_c = a_0 + a_1(T_{bF}) + a_2(T_{bF})^2 + a_3(API)(T_{bF}) + a_4(T_{bF})^3 + a_5(API)(T_{bF})^2 + a_6(API)^2(T_{bF})^2 \qquad \text{Eq.(100)}$$

$$\log(p_c) = b_0 + b_1(T_{bF}) + b_2(T_{bF})^2 + b_3(API)(T_{bF}) + b_4(T_{bF})^3 + b_5(API)(T_{bF})^2 + b_6(API)^2(T_{bF}) + b_7(API)^2(T_{bF})^2 \qquad \text{Eq.(101)}$$

Where, T_c is the critical temperature "ºR".

p_c is the critical pressure "psia".

T_{bF} is the normal boiling point "ºF".

API is the API gravity of the fraction.

$a_1 - a_7$ & b_1-b_7 are values from Table 12.

Table 12: Coefficient values of Cavett's correlations

i	a_i	b_i
0	768.0712100000	2.82904060
1	1.7133693000	$0.94120109 \times 10^{-3}$
2	-0.0010834003	$-0.30474749 \times 10^{-5}$
3	-0.0089212579	$-0.20876110 \times 10^{-4}$
4	$0.3889058400 \times 10^{-6}$	$0.15184103 \times 10^{-8}$
5	$0.5309492000 \times 10^{-5}$	$0.11047899 \times 10^{-7}$
6	$0.3271160000 \times 10^{-7}$	$-0.48271599 \times 10^{-7}$
7		$0.13949619 \times 10^{-9}$

4.4 Kesler and Le Correlations

Kesler and Lee (1976)[23] proposed a set of equations using the specific gravity (γ) and boiling point (T_b) as input parameters, to estimate the critical pressure, critical temperature and molecular weight of petroleum fractions. These expressions are as following:

$$\ln(p_c) = 8.3634 - \frac{0.0566}{\gamma} - [0.24244 + \frac{2.2898}{\gamma} + \frac{0.11857}{\gamma^2}]10^{-3}T_b + [1.4685 + \frac{3.648}{\gamma} + \frac{0.47227}{\gamma^2}]10^{-7}T_b^2 - [0.42019 + \frac{1.6977}{\gamma^2}]10^{-10}T_b^3 \qquad \text{Eq.(102)}$$

$$T_c = 341.7 + 811.1\gamma + [0.4244 + 0.1174\ \gamma]T_b + \frac{[0.4669 - 3.26238\gamma]10^5}{T_b} \qquad \text{Eq.(103)}$$

$$M = -12272.6 + 9486.4\gamma + [4.6523 - 3.3287\gamma]T_b + [1 - 0.77084\gamma - 0.02058\gamma^2][1.3437 - \frac{720.79}{T_b}]\frac{10^7}{T_b} + [1 - 0.80882\gamma - 0.02226\gamma^2][1.8828 - \frac{181.98}{T_b}]\frac{10^{12}}{T_b^3} \qquad \text{Eq.(104)}$$

Kesler and Lee (1976) proposed two expressions for calculating the acentric factor, by introducing the Watson characterization factor and the reduced boiling point temperature as correlating parameters. These expressions are as following:

1- For $\theta > 0,8$:

$$\omega = -7.904 + 0.1352K_w - 0.007456K_w^2 + 8.359\ \theta + \frac{1.408 - 0.01063K_w}{\theta}$$
Eq.(105)

2- For $\theta < 0,8$:

$$\omega = \frac{-ln\frac{p_c}{14.7} - 5.92714 + \frac{6.09648}{\theta} + 1.28862\ \ln(\theta) - 0.169347\theta^6}{15.2518 - \frac{15,6875}{\theta} - 13,4721\ \ln(\theta) + 0.43577\theta^6}$$
Eq.(106)

Where,

p_c is the critical pressure "psia".

T_c is the critical temperature "°R".

T_b is the boiling temperature "°R".

ω is the acentric factor.

M is the molecular weight.

γ is the specific gravity.

4.5 Edmister's Correlation

Edmister (1958)[24] proposed a correlation for estimating the acentric factor "ω" of pure fluids and petroleum fractions. The correlation uses the critical pressure "p_c" in psia, critical temperature "T_c" in °R and boiling point in °R. This correlation has the following expression:

$$\omega = \frac{3[\log\left(\frac{p_c}{14.70}\right)]}{7(\frac{T_c}{T_b} - 1)} - 1$$
Eq.(107)

4.6 Standing's correlations

Standing (1977)[25] expressed in a mathematical form the graphical correlations presented by Matthews et al (1942)[26] to determine the critical temperature and critical pressure of the heptanes-plus fraction. These correlations are as following:

$$(T_c)_{C7+} = 608 + 364\log[M_{C7+} - 71.2] + [2450\log(M_{C7+}) - 3800]\log(\gamma)_{C7+}$$
Eq.(108)

$$(p_c)_{C7+} = 1188 - 431\log[M_{C7+} - 61.1] + 2319 - 852\log[M_{C7+} - 53.7][\gamma_{C7+} - 0.8]$$
Eq.(109)

Where,

M_{C7+} is the molecular weight of the C_{7+}.

γ_{C7+} is the specific gravity of the C_{7+}.

4.7 Hall and Yarborough Correlations

Hall and Yarborough (1971)[27] proposed an expression for determining the critical volume of a fraction from its molecular weight and specific gravity:

$$v_c = \frac{0,025 M^{1.15}}{\gamma^{0.7935}}$$

<div align="right">Eq.(110)</div>

$$v_c = MV_c$$

<div align="right">Eq.(111)</div>

Where,

V_c is the critical volume in "ft^3/lb".

v_c is the critical volume in "$ft^3/lb.mol$".

M is the molecular weight.

The critical volume could also be calculated using the real gas equation of state at the critical point of the component, as following:

$$pV = ZRT\left[\frac{m}{M}\right]$$

<div align="right">Eq.(112)</div>

And by applying the real gas equation at the critical point, it gives:

$$V_c = (Z_c RT_c) / (p_c M)$$

<div align="right">Eq.(113)</div>

4.8 Twu's Correlations

Twu (1984)[28] developed a suite of critical properties, based on perturbation expansion theory with normal paraffins as the reference states, which can be used in determining the critical and physical properties of the undefined hydrocarbon fractions, such as C_{7+}. The methodology is based on selecting (finding) a normal paraffin fraction with a boiling temperature T_{bP} identical and similar to that of the hydrocarbon-plus fraction such as C_{7+}. This methodology requires the availability of the boiling point temperature of the plus fraction "T_{bC+}, molecular weight of the plus fraction "M_{C+}", and the specific gravity of the plus fraction "γ_{C+}". If the boiling point temperature is not available, it can be estimated from the correlation that was proposed by Soreide (1989)[29].

$$T_{bC+} = a_1 + a_2(M_{C+})^{a_3}(\gamma_{C+})^{a_4} \exp[a_5 M_{C+} + a_6 \gamma_{C+} + a_7 M_{C+}\gamma_{C+}]$$

<div align="right">Eq.(114)</div>

Where,

$a_1 = 1928.3$

$a_2 = -1.695(10^5)$

$a_3 = -0.03522$

$a_4 = 3.266$

$a_5 = -4.922(10^{-3})$

$a_6 = -4.7685$

$a_7 = 3.462(10^{-3})$

The following steps should be followed in order to use Twu's approach:

1- Normal paraffins properties should be calculated using the following expressions:

a- The critical temperature of normal paraffin (T_{cP}) in "ºR" :

$$T_{cP} = T_{bC+} [\ A_1 + A_2 T_{bC+} + A_3 T^2{}_{bC+} + A_4 T^3{}_{bC+} + \frac{A_5}{(A_6 T_{bC+})^{13}}]^{-1} \quad \text{Eq.(115)}$$

Where,

$A_1 = 0.533272$

$A_2 = 0.191017(10^{-3})$

$A_3 = 0.779681(10^{-7})$

$A_4 = -0.284376(10^{-10})$

$A_5 = 0.959468(10^2)$

$A_6 = 0.01$

b- The critical pressure of normal paraffins (P_{cP}) in "psia":

$$p_{cP} = [A_{1\,+}\, A_2 a_i^{0.5} + A_3 a_i + A_4 a_i^2 + A_5 a_i^4]^2 \qquad \text{Eq.(116)}$$

$$a_i = 1 - (T_{bC+} \ / \ T_{cP}) \qquad \text{Eq.(117)}$$

Where,

$A_1 = 3.83354$

$A_2 = 1.19629$

$A_3 = 34.8888$

$A_4 = 36.1952$

$A_5 = 104.193$

c- The specific gravity of normal paraffins (v_{cP}) in "ft³/lbm-mol":

$$\gamma_P = A_1 + A_2 a_i + A_3 a_i{}^3 + A_4 a_i{}^{12} \qquad \text{Eq.(118)}$$

Where,

$A_1 = -0.419869$

$A_2 = 0.505839$

$A_3 = 1.56436$

$A_4 = 9481.7$

2- The properties of the plus fraction should be found using the following expressions:

a- The critical temperature of the plus fraction in °R:

$$T_{C+} = T_{cP} \left[\frac{1+2f_T}{1-2f_T} \right]^2 \qquad\qquad \text{Eq.(119)}$$

$$f_T = \{\exp[5(\gamma_P - \gamma_{C+})]\text{-}1\}\left[\frac{A_1}{T_{bC+}^{0.5}} + \left(A_2 + \frac{A_3}{T_{bC+}^{0.5}}\right)\{\exp[5(\gamma_P - \gamma_{C+})] - 1\}\right] \qquad \text{Eq.(120)}$$

Where,

$A_1 = -0.362456$

$A_2 = 0.0398285$

$A_3 = -0.948125$

b- The critical volume of the plus fraction in "ft^3/lbm-mol":

$$v_{C+} = v_{cP} \left[\frac{1+2f_v}{1-2f_v} \right]^2 \qquad\qquad \text{Eq.(121)}$$

$$f_v = \{\exp[4(\gamma_P^2 - \gamma_{C+}^2)]\text{-}1\}\left[\frac{A_1}{T_{bC+}^{0.5}} + \left(A_2 + \frac{A_3}{T_{bC+}^{0.5}}\right)\{\exp[4(\gamma_P^2 - \gamma_{C+}^2)] - 1\}\right] \qquad \text{Eq.(122)}$$

Where,

$A_1 = 0.466590$

$A_2 = -0.182421$

$A_3 = 3.01721$

c- The critical pressure of the plus fraction in "psia":

$$p_{C+} = p_{cP} \left(\frac{T_{C+}}{T_{cP}}\right)\left(\frac{v_{cP}}{v_{C+}}\right)\left[\frac{1+2f_P}{1-2f_P}\right]^2 \qquad\qquad \text{Eq.(123)}$$

$$f_P = \{\exp[0.5(\gamma_P - \gamma_{C+})]\text{-}1\}\left((A_1 + \frac{A_2}{T_{bC+}^{0.5}} + A_3 T_{bC+}) + (A_4 + \frac{A_5}{T_{bC+}^{0.5}} + A_6 T_{bC+})\{\exp[0.5(\gamma_P - \gamma_{C+})]\text{-}1\}\right) \qquad \text{Eq.(124)}$$

Where,

$A_1 = 2.53262$

$A_2 = -46.19553$

$A_3 = -0.00127885$

$$A_4 = -11.4277$$
$$A_5 = 252.14$$
$$A_6 = 0.00230535$$

5. *Mixture Mixing Rule*

In order to use Soave-Redlich-Kwong cubic EOS with mixtures, determination of the two parameters $\alpha\alpha(T)$ and b of this equation should be done, using the following equations:

$$\alpha\alpha(T)_m = \sum_i \sum_j \left(x_i x_j \sqrt{\alpha_i \alpha_j \alpha_i \alpha_j} (1 - k_{ij}) \right) \qquad \text{Eq.(125)}$$

$$b_m = \sum_i (x_i b_i) \qquad \text{Eq.(126)}$$

With

$$A = \frac{(\alpha\alpha)_m p}{(RT)^2} \qquad \text{Eq.(127)}$$

$$B = \frac{b_m p}{RT} \qquad \text{Eq.(128)}$$

Where k_{ij} is an empirically determined correction factor, known as the binary interaction coefficient "BIC", that characterizes any binary system with i and j components in the hydrocarbon mixture.

Binary interaction coefficients are used to model the intermolecular interaction through empirical adjustment of $\alpha\alpha(T)_m$ terms. They depend on the difference in molecular size of components in a binary system and they are characterized by the following properties:

1- The interaction between hydrocarbon components increases as the relative difference between their molecular weights increases:

$$k_{i,j+1} > k_{i,j}$$

2- Hydrocarbon components with the same molecular weight have a binary interaction coefficient of zero:

$$k_{i,j} = 0$$

3- Binary interaction coefficients have symmetric matrix:

$$k_{i,j} = k_{j,i}$$

Soave (1972)[3] and Graboski and Daubert (1978)[30] suggested that the binary interaction coefficients should have a value of zero between hydrocarbon-hydrocarbon pairs, except between methane and "C_1" and C_7^+.

Techniques for determining the binary interaction coefficients were presented by Vidal and Daubert (1978)[31] and Slot-Petersen (1978)[32].

The following expression was proposed by Whitson and Brule (2000)[33] to calculate the binary interaction coefficient between methane and the heavy fractions:

$$K_{C1\text{-}C7+} = 0.18 - \frac{16.668\, V_{ci}}{\left[1.1311 + (V_{ci})^{1/3}\right]^6} \qquad\qquad \text{Eq.(129)}$$

$$V_{ci} = 0.4804 + 0.06011 M_i + 0.00001076\, M_i^2 \qquad\qquad \text{Eq.(130)}$$

Where, V_{ci} is the critical volume of the heavy fraction C_{7+} "ft^3/lbm".
$\quad$ M_i is the molecular weight

Reid et al (1987)[34] proposed Table 13, which contains the values of binary interaction coefficients of non-hydrocarbons to be used with SRK EOS:

Table 13: Binary Interaction Coefficients of non-hydrocarbons

Component	N_2	CO_2	H_2S
N2	0	0	0
CO2	0	0	0
H2S	0.12	0.12	0
C1	0.02	0.12	0.08
C2	0.06	0.15	0.07
C3	0.08	0.15	0.07
i-C4	0.08	0.15	0.06
n-C4	0.08	0.15	0.06
i-C5	0.08	0.15	0.06
n-C5	0.08	0.15	0.06
C6	0.08	0.15	0.05
C7 +	0.08	0.15	0.03

6. Lee's Mixing Rules

Lee et al (1979)[35] proposed a lumping scheme to determine the properties of the lumped fractions, by using Kay's mixing rules approach. They defined the normalized mole fraction of a component "i" within the set of the lumped fraction, that is, $i \in L$, as:

$$z_i^* = z_i / \sum_{i \in L}^{L} z_i \qquad\qquad \text{Eq.(131)}$$

They proposed the following rules:

$$\text{ML} = \sum_{i \in L}^{L} z_i^* M_i \qquad \text{Eq.(132)}$$

$$\gamma_L = M_L / \sum_{i \in L}^{L} [z_i^* M_i / \gamma_i] \qquad \text{Eq.(133)}$$

$$V_{cL} = \sum_{i \in L}^{L} [z_i^* M_i V_{ci} / M_L] \qquad \text{Eq.(134)}$$

$$p_{cL} = \sum_{i \in L}^{L} z_i^* p_{ci} \qquad \text{Eq.(135)}$$

$$T_{cL} = \sum_{i \in L}^{L} z_i^* T_{ci} \qquad \text{Eq.(136)}$$

$$\omega_L = \sum_{i \in L}^{L} z_i^* \omega_i \qquad \text{Eq.(137)}$$

Where,

p_{cL} is the pseudo-critical pressure.

T_{cL} is the pseudo-critical temperature.

V_{cL} is the pseudo-critical volume.

ω_L is the pseudo-acentric factor.

M_L is the pseudo-molecular weight.

γ_L is the pseudo-specific gravity.

z_i^* is the normalized mole fraction of a component "i" in the lumped set.

The subscript L denotes the lumped fraction.

7. Hong's Mixing Rule

Hong (1982)[36] concluded that the best mixing parameter in characterizing the C_{7+} fractions is the weight fraction average w_i. Defining the normalized weight fraction of a component "i" to be within the set of lumped fraction $i \in$ L, as:

$$\text{wi} * = \text{ziMi} / \sum_{i \in L}^{L} z_i M_i \qquad \text{Eq.(138)}$$

Hong's proposed the following mixing rules:

$$p_{cL} = \sum_{i \in L}^{L} w_i^* p_{ci} \qquad \text{Eq.(139)}$$

$$T_{cL} = \sum_{i \in L}^{L} w_i^* T_{ci} \qquad \text{Eq.(140)}$$

$$V_{cL} = \sum_{i \in L}^{L} w_i^* v_{ci} \qquad \text{Eq.(141)}$$

$$\omega_L = \sum_{i \in L}^{L} w_i^* \omega_i \qquad \text{Eq.(142)}$$

$$M_L = \sum_{i \in L}^{L} v_i^* M_i \qquad \text{Eq.(143)}$$

$$k_{kL} = 1 - \sum_{i \in L}^{L} \sum_{j \in L}^{L} w_i^* w_j^* (1 - k_{ij}) \qquad \text{Eq.(144)}$$

Where,

w_i^* is the normalized weight fraction of a component "i" in the lumped set.

k_{kL} is the binary interaction coefficient between the kth component and the lumped fraction.

The subscript L denotes the lumped fraction.

8. Splitting and Lumping the plus-fraction

Most hydrocarbon fluids contain hundreds of different components that are difficult to be identified and characterized using laboratory separation techniques. This is the reason why this large number of components are lumped together and categorized as "plus-fractions".

These "plus-fractions" are difficult to have a proper characterization in terms of critical properties (temperature and pressure) and in terms of acentric factor. The only thing that could be known for these plus fraction components (known also as heavy-end components) is their molecular weight and their specific gravity from laboratory analysis. It is also known that these measured properties values of the plus fractions have an uncertainty of as much as 20%, and this makes their characterization more difficult. This means that it can lead to a large prediction error. For example, EOS calculation could sometimes predict a bubble point pressure instead of a dew point pressure in a rich gas condensate sample.

One way of characterizing the heavy-end components is to split them into single carbon number groups with well-defined properties, in other words, to break down the plus fraction into certain "optimum" number of SCN groups. An optimum number of SCN should be found first, in other words, the minimum number of SCNs, because a large number of SCN groups will lead to a satisfactory prediction of the PVT behavior by the EOS, but at the same time, in compositional models, the cost and the computing time will increase significantly with the increasing number of the components in the system, so a strict limitation is set on the number of components used in the system.

There are some important requirements and constraints that should be followed while applying any splitting model, which are the following:

1- The summation of the mole fractions of the individual pseudo-components should be equal to the mole fraction of the plus-fraction. This is expressed mathematically as following:

$$\sum_{n=7}^{n+} Z_n = Z_{Cn}{}^+$$

Eq.(145)

2- The summation of the products of the mole fraction and the molecular weight of the individual pseudo-components should be equal to the product of the mole fraction and the molecular weight of the plus-fraction. This is expressed mathematically as following:

$$\sum_{n=7}^{n+} Z_n . MW_n = Z_{Cn}{}^+ . MW_{Cn}{}^+$$

Eq.(146)

3- The summation of the product of the mole fraction and the molecular weight divided by the specific gravity of each individual pseudo-component should be equal to that of the plus-fraction. This can be expressed mathematically as following:

$$\sum_{n=7}^{n+}(Z_n . MW_n/\gamma_n) = (Z_{Cn+} . MW_{Cn+}/\gamma_{Cn+}) \qquad \text{Eq.(147)}$$

Where,

n is the number of carbon atoms.

Z_{Cn}^+ is the mole fraction of the plus-fraction component.

Z_n is the mole fraction of the each individual pseudo-component.

MW_n is the molecular weight of each individual pseudo-component.

MW_{Cn}^+ is the molecular weight of the plus-fraction component.

γ_{Cn}^+ is the specific gravity of the plus fraction component.

γ_n is the specific gravity of each individual pseudo-component.

N is the last hydrocarbon group in the plus-fraction.

9. Splitting Schemes

Splitting is the process of breaking the plus fraction into hydrocarbon groups, with well-defined properties. In other words, splitting the plus fraction into hydrocarbon groups will decrease the uncertainty in the properties that were assigned to the plus fraction, and this will lead to build a more accurate EOS model. This means that the predictions that will be made, based on the EOS model that was built, will be very close to the reality.

Below, there are some of the schemes that are used nowadays in splitting the plus fraction into hydrocarbon groups:

1- Katz (1983)[37] who proposed an exponential function which requires the mole fraction of C_7^+ only. This function has the following expression:

$$Z_n = (1.269831 Z_{C7+}) \exp(-0.26721n) + 0.0060884 Z_{C7+} + 10.4275*10^{-6} \qquad \text{Eq.(148)}$$

2- Lohrenz et al (1964)[38] who proposed that the heptanes-plus fraction could be divided into pseudo-components with carbon number ranges from 7 to 40. They stated that the mole faction Z_n is related to its number of carbon atoms n and the mole fraction of the hexane fraction Z_6 with the following mathematical expression:

$$Z_n = Z_6 \exp[A(n-6)^2 + B(n-6)] \qquad \text{Eq.(149)}$$

Where A and B are correlating parameters.

3- Pedersen et al (1982)[39] who proposed a logarithmic relationship between the mole fraction and the carbon number.

$$\ln (Z_n) = An + B \qquad\qquad Eq.(150)$$

Where A and B are constants.

4- Whitson (1983)[40] who proposed a three parameter gamma distribution function to describe the relation between the mole fraction and the molecular weight of SCN components of the plus fraction.

$$P(M) = \frac{(M - \eta)^{\alpha-1} \exp[-\frac{M-\eta}{\beta}]}{\beta^{\alpha}.\Gamma(\alpha)} \qquad Eq.(151)$$
$$\beta = (M_{Cn}{}^{+} - \eta) / \alpha \qquad\qquad Eq.(152)$$

Where,
P(M): is the probability function of the molecular weight.
η: is an adjustable parameter with different values, used to see which value will increase the agreement between the experimental and the calculated mole fraction.
M: is the molecular weight of the component.
Γ: is the gamma function.
α : it affects the shape of the distribution, in this study it is equal to unity, because it is believed that the distribution of the mole fractions for the hydrocarbon components heavier than C_7 is exponential. Figure 3 shows Whitson's model for several values of parameter α.
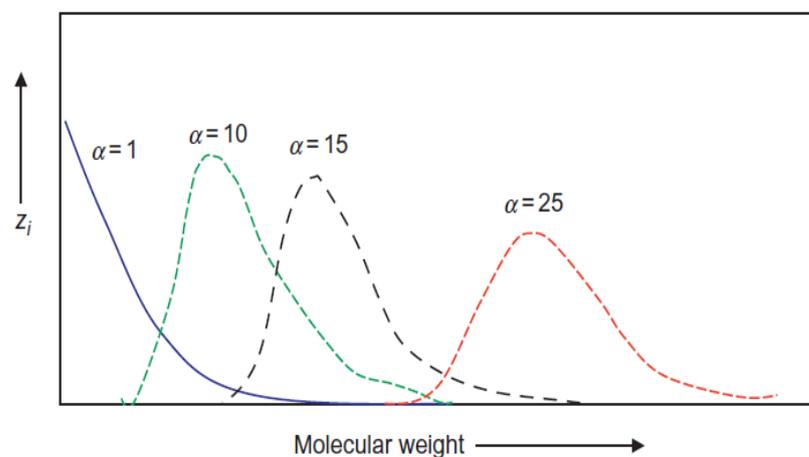
Figure 3: Gamma distribution for C7+.

Whitson indicates that the parameter "η" could be physically interpreted as the minimum molecular weight found in the plus-fraction. It can be found using the following expression:

$$\eta \approx 14n - 6 \qquad\qquad\qquad \text{Eq.(153)}$$

The cumulative frequency of occurrence for each single carbon number with molecular weight boundaries between M_{n-} and M_{n-1}, is calculated from the integration of the probability function.

$$f_n = \int_{M_{n-1}}^{M_n} P(M)dM = P(M_n) - P(M_{n-1}) \qquad\qquad \text{Eq.(154)}$$

After integrating the above equation, the following expression is given:

$$f_n = -e^{\left(\frac{\eta}{\beta}\right)} \cdot \left[e^{\left(\frac{M_n}{-\beta}\right)} - e^{\left(\frac{M_{n-1}}{-\beta}\right)} \right] \qquad\qquad \text{Eq.(155)}$$

The mole fraction Z_n for each SCN group is given by the following expression:

$$Z_n = Z_{Cn+} \cdot f_n \qquad\qquad\qquad \text{Eq.(156)}$$

5- Ahmed (2014)[41], who proposed a system of equations, the first equation uses the experimental specific gravity of the plus fraction (C_7^+) to find the slope, and the second equation is to calculate the molecular weight of the octanes plus fraction by using the slope which was found from the first equation.

10. Lumping Schemes

Lumping is the process of reducing the number of the components used in the equation of state calculations for reservoir fluid by employing the concept of pseudo-component, this process is also known as pseudoization.

10.1 Whitson's Lumping Scheme

Whitson (1980)[42] proposed a lumping scheme whereby the compositional distribution of the C_{7+} fraction is reduced to only few multiple carbon number (MCN) groups. Whitson suggested that the number of MCN groups necessary to describe the plus fraction is given by the following empirical equation:

$$N_g = Int[1 + 3.3\log(N - n)] \hspace{4cm} Eq.(157)$$

Where,

N_g: represents the number of MCN groups.

Int: represents an integer function.

N: is the number of carbon atoms of the last component in the hydrocarbon system.

n: is the number of carbon atoms of the first component "lighter component" in the plus fraction.

The molecular weights separating each multiple carbon number (MCN) group are calculated using the following expression:

$$M_I = M_{C7} \left(\frac{M_{N+}}{M_{C7}}\right)^{1/N_g} \hspace{3cm} Eq.(158)$$

Where,

M_{N+}: is the molecular weight of the last reported component in the extended analysis of the hydrocarbon system.

M_{C7}: is the molecular weight of C_7.

I: has values 1,2…, N_g.

10.2 Lee's Lumping Scheme

Lee et al (1979)[43] proposed a simple procedure for regrouping the oil fractions into pseudo-components. They employed the physical reasoning that crude oil fractions having relatively close physicochemical properties (such as molecular weight and specific gravity) can be accurately represented by a single fraction. Having observed that the closeness of these properties is reflected by the slopes of curves when the properties are plotted against the weight-averaged boiling point of each fraction, Lee et al. used the weighted sum of the slopes of these curves as a criterion for lumping the crude oil fractions. The authors proposed the following computational steps:

1- Plot the available physical and chemical properties of each original fraction versus its weight-averaged boiling point.

2- Calculate numerically the slope "m_{ij}" for each fraction at each weight-averaged boiling point, where:

   m_{ij}: is the slope of the property curve versus boiling point.
   i: has values from 1 to n_f.
   j: has values from 1 to n_p.
   n_f : is the number of original oil fractions
   n_p : is the number of available physiochemical properties.

3- The normalized absolute slope should be found using the

following expression:

$$\overline{m}_{ij} = \frac{m_{ij}}{max_{i=1,..,n_f} m_{ij}}$$
Eq.(159)

4- The weighted sum of slopes for each fraction should be found using the following expression:

$$\overline{M}_i = (\sum_{j=1}^{n_p} \overline{m}_{ij}) / n_p$$
Eq.(160)

Where, $\overline{M}_i$ is the averaged change of physicochemical properties of the crude oil fractions along the boiling point axis.

5- Group the fractions that share the same value of $\overline{M}_i$.
6- Calculate the physical properties of the pseudo-components using the Lee's et al (1979) mixing rules equations.

10.3 Behrens and Sandler's Lumping Scheme

Behrens and Sandler (1986)[44] suggested that the heptanes-plus fraction can be fully described with two pseudo-components only. They used the semi-continuous thermodynamic distribution theory to model the heptanes-plus fraction for EOS calculations. That means that the mole fraction of some components (well-defined components) such as C_1 through C_6 have discrete values , while the unidentifiable components such as C_{7+} are described as continuous distribution functions. This is expressed in Figure 4.
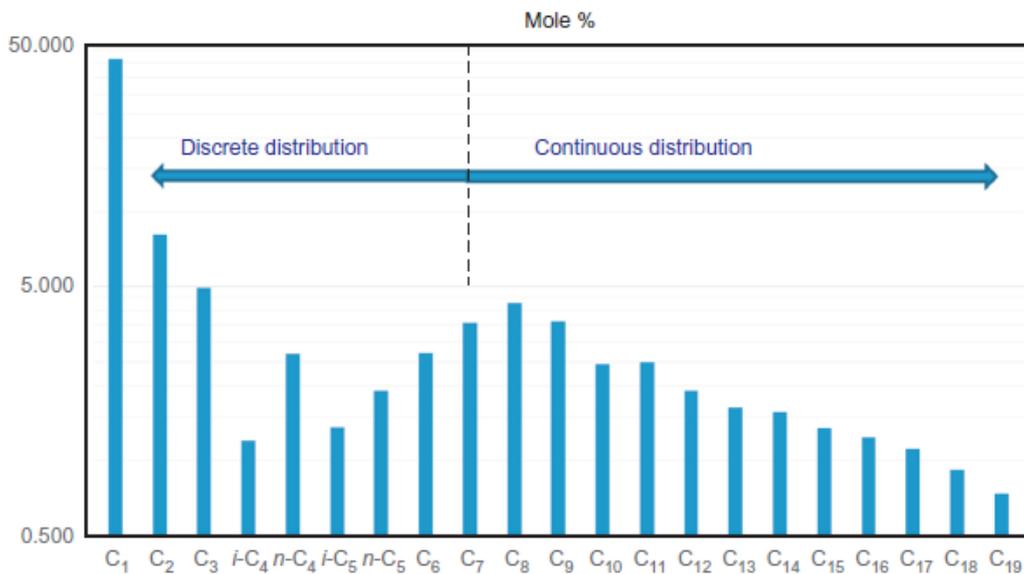
Figure 4: Discrete and continuous compositional distribution.

- For a hydrocarbon system with k discrete components, the following relationship applies:

$$\sum_{i=1}^{C_6} z_i + z_{7+} = 1.0$$
Eq.(161)

- The mole fraction of C_{7+} in this equation is replaced with the selected distribution function, to give the following expression:

$$\sum_{i=1}^{C_6} z_i + \int_A^B F(I)dI \ = \ 1.0 \qquad\qquad \text{Eq.(162)}$$

Where,

F(I) is the continuous distribution function, which describes the heavy fractions according to index "I", chosen to be a property of individual components, like boiling point, molecular weight or the carbon number.

A is the beginning of the continuous distribution function, for example C_7.
B is the upper cutoff of the continuous distribution, for example C_{45}.

This molar distribution behavior is shown schematically in Figure 5, which shows a semi-log plot of the composition "z_i" versus the carbon number "n" of the individual components in a hydrocarbon system. The parameter "A" can be determined from the plot or defaulted to C_7; that is, A = 7. The value of the second parameter, B, ranges from 50 to infinity; that is, $50 \le B \le 1$. However, Behrens and Sandler pointed out that the exact choice of the cutoff is not critical.

Selecting the index, I, of the distribution function F(I) to be the carbon number, n, Behrens and Sandler proposed the following exponential form of F(I):

$$F(n) = D(n)e^{an}dn \qquad\qquad \text{Eq.(163)}$$

Where,
$A \le n \le B$

Parameter (a) is found using the following function:

$$f(a) = \left(\frac{1}{a}\right) - \bar{c}_n + A - \frac{[A-B]e^{-Ba}}{e^{-Aa} - e^{-Ba}} = 0 \qquad\qquad \text{Eq.(164)}$$

Where $\bar{c}_n$ represents the average carbon number, as is found by the following equation:

$$\bar{c}_n = (M_{C7+} + 4) / 14 \qquad\qquad \text{Eq.(165)}$$

An initial value of "a" is given by the following equation:

$$a \ = \ [1 / \bar{c}n] - A \qquad\qquad \text{Eq.(166)}$$

Using the Newton-Raphson method to solve for the function $f(a)$, the initial value of "a" which was previously calculated and substituting the average carbon number equation into $f(a)$, the following equation results:

$$z_{7+} = \int_A^B D(n)e^{-an}dn = 1.0 \qquad\qquad \text{Eq.(167)}$$

After changing the range of integration from A to 0 and from B to c, and after transforming the variables, the following expression results:

$$z_{7+} = \int_0^c D(r)e^{-r}dr \qquad\qquad \text{Eq.(168)}$$

Where,
$c = a(B - A)$

r: is the dummy variable of integration.

Gaussian quadrature numerical integration method was applied with two-point integration to the above equation, and this gave the following expression:

$$z_{7+} = \sum_{i=1}^{2} D(r_i)w_i = D(r_1)w_1 + D(r_2)w_2 \qquad \text{Eq.(169)}$$

Where,
r_i: are the roots for quadrature of integrals after variable transformation.
w_i: is the weighting factor of Gaussian quadrature at point "i".
The values of r_1, r_2, w_1 and w_2 are given in Table 14.
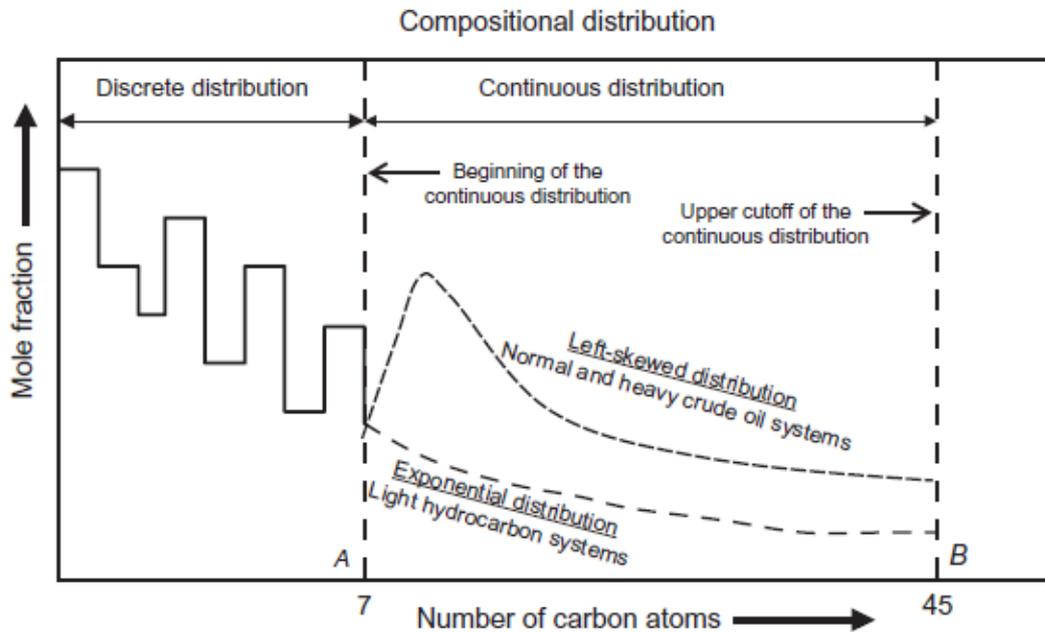
Figure 5: Schematic illustration of the semi-continuous distribution model.

Table 14: Behrens and Sandler Roots and Weights for Two-Point Integration.

C	r_1	r_2	w_1	w_2	c	r_1	r_2	w_1	w_2
0.30	0.0615	0.2347	0.5324	0.4676	4.40	0.4869	2.5954	0.7826	0.2174
0.40	0.0795	0.3101	0.5353	0.4647	4.50	0.4914	2.6304	0.7858	0.2142
0.50	0.0977	0.3857	0.5431	0.4569	4.60	0.4957	2.6643	0.7890	0.2110
0.60	0.1155	0.4607	0.5518	0.4482	4.70	0.4998	2.6971	0.7920	0.2080
0.70	0.1326	0.5347	0.5601	0.4399	4.80	0.5038	2.7289	0.7949	0.2051
0.80	0.1492	0.6082	0.5685	0.4315	4.90	0.5076	2.7596	0.7977	0.2023
0.90	0.1652	0.6807	0.5767	0.4233	5.00	0.5112	2.7893	0.8003	0.1997
1.00	0.1808	0.7524	0.5849	0.4151	5.10	0.5148	2.8179	0.8029	0.1971
1.10	0.1959	0.8233	0.5932	0.4068	5.20	0.5181	2.8456	0.8054	0.1946
1.20	0.2104	0.8933	0.6011	0.3989	5.30	0.5214	2.8722	0.8077	0.1923
1.30	0.2245	0.9625	0.6091	0.3909	5.40	0.5245	2.8979	0.8100	0.1900
1.40	0.2381	1.0307	0.6169	0.3831	5.50	0.5274	2.9226	0.8121	0.1879
1.50	0.2512	1.0980	0.6245	0.3755	5.60	0.5303	2.9464	0.8142	0.1858
1.60	0.2639	1.1644	0.6321	0.3679	5.70	0.5330	2.9693	0.8162	0.1838

1.70	0.2763	1.2299	0.6395	0.3605	5.80	0.5356	2.9913	0.8181	0.1819
1.80	0.2881	1.2944	0.6468	0.3532	5.90	0.5381	3.0124	0.8199	0.1801
1.90	0.2996	1.3579	0.6539	0.3461	6.00	0.5405	3.0327	0.8216	0.1784
2.00	0.3107	1.4204	0.6610	0.3390	6.20	0.5450	3.0707	0.8248	0.1754
2.10	0.3215	1.4819	0.6678	0.3322	6.40	0.5491	3.1056	0.8278	0.1722
2.20	0.3318	1.5424	0.6745	0.3255	6.60	0.5528	3.1375	0.8305	0.1695
2.30	0.3418	1.6018	0.6810	0.3190	6.80	0.5562	3.1686	0.8329	0.1671
2.40	0.3515	1.6602	0.6874	0.3126	7.00	0.5593	3.1930	0.8351	0.1649
2.50	0.3608	1.7175	0.6937	0.3063	7.20	0.5621	3.2170	0.8371	0.1629
2.60	0.3699	1.7738	0.6997	0.3003	7.40	0.5646	3.2388	0.8389	0.1611
2.70	0.3786	1.8289	0.7056	0.2944	7.70	0.5680	3.2674	0.8413	0.1587
2.80	0.3870	1.8830	0.7114	0.2886	8.10	0.5717	3.2992	0.8439	0.1561
2.90	0.3951	1.9360	0.7170	0.2830	8.50	0.5748	3.3247	0.8460	0.1540
3.00	0.4029	1.9878	0.7224	0.2776	9.00	0.5777	3.3494	0.8480	0.1520
3.10	0.4104	2.0386	0.7277	0.2723	10.00	0.5816	3.3811	0.8507	0.1493
3.20	0.4177	2.0882	0.7328	0.2672	11.00	0.5836	3.3978	0.8521	0.1479
3.30	0.4247	2.1367	0.7378	0.2622	12.00	0.5847	3.4063	0.8529	0.1471
3.40	0.4315	2.1840	0.7426	0.2574	14.00	0.5856	3.4125	0.8534	0.1466
3.50	0.4380	2.2303	0.7472	0.2528	16.00	0.5857	3.4139	0.8535	0.1465
3.60	0.4443	2.2754	0.7517	0.2483	18.00	0.5858	3.4141	0.8536	0.1464
3.70	0.4504	2.3193	0.7561	0.2439	20.00	0.5858	3.4142	0.8536	0.1464
3.80	0.4562	2.3621	0.7603	0.2397	25.00	0.5858	3.4142	0.8536	0.1464
3.90	0.4618	2.4038	0.7644	0.2356	30.00	0.5858	3.4142	0.8536	0.1464
4.00	0.4672	2.4444	0.7683	0.2317	40.00	0.5858	3.4142	0.8536	0.1464
4.10	0.4724	2.4838	0.7721	0.2279	60.00	0.5858	3.4142	0.8536	0.1464
4.20	0.4775	2.5221	0.7757	0.2243	100.00	0.5858	3.4142	0.8536	0.1464
4.30	0.4823	2.5593	0.7792	0.2208	1	0.5858	3.4142	0.8536	0.1464

The following steps are the computational sequences of Behrens and Sandler's lumping method:

1- The endpoints of the distribution (A and B) are found using the following expression:

A = (starting carbon number) – 0.5

B = (ending carbon number) + 0.5

2- Solving the function $f(a)$ in order to calculate the value of parameter (a).

3- Determine the upper limit of the integration (c) using the following expression:

$$c = a(A - B) \qquad \text{Eq.(170)}$$

4- Find the integration point r_1, r_2 and the weighting factors w_1 and w_2 from table (1.7).

5- Find the pseudo-component carbon numbers "n_i" and mole fractions "z_i" from the following expressions:

For the first pseudo-component:

$$n_1 = (r_1/a) + A \qquad \text{Eq.(171)}$$

$$z_1 = w_1 z_{7+} \qquad \text{Eq.(172)}$$

For the second pseudo-component:

$$n_2 = (r_2/a) + A \qquad \text{Eq.(173)}$$

$$z_2 = w_2 z_{7+} \qquad \text{Eq.(174)}$$

6- Assign the critical and physical properties of the two pseudo-components from Table 15 [10].

Table 15: Generalized Physical Properties.

Group SCN	T_b (°R)	γ	K_w	M	T_c (°R)	p_c (psia)	ω	V_c (ft³/lb)
C_6	607	0.69	12.27	84	914	476	0.271	5.6
C_7	658	0.727	11.96	96	976	457	0.310	6.2
C_8	702	0.749	11.87	107	1027	428	0.349	6.9
C_9	748	0.768	11.82	121	1077	397	0.392	7.7
C_{10}	791	0.782	11.83	134	1120	367	0.437	8.6
C_{11}	829	0.793	11.85	147	1158	341	0.479	9.4
C_{12}	867	0.804	11.86	161	1195	318	0.523	10.2
C_{13}	901	0.815	11.85	175	1228	301	0.561	10.9
C_{14}	936	0.826	11.84	190	1261	284	0.601	11.7
C_{15}	971	0.836	11.84	206	1294	268	0.644	12.5
C_{16}	1002	0.843	11.87	222	1321	253	0.684	13.3
C_{17}	1032	0.851	11.87	237	1349	240	0.723	14
C_{18}	1055	0.856	11.89	251	1369	230	0.754	14.6
C_{19}	1077	0.861	11.91	263	1388	221	0.784	15.2
C_{20}	1101	0.866	11.92	275	1408	212	0.816	15.9
C_{21}	1124	0.871	11.94	291	1428	203	0.849	16.5
C_{22}	1146	0.876	11.95	300	1447	195	0.879	17.1
C_{23}	1167	0.881	11.95	312	1466	188	0.909	17.7
C_{24}	1187	0.885	11.96	324	1482	182	0.936	18.3
C_{25}	1207	0.888	11.99	337	1498	175	0.965	18.9
C_{26}	1226	0.892	12.00	349	1515	168	0.992	19.5
C_{27}	1244	0.896	12.00	360	1531	163	1.019	20.1
C_{28}	1262	0.899	12.02	372	1545	157	1.044	20.7
C_{29}	1277	0.902	12.03	382	1559	152	1.065	21.3
C_{30}	1294	0.905	12.04	394	1571	149	1.084	21.7
C_{31}	1310	0.909	12.04	404	1584	145	1.104	22.2
C_{30}	1326	0.912	12.05	415	1596	141	1.122	22.7
C_{33}	1341	0.915	12.05	426	1608	138	1.141	23.1
C_{34}	1355	0.917	12.07	437	1618	135	1.157	23.5
C_{35}	1368	0.92	12.07	445	1630	131	1.175	24
C_{36}	1382	0.922	12.08	456	1640	128	1.192	24.5
C_{37}	1394	0.925	12.08	464	1650	126	1.207	24.9
C_{38}	1407	0.927	12.09	475	1661	122	1.226	25.4
C_{39}	1419	0.929	12.10	484	1671	119	1.242	25.8
C_{40}	1432	0.931	12.11	495	1681	116	1.258	26.3
C_{41}	1442	0.933	12.11	502	1690	114	1.272	26.7
C_{42}	1453	0.934	12.13	512	1697	112	1.287	27.1
C_{43}	1464	0.936	12.13	521	1706	109	1.300	27.5
C_{44}	1477	0.938	12.14	531	1716	107	1.316	27.9

11. Tuning an Equation of State

Tuning an EOS is the process of adjusting the parameters of the EOS in order to achieve a satisfactory match between the laboratory fluid PVT "pressure-volume-temperature" data and the data resulted from the equation of state used. The laboratory data are from several lab tests made on the reservoir's fluid, such as; constant composition expansion test "CCE", constant volume depletion test "CVD", swelling test, separator test, minimum miscibility pressure test "MMP", differential liberation test "DL", etc.

Equations of state are used as mentioned before, to determine the volumetric and phase behavior of petroleum reservoir fluids, and to predict the performance of surface separation facilities. This means, that in order to provide a meaningful and a reliable prediction from the equation of state, tuning should be done first.

Manual adjustments (by directly changing the value of the property in the component table) through trial and error or an automatic nonlinear regression algorithm are used to adjust the equations of state parameters to achieve a match between laboratory and equation of state results. Regression variables are based on selecting a number of EOS parameters that may be adjusted or tuned to achieve a match between the experimental and EOS predictions.

11.1 Equation of State tuning parameters

There are several parameters in each EOS available for tuning and here are the most commonly used tuneable parameters "parameters used as regression variables:

1- Critical properties of the undefined fraction components, such as; critical pressure - "p_c", critical temperature "T_c" and critical volume "V_c".
2- The acentric factor "ω" of the undefined fraction components.
3- The Ω modifications of the undefined fraction components
4- Binary Interaction Coefficients "k_{ij}" between the methane and the plus fractions.
5- Binary Interaction Coefficients "k_{ij}" between the methane and the non-hydrocarbon components.

The weight factors are important options that are used in WinProp, these weight factors are assigned for each of the tuneable properties, and they play a very important role in the tuning process. In other words, the weight factors give the user the opportunity to give more emphasis on some data that he/she prefers to be better tuned, and this is done by simply increase the weight factor of the property that he/she wants from the software to focus on, and bring its predicted value

closer to the laboratory measured value. The default value of the weight factor is 1.0.

WinProp uses a set of upper and lower bounds, these bounds corresponds to upper and lower values of each property that it is allowed to reach during the regression process. For most properties, these bounds are assigned to 20% above or below the original value. These bounds can be easily adjusted by the user, by the user should be careful not to give flexibility to the regression and gives values for the regression parameters that have no physical explanations.

The regression feature of WinProp is used to tune the equation of state to match the experimental measurements. WinProp uses the regression procedure of Agarwal et al.[45]. To start the regression process, the software will look at the regression parameters which were chosen and will order the most sensitive parameters to be used first. The regression is performed on a small number of parameters at a time. The default is to use a subset of five parameters, although this number can be modified. Once a parameter reaches the maximum or minimum value allowed (upper or lower bounds) or when it reaches to a point when no more improvement in the matching is resulted, the parameter is replaced by the next parameter that hasn't been used from the ordered list.

Tuning an equation of state could be done using two different methods; the stepwise method and the sequential method. The stepwise tuning method, is tuning the equation of state for each laboratory test individually, in other words, for example, tuning against the saturation pressure of the fluid sample, and after having this property well-tuned, or when no more significant improvements could be done, an update of the component properties is made, and after that the properties of the next laboratory test data are tuned like CCE, DV…etc, and so on. On the other hand, the sequential tuning consists in tuning the equation of state to match the laboratory data from more than one test at the same time until no more significant improvements could be done. Till today, several studies have been done to find the difference between these two methods, and when should each method be used in order to get a better match, but without any solid and undisputable conclusions. Usually experience is used to decide to follow the stepwise or the sequential method or any other one.

12.   Previous Work "Literature Review"

12.1 Validation of splitting the hydrocarbon plus fraction: First step in tuning equation of state.[46]

To tune an EOS the following steps are needed:

1- Extend the measured composition (split the plus fraction) into single carbon number (SNC)."Most of the literatures propose to split the plus fraction to SCN 45+".

2- Match the saturation pressure using the extended composition at the reservoir temperature by changing the molecular weight of the plus fraction.

3- Group the SCN into multiple carbon number groups (MCN) or pseudo-components, and assign the critical properties and the acentric factor for these pseudo-components.

4- Match the saturation pressure using the MCN groups composition at the reservoir temperature.

5- Match the pressure-volume-temperature (PVT) properties.

Constraints for splitting the plus fraction or for grouping the experimental composition to a plus fraction:

1- $\sum_{i=7}^{N} Zi = Z_{Cn}^{+}$

2- $\sum_{i=7}^{N} Zi . MWi = Z_{Cn}^{+} . MW_{Cn}^{+}$

3- $\sum_{i=7}^{N} (Zi . MWi / \gamma i) = (Z_{Cn}^{+} . MW_{Cn}^{+} / \gamma_{Cn}^{+})$

Katz and Firoozabadi[47] verified that the use of the extended composition of C_7^+ with Peng-Robinson EOS, will give more accurate PVT predictions for crude oil and gas condensate mixtures.

Methods for splitting the plus fraction, based on the distribution function proposed:

1- Whitson[48], who proposed a three parameter gamma distribution function to describe the relation between the mole fraction and the molecular weight of SCN components of the plus fraction.

2- Pedersen et al[49], who proposed a logarithmic relationship between the mole fraction and the carbon number.

3- Ahmed et al[50,51], who proposed a system of equations, the first equation uses the experimental specific gravity of the plus fraction (C_7^+) to find the slope, and the second equation is to calculate the molecular weight of the octanes plus fraction by using the slope which was found from the first equation.

4- Katz[52], who proposed an exponential function which requires the mole fraction of C_7^+ only.

Most of the proposed methods split the plus fraction to C_{45}^+.

In industry, it is believed that the distribution of the mole fraction of components that are heavier that heptane (C_7) has an exponential trend line.

In this paper, they used the method which was proposed by Whitson to split the plus fraction into single carbon number groups. As mentioned above, Whitson used a three-parameter gamma distribution function:

$$P(M) = \frac{(M-\eta)^{\alpha-1}\exp[-\frac{M-\eta}{\beta}]}{\beta^{\alpha}.\Gamma(\alpha)}$$

$$\beta = (M_{Cn}{}^{+} - \eta) / \alpha$$

Where,

η: is an adjustable variable with different values, used to see which value will increase the agreement between the experimental and the calculated mole fraction.

M: is the molecular weight of the component.

Γ: is the gamma function.

α : it affects the shape of the distribution, in this study it is equal to unity, because it is believed that the distribution of the mole fractions for the hydrocarbon components heavier than C_7 is exponential.

The cumulative frequency of occurrence for each single carbon number with molecular weight boundaries between M_{i-1} and M_i, is calculated from the integration of the probability function.

$$f = \int_{Mi-1}^{Mi} P(M)dM = P(M_i) - P(M_{i-1})$$

In order to find the integration, the molecular weight boundaries should be found, in this paper, two methods were introduced in order to find the value of the integration.

The Mid Point Average Method which calculates the cumulative frequency of occurrence for component "i" by integrating the distribution function. In this paper the molecular weights that were used are those proposed by Katz and Firoozabadi[47], and those proposed by Whitson[48]. These midpoints are used as the lower and the upper limits for the integration.

$$f_i = -e^{(\frac{\eta}{\beta})}. (e^{(\frac{Mi+0,5}{-\beta})} - e^{(\frac{Mi-0,5}{-\beta})}) \qquad\qquad \text{Eq.(175)}$$

The Normal Cut Method is the second method for calculating the cumulative frequency of occurrence by integrating the gamma distribution function. This method uses for the integration boundaries the molecular weight of component i and the previous component (i-1).

$$f_i = -e^{(\frac{\eta}{\beta})}. (e^{(\frac{Mi}{-\beta})} - e^{(\frac{Mi-1}{-\beta})}) \qquad\qquad \text{Eq.(176)}$$

The value of η could be calculated using one of the following methods:

1- Midpoints between SCN molecular weights of the lighter component in the plus fraction and the previous component. This method uses the molecular weights that were proposed by Whitson[48] and Katz and Firoozabadi[47].

2- This method is the same as the previous one, except that the molecular weights that are going to be used are those of the normal paraffin.

3- This method will give η the value of the molecular weight of the normal paraffin which is smaller than the plus fraction.
4- This method will give η the value of the average molecular weight for SCN groups that were proposed by Whitson[48] and Katz and Firoozabadi[47] which is smaller than the plus fraction.
5- η is calculated as recommended by Whitson, using the following equation:
$$\eta = (14*n) - 6$$
Where, n represents the plus fraction number.

The mole fraction of each SCN is calculated using the following equation:

$$z_i = z_{plus} \cdot f_i \qquad\qquad Eq.(177)$$

The mole fraction of the heaviest SCN group of the extended components is calculated using the following equation:

$$z_{Cn+} = z_{plus} - \sum_{i=1}^{ne-1} zi \qquad\qquad Eq.(178)$$

The molecular weight of the heaviest fraction is calculated using the following equation:

$$M_{Cn+} = \frac{z_{plus} \cdot M_{plus} - \sum_{i=1}^{ns-1} Z_i \cdot M_i}{Z_{cn+}} \qquad\qquad Eq.(179)$$

From this research, it was concluded that:
1- When splitting a fluid composition with a plus fraction either C_7^+ or C_{11}^+ the cumulative frequency of occurrence is better calculated using the Normal Cut Method than using the Mid-Point Average Method, with a value of η equal to the molecular weight of the normal alkane smaller than the plus fraction.
2- When assigning average molecular weight to the SCN groups, Katz and Firoozabadi correlations gave more accurate molecular weights of the extended plus fraction (C_{45}^+) than those calculated with Whistson correlation.
3- The method Whitson proposed was the most accurate method to split the hydrocarbon plus fraction compared to the other three methods used in this study.

12.2 Tuning an equation of state – The critical importance of correctly grouping.[53]

The selection of single carbon number groups that are grouped into multiple carbon number groups has a severe effect on the calculation of the critical point of the mixture. This in turn affects the maximum constant volume line of the phase diagram at reservoir temperature.

The position of the critical point is important due to the fact that, it controls the shape of the phase diagram, since the bubble point pressure and the dew point pressure lines converge at the critical point. Also the quality lines all converge at the critical point.

Grouping the extended composition into MCN:

The decision of how many MCN groups is there going to be from the extended SCN groups, and the split of the composition assigned to each of these MCN groups is more of an art than of a science.

In this study the extended SCN groups are grouped into two MCN groups, MCN1 and MCN2, and the intermediates were grouped as recommended by Pedersen et al[54] into, ethane-propane and butanes- pentanes-hexanes. The pure components (N2, H2S, CO2 and CH4) were not grouped and they stayed as they are. In other words, this resulted into a maximum of four pure components and four grouped pseudo-components.

To group the critical properties of MCN1 and MCN2 as well as the two pseudo-components from the combined intermediate components, the procedure proposed by Leiboviri[55] was used. Twu and Coon[56] procedure was used in grouping the acentric factor of the four pseudo-components. The resulting compositions and properties were used to calculate the saturation pressure of the mixture and it was found that it gave a value close to that measured experimentally. So a correction factor (Ψ_b) was introduced, that is a ratio between the critical temperature and the critical pressure of the heaviest component MCN2. This correction factor was altered according to the procedure of Aguilar[57] to regain the match of the saturation pressure.

The values of critical temperature and critical pressure of the mixture calculated with the equation of state were strongly affected by the way the two MSN`s were split.

In this study, it was found that the alteration of the acentric factor of MCN2 to match the saturation pressure was as effective as the alteration of the critical temperature to critical pressure ratio (Ψ_b). Alteration of the acentric factor value is much easier than that of the (Ψ_b).

From this work, the main conclusion was that the grouping scheme used to prepare composition for EOS calculations is very important in order to get satisfactory results. Eight components or pseudo-components are enough to get and obtain acceptable results in EOS calculations

12.3 A Comparison of EOS Tuning Simulation.[58]

Hoffman plots[59] are useful to identify trends in the data.

The Peng- Robinson EOS generally under predicts the "K" value for methane from 14.7 to 1000 psia and 100±50F.

Binary Interaction Coefficients (BIC) is determined using a modified Chueh-Prausnitz relationship:

$$\delta_{ij} = A_i . \left\{ 1 - \left[\frac{\sqrt{2Vc i^{\frac{1}{3}} * Vc j^{\frac{1}{3}}}}{Vc i^{\frac{1}{3}} + Vc j^{\frac{1}{3}}} \right]^P \right\} \qquad \text{Eq.(180)}$$

Where, Ai and P are the two tuning parameters for BIC.

Omegas are determined using the following relation:

$$a_c = \Omega_a \frac{(RTc)^2}{Pc} \qquad \text{Eq.(181)}$$
$$b_c = \Omega_b \frac{(RTc)^2}{Pc} \qquad \text{Eq.(182)}$$

Where Ωa was given a value of 0.45724 and by finding the values of T_c and P_c we find the value of Ω_b.

Material Balance calculations serve two purposes:
1- As a quality check of the data.
2- The equation of state is tuned to match the incremental mass value of V/F determined for the differential liberation, contact and separator experiments. (V/F = mass fraction of vapor from a flash).

The equation of state's strength lies in its ability to match the compositional paths in mass or molar units.

12.4 Monitoring PVT Properties Derivatives Ensures Physically Sound Tuned EOS Behaviour over Entire Operating Conditions Range.[60]

Equation of state accuracy depends on the following:
1- The nature if the fluids.
2- The type of equation selected.
3- Operator-dependent tuning procedure.

Pedersen[61] recommends tuning solely the molecular weights of the plus fractions rather than the entire list of tunable EOS parameters.

Wang[62] proposes that the adjusted parameters be maintained within reasonable physical limits and with a monotonically decreasing or increasing trend with carbon number.

Differentiation with respect to composition provides properties derivatives which are only slightly affected by the normalization in the concentration of the remaining (n-1) components, which means that its effects are negligible.

The derivatives were produced from the Peng Robinson EOS.
The properties of the components were obtained by using the Kesler Lee[63] correlations.
The properties of the heavy end where obtained from the Twu[64] correlations using the reported molecular weight and specific gravity.
The interaction coefficients used were obtained from the Oellrich[65] correlation.

Using the derivatives is one way of checking the sensitivity of a specific PVT property with respect to component properties. In other words, based on the value of the derivative, we can have an idea of how much that component property affects our PVT property; the higher the value of the derivative the more sensitive the PVT property is to it.

12.5 Fully Automatic Procedure for Efficient Reservoir Fluid Characterization.[66]

Coats, K.H and Smart, G.T[67] summarized some important observations involved in a manual EOS-tuning processes, which include:

1- Do not include any regression variable that, by inspection, can have only a negligible effect on calculated results.
2- Use an optimal regression variable set. Too many variables may result in no convergence of nonlinear regression or a drift of regression to the maximum number of iterations. Too few regression variables may yield poor match to the lab data.
3- The characteristics of an optimal regression variable set are that the regression converges; the variable values converged upon are realistic; deletion of any member of variable set results in either or both of (1) a significant worse match and (2) unrealistic variable values; and addition of any other EOS parameter results in either or both of (1) no convergence and (2) insignificantly better data match.

When multiple fluid samples exist, the "MASTER" fluid sample is determined first. Usually, the master fluid sample is the reservoir fluid sample at the reservoir pressure and temperature. When different reservoir fluid samples exist, the one that dominates the simulation process should be chosen as the master fluid sample.

For a given cubic equation of state (PR EOS, for example), the parameters, which may be tuned, include: EOS parameters Ω_a and Ω_b, critical temperature T_c, acentric factor A_c, volume correction parameter V_{cr}, molecular weight MW, and binary interaction parameters (BIN).

12.6 An Efficient Tuning Strategy to Calibrate Cubic EOS.[68]

In this study the plus fraction is extended into 45 single carbon number groups (SCN) using a gamma probability function. Then critical pressure, critical temperature, and acentric factor are assigned to each SCN using the best available correlations. And the laboratory measured saturation pressure of the fluid is matched by adjusting the molecular weight of the heaviest SCN.

The critical properties for the grouped components are assigned with a methodology that preserves the coefficients, *a* and *b*, of the equation of state that previously matched the saturation pressure.

Peng- Robinson equation of state is claimed to be more suitable for volumetric predictions. In this study, volume shift parameters are used to improve the volumetric capability of the Peng-Robinson EOS.

Binary interaction coefficients (BIC) between hydrocarbon components are assumed to be zero while between non- hydrocarbons and hydrocarbon components are set different than zero.

The gamma probability function is used to extend the plus fraction into 45 single carbon number groups (SCN). This model is useful for extending the plus fraction because it preserves the measured molecular weight of the plus fraction.

In this study the parameter η was calculated as the average molecular weight between the first single carbon number group at which the molar extension starts and the previous SCN group.

Whitson[69] defined the Watson characterization factor, *K*, as a function of molecular weight and specific gravity. And this can be calculated with the following equation:

$$K = 4.5579 \cdot M_t^{\,0.15178} \cdot \gamma_t^{\,-0.84573} \qquad \text{Eq.(183)}$$

$$\gamma_i = \left[\frac{K}{4.5579 * Mi^{0.15178}}\right]^{-1/0.84573} \qquad \text{Eq.(184)}$$

A value for the constant characterization factor "K" should be assumed first and then the specific gravity for each SCN should be found using equation (181), and then the specific gravity of the heaviest plus fraction should be found using the following equation:

$$\gamma_{plus} = \frac{Zplus * Mplus}{\sum_{i=1}^{m} Zi * \frac{Mi}{\gamma i}} \qquad \text{Eq.(185)}$$

In order to simplify the equations and for a direct calculation of the characterization factor "K" some rearrangements of the above equations were done and the following equations were concluded:

$$K = \left[\frac{\xi. \gamma plus}{Zplus . M\,plus}\right]^{-0.84573} \qquad \text{Eq.(186)}$$

$$\xi = \left(\sum_{i=1}^{m} [4.5579 * Mi^{0.15178}]^{-1/0.84573}\right) * zi * Mi \qquad \text{Eq.(187)}$$

Starting from the above equations (184 & 185), the value of "K" should be calculated first and then the specific gravity for each SCN should be found using equation (182). With this way the value of the specific gravity of the plus fraction was preserved.

Using the extended composition to match the saturation pressure:

The molecular weight of the plus fraction is the first parameter that is going to be used for the tuning process. This is due to the fact that a 20% experimental error is most likely inherited to the molecular weight determination.

The laboratory analysis measures the fluid composition in weight fraction, while EOS calculations require the composition in mole fraction. This means that if the molecular weight of any component "the plus fraction "is changed, the mole fraction must be recalculated. In other words, the accuracy of the molar composition to be used in the phase behavior calculations depends on the accuracy of the molecular weight of the plus fraction.

To match the saturation pressure the following steps were followed:
1- Calculate the apparent molecular weight of the fluid using the following equation:

$$M_a = \sum_{i=1}^{n} z_i \, M_i \qquad\qquad \text{Eq.(188)}$$

2- Calculate the weight fraction of each component of the fluid using the following equation:

$$w_i = z_i.M_i \, / M_a \qquad\qquad \text{Eq.(189)}$$

3- The weight fractions are maintained constant, and the molar composition is recalculated with each change in the molecular weight of the plus fraction. The new molar composition of all components except the plus fraction is calculated after each adjustment of the apparent molecular weight of the fluid.

$$Z_i = w_i \, *M_a/M_i \qquad\qquad \text{Eq.(190)}$$

4- The mole fraction and the molecular weight of the plus fraction is calculated using the following equations:

$$z_{plus} = 1 - \sum_{i=1}^{n} z_i \qquad\qquad \text{Eq.(191)}$$

$$M_{plus} = \frac{Ma - \sum_{i=1}^{n} z_i.M_i}{zplus} \qquad\qquad \text{Eq.(192)}$$

5- The mole fraction and the molecular weight of the heaviest SCN group of the extended components is calculated using the following equation:

$$z_{Cn+} = z_{plus} - \sum_{i=1}^{ne-1} z_i \qquad\qquad \text{Eq.(193)}$$

$$M_{Cn+} = \frac{Zplus.Mplus - \sum_{i=1}^{ns-1} Z_i.Mi}{Zcn+} \qquad\qquad \text{Eq.(194)}$$

6- The apparent molecular weight is changed until the calculated saturation pressure equals to the measured saturation pressure.

The magnitude of the adjustment of the molecular weight of the plus fraction required to match the measured saturation pressure depends in the choice of equation of state,

the number of pseudo-components representing the plus fraction, the selection of critical property correlations, and the accuracy of the experimental data.

Assigning critical properties and acentric factor

Critical pressure and critical temperature were calculated using the following correlations:

1. Riazi-Daubert[20]
2. Twu[64]
3. Cavett[22]
4. Lee-Kesler[70]
5. Riazi-Al-Hassaf[71]
6. Pedersen et al[61]

Acentric factors to each SCN were assigned using the following correlations:

1. Lee-Kesler[70]
2. Kesler- Lee[63]
3. Edminister[24]
4. Pedersen et al[61]
5. Riazi-Al-Hassaf[71]

The critical properties of each MCN is determined by Leibovici's[55] method using the equation of state mixing rules to minimize the changes to the grouped EOS parameters a and b which had been calculated previously with the extended composition.

1. An initial trial value of T_{cm} "critical temperature of each MCN" using the following equation:

$$T_{cm} = [\sum_{i=1}^{m} \sum_{j=1}^{m} \frac{Tci*Tcj}{\sqrt{Pci*Pcj}}] / [\sum_{i=1}^{m} zi.\frac{Tci}{Pci}] \qquad \text{Eq.(195)}$$

2. The critical pressure for each MCN is calculated using the following equation:

$$\frac{Tcm}{Pcm} = \sum_{i=1}^{m} zi.\frac{Tci}{Pci} \qquad \text{Eq.(196)}$$

3. The values of the constants for each MCN, a_{cm} and b_m, can be determined using the following equations:

$$a_{cm} = 0.45724 \frac{R^2*Tcm^2}{Pcm} \qquad \text{Eq.(197)}$$

$$b_m = 0.07780 \frac{R*Tcm}{Pcm} \qquad \text{Eq.(198)}$$

Twu and Coon[56] derived an equation to determine the temperature dependent term, a_m, for each MCN.

Setting the binary interaction coefficients to zero for hydrocarbon to hydrocarbon interactions and nonzero for non-hydrocarbon to hydrocarbon interactions reduces the computational time and gives excellent results.

Volume translation parameters are correction terms that are applied to the molar volume calculated with the equation of state, and they improve the volumetric capability of the equations of state.

Splitting MCN1 into MCN1a and MCN1b may improve the match of volumetric data. Approximately 60% and 5% of the former MCN1 mole fraction should be assigned to the MCN1b pseudo-component for volatile oils and retrograde gases, respectively.

Properly distributing the SCN into the two MCN groups is of vital importance because the grouping scheme has a strong influence on the calculated critical locus. Thus, the grouping scheme affects the performance of regression on volumetric data.

Setting the binary interaction coefficients to zero for hydrocarbon-to-hydrocarbon interactions and nonzero for non-hydrocarbon-to-hydrocarbon interactions reduces the computational time and gives excellent results.

12.7 Application of a Regression-Based EOS PVT program to Laboratory Data.[72]

This paper states that splitting the C_7^+ fraction to match the laboratory PVT data in not necessary.

The PVT program has internally stored binary interaction coefficients (BIC) closely resemble values given by Yarborough[73] for Redlich-Kwong (RK) EOS and values given by Ktaz et al for Peng-Robinson (PR) EOS. But for user components which are not assigned in the internal table, it can either be entered by the user, or it can be determined by interpolation on the basis of molecular weight (MW).

The PVT program preserves the molecular weight, the mole fraction and the specific gravity of the plus fraction, when the plus fraction is split into extended fractions.

The default weight factors are one (1) with the exceptions of values of forty (40) and twenty (20) for the saturation pressure and the density, respectively.

If several samples are in a data set, each with saturation pressure and density, then the first sample will get weight factors of forty and twenty for its saturation pressure and density, respectively, and the other samples will get values of twelve and two for saturation pressure and density.

The theoretical values of $\Omega_{a \text{ and }} \Omega_b$ for Peng-Robinson EOS are roughly 0.4572 and 0.0778, respectively.

And those for Redlich-Kwong are 0.4275 and 0.0866, respectively.

The default lower and upper limits of the omegas are as follows:

$\Omega_a = (0..1, 1.3)$

$\Omega_b = (0..02, 0.25)$

The default limits on binary interaction coefficients (BIC) are (-1.0, 0.9).

12.8 On the Dangers of Tuning EOS Parameters.[74]

Tuning an equation of state (EOS) to measure the PVT data and the measured bubble and dew points is used to find the EOS parameters to needed to describe the properties of the mixture.

The tuned EOS must give reliable predictions over a wide range of pressure, temperature and the composition of the fluid being tuned.

The tuned EOS is suitable for a specific pressure and temperature conditions (the reservoir conditions), and having a tuned EOS doesn't mean that it will improve the prediction of K-values, enthalpies or other properties of the fluid at a pressure-temperature range different than the reservoirs' one.

Pedersen at el (1984) have presented a purely predictive procedure for the determination of EOS parameters of mixtures containing undefined heavy hydrocarbons. The procedure is based in the Soave-Redlich-Kwong equation of state (Soave 1972) and uses binary interaction parameters k_{ij} equal to zero for all hydrocarbon-hydrocarbon interactions, while non-zero values may be used for interactions with non-hydrocarbons.

In order to have a successful characterization of the fluid sample, a comprehensive and an accurate analytical data is required. This is due to the fact that PVT properties are very sensitive to even small differences in the analytical data that are reported especially for the heavy end fractions. In other words, the reported analytical data should be as accurate as possible for estimating the component properties and the molar distribution of the heavy end (residue).

The analyzed reservoir fluid samples are either bottom hole sample or gas and liquid stream samples from a well-head separator. Bottom hole samples are flashed in the laboratory to standard conditions (pressure of 1 atmosphere & temperature of 15 ℃). Then the two phases of the samples are analyzed separately, and from the gas-liquid ratio the reservoir fluid composition is calculated. Gas and liquid samples are also flashed to standard conditions, and the two gas phases with the combined liquid phase are analyzed separately.

To analyze the gas phases and the lighter components of the liquid phase, gas chromatographic analysis "GC" are used. Mass spectroscopy is used as a supplementary technique to quantitatively identify components like; N2, CO2 and C1-

C9. The molecular weight and the mole fraction of the heavier components (C_{10}^+, in case the C_{10}^+ fraction is not further analyzed), must be determined based on the molecular weight of the total liquid phase at standard conditions. True boiling point distillation (TBP) is commonly used to analyze oil samples.

The composition resulting from the gas chromatography and the true boiling point distillation analyses are in weight percent, which means that in order to convert this value into molecular percentage, the molecular weight of each component should be known. For the components that were analyzed using the chromatography "the well-defined components" knowing the molecular weight is not a problem at all, as these components are well defined. But for the boiling point fractions the accuracy of the molecular composition depends on the accuracy of the measured molecular weight.

Material balance is used to check the consistency of the molecular weights knowing the measured average molecular weights and the composition of the fluid.

Physical properties of the heavy components like density and molecular weight are measured using liquid-liquid chromatography to split the TBP-fraction into saturated (paraffin) and unsaturated compounds like naphthenes and aromatics.

The procedure of Pedersen et al (1984) was used to characterize the fluid in this paper.

The procedure of Peneloux et al (1982) was used to calculate the oil densities. And a Peneloux's c-parameter of the C_7^+ fractions here was found using the following equation:

$$c = 0.597 \, MW^{0.686} \qquad\qquad\qquad\qquad \text{Eq.(199)}$$

Where, MW is the molecular weight.

12.9 Regression to Experimental PVT Data.[75]

PVT simulation programs are used to predict the volumetric properties, phase fractions and saturations points at reservoir conditions. They are also expected to be able to predict the phase behavior at process plant and transport conditions.
Standard composition analysis most often stops at either C_7^+, C_{10}^+ or C_{20}^+, due to the fact that as the carbon number increase, the diversity in chemical structure increases. In PVT simulators the plus fraction is usually represented through a number of pseudo-components with the experimental PVT data that should be assigned to the equation of state parameters. These experimental PVT data are often originated from Constant Mass Expansion, Constant Volume Depletion and Differential Liberation which are carried out at reservoir temperature.

Potential problems with Regression to PVT experimental data:

The only regression parameters are saturation points and volumetric properties.
There is no reason to believe that these parameters are valid for other properties than those used in the fit, and there is no reason to believe that the parameters are valid for

the properties of the fit outside the temperature and pressure ranges covered in the parameter estimation. This may, for example, lead to erroneous results when the program is used to generate input for conditions much different from those of the PVT experiment.

Handling of the Plus-fraction Prior to Regression:

Pedersen et al procedure for the characterization of a C_7^+ is developed from the Soave-Redlich-Kwong equation of state, with the volume translation principle as proposed by Peneloux et al.
Fortunately, reservoir fluid compositions are not completely random. Extensive composition analyses comprising very many reservoir fluids from all over the world have shown that the natural logarithm of the mole fraction of a given C_{7+} fraction is approximately a linear function of the carbon number· The density, ρ, of a given C_{7+} fraction is a measure of its aromaticity. A large density indicates a high content of aromatic compounds and a low density a high content of paraffinic and naphthenic compounds. By making the correlations for T_c, P_c and ω functions of the density, it is ensured that the distribution between paraffinic, naphthenic and aromatic compounds is taken into account.

Pedersen et al correlations

$$T_c = c_1\rho + c_2\ln MW + c_3 MW + (c_4/MW) \qquad \text{Eq.(200)}$$
$$\ln P_c = d_1 + d_2\rho + (d_3/MW) + (d_4/MW^2) \qquad \text{Eq.(201)}$$
$$m = e_1 + e_2 MW + e_3\rho + e_4 MW^2 \qquad \text{Eq.(202)}$$

Where,
$$m = 0.480 + 1.574\omega - 0.176\,\omega^2 \qquad \text{Eq.(203)}$$

and,

$c_1 = 1.6312 * 10^2$ $d_1 = -1.3408 *10^{-1}$ $e_1 = 7.4310 * 10^{-1}$

$c_2 = 8.6052 * 10$ $d_2 = 2.5019$ $e_2 = 4.8122 * 10^{-3}$

$c_3 = 4.3475 *10^{-1}$ $d_3 = 2.0846 *10^2$ $e_3 = 9.6707 *10^{-3}$

$c_4 = -1.8774 * 10^3$ $d_4 = -3.9872 * 10^3$ $e_4 = -3.7184 * 10^{-6}$

ρ is in g/cm^3, T_c in K and P_c in atm.

The coefficients in these expressions have been determined using comprehensive experimental data comprising both gas condensate and oil mixtures.

The Volume Translation Parameter as a Regression Parameter
The extended SRK equation of state suggested by Peneloux et al has the following form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+c)(V+b+2c)} \qquad \text{Eq.(204)}$$

Where P is the pressure, R is the gas constant, T is the temperature, a and b are the usual equation of state parameters and c is a volume translation parameter.
Volume translation parameter influences the density without affecting the phase equilibrium results: saturation points, phase compositions and phase amounts.
For a pure component, the molar volume calculated using the Peneloux equation equals the SRK molar volume minus the c-parameter. For a mixture, the molar volume calculated using the Peneloux equation equals the SRK molar volume minus

the molar average of the c-parameters of each component. For defined components the c-parameter may be found as suggested by Peneloux et al.:

$$c = 0.40768 \frac{RTc}{Pc}(0.29441 - Z_{RA})$$ Eq.(205)

$$Z_{RA} = 0.29056 - 0.0877\omega$$ Eq.(206)

Where, Z_{RA} is the Racket compressibility factor.

For C_{7+} pseudo components, the c-parameter may be deter- mined as the difference in the molar volume calculated using the SRK equation and the real molar volume. The latter volume may be calculated from the density at standard conditions which is available from the C_{7+} characterization. By determining the C_{7+} c- parameters in this manner, it is implicitly assumed that the difference between the real molar volume and that calculated using the SRK equation is constant, independent of T and P. This is not necessarily the case. The c-parameter is, therefore, an appropriate regression parameter in those cases when satisfactory phase equilibrium results but unsatisfactory volumetric results are obtained.

Adjustments of T_C, P_C and ω Correlations

Pedersen et al warn against the use of non-zero binary interaction coefficients as regression parameters because hydrocarbon-hydrocarbon non-zero binary interaction coefficients will often result in predictions of false liquid- liquid phase splits.

the correlations used for T_c, P_c and ω of the C_{7+} fractions are not, as is the case with T_c, P_c and ω of the defined components, founded on fundamental physical considerations. They are only empirical correlations which have been found to represent a large set of reservoir fluid PVT data very well.

Unfortunately, it is not always possible by comparing measured and calculated PVT data to decide whether deviations between measured and calculated volumetric data are due to erroneous density calculations, erroneous phase equilibrium calculations or both. This is because the volumetric results are often presented as relative volumes. For example, for gas condensate mixtures, the liquid phase volume is often recorded in percent of the saturation point volume at the same temperature. In those cases a three parameter regression is recommended with the volume translation parameter and the two most sensitive coefficients of the T_c, P_c and ω correlations as the three regression parameters.

The optimization of the equation of state against the experimental PVT data was accomplished by a stepwise regression procedure, first critically evaluating the composition data, and secondly adjusting the volume translation parameter to match experimental phase densities. For many mixtures these adjustments will be sufficient to obtain satisfactory PVT simulation results. For mixtures for which this is not the case, small adjustments in two of the coefficients of the T_c, P_c and ω correlations will usually give the desired agreement between experimental and calculated PVT data.

12.10   A simple and efficient approach for improving the prediction of reservoir fluid viscosity.[76]

In equation of state based reservoir simulators, accurate predictions of liquid and gas phase viscosities are required.

Probably the most used correlation used in reservoir simulation models is Lohrenz-Bray-Clark (LBC)[77] which was based on Jossi-Stiel-Thodos correlation[78]. LBC is a fourth-degree polynomial in the reduced density, and has the disadVantage of that the predicted viscosity is very sensitive to the density which is determined by a cubic equation of state, and it could be very inaccurate for high viscosity fluids.

Ely and Hanley[79] presented a model for predicting the viscosity of non-polar pure fluids and their mixtures. Pedersen and Fredenslund[80] proposed a new corresponding states method that is bases on the principle of corresponding states with methane as the reference component. Later Aasberg-Petersen et al[81] improved the model by introducing n-decane at the second reference component. Little and Kennedy[82] by used an analogy with the Van der Waals equation of state to correlate the viscosity of reservoir fluids. Lawal[83] applied the Lawal-Lake-Silberberg equation of state to correlate the viscosity as well.

In this paper a new method was proposed to improve the gas and liquid viscosities predictions based on the LBC correlation, this was done by introducing an exponential term and incorporating a cubic equation of state.

13.   Methodology of Tuning

In this section, the gas-oil ratio (GOR) and the oil volume factor (Bo) from separator test and differential vaporization test equations were written in a form that contains only the fundamental PVT properties. Doing so, will help us understand how each fundamental property affects the GOR and Bo values.

The following steps were followed in order to write the GOR equation in a more general form with only the fundamental properties being as inputs for the equation:

$$GOR = \frac{V_g^{sc}}{V_o^{sc}}$$
$$\text{Eq.(207)}$$

$$V = \frac{m}{\rho}$$
$$\text{Eq.(208)}$$

Where,

$V_g{}^{sc}$ represents the volume of gas at standard conditions.

$V_o{}^{sc}$ represents the volume of oil at standard conditions.

m represents the mass.

ρ represents the density.

Using Eq.2 within Eq.1 led to the following expression:

$$GOR = \frac{m_g^{sc}/\rho_g^{sc}}{m_o^{sc}/\rho_o^{sc}}$$
$$\text{Eq.(209)}$$

The following equations are used within Eq.3:

$$m_g^{sc} = n_g * MW_g^{sc}$$
$$\text{Eq.(210)}$$

$$m_o^{sc} = n_o * MW_o^{sc}$$
$$\text{Eq.(211)}$$

$$\rho_g^{sc} = \frac{p^{sc} * MW_g^{sc}}{Z * R * T^{sc}}$$
$$\text{Eq.(212)}$$

$$\rho_o^{sc} = \frac{p^{sc} * MW_o^{sc}}{Z * R * T^{sc}}$$
$$\text{Eq.(213)}$$

$$n_o = N_o/(N_o + N_g)$$
$$\text{Eq.(214)}$$

$$n_g = N_g/(N_o + N_g)$$
$$\text{Eq.(215)}$$

$$n_o + n_g = 1$$
$$\text{Eq.(216)}$$

Where,

n_o represents oil mole fraction.

n_g represents gas mole fraction.

p^{sc} represents the pressure at standard conditions.

T^{sc} represents the temperature at standard conditions.

$MW_g{}^{sc}$ represents the molecular weight of gas at standard conditions.

$MW_o{}^{sc}$ represents the molecular weight of oil at standard conditions.

R represents the universal gas constant.

Introducing Eq.4-Eq.7 into Eq.3 led to the following final expression for GOR:

$$GOR = \left(\frac{n_g}{1 - n_g}\right) * \left(\frac{Z_g^{atm}}{Z_L^{atm}}\right)$$

Eq.(217)

Where L represents the liquid phase and g represents the gas phase.

The following steps were followed in order to write Bo equation in a more general form with only the fundamental properties being as inputs for the equation:

$$Bo = \frac{V_o}{V_o^{sc}}$$

Eq.(218)

$$Bo = \frac{m_o/\rho_o}{m_o^{sc}/\rho_o^{sc}}$$

Eq.(219)

$$Bo = \left(\frac{p_{atm} * T}{T_{atm}}\right) * \left(\frac{p_{sat} * Z_L}{Z_L^{atm}}\right) * \left(\frac{1}{1 - n_g}\right)$$

Eq.(220)

From the sensitivity analysis we made in the previous section against Omega A, Omega B, the acentric factor, the critical pressure and temperature of the heavy-end component, we have found that $Z_g{}^{atm}$ through all the trials we made is almost constant. In other words, $Z_g{}^{atm}$ can be considered as constant with a value equal to unity.

By looking at Eq.8 and Eq.14, it is obvious that GOR depends mainly on (n_g) and $Z_L{}^{atm}$, whereas Bo depends mainly on (n_g), psat, $Z_L{}^{atm}$ and Z_L.

First of all, the laboratory measured n_g was calculated for both GOR and Bo that were measured from the separator test. After that $Z_L{}^{sat}$ was calculated by applying Eq. 15, using the oil density at saturation pressure that was measured from the Differential Liberation Test, and a molecular weight with a value equal to the molecular weight of the fluid reported in the Reservoir Fluid Analysis.

$$Z_L = \frac{p_{sat} * MW_o}{\rho_o^{sat} * R * T_{sat}}$$

Eq.(221)

Then, $Z_L{}^{atm}$ was calculated using Eq.16, with a molecular weight equals to the molecular weight of the fluid as measured in the Separator Fluid Analysis, and a liquid density equals to the tank liquid density measured from Separation Test.

$$Z_L^{atm} = \frac{p_{atm} * MW_o}{\rho_o^{atm} * R * T_{atm}}$$

Eq.(222)

After that, a table was made that includes the fundamental properties of the oil, and a comparison between the laboratory values and the values that were predicted from

WinProp software without any tuning or any regression process. This was done in order to see how far are the fundamental properties as predicted from the software from the laboratory values.

Then, a sensitivity table for each oil sample was made, which shows the effect of changing the properties of the heavy-end component (C12+) and those of methane (CH4) on the fundamental PVT properties. These tables were made in order to see and check which parameter affects more each property, and also to check and understand the direction each and every fundamental property of the oil follows after changing a specific parameter with a specific amount of each property of the heavy-end and methane components. Sensitivity tables show us the percentage by which each fundamental property will change after perturbing each parameter by five percent of its original (initial) value that was given from the WinProp; where the minus sign indicates a decrease way. Tables (16 – 27) represent the sensitivity tables that were made for each oil sample.

Table 16: Sensitivity Table for Oil Sample I_Part I.

Property	Pc_C12+	Pc_C1	Vc_C12+	Vc_C1	Tc_C12+	Tc_C1
ZL(atm)	-2.484	0.000	0.131	0.000	2.222	0.000
ZL(sat)	1.066	-1.149	0.323	-1.066	6.885	-5.232
MWL(atm)"g/mol"	0.040	-0.019	0.057	0.000	0.069	0.036
MWL(sat)"g/mol"	0.000	0.000	0.000	0.000	0.000	0.000
ρo (atm) "lb/ft3"	2.590	-0.004	0.004	0.000	-2.058	0.005
ρo (sat) "lb/ft3"	1.827	0.774	0.046	-0.113	1.737	-1.749
Psat"psia"	2.914	-0.387	0.372	-0.634	8.740	-6.893
Separator ng-Bo	0.018	-0.035	0.048	0.145	0.043	0.010
Separator ng-GOR	0.017	-0.006	0.043	0.000	0.040	0.006
ng'-DL	0.079	-0.071	0.044	-0.014	-0.005	-0.027
Residual Oil Density_DL	3.528	0.000	0.012	0.000	-2.926	0.012
ZL' atm- DL	-3.369	0.085	0.044	0.000	3.085	0.023
ng'/1-ng'	0.591	-0.526	0.326	-0.101	-0.039	-0.201
ng/1-ng	0.080	-0.027	0.203	0.000	0.192	0.028

Table 17: Sensitivity Table for Oil Sample I_Part II.

Property	Acentric Factor C12+	Acentric Factor C1	MW C12+	MW C1
ZL(atm)	-0.131	0.000	-0.915	0.000
ZL(sat)	1.676	0.048	0.000	0.000
MWL(atm)"g/mol"	0.030	0.000	2.625	0.000
MWL(sat)"g/mol"	0.000	0.000	1.558	0.739
ρo (atm) "lb/ft3"	0.161	0.000	2.625	0.000
ρo (sat) "lb/ft3"	0.812	0.007	1.568	0.738
Psat"psia"	2.500	0.057	0.000	0.000
Separator ng-Bo	0.013	0.000	-0.245	0.000

Separator ng-GOR	0.013	0.000	-0.194	0.000
ng'-DL	0.023	0.000	-0.119	0.000
Residual Oil Density_DL	0.172	0.000	3.540	0.000
ZL' atm- DL	-0.142	0.000	-0.884	0.000
ng'/1-ng'	0.175	0.003	-0.884	0.000
ng/1-ng	0.060	0.000	-0.915	0.000

Table 18: Sensitivity Table for Oil Sample I_Part III.

Property	Volume shift C12+	Volume shift C1	Omega A C12+	Omega A C1
ZL(atm)	-0.392	0.000	-0.261	0.000
ZL(sat)	-0.168	0.000	4.741	-3.855
MWL(atm)"g/mol"	0.000	0.000	0.072	0.008
MWL(sat)"g/mol"	0.000	0.000	0.000	0.000
ρo (atm) "lb/ft3"	0.459	0.000	0.353	0.001
ρo (sat) "lb/ft3"	0.173	0.000	2.194	-0.578
Psat"psia"	0.000	0.000	7.041	-4.409
Separator ng-Bo	0.016	0.000	0.036	0.002
Separator ng-GOR	0.014	0.000	0.035	-0.001
ng'-DL	-0.001	0.000	0.039	-0.080
Residual Oil Density_DL	0.652	0.000	0.369	0.000
ZL' atm- DL	-0.647	0.000	-0.295	0.008
ng'/1-ng'	-0.010	0.000	0.294	-0.597
ng/1-ng	0.065	0.000	0.165	-0.003

Table 19: Sensitivity Table for Oil Sample I_Part IV.

Property	Omega B C12+	Omega B C1	Exp. Value (kijs)
ZL(atm)	3.007	0.000	-0.915
ZL(sat)	-4.801	5.388	0.587
MWL(atm)"g/mol"	-0.075	0.013	0.048
MWL(sat)"g/mol"	0.000	0.000	0.000
ρo (atm) "lb/ft3"	-2.933	0.004	0.007
ρo (sat) "lb/ft3"	-3.947	-0.172	0.114
psat"psia"	-8.559	5.211	0.707
Separator ng-Bo	-0.014	0.006	-0.234
Separator ng-GOR	-0.017	0.007	-0.182
ng'-DL	-0.144	0.062	0.032
Residual Oil Density_DL	-3.798	0.012	0.012
ZL' atm- DL	3.870	0.001	0.035
ng'/1-ng'	-1.068	0.467	0.238
ng/1-ng	-0.078	0.032	-0.856

Table 20: Sensitivity Table for Oil Sample III_Part I.

Property	Pc_C12+	Pc_C1	Vc_C12+	Vc_C1	Tc_C12+	Tc_C1
ZL(atm)	-2.703	0.000	0.000	0.000	2.334	0.123
ZL(sat)	0.980	-1.095	0.504	-0.937	6.095	-9.452
MWL(atm)"g/mol"	0.005	-0.008	0.030	0.010	0.021	0.150
MWL(sat)"g/mol"	0.000	-0.211	0.000	0.000	0.000	0.000
Separator ng-GOR	-0.001	-0.006	0.039	0.016	0.036	0.276
Separator ng-Bo	-0.010	0.886	0.022	0.009	0.044	0.294
ρo (atm) "lb/ft3"	2.779	0.000	-0.002	0.002	-2.255	0.028
ρo (sat) "lb/ft3"	2.461	0.415	-0.002	-0.026	-1.275	-0.695
Psat"psia"	3.465	-0.673	0.506	-0.960	4.747	-10.084
ng'-DL	-0.065	-0.016	0.061	0.024	-0.028	0.352
Residual Oil Density_DL	2.967	0.000	0.000	0.000	-2.456	0.025
ZL' atm- DL	-2.877	-0.008	0.030	0.010	2.539	0.125
ng'/1-ng'	-0.135	-0.033	0.127	0.050	-0.058	0.731
ng/1-ng	-0.002	-0.011	0.069	0.028	0.065	0.492

Table 21: Sensitivity Table for Oil Sample III_Part II.

Property	Accentric Factor C12+	Accentric Factor C1	MW C12+	MW C1
ZL(atm)	-0.246	0.000	0.000	0.000
ZL(sat)	1.787	0.058	0.000	0.000
MWL(atm)"g/mol"	0.008	-0.001	2.813	0.001
MWL(sat)"g/mol"	0.000	0.000	2.546	0.306
Separator ng-GOR	-0.042	-0.001	0.000	0.000
Separator ng-Bo	-0.110	0.005	0.000	0.000
ρo (atm) "lb/ft3"	0.159	0.000	2.813	0.001
ρo (sat) "lb/ft3"	0.319	0.002	2.544	0.303
Psat"psia"	2.116	0.069	0.000	0.000
ng'-DL	-0.024	-0.002	-0.084	0.000
Residual Oil Density_DL	0.150	0.000	2.992	0.000
ZL' atm- DL	-0.142	-0.001	-0.174	0.001
ng'/1-ng'	-0.051	-0.004	-0.174	0.001
ng/1-ng	-0.075	-0.002	0.000	0.000

Table 22: Sensitivity Table for Oil Sample III_Part III.

Property	Volume shift C12+	Volume shift C1	Omega A C12+	Omega A C1
ZL(atm)	-0.614	0.000	-0.369	0.000
ZL(sat)	-0.403	0.043	4.380	-6.614
MWL(atm)"g/mol"	0.000	0.000	0.018	0.090
MWL(sat)"g/mol"	0.000	0.000	0.000	0.000
Separator ng-GOR	-0.055	0.000	-0.002	0.126
Separator ng-Bo	-0.123	0.014	-0.031	0.096
ρo (atm) "lb/ft3"	0.518	0.000	0.340	0.017
ρo (sat) "lb/ft3"	0.400	-0.053	0.756	-0.166
Psat"psia"	0.000	0.000	5.180	-6.760
ng'-DL	0.000	0.000	-0.055	0.207
Residual Oil Density_DL	0.561	0.000	0.324	0.012
ZL' atm- DL	-0.558	0.000	-0.305	0.077
ng'/1-ng'	-0.001	0.000	-0.115	0.430
ng/1-ng	-0.098	0.000	-0.003	0.225

Table 23: Sensitivity Table for Oil Sample III_Part IV.

Property	Omega B C12+	Omega B C1	Exp. Value (kijs)
ZL(atm)	3.194	-0.123	0.000
ZL(sat)	-4.726	8.559	0.994
MWL(atm)"g/mol"	-0.003	-0.080	0.026
MWL(sat)"g/mol"	0.000	0.000	0.000
Separator ng-GOR	0.010	-0.186	0.032
Separator ng-Bo	0.000	-0.225	0.018
ρo (atm) "lb/ft3"	-3.104	-0.017	0.001
ρo (sat) "lb/ft3"	-3.220	-0.242	0.020
Psat"psia"	-7.796	8.301	1.016
ng'-DL	0.200	-0.178	0.025
Residual Oil Density_DL	-3.279	-0.025	0.000
ZL' atm- DL	3.387	-0.055	0.026
ng'/1-ng'	0.416	-0.369	0.052
ng/1-ng	0.018	-0.331	0.058

Table 24: Sensitivity Table for Oil Sample IV_Part I.

Property	Pc_C12+	Pc_C1	Vc_C12+	Vc_C1	Tc_C12+	Tc_C1
ZL(atm)	-2.844	0.000	0.114	0.000	2.617	0.114

ZL(sat)	2.454	-2.376	0.993	-1.305	9.592	-8.618
MWL(atm)"g/mol"	0.014	-0.015	0.071	0.008	0.056	0.136
MWL(sat)"g/mol"	0.000	0.000	0.000	0.000	0.000	0.000
Separator ng-GOR	0.041	-0.007	0.080	0.005	0.050	0.113
Separator ng-Bo	0.060	-0.011	0.086	0.000	0.050	0.126
ρo (atm) "lb/ft3"	3.041	-0.002	0.004	0.001	-2.482	0.023
ρo (sat) "lb/ft3"	2.490	0.576	0.045	-0.083	-0.702	-1.178
Psat"psia"	5.001	-1.819	1.034	-1.394	8.822	-9.697
ng'-DL	-0.019	-0.031	0.070	0.009	0.034	0.200
Residual Oil Density_DL	3.356	-0.012	0.000	0.000	-2.827	0.037
ZL' atm- DL	-3.234	-0.003	0.071	0.008	2.967	0.099
ng'/1-ng'	-0.062	-0.104	0.233	0.030	0.115	0.667
ng/1-ng	0.112	-0.018	0.217	0.013	0.135	0.308

Table 25: Sensitivity Table for Oil Sample IV_Part II.

Property	Acentric Factor C12+	Acentric Factor C1	MW C12+	MW C1
ZL(atm)	-0.114	0.000	0.000	0.000
ZL(sat)	3.399	0.068	0.000	0.000
MWL(atm)"g/mol"	0.022	-0.001	3.087	0.000
MWL(sat)"g/mol"	0.000	0.000	2.513	0.518
Separator ng-GOR	0.033	0.000	0.000	0.000
Separator ng-Bo	0.040	-0.003	0.000	-0.002
ρo (atm) "lb/ft3"	0.184	0.000	3.087	0.000
ρo (sat) "lb/ft3"	0.540	0.004	2.509	0.519
Psat"psia"	3.950	0.069	0.000	-0.003
ng'-DL	0.002	-0.001	-0.089	0.000
Residual Oil Density_DL	0.172	0.000	3.393	0.000
ZL' atm- DL	-0.150	-0.001	-0.295	0.000
ng'/1-ng'	0.006	-0.004	-0.295	-0.001
ng/1-ng	0.091	-0.001	0.000	0.000

Table 26: Sensitivity Table for Oil Sample IV_Part III.

Property	Volume shift C12+	Volume shift C1	Omega A C12+	Omega A C1
ZL(atm)	-0.683	0.000	-0.228	0.114
ZL(sat)	-0.428	0.088	7.498	-6.904
MWL(atm)"g/mol"	0.000	0.000	0.047	0.072
MWL(sat)"g/mol"	0.000	0.000	0.000	0.000
Separator ng-GOR	-0.007	0.000	0.062	0.080
Separator ng-Bo	-0.010	-0.004	0.076	0.095
ρo (atm) "lb/ft3"	0.670	0.000	0.352	0.013

ρo (sat) "lb/ft3"	0.430	-0.084	1.137	-0.366
Psat"psia"	0.000	-0.003	8.716	-7.251
ng'-DL	0.001	0.000	0.012	0.105
Residual Oil Density_DL	0.750	0.000	0.320	0.012
ZL' atm- DL	-0.744	0.000	-0.272	0.060
ng'/1-ng'	0.003	-0.001	0.040	0.350
ng/1-ng	-0.018	0.000	0.169	0.218

Table 27: Sensitivity Table for Oil Sample IV_Part IV.

Property	Omega B C12+	Omega B C1	Exp. Value (kijs)
ZL(atm)	3.527	0.000	0.114
ZL(sat)	-7.859	10.400	1.665
MWL(atm)"g/mol"	-0.013	-0.050	0.057
MWL(sat)"g/mol"	0.000	0.000	0.000
Separator ng-GOR	0.029	-0.028	0.071
Separator ng-Bo	0.042	-0.024	0.082
ρo (atm) "lb/ft3"	-3.356	-0.009	0.005
ρo (sat) "lb/ft3"	-3.553	-0.185	0.094
Psat"psia"	-11.133	10.193	1.758
ng'-DL	0.073	-0.077	0.041
Residual Oil Density_DL	-3.639	-0.025	0.000
ZL' atm- DL	3.763	-0.025	0.057
ng'/1-ng'	0.244	-0.256	0.136
ng/1-ng	0.078	-0.075	0.193

Tables (16-27) were made in order to understand how each parameter affects the fundamental properties of the oil. For instance, if the saturation pressure is our target, and we aim to tune only the saturation pressure without affecting the other properties, we can have a look at these sensitivity tables, to see which parameters should be changed in order to have a better match for the saturation pressure. This is the main aim of making these sensitivity tables. In other words, these sensitivity tables are important as they give us an idea of how each parameter is going to affect each and every fundamental property of the oil.

In this study, the tuning of the saturation pressure, the constant composition expansion (CCE), differential liberation (DL) and separator tests was divided into two main steps; first of all the fundamental properties (Z_L^{atm}, Z_L^{sat}, MW_L^{atm}, MW_L^{sat}, ρ_o^{atm}, ρ_o^{sat}, psat, ng calculated from separation test for both GOR and Bo, ng calculated for both GOR and Bo from differential vaporization test) of the fluid were the target, in other words, the fundamental properties of the fluid were to be tuned. Then, after reaching to a good match of the fundamental oil properties, the other properties of the oil were to be tuned.

To be more specific, the first step was made by looking at the sensitivity table that was previously made, and at the fundamental properties that were predicted by WinProp without any tuning (the values that WinProp predicted after introducing the fluid's composition and the values of the laboratory tests). In other words, by looking at the sensitivity table and at the values of the fundamental properties, an appropriate parameter was chosen to tune the predicted values and bring them closer to the laboratory extracted values of the fundamental properties.

To start with, the binary interaction coefficients between hydrocarbon pairs was given a value of zero, and then the tuning process started, firstly, by looking at the values of the molecular weight of the oil at atmospheric conditions from the laboratory report, in other words, from the separation test data, and the molecular weight predicted from the WinProp software. If these two values were relatively close to each other, then we should move to the next step. After that, the density of the oil at atmospheric conditions was to be tuned, and this was done by tuning against the volume shift of the heavy-end component.

Then the saturation pressure was the next target, which means that the saturation pressure of the fluid was to be tuned, and this was done by using the regression process option that WinProp provides by using the binary interaction coefficient of the hydrocarbon pairs as a regression parameter. This could be achieved by excluding all the other tests from the regression loop, and keep only the saturation pressure as an active test. By doing so, the Winprop will understand that our aim from this regression process is to tune against the saturation pressure only. Otherwise, if the other tests were kept within the regression loop, WinProp will try to find the best possible value for the binary interaction coefficient of the hydrocarbon pairs that will reduce the error between all the data that were within these tests in the regression loop, and may end-up with a saturation pressure that is not equal to the real one (measured in the laboratory).

After that, a closer look at the fundamental properties will show if these two regressions that were previously made and these changes on the properties of the fluid had affected the other fundamental properties of the fluid. If yes, a comparison should be made between these predicted values and the laboratory extracted ones, to check which parameter the next regression process should be used in the regression process so that the other fundamental properties of the oil would come closer to the laboratory ones.

14.   Fluid samples tuning process

In the way of finding a road map that could be used in order to tune any oil sample, three reservoir oils with totally different compositions were used.

14.1 PVT study oil sample #1

The laboratory data that were reported by the PVT report are shown in Appendix A.

First of all, the oil sample composition was introduced in WinProp software with zero value for binary interaction coefficients between the hydrocarbon pairs, and it run without any regression, in other words, the regression option was not activated yet. A record was kept of the predicted values for the fundamental properties of the sample, and a comparison was made between the predicted and the laboratory (original) values. This is shown in Table 28.

Table 28: The fundamental properties of the oil sample as extracted form laboratory and as predicted by WinProp without any regression process _Oil Sample I.

Property	Lab. Extracted Data	Predicted by Winprop "no tuning"
ZL(atm)	0.0084153	0.00759
ZL(sat)	0.826850486	0.7521
MWL(atm)"g/mol"	159.49	141.122
MWL(sat)"g/mol"	50.02	50.06
Separator ng-GOR	0.802559773	0.785987739
Separator ng-Bo	0.808972372	0.786797255
ρo (atm) "lb/ft3"	49.94225427	49.01677
ρo (sat) "lb/ft3"	32.08789837	30.4558
ng'-DL Test	0.863614019	0.860605246
Patm"psi"	14.7	14.7
Psat"psia"	3954	3411.371
Tatm"K"	288.706	288.706
Tsat"K"	385.9	385.9
GOR " sm3/sm3"	483.0278293	483.8774026
Separator Bo	2.556	2.677
ρo (atm) "kg/m3"	800	785.1751302
ρo (sat)"kg/m3"	514	487.8562323
Separator GOR "scf/stb"	2712	2716.77
DL-GOR	3999	4301.27
Residual oil density	833	813.1
DL-MW (1.1*residual)"kg/mol"	0.175439	0.1552342
Z'L atm - DL	0.008890113	0.008058785
Error% (ZL&ZL')	-5.642256903	-6.176349979
Lab (ng'/1-ng') Error%	6.332131904	6.173871115
Lab (ng/1-ng) Error%	4.064823987	3.672629486

First of all, the oil density at atmospheric conditions was tuned using the volume shift of the plus fraction (C12+), which had an initial value of about 0.164275 and after the regression process it got a value of 0.19785. The fundamental properties of the fluid after the regression are shown in Table 29.

Table 29: Fundamental properties values after changing the molecular weight of C12+_Oil Sample I.

Property	Lab. Extracted Data	Volume Shift C12+
ZL(atm)	0.0084153	0.00745
ZL(sat)	0.826850486	0.7469
MWL(atm)"g/mol"	159.49	141.122
MWL(sat)"g/mol"	50.02	50.06
Separator ng-GOR	0.802559773	0.786002725
Separator ng-Bo	0.808972372	0.786816971
ρo (atm) "lb/ft3"	49.94225427	49.94225
ρo (sat) "lb/ft3"	32.08789837	30.6681
ng'-DL Test	0.863614019	0.860600783
Patm"psi"	14.7	14.7
Psat"psia"	3954	3411.371
Tatm"K"	288.706	288.706
Tsat"K"	385.9	385.9
GOR " sm3/sm3"	483.0278293	493.0143228
Separator Bo	2.556	2.7087
ρo (atm) "kg/m3"	800	799.9999316
ρo (sat)"kg/m3"	514	491.2569599
Separator GOR "scf/stb"	2712	2768.07
DL-GOR	3999	4414.84
Residual oil density	833	834.6
DL-MW (1.1*residual)"kg/mol"	0.175439	0.1552342
Z'L atm - DL	0.008890113	0.007851184
Error% (ZL&ZL')	-5.642256903	-5.385018323
Lab (ng'/1-ng') Error%	6.332131904	6.173641454
Lab (ng/1-ng) Error%	4.064823987	3.672956705

Then, the saturation pressure of the fluid was tuned by using the binary interaction coefficients between hydrocarbon pairs as regression parameter. Before the regression, the exponential value that defines the values of the binary interaction coefficients was zero and after the regression it got a value of 1.4054237. The values of the fundamental properties after the regression are shown inTable 30.

Table 30: Fundamental properties values after changing the binary interaction coefficients between hydrocarbon pairs_Oil Sample I.

Property	Lab. Extracted Data	kijs (hydrocarbon pairs)
ZL(atm)	0.0084153	0.00752
ZL(sat)	0.826850486	0.8465
MWL(atm)"g/mol"	159.49	142.7527

MWL(sat)"g/mol"	50.02	50.06
Separator ng-GOR	0.802559773	0.789961375
Separator ng-Bo	0.808972372	0.790754715
ρo (atm) "lb/ft3"	49.94225427	50.03274
ρo (sat) "lb/ft3"	32.08789837	31.3645
ng'-DL Test	0.863614019	0.867092413
Patm"psi"	14.7	14.7
Psat"psia"	3954	3954.049
Tatm"K"	288.706	288.706
Tsat"K"	385.9	385.9
GOR " sm3/sm3"	483.0278293	500.136846
Separator Bo	2.556	2.6733
ρo (atm) "kg/m3"	800	801.4494457
ρo (sat)"kg/m3"	514	502.4122433
Separator GOR "scf/stb"	2712	2808.06
DL-GOR	3999	4616.53
Residual oil density	833	835.4
DL-MW (1.1*residual)"kg/mol"	0.175439	0.15702797
Z'L atm - DL	0.008890113	0.007934301
Error% (ZL&ZL')	-5.642256903	-5.509320336
Lab (ng'/1-ng') Error%	6.332131904	6.524024971
Lab (ng/1-ng) Error%	4.064823987	3.761029082

After that, the critical temperature of the plus fraction (C12+) and the methane (C1) were introduced in the regression process as regression parameters, so that the predicted gas-oil ratio (GOR) values and the oil volume factor (Bo) values measured from the differential vaporization test will come closer to the laboratory ones. Weight factor for all the tests were equal to unity at this step. The fundamental properties after this regression step are shown in Table 31.

Table 31: Fundamental properties values after changing the critical temperature of C12+ and CH4_Oil Sample I.

Property	Lab. Extracted Data	Tc (C12+ and C1)
ZL(atm)	0.0084153	0.00784
ZL(sat)	0.826850486	0.9093
MWL(atm)"g/mol"	159.49	142.9637
MWL(sat)"g/mol"	50.02	50.06
Separator ng-GOR	0.802559773	0.790481529
Separator ng-Bo	0.808972372	0.791336844
ρo (atm) "lb/ft3"	49.94225427	48.07074
ρo (sat) "lb/ft3"	32.08789837	31.7191

ng'-DL Test	0.863614019	0.868069973
Patm"psi"	14.7	14.7
Psat"psia"	3954	4295.569
Tatm"K"	288.706	288.706
Tsat"K"	385.9	385.9
GOR " sm3/sm3"	483.0278293	481.2307236
Separator Bo	2.556	2.5425
ρo (atm) "kg/m3"	800	770.0211487
ρo (sat)"kg/m3"	514	508.0924034
Separator GOR "scf/stb"	2712	2701.91
DL-GOR	3999	4390.33
Residual oil density	833	788.9
DL-MW (1.1*residual)"kg/mol"	0.175439	0.15726007
Z'L atm - DL	0.008890113	0.00841439
Error% (ZL&ZL')	-5.642256903	-7.32640105
Lab (ng'/1-ng') Error%	6.332131904	6.579775578
Lab (ng/1-ng) Error%	4.064823987	3.772848873

After that, it was decided to tune the saturation pressure of the fluid as in the previous step, the predicted saturation pressure was not equal to the measured one. So, the binary interaction coefficients between hydrocarbon pairs were used in the regression process. The exponential value that determines the binary interaction coefficient values between hydrocarbon pairs got a value of 0.902873 instead of 1.4054237.

Then, the critical pressure, the critical temperature, and the molecular weight of the plus fraction (C12+), with the critical temperature of CO_2, H_2S, C_2H_6 and C_3H_8 were used as regression parameters get a better math for the constant mass study test, differential vaporization test and separator test as well. The saturation pressure had a weight factor of 35, API gravity from the separator test had a weight factor of 2 and the constant mass study had a weight factor of 1. For the differential vaporization test, the oil volume factor had a weight factor of 10, whereas, the gas-oil ratio as well as the liquid density and API gravity had a weight factor of 5, and the residual oil specific gravity had a weight factor of 2. Table 32 shows the fundamental properties after this tuning step.

Table 32: Fundamental properties of the fluid after using the critical temperature of (CO2, H2S, C2H6, C3H8 and C12+), the molecular weight and the critical pressure of C12+ as regression parameters.

Property	Lab. Extracted Data	Tc (C12+,CO2,H2S,C2H6,C3H8) _ Pc (C12+)_MW (C12+)
ZL(atm)	0.0084153	0.00837
ZL(sat)	0.826850486	0.8869
MWL(atm)"g/mol"	159.49	157.852

MWL(sat)"g/mol"	50.02	53.2
Separator ng-GOR	0.802559773	0.78934117
Separator ng-Bo	0.808972372	0.790115395
ρo (atm) "lb/ft3"	49.94225427	49.71358
ρo (sat) "lb/ft3"	32.08789837	32.3048
ng'-DL Test	0.863614019	0.860469423
Patm"psi"	14.7	14.7
Psat"psia"	3954	4014.994
Tatm"K"	288.706	288.706
Tsat"K"	385.9	385.9
GOR " sm3/sm3"	483.0278293	447.6716883
Separator Bo	2.556	2.4707
ρo (atm) "kg/m3"	800	796.3369812
ρo (sat)"kg/m3"	514	517.4744388
Separator GOR "scf/stb"	2712	2513.49
DL-GOR	3999	3892.54
Residual oil density	833	824
DL-MW (1.1*residual)"kg/mol"	0.175439	0.1736372
Z'L atm - DL	0.008890113	0.008894913
Error% (ZL&ZL')	-5.642256903	-6.271356683
Lab (ng'/1-ng') Error%	6.332131904	6.166887893
Lab (ng/1-ng) Error%	4.064823987	3.747012031

To conclude with this tuning, the saturation pressure was to be tuned by using the binary interaction coefficients between hydrocarbon pairs as regression parameter. The final tables that show the values of the fundamental properties of the fluid are shown in tables (21-25) and figures (6-9).

Table 33: Fundamental properties of the fluid after the final tuning process_ Oil sample I.

Property	Lab. Extracted Data	Final Tuning
ZL(atm)	0.0084153	0.00836
ZL(sat)	0.826850486	0.8755
MWL(atm)"g/mol"	159.49	157.7246
MWL(sat)"g/mol"	50.02	53.2
Separator ng-GOR	0.802559773	0.788987293
Separator ng-Bo	0.808972372	0.789722853
ρo (atm) "lb/ft3"	49.94225427	49.70907
ρo (sat) "lb/ft3"	32.08789837	32.2267
ng'-DL Test	0.863614019	0.860026874

Patm"psi"	14.7	14.7
Psat"psia"	3954	3953.998
Tatm"K"	288.706	288.706
Tsat"K"	385.9	385.9
GOR " sm3/sm3"	483.0278293	447.2549165
Separator Bo	2.556	2.4749
ρo (atm) "kg/m3"	800	796.2647378
ρo (sat)"kg/m3"	514	516.223394
Separator GOR "scf/stb"	2712	2511.15
DL-GOR	3999	3881.37
Residual oil density	833	824
DL-MW (1.1*residual)"kg/mol"	0.175439	0.17349706
Z'L atm - DL	0.008890113	0.008887734
Error% (ZL&ZL')	-5.642256903	-6.312602904
Lab (ng'/1-ng') Error%	6.332131904	6.144228522
Lab (ng/1-ng) Error%	4.064823987	3.739051102

Table 34: Oil volume factor (Bo) - Constant Mass Study results _Oil Sample I.

Lab. Extracted Data		Predicted by WinProp "no tuning"		Final Tuning	
Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"
6015	0.924	6015	0.890324	6015	0.921393
5535	0.9379	5535	0.904431	5535	0.93569
5215	0.9477	5215	0.914903	5215	0.946293
4833	0.9604	4833	0.928753	4833	0.960302
4610	0.9682	4610	0.937635	4610	0.969276
4415	0.9759	4415	0.945958	4415	0.977678
4211	0.9855	4211	0.955294	4211	0.987095
4040	0.9945	4040	0.963677	4040	0.995542
3954	1	3954	0.968105	3954	1
3873	1.0107	3873	0.972415	3954	1
3821	1.0182	3821	0.975257	3873	1.01086
3766	1.0264	3766	0.97833	3821	1.01816
3720	1.0336	3720	0.980955	3766	1.02618
3669	1.0418	3669	0.983926	3720	1.03314
3578	1.0572	3578	0.989393	3669	1.04112
3354	1.0995	3411.37	1	3578	1.05614
2971	1.1916	3354	1.0116	3354	1.09785
2437	1.3896	2971	1.10406	2971	1.18937
1890	1.7408	2437	1.29755	2437	1.38379
1604	2.0485	1890	1.64396	1890	1.73538
		1604	1.9405	1604	2.03678

Table 35: Oil volume factor (Bo) – Differential Vaporization results _Oil Sample I.

Lab. Extracted Data		Predicted by WinProp "no tuning"		Final Tuning	
Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"
3954	3.416	3715	3.70905	3954	3.41894
3715	2.811	3415	3.77904	3715	2.97413
3415	2.43	3411.37	3.77995	3415	2.61906
2815	2.072	2815	2.80965	2815	2.18757
2215	1.833	2215	2.31817	2215	1.90871
1615	1.663	1615	1.99492	1615	1.70202
1015	1.516	1015	1.74798	1015	1.53414
515	1.391	515	1.56272	515	1.40725
15	1.088	15	1.06708	15	1.05953

Table 36: Gas-Oil Ratio – Differential Vaporization results _Oil Sample I.

Lab. Extracted Data		Predicted by WinProp "no tuning"		Final Tuning	
Pressure"psia"	GOR "scf/stb"	Pressure"psia"	GOR "scf/stb"	Pressure"psia"	GOR "scf/stb"
3954	3999	3715	4301.27	3954	3881.37
3715	3054	3415	4301.27	3715	3160.19
3415	2429	3411.37	4301.27	3415	2567.49
2815	1779	2815	2746.37	2815	1820.33
2215	1339	2215	1919.38	2215	1324.33
1615	994	1615	1360	1615	951.602
1015	691	1015	928.233	1015	648.453
515	438	515	609.739	515	423.82
15	0	15	0	15	0

Table 37: Oil density – Differential Vaporization results _Oil Sample I.

Lab. Extracted Data		Predicted by WinProp "no tuning"		Final Tuning	
Pressure"psia"	ρ_o "kg/m3"	Pressure"psia"	ρ_o "kg/m3"	Pressure"psia"	ρ_o "kg/m3"
3954	514	3715	497.18	3954	516.222
3715	545	3415	487.972	3715	537.977
3415	573	3411.37	487.855	3415	561.111
2815	608	2815	542.512	2815	600.354
2215	640	2215	586.443	2215	635.149
1615	666	1615	625.766	1615	667.8
1015	689	1015	663.287	1015	699.349
515	711	515	695.467	515	725.531
15	765	15	761.981	15	777.675
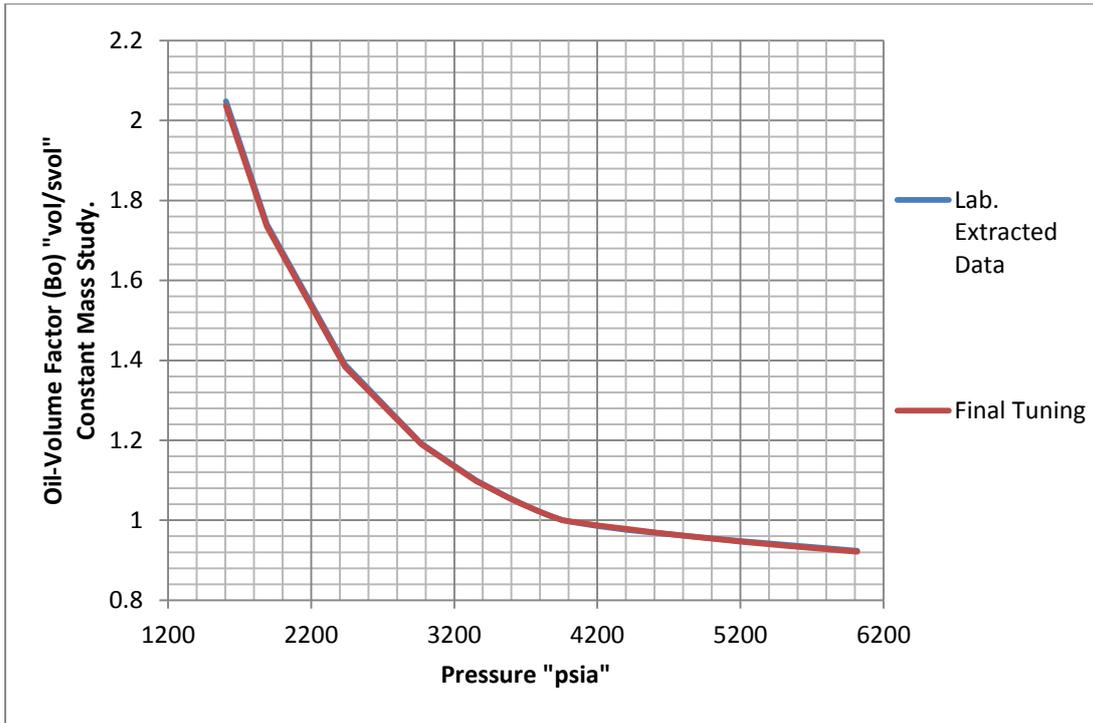
Figure 6: Oil Volume Factor (Bo) - Constant Mass Study_Oil sample I.
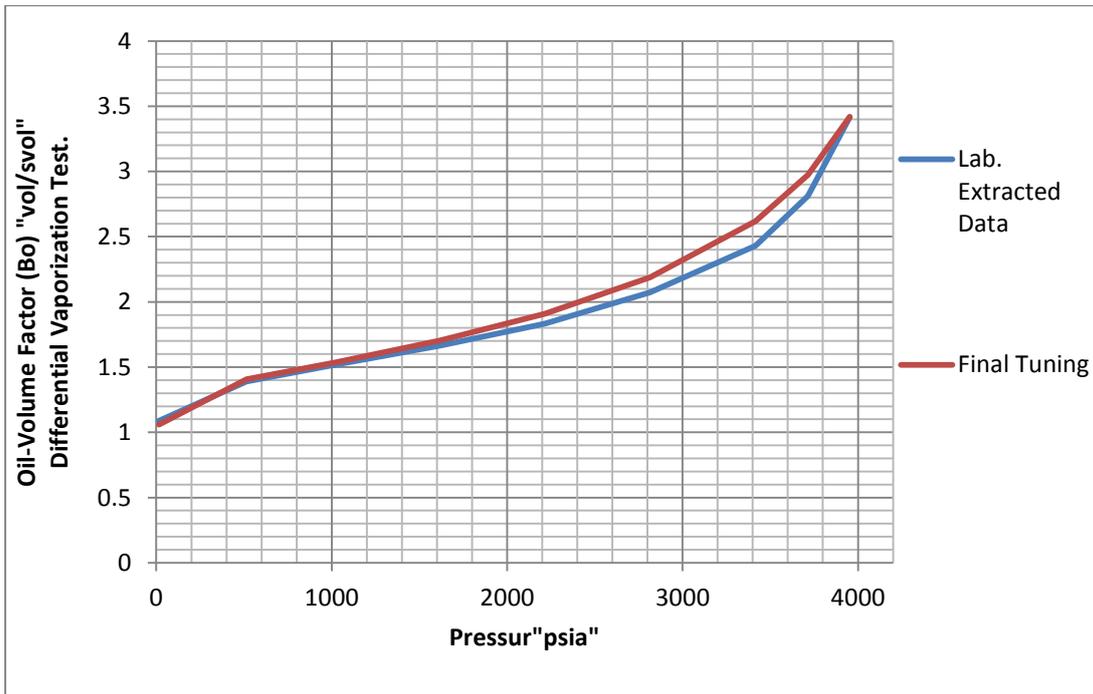
Figure 7: Oil Volume Factor (Bo) – Differential Vaporization Test_Oil sample I.
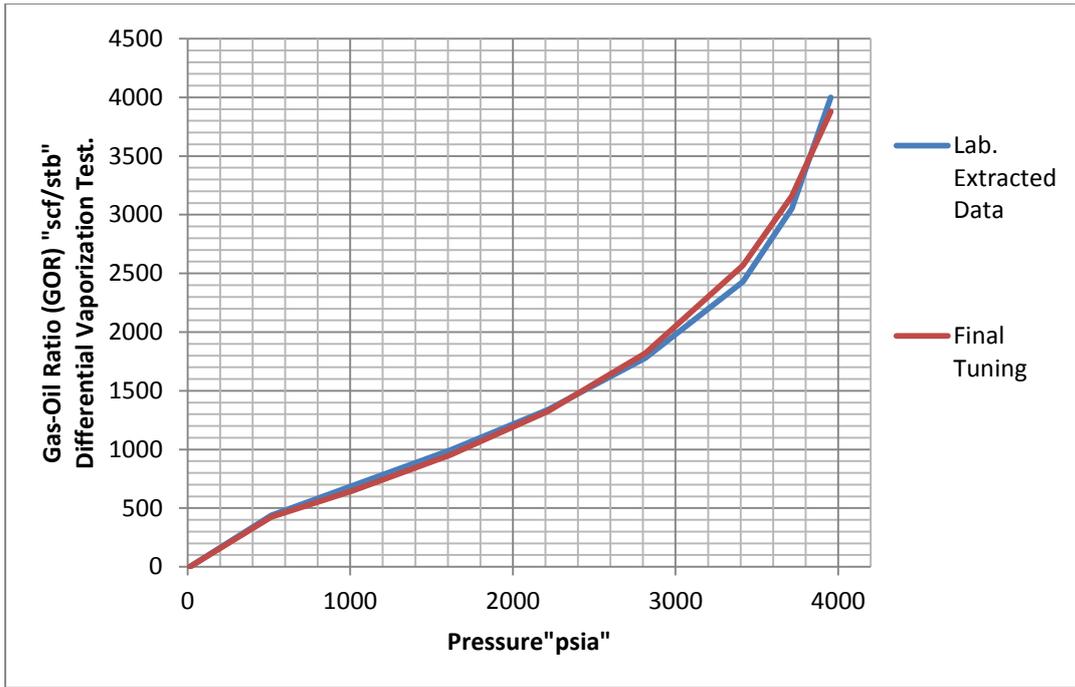
Figure 8: Gas-Oil Ratio (GOR) –Differential Vaporization Study_Oil sample I.
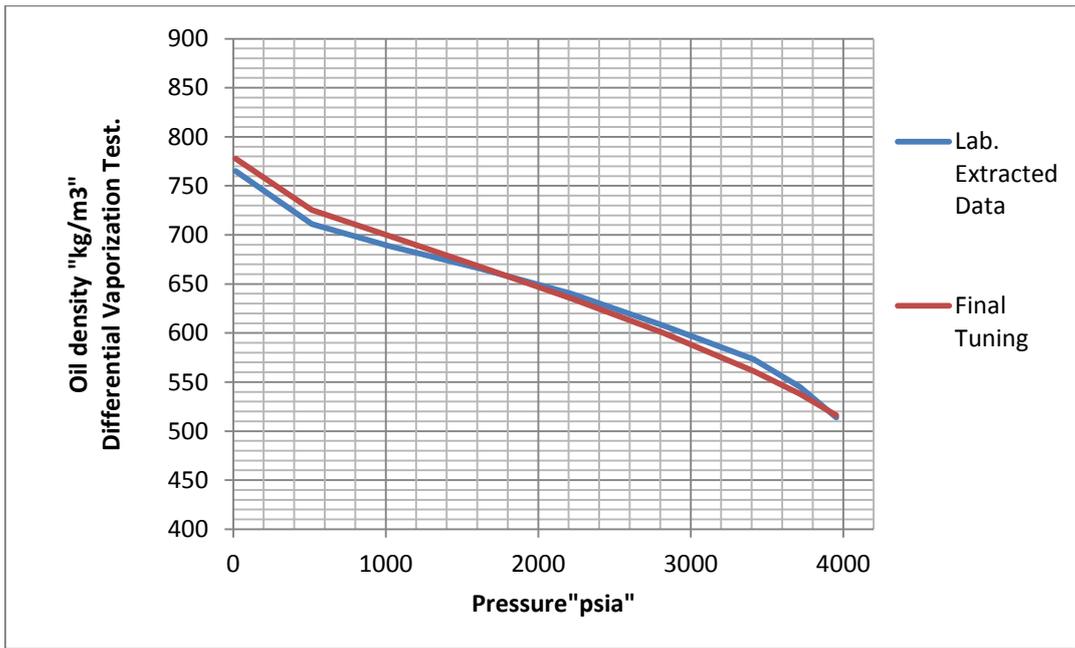
Figure 9: Oil density –Differential Vaporization Study_Oil sample I.

14.2 PVT study oil sample #3

The laboratory data that were measured are shown in Appendix C.

First of all, the oil sample was introduced in WinProp software with zero value for binary interaction coefficients between the hydrocarbon pairs, and it run without any regression

processes, in other words, the regression option was not activated yet. A record was kept for the predicted values of the fundamental properties of the sample, and a comparison was made between the predicted and the laboratory (original) values. This is shown in Table 38.

Table 38: The fundamental properties of the oil sample as extracted form laboratory and as predicted by WinProp without any regression process _Oil Sample III.

Property	Lab. Extracted Data	Predicted by Winprop "no tuning"
ZL(atm)	0.008316675	0.0081
ZL(sat)	0.690851988	0.5726
MWL(atm)"g/mol"	159	151.7841
MWL(sat)"g/mol"	96.6	94.67
Sep. ng-GOR	0.443492043	0.433901489
Sep. ng-Bo	0.448420384	0.434744731
ρo (atm) "lb/ft3"	50.50422	49.40291
ρo (sat) "lb/ft3"	42.76305522	42.08
ng'-DL Test	0.49208178	0.514370972
Patm"psi"	14.7	14.7
Psat"psia"	2034	1692.452
Tatm"K"	288.706	288.706
Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	94.62679035
Sep. Bo	1.298	1.2954
ρo (atm) "kg/m3"	807	49.40291
ρo (sat)"kg/m3"	685	42.08
Sep.GOR "scf/stb"	538	531.29
DL-GOR	599	676.89
Residual oil density	813	802.2
DL-MW (1.1*residual)"kg/mol"	0.1749	0.16696251
Z'L atm - DL	0.009080827	0.008785418
Error% (ZL&ZL')	-9.188191882	-8.461950223
Lab (ng'/1-ng') Error%	0.968820887	1.059184978
Lab (ng/1-ng) Error%	0.7969195	0.766477002

After looking at the laboratory measured molecular weight at saturation conditions and at the molecular weight that was predicted from WinProp, it was decided to tune this property first. To do so, the molecular weight of the plus fraction C12+ was used as a regression parameter to bring these two values closer to each other. The initial value of the molecular weight of C12+ was 242 g/mol, after the regression process it got a value of 252 g/mol, which means an increase of about 4.1322% from its initial value. The fundamental properties of the fluid after this tuning step are show in Table 39.

Table 39: Fundamental properties values after changing the molecular weight of C12+_Oil Sample III.

Property	Lab. Extracted Data	Molecular Weight of C12+
ZL(atm)	0.008316675	0.0081
ZL(sat)	0.690851988	0.5726
MWL(atm)"g/mol"	159	155.3056
MWL(sat)"g/mol"	96.6	96.66
Separator ng-GOR	0.443492043	0.433901489
Separator ng-Bo	0.448420384	0.434744731
ρo (atm) "lb/ft3"	50.50422	50.54908
ρo (sat) "lb/ft3"	42.76305522	42.964
ng'-DL Test	0.49208178	0.514009571
Patm"psi"	14.7	14.7
Psat"psia"	2034	1692.452
Tatm"K"	288.706	288.706
Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	94.62679035
Separator Bo	1.298	1.2954
ρo (atm) "kg/m3"	807	809.720438
ρo (sat)"kg/m3"	685	688.218834
Separator GOR "scf/stb"	538	531.29
DL-GOR	599	676.89
Residual oil density	813	822
DL-MW (1.1*residual)"kg/mol"	0.1749	0.17083616
Z'L atm - DL	0.009080827	0.008772717
Error% (ZL&ZL')	-9.188191882	-8.305144255
Lab (ng'/1-ng') Error%	0.968820887	1.057653689
Lab (ng/1-ng) Error%	0.7969195	0.766477002

After that, the saturation pressure of the fluid was to be tuned, and to do so, the binary interaction coefficients between hydrocarbon pairs were used as a regression parameter. The exponential value that determines the binary interaction coefficients between hydrocarbon pairs was zero before the regression process, and after the regression process took place, it became about 1.1342. The values of the fundamental properties of the sample after the regression are show in Table 40.

Table 40: Fundamental properties values after changing the binary interaction coefficients between hydrocarbon pairs_Oil Sample III.

Property	Lab. Extracted Data	kijs (hydrocarbon pairs)
ZL(atm)	0.008316675	0.00813

ZL(sat)	0.690851988	0.6865
MWL(atm)"g/mol"	159	156.0875
MWL(sat)"g/mol"	96.6	96.66
Separator ng-GOR	0.443492043	0.437489076
Separator ng-Bo	0.448420384	0.438058363
ρo (atm) "lb/ft3"	50.50422	50.5634
ρo (sat) "lb/ft3"	42.76305522	43.0839
ng'-DL Test	0.49208178	0.516343717
Patm"psi"	14.7	14.7
Psat"psia"	2034	2034.8
Tatm"K"	288.706	288.706
Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	95.66337662
Separator Bo	1.298	1.2946
ρo (atm) "kg/m3"	807	809.9498229
ρo (sat)"kg/m3"	685	690.1394522
Separator GOR "scf/stb"	538	537.11
DL-GOR	599	679.74
Residual oil density	813	821.9
DL-MW (1.1*residual)"kg/mol"	0.1749	0.17169625
Z'L atm - DL	0.009080827	0.008817956
Error% (ZL&ZL')	-9.188191882	-8.461949068
Lab (ng'/1-ng') Error%	0.968820887	1.067584018
Lab (ng/1-ng) Error%	0.7969195	0.777743252

After that, the critical temperature for both the plus fraction (C12+) and ethane (C2H6) were used as regression parameters to bring the predicted gas-oil ration (GOR) and the predicted oil volume factor (Bo) of the differential vaporization test closer to the laboratory data. In this regression process, it was used a weight factor of 30 for saturation pressure, a weight factor of 3 for constant mass study and a weight factor of 10 for differential vaporization test.

The initial values of the critical temperature of C12+, CH4 and C2H6 were 775.4090 K, 305.4 K respectively. After the regression, the values became 881.51 K and 250.73 K respectively. The values of the fundamental properties of the oil sample are shown in Table 41.

Table 41: Fundamental properties values after changing the critical temperature of C12+ and C2H6_Oil Sample III.

Property	Lab. Extracted Data	Tc of [C12+ ,C2H6]
ZL(atm)	0.008316675	0.00831
ZL(sat)	0.690851988	0.7476

MWL(atm)"g/mol"	159	156.3777
MWL(sat)"g/mol"	96.6	96.66
Separator ng-GOR	0.443492043	0.438608081
Separator ng-Bo	0.448420384	0.439351966
ρo (atm) "lb/ft3"	50.50422	49.59648
ρo (sat) "lb/ft3"	42.76305522	42.7149
ng'-DL Test	0.49208178	0.514618753
Patm"psi"	14.7	14.7
Psat"psia"	2034	2197.004
Tatm"K"	288.706	288.706
Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	94.01766234
Separator Bo	1.298	1.2804
ρo (atm) "kg/m3"	807	794.4612149
ρo (sat)"kg/m3"	685	684.2286257
Separator GOR "scf/stb"	538	527.87
DL-GOR	599	659.38
Residual oil density	813	804.3
DL-MW (1.1*residual)"kg/mol"	0.1749	0.17201547
Z'L atm - DL	0.009080827	0.009027668
Error% (ZL&ZL')	-9.188191882	-8.636192142
Lab (ng'/1-ng') Error%	0.968820887	1.060236167
Lab (ng/1-ng) Error%	0.7969195	0.781286774

After that, the molecular weight of the plus fraction was used in the regression, and it took a value of 272 g/mol instead of 252 g/mol. This was done in order the bring the predicted oil density measured from the differential vaporization test closer to the laboratory ones. The fundamental properties are shown in Table 42.

Table 42: Fundamental properties values after changing molecular weight of C12+_Oil Sample III.

Property	Lab. Extracted Data	MW of C12+
ZL(atm)	0.008316675	0.00876
ZL(sat)	0.690851988	0.7286
MWL(atm)"g/mol"	159	163.0393
MWL(sat)"g/mol"	96.6	100.65
Separator ng-GOR	0.443492043	0.436563
Separator ng-Bo	0.448420384	0.437348
ρo (atm) "lb/ft3"	50.50422	49.06728
ρo (sat) "lb/ft3"	42.76305522	42.8427
ng'-DL Test	0.49208178	0.511883

Patm"psi"	14.7	14.7
Psat"psia"	2034	2062.602
Tatm"K"	288.706	288.706
Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	88.45002
Separator Bo	1.298	1.2564
ρo (atm) "kg/m3"	807	785.9842
ρo (sat)"kg/m3"	685	686.2758
Separator GOR "scf/stb"	538	496.61
DL-GOR	599	617.85
Residual oil density	813	794.4
DL-MW (1.1*residual)"kg/mol"	0.1749	0.179343
Z'L atm - DL	0.009080827	0.00953
Error% (ZL&ZL')	-9.188191882	-8.784687
Lab (ng'/1-ng') Error%	0.968820887	1.048688
Lab (ng/1-ng) Error%	0.7969195	0.774822

So far, the predicted gas-oil ratio (GOR) and oil volume factor (Bo) values from differential vaporization are very close, but in at the same time, the predicted API gravity from the separator test had an error of about 10.68%. To decrease this error percentage, the critical temperature of C12+ and the molecular weight of C12+ and N2, were regressed and got a value of 890 K, 280 g/mol and 22 g/mol, respectively. Weight factors of 5,2 and 1 were used for the saturation pressure, differential vaporization test and constant mass study, respectively. The fundamental properties after the regression are shown in Table 43.

Table 43: Fundamental properties values after changing molecular weight of C12+ and N2 and the critical temperature of C12+_Oil Sample III.

Property	Lab. Extracted Data	Tc (C12+) _ MW (C12+,N2)
ZL(atm)	0.008316675	0.0088
ZL(sat)	0.690851988	0.7366
MWL(atm)"g/mol"	159	166.0009
MWL(sat)"g/mol"	96.6	102.31
Separator ng-GOR	0.443492043	0.436487287
Separator ng-Bo	0.448420384	0.437198647
ρo (atm) "lb/ft3"	50.50422	49.71524
ρo (sat) "lb/ft3"	42.76305522	43.417
ng'-DL Test	0.49208178	0.511598342
Patm"psi"	14.7	14.7
Psat"psia"	2034	2078.862
Tatm"K"	288.706	288.706

Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	88.02077922
Separator Bo	1.298	1.2542
ρo (atm) "kg/m3"	807	796.3635719
ρo (sat)"kg/m3"	685	695.4752145
Separator GOR "scf/stb"	538	494.2
DL-GOR	599	614.53
Residual oil density	813	805.4
DL-MW (1.1*residual)"kg/mol"	0.1749	0.18260099
Z'L atm - DL	0.009080827	0.009570125
Error% (ZL&ZL')	-9.188191882	-8.751423663
Lab (ng'/1-ng') Error%	0.968820887	1.047495097
Lab (ng/1-ng) Error%	0.7969195	0.774582857

After that, the saturation pressure was to be tuned by changing the binary interaction coefficients value between the hydrocarbon values, as the exponential value got a value of 0.2 instead of 0.298988. The values of the fundamental properties after this regression are shown in Table 44.

Table 44: Fundamental properties values after changing the binary interaction coefficients between hydrocarbon pairs_Oil Sample III.

Property	Lab. Extracted Data	kijs (hydrocarbon pairs)
ZL(atm)	0.008316675	0.0088
ZL(sat)	0.690851988	0.7366
MWL(atm)"g/mol"	159	166.0009
MWL(sat)"g/mol"	96.6	102.31
Sep. ng-GOR	0.443492043	0.436487287
Sep. ng-Bo	0.448420384	0.437198647
ρo (atm) "lb/ft3"	50.50422	49.71524
ρo (sat) "lb/ft3"	42.76305522	43.417
ng'-DL Test	0.49208178	0.511598342
Patm"psi"	14.7	14.7
Psat"psia"	2034	2078.862
Tatm"K"	288.706	288.706
Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	88.02077922
Sep. Bo	1.298	1.2542
ρo (atm) "kg/m3"	807	796.3635719
ρo (sat)"kg/m3"	685	695.4752145

Sep.GOR "scf/stb"	538	494.2
DL-GOR	599	614.53
Residual oil density	813	805.4
DL-MW (1.1*residual)"kg/mol"	0.1749	0.18260099
Z'L atm - DL	0.009080827	0.009570125
Error% (ZL&ZL')	-9.188191882	-8.751423663
Lab (ng'/1-ng') Error%	0.968820887	1.047495097
Lab (ng/1-ng) Error%	0.7969195	0.774582857

To finalize the tuning process, the predicted oil density values from the differential vaporization test were to be tuned by regressing against the molecular weight of the plus fraction (C12+), as it got a value of 273.5 g/mol instead of 280.37 g/mol. The values of the fundamental properties of the sample are shown in

Table 45: Fundamental properties values after changing the molecular weight of the plus fraction (C12+)_Oil Sample III.

Property	Lab. Extracted Data	MW (C12+)
ZL(atm)	0.008316675	0.0088
ZL(sat)	0.690851988	0.7233
MWL(atm)"g/mol"	159	163.5161
MWL(sat)"g/mol"	96.6	100.94
Sep. ng-GOR	0.443492043	0.436310048
Sep. ng-Bo	0.448420384	0.437072673
ρo (atm) "lb/ft3"	50.50422	48.98758
ρo (sat) "lb/ft3"	42.76305522	42.8246
ng'-DL Test	0.49208178	0.511592929
Patm"psi"	14.7	14.7
Psat"psia"	2034	2040.544
Tatm"K"	288.706	288.706
Tsat"K"	344.3	344.3
GOR " sm3/sm3"	95.82189239	87.95737291
Sep. Bo	1.298	1.2544
ρo (atm) "kg/m3"	807	784.7075502
ρo (sat)"kg/m3"	685	685.9858551
Sep.GOR "scf/stb"	538	493.844
DL-GOR	599	614.25
Residual oil density	813	793
DL-MW (1.1*residual)"kg/mol"	0.1749	0.17986771
Z'L atm - DL	0.009080827	0.00957428
Error% (ZL&ZL')	-9.188191882	-8.798639988
Lab (ng'/1-ng') Error%	0.968820887	1.047472405

| Lab (ng/1-ng) Error% | 0.7969195 | 0.774024882 |

Table 46: Oil volume factor (Bo) - Constant Mass Study result _Oil Sample IV.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"
5015	0.9668	5015	0.955306	5015	0.968044
4515	0.9712	4515	0.960423	4515	0.97239
4015	0.9763	4015	0.965976	4015	0.977076
3765	0.9789	3765	0.968937	3765	0.979561
3515	0.9817	3515	0.972034	3515	0.982149
3265	0.9845	3265	0.975278	3265	0.98485
3015	0.9875	3015	0.978681	3015	0.98767
2765	0.9906	2765	0.982258	2765	0.990619
2515	0.9937	2515	0.986024	2515	0.993708
2258	0.997	2258	0.990112	2258	0.997043
2034	1	2034	0.993873	2040.54	1
2022	1.0023	2022	0.99408	2034	1.00131
2000	1.0069	2000	0.99446	2022	1.00375
1979	1.0114	1979	0.994826	2000	1.00832
1938	1.0206	1938	0.995545	1979	1.01281
1862	1.0389	1862	0.996895	1938	1.02196
1730	1.0763	1730	0.999301	1862	1.04034
1515	1.1555	1692.45	1	1730	1.07736
1243	1.3059	1515	1.06678	1515	1.15562
931	1.609	1243	1.21556	1243	1.30324
595	2.3598	931	1.51529	931	1.5994
		595	2.24412	595	2.31385

Table 47 Oil volume factor (Bo) – Differential Vaporization results _Oil Sample III.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"
2034	1.339	1982	1.39273	2040.54	1.33983
1982	1.328	1715	1.39946	1982	1.33209
1715	1.295	1692.45	1.40005	1715	1.29788
1315	1.249	1315	1.33265	1315	1.24947
915	1.205	915	1.2678	915	1.20384
465	1.156	465	1.19899	465	1.15396
15	1.051	15	1.0381	15	1.03108

Table 48: Gas-Oil Ratio (GOR) – Differential Vaporization results _Oil Sample III.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure"psia"	GOR"scf/stb"	Pressure"psia"	GOR"scf/stb"	Pressure"psia"	GOR"scf/stb"
2034	599	1982	676.894	2040.54	614.247
1982	584	1715	676.894	1982	596.458
1715	506	1692.45	676.894	1715	517.825
1315	396	1315	531.396	1315	406.841
915	291	915	391.812	915	302.947
465	177	465	246.411	465	191.778
15	0	15	0	15	0

Table 49: Oil specific gravity – Differential Vaporization results _Oil Sample III.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure	SG	Pressure	SG	Pressure	SG
2034	0.685	1982	0.677599	2040.54	0.685984
1982	0.689	1715	0.674341	1982	0.688015
1715	0.698	1692.45	0.674057	1715	0.697316
1315	0.712	1315	0.6927	1315	0.711385
915	0.726	915	0.71235	915	0.725612
465	0.741	465	0.734833	465	0.741976
15	0.773	15	0.77274	15	0.769075
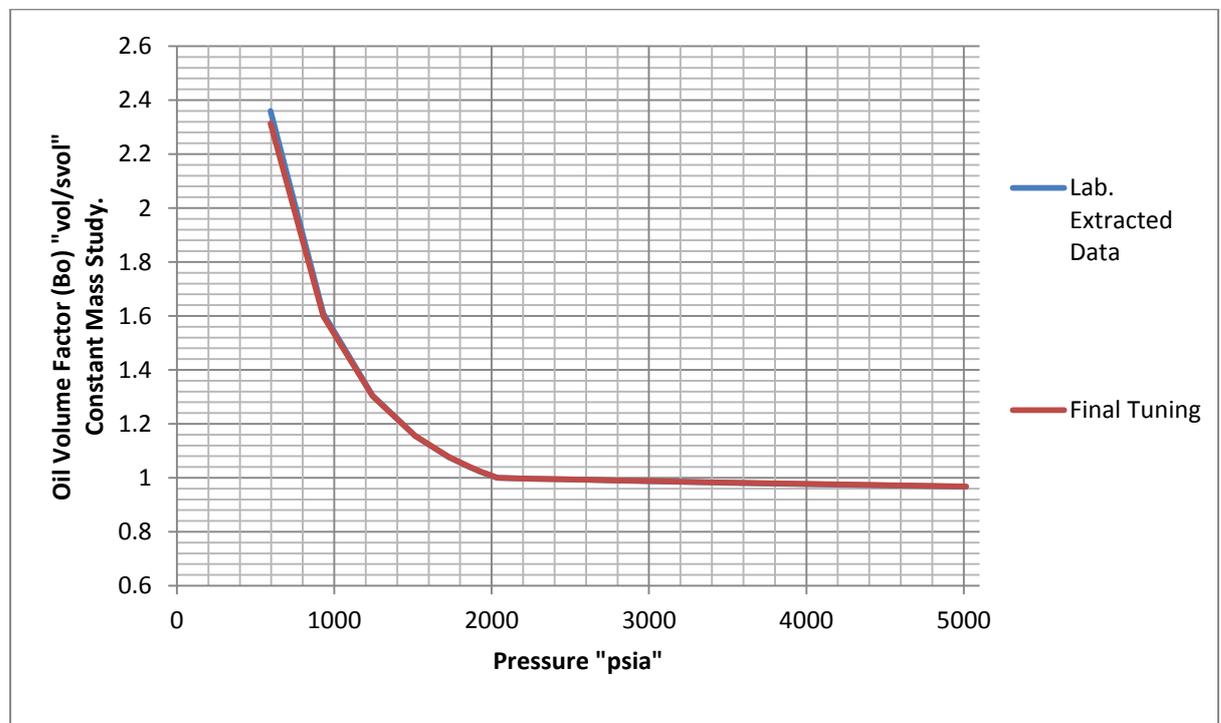
Figure 10: Oil Volume Factor (Bo) - Constant Mass Study_Oil sample III.
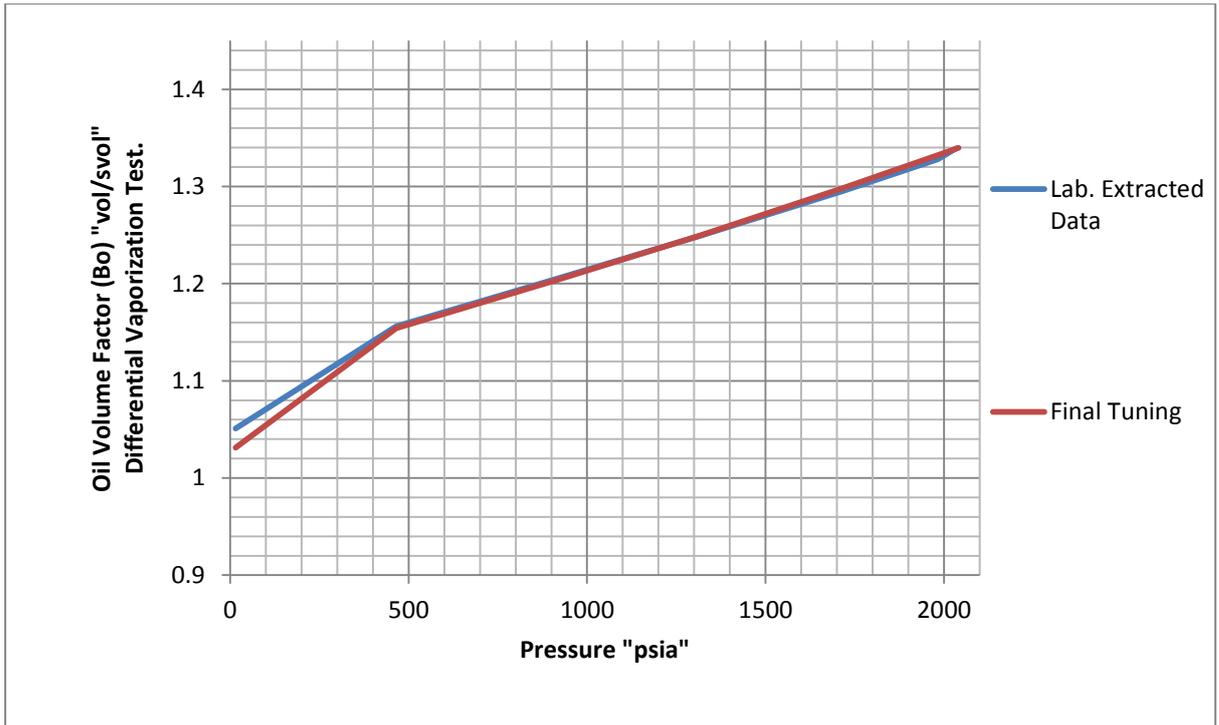
Figure 11: Oil Volume Factor (Bo) – Differential Vaporization Test _Oil sample III.
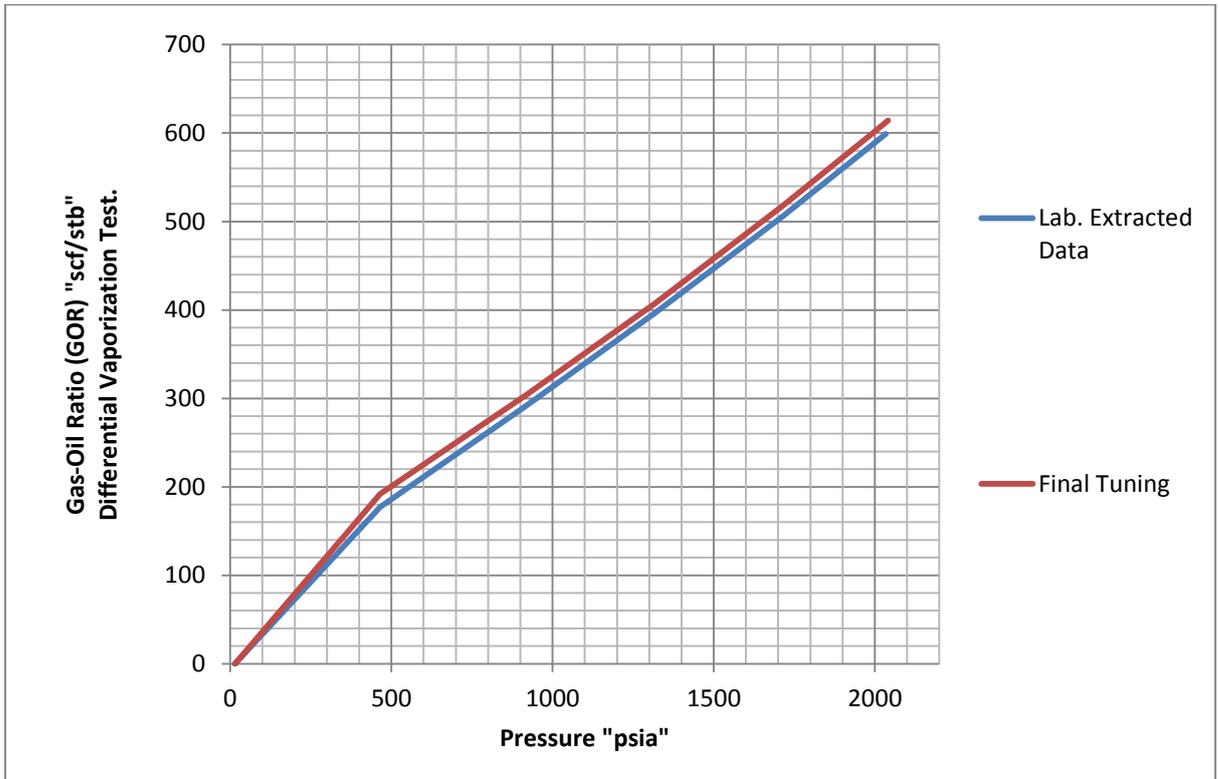
Figure 12: Gas-Oil Ratio (GOR) –Differential Vaporization Study_Oil sample III.
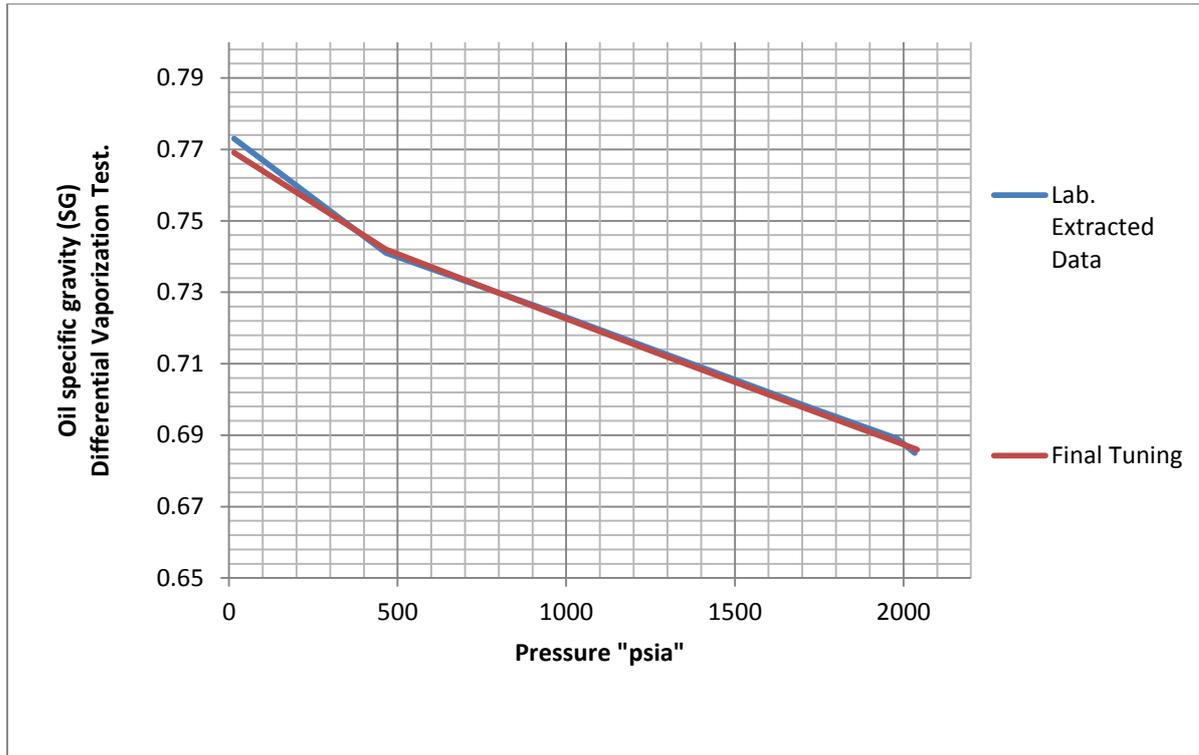
Figure 13: Oil specific gravity (SG) –Differential Vaporization Study_Oil sample III.

14.3 PVT study oil sample #4

The laboratory data that were measured are shown in Appendix D.

In order to show the importance of the tuning process and the sequence of tuning process, two tuning procedures with small changes were made.

➤ *Procedure A:*

First of all, the oil sample was introduced in WinProp software with zero value for binary interaction coefficients between the hydrocarbon pairs, and it run without any regression processes, in other words, the regression option was not activated yet. A record was kept of the predicted values for the fundamental properties of the sample, and a comparison was made between the predicted and the laboratory (original) values. This is shown in table ( ).

After that, and by looking at the molecular weight of the fluid at saturation conditions, it was noticed that the predicted value and the lab extracted value were relatively close. So, the next step was to look at the density of oil at atmospheric conditions, which was also close to the lab value, but by using the volume shift of the plus fraction only as a regression parameter, it was managed to perfectly match these two values. Table 50 shows the fundamental properties values before and after using the volume shift of C12+.

Table 50: Fundamental properties values after changing the volume shift of C12+_Oil Sample IV.

Property	Lab. Extracted Data	Volume Shift C12+
ZL(atm)	0.008631951	0.00855
ZL(sat)	0.961359067	0.7737
MWL(atm)"g/mol"	166.05	164.3954
MWL(sat)"g/mol"	76.3	75.22
Separator ng-GOR	0.625200966	0.62531866
Separator ng-Bo	0.622799587	0.626348378
ρo (atm) "lb/ft3"	50.69138808	50.69138
ρo (sat) "lb/ft3"	39.95380341	39.4402
ng'-DL Test	0.668494562	0.694632182
Patm"psi"	14.7	14.7
Psat"psia"	3315	2671.708
Tatm"K"	288.706	288.706
Tsat"K"	340.9	340.9
GOR " sm3/sm3"	193.2467532	195.1970315
Sep. Bo	1.546	1.5734
ρo (atm) "kg/m3"	812	811.9998705
ρo (sat)"kg/m3"	640	631.7728437
Sep.GOR "scf/stb"	1085	1095.95
DL-GOR	1210	1388.37
Residual oil density	824	829.8
DL-MW (1.1*residual)"kg/mol"	0.182655	0.18083494
Z'L atm - DL	0.009356867	0.009198882
Error% (ZL&ZL')	-8.398058252	-7.589260338
Lab (ng'/1-ng') Error%	2.016541768	2.274739321
Lab (ng/1-ng) Error%	1.668096524	1.66893462

The value of the volume shift of the C12+ was 0.1939355 before the regression, and it went to 0.2202595 after the regression, which means that the volume shift had a deviation of almost 13.57% from its original value that was given by the software.

After that the saturation pressure of the fluid was the second target to be tuned. This was done by setting the binary interaction coefficients of the hydrocarbon pairs as a regression parameter. The fundamental properties values before and after the regression are shown in Table 51.

Property	Lab. Extracted Data	kijs (hydrocarbon pairs)
ZL(atm)	0.008631951	0.00862
ZL(sat)	0.961359067	0.9516
MWL(atm)"g/mol"	166.05	165.9165
MWL(sat)"g/mol"	76.3	75.22
Separator ng-GOR	0.625200966	0.630267828
Separator ng-Bo	0.622799587	0.63131083
ρo (atm) "lb/ft3"	50.69138808	50.74102
ρo (sat) "lb/ft3"	39.95380341	39.7936
ng'-DL Test	0.668494562	0.702127614
Patm"psi"	14.7	14.7
Psat"psia"	3315	3315.643
Tatm"K"	288.706	288.706
Tsat"K"	340.9	340.9
GOR " sm3/sm3"	193.2467532	197.7564378
Separator Bo	1.546	1.5675
ρo (atm) "kg/m3"	812	812.7950289
ρo (sat)"kg/m3"	640	637.4337816
Separator GOR "scf/stb"	1085	1110.32
DL-GOR	1210	1401.94
Residual oil density	824	816.1
DL-MW (1.1*residual)"kg/mol"	0.182655	0.18250815
Z'L atm - DL	0.009356867	0.009439848
Error% (ZL&ZL')	-8.398058252	-9.510998761
Lab (ng'/1-ng') Error%	2.016541768	2.357142348
Lab (ng/1-ng) Error%	1.668096524	1.704660494

The initial exponential value of the binary interaction coefficients of the hydrocarbon pairs was zero before the regression, and after the regression it got a value of 0.95036142.

After that and by looking at the fundamental properties values, it was decided that a good match was made for almost all these properties, so it was decided to have a look at the constant mass study test and the differential vaporization test curves. By looking at the differential vaporization curves of both oil volume factor (Bo) and gas-oil ratio (GOR), it was noticed that their predicted values were higher than those measured in the laboratory. For this reason, it was decided to use the critical temperature of C12+ as a regression parameter, since it was noticed that by increasing the critical temperature of C12+ will shift these two curves downwards and they will get smaller values. This is shown in Table 52.

Property	Lab. Extracted Data	Tc C12+
ZL(atm)	0.008631951	0.00891
ZL(sat)	0.961359067	1.039
MWL(atm)"g/mol"	166.05	165.9947
MWL(sat)"g/mol"	76.3	75.22
Separator ng-GOR	0.625200966	0.630399757
Separator ng-Bo	0.622799587	0.631387065
ρo (atm) "lb/ft3"	50.69138808	49.09154
ρo (sat) "lb/ft3"	39.95380341	39.304
ng'-DL Test	0.668494562	0.698691678
Patm"psi"	14.7	14.7
Psat"psia"	3315	3575.604
Tatm"K"	288.706	288.706
Tsat"K"	340.9	340.9
GOR " sm3/sm3"	193.2467532	191.4282746
Separator Bo	1.546	1.5357
ρo (atm) "kg/m3"	812	786.3728335
ρo (sat)"kg/m3"	640	629.591124
Separator GOR "scf/stb"	1085	1074.79
DL-GOR	1210	1350.65
Residual oil density	824	799.6
DL-MW (1.1*residual)"kg/mol"	0.182655	0.18259417
Z'L atm - DL	0.009356867	0.009639183
Error% (ZL&ZL')	-8.398058252	-8.18387621
Lab (ng'/1-ng') Error%	2.016541768	2.318859538
Lab (ng/1-ng) Error%	1.668096524	1.705625927

The initial value of the critical temperature of C12+ was 818.32748 K, after the regression it got a value of 860.41005 K, which means that the deviation percentage from the original value was about 5.1425%.

By looking at the fundamental properties after the regression, it was noticed that the saturation pressure had a value that is far from the laboratory one. To tune the saturation pressure, the binary interaction coefficient between hydrocarbon pairs was chosen again as a regression parameter. The values of the fundamental properties after the regression are shown in Table 53 with the exponential value of the binary interaction coefficients equals to 0.68324.

Property	Lab. Extracted Data	kijs (hydrocarbon pairs)
ZL(atm)	0.008631951	0.00889
ZL(sat)	0.961359067	0.9668
MWL(atm)"g/mol"	166.05	165.552
MWL(sat)"g/mol"	76.3	75.22
Separator ng-GOR	0.625200966	0.628997623
Separator ng-Bo	0.622799587	0.629993992
ρo (atm) "lb/ft3"	50.69138808	49.07941
ρo (sat) "lb/ft3"	39.95380341	39.1637
ng'-DL Test	0.668494562	0.697395347
Patm"psi"	14.7	14.7
Psat"psia"	3315	3315.158
Tatm"K"	288.706	288.706
Tsat"K"	340.9	340.9
GOR " sm3/sm3"	193.2467532	190.7087199
Separator Bo	1.546	1.5389
ρo (atm) "kg/m3"	812	786.1785291
ρo (sat)"kg/m3"	640	627.3437285
Separator GOR "scf/stb"	1085	1070.75
DL-GOR	1210	1345.79
Residual oil density	824	799.5
DL-MW (1.1*residual)"kg/mol"	0.182655	0.1821072
Z'L atm - DL	0.009356867	0.009614679
Error% (ZL&ZL')	-8.398058252	-8.151614862
Lab (ng'/1-ng') Error%	2.016541768	2.30464185
Lab (ng/1-ng) Error%	1.668096524	1.695400519

The next target was to tune the oil density at all the pressure steps of the differential vaporization test and the API gravity of the separator test, and to do so, the molecular weight of C12+ was chosen as a regression parameter. The molecular weight of the plus fraction will have zero effects on both the differential vaporization Bo and GOR values and on the constant mass study values, it will affect only the density, and it will bring the predicted values closer to the laboratory values. The fundamental properties values after the regression are shown in Table 54.

Table 54: Fundamental properties values after changing the molecular weight of C12+_Oil Sample IV.

Property	Lab. Extracted Data	MW C12+
ZL(atm)	0.008631951	0.00889
ZL(sat)	0.961359067	0.9668
MWL(atm)"g/mol"	166.05	170.5904
MWL(sat)"g/mol"	76.3	77.08
Separator ng-GOR	0.625200966	0.628998
Separator ng-Bo	0.622799587	0.629994
ρo (atm) "lb/ft3"	50.69138808	50.57307
ρo (sat) "lb/ft3"	39.95380341	40.1343
ng'-DL Test	0.668494562	0.696764
Patm"psi"	14.7	14.7
Psat"psia"	3315	3315.158
Tatm"K"	288.706	288.706
Tsat"K"	340.9	340.9
GOR " sm3/sm3"	193.2467532	190.7087
Separator Bo	1.546	1.5389
ρo (atm) "kg/m3"	812	810.1047
ρo (sat)"kg/m3"	640	642.8913
Separator GOR "scf/stb"	1085	1070.75
DL-GOR	1210	1345.79
Residual oil density	824	826.3
DL-MW (1.1*residual)"kg/mol"	0.182655	0.187649
Z'L atm - DL	0.009356867	0.009586
Error% (ZL&ZL')	-8.398058252	-7.828578
Lab (ng'/1-ng') Error%	2.016541768	2.297758
Lab (ng/1-ng) Error%	1.668096524	1.695401

The value of the molecular weight of C12+ before the regression was 284.41 g/mol, and after the regression it got a value of 298.4582 g/mol, which means the it had a deviation of almost 4.939%.

After that, the critical pressure and the critical temperature of C12+ were used as regression parameters in order to bring the predicted GOR and Bo measured from the differential vaporization test closer to those measured in the laboratory. The fundamental properties values after the regression are shown in Table 55. The critical temperature of C12+ got a value of 905.26 K instead of 860.41 K, and the critical pressure got a value of 13.573 atm instead of 13.194 atm.

Property	Lab. Extracted Data	Pc C12+__Tc C12+
ZL(atm)	0.008631951	0.009
ZL(sat)	0.961359067	1.0673
MWL(atm)"g/mol"	166.05	170.6993
MWL(sat)"g/mol"	76.3	77.08
Separator ng-GOR	0.625200966	0.629197621
Separator ng-Bo	0.622799587	0.630144712
ρo (atm) "lb/ft3"	50.69138808	49.96467
ρo (sat) "lb/ft3"	39.95380341	40.2643
ng'-DL Test	0.668494562	0.696952
Patm"psi"	14.7	14.7
Psat"psia"	3315	3671.629
Tatm"K"	288.706	288.706
Tsat"K"	340.9	340.9
GOR " sm3/sm3"	193.2467532	188.5393692
Separator Bo	1.546	1.5158
ρo (atm) "kg/m3"	812	800.3590664
ρo (sat)"kg/m3"	640	644.9736896
Separator GOR "scf/stb"	1085	1058.57
DL-GOR	1210	1327.07
Residual oil density	824	814.6
DL-MW (1.1*residual)"kg/mol"	0.182655	0.18776923
Z'L atm - DL	0.009356867	0.00972985
Error% (ZL&ZL')	-8.398058252	-8.109443244
Lab (ng'/1-ng') Error%	2.016541768	2.299806776
Lab (ng/1-ng) Error%	1.668096524	1.696854323

After that, it was noticed that the predicted saturation pressure value was not equal to that of the laboratory measured, so again the binary interaction coefficients of the hydrocarbon pairs were used as a regression parameter. After the regression was done, the exponential value of the binary interaction coefficient of the hydrocarbon pairs got a value of 0.33893 instead of 0.68324. The fundamental properties values are shown in Table 56.

Table 56: Fundamental properties values after changing the binary interaction coefficients between the hydrocarbon pairs_Oil Sample IV.

Property	Lab. Extracted Data	kijs (hydrocarbon pairs)
ZL(atm)	0.008631951	0.00897
ZL(sat)	0.961359067	0.968

MWL(atm)"g/mol"	166.05	170.0704
MWL(sat)"g/mol"	76.3	77.08
Separator ng-GOR	0.625200966	0.627223282
Separator ng-Bo	0.622799587	0.628160497
ρo (atm) "lb/ft3"	50.69138808	49.94605
ρo (sat) "lb/ft3"	39.95380341	40.0878
ng'-DL Test	0.668494562	0.69519551
Patm"psi"	14.7	14.7
Psat"psia"	3315	3315.46
Tatm"K"	288.706	288.706
Tsat"K"	340.9	340.9
GOR " sm3/sm3"	193.2467532	187.5775881
Separator Bo "vol/svol"	1.546	1.5194
ρo (atm) "kg/m3"	812	800.0608019
ρo (sat)"kg/m3"	640	642.1464243
Separator GOR "scf/stb"	1085	1053.17
DL-GOR "scf/stb"	1210	1320.64
Residual oil density "kg/m3"	824	814.4
DL-MW (1.1*residual)"kg/mol"	0.182655	0.18707744
Z'L atm - DL	0.009356867	0.009696383
Error% (ZL&ZL')	-8.398058252	-8.097918379
Lab (ng'/1-ng') Error%	2.016541768	2.280791568
Lab (ng/1-ng) Error%	1.668096524	1.682570965

Table 57: Oil volume factor (Bo) - Constant Mass Study results _Oil Sample IV.

Laboratory Extracted Data		Predicted by Winprop without tuning		Final Tuning	
Pressure"psia"	*Bo"vol/svol"*	*Pressure"psia"*	*Bo"vol/svol"*	*Pressure"psia"*	*Bo"vol/svol"*
5015	0.9745	5015	0.958978	5015	0.975387
4515	0.981	4515	0.966146	4515	0.981844
4265	0.9848	4265	0.969993	4265	0.985293
4015	0.9885	4015	0.974036	4015	0.988905
3765	0.9925	3765	0.978293	3765	0.992693
3515	0.9966	3515	0.982784	3515	0.996674
3315	1	3315	0.986561	3315.46	1
3300	1.0018	3300	0.986851	3315	1.00004
3252	1.006	3252	0.987787	3300	1.00138
3165	1.0145	3165	0.98951	3252	1.00579
3004	1.0319	3004	0.992794	3165	1.01432
2745	1.0668	2745	0.998358	3004	1.03211
2398	1.1337	2671.71	1	2745	1.06754

1938	1.2787	2398	1.05445	2398	1.13344
1453	1.5723	1938	1.19547	1938	1.27452
972	2.173	1453	1.47503	1453	1.5556
615	3.2866	972	2.09494	972	2.18005
		615	3.27778	615	3.37239

Table 58: Oil volume factor (Bo) - Differential Vaporization Test_Oil Sample IV.

Laboratory Extracted Data		Predicted by WinProp without tuning		Final Tuning	
Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"
3315	1.634	3115	1.73843	3315.46	1.69659
3115	1.589	2715	1.75336	3115	1.65668
2715	1.515	2671.71	1.75507	2715	1.58355
2115	1.423	2115	1.6081	2115	1.48517
1515	1.342	1515	1.47634	1515	1.3957
765	1.247	765	1.33408	765	1.29015
15	1.047	15	1.0315	15	1.02719

Table 59: Gas-Oil Ratio (GOR) - Differential Vaporization Test_Oil Sample IV.

Laboratory Extracted Data		Predicted by WinProp without tuning		Final Tuning	
Pressure"psia"	GOR "scf/stb"	Pressure"psia"	GOR "scf/stb"	Pressure"psia"	GOR "scf/stb"
3315	1210	3115	1360.39	3315.46	1320.64
3115	1120	2715	1360.39	3115	1231.26
2715	962	2671.71	1360.39	2715	1066.33
2115	750	2115	1047.68	2115	843.483
1515	560	1515	766.355	1515	641.681
765	337	765	466.184	765	408.715
15	0	15	0	15	0

Table 60: Oil density - Differential Vaporization Test_Oil Sample IV.

Laboratory Extracted Data		Predicted by WinProp without tuning		Final Tuning	
Pressure"psia"	ρ_o "kg/m3"	Pressure"psia"	ρ_o "kg/m3"	Pressure"psia"	ρ_o "kg/m3"
3315	640	3115	630.496	3315.46	642.145
3115	649	2715	625.125	3115	648.838
2715	665	2671.71	624.517	2715	662.311
2115	687	2115	652.309	2115	683.166
1515	707	1515	682.135	1515	705.118
765	734	765	720.316	765	734.706
15	787	15	788.294	15	792.878
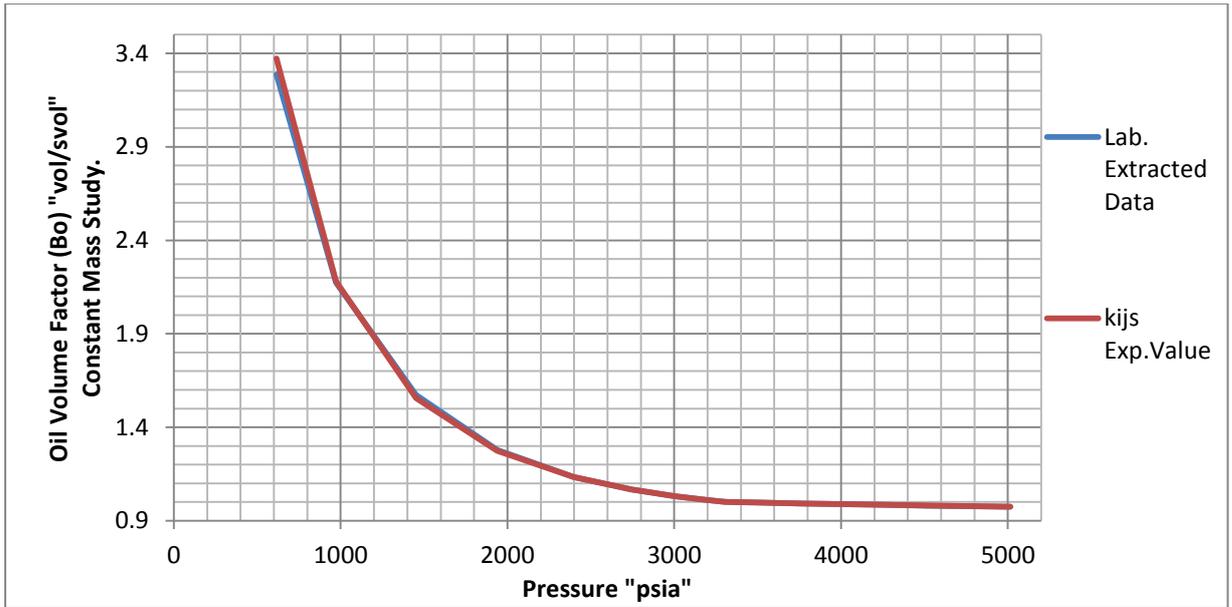
Figure 14: Oil Volume Factor (Bo) - Constant Mass Study_Oil sample IV.
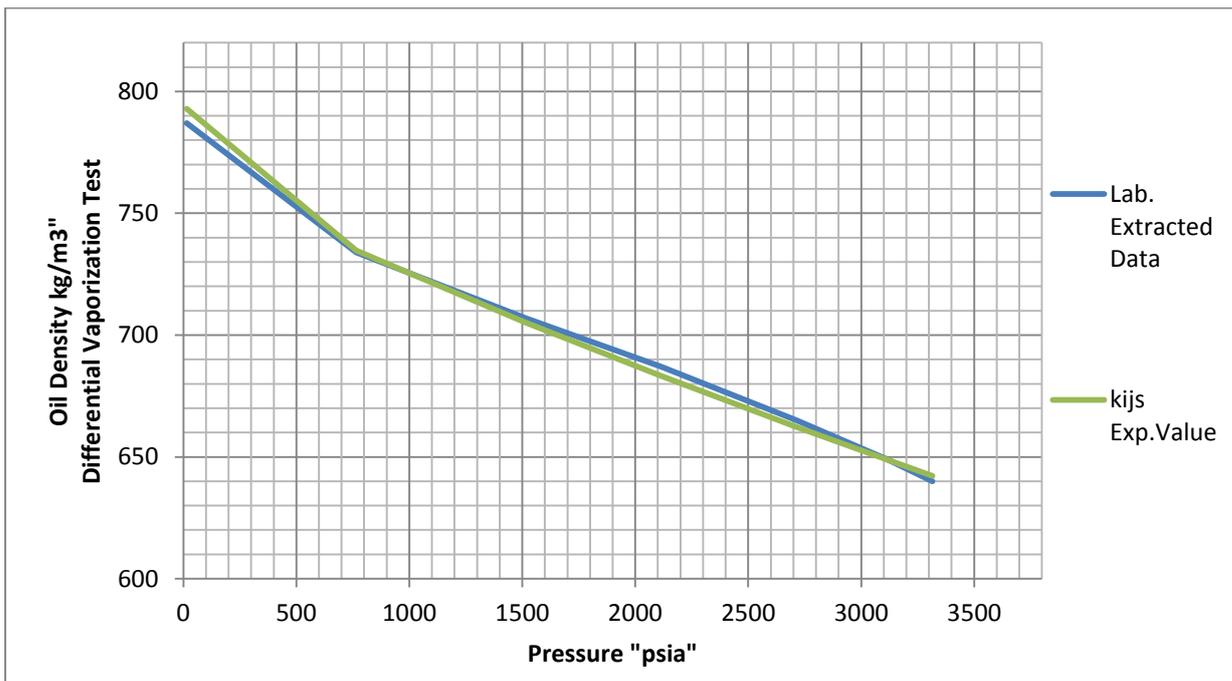
Figure 15: Oil Density - Differential Vaporization Test_Oil Sample IV.
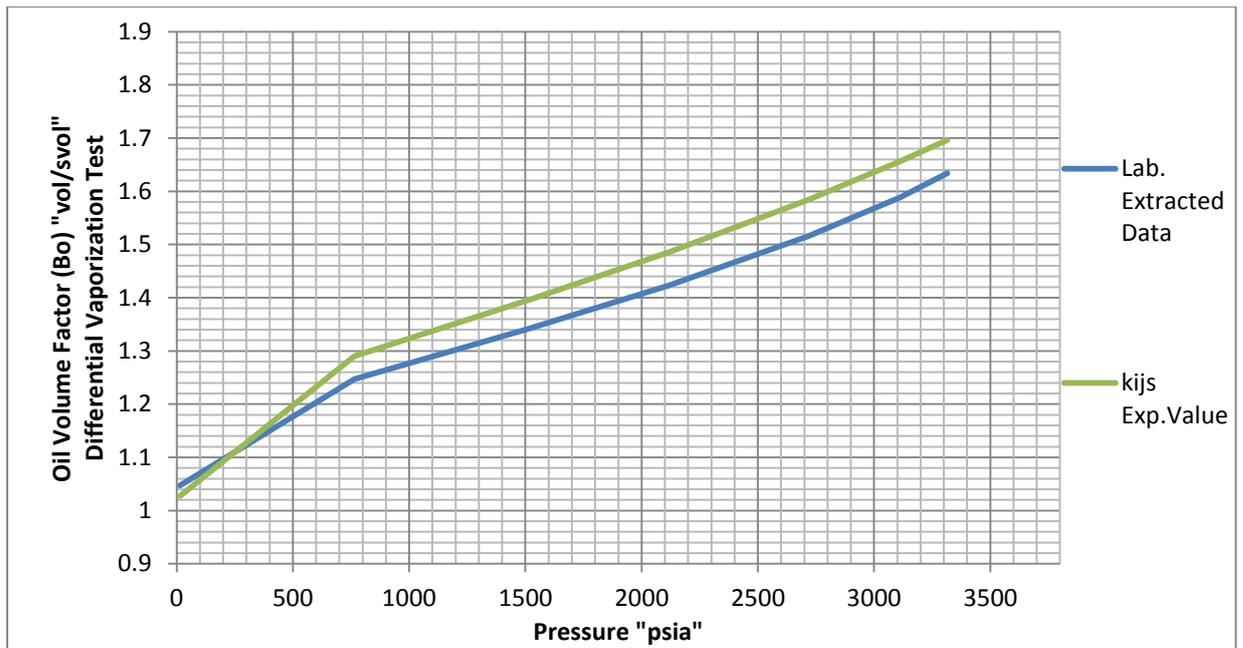
Figure 16: Oil Volume Factor (Bo) - Differential Vaporization Test_Oil Sample IV.
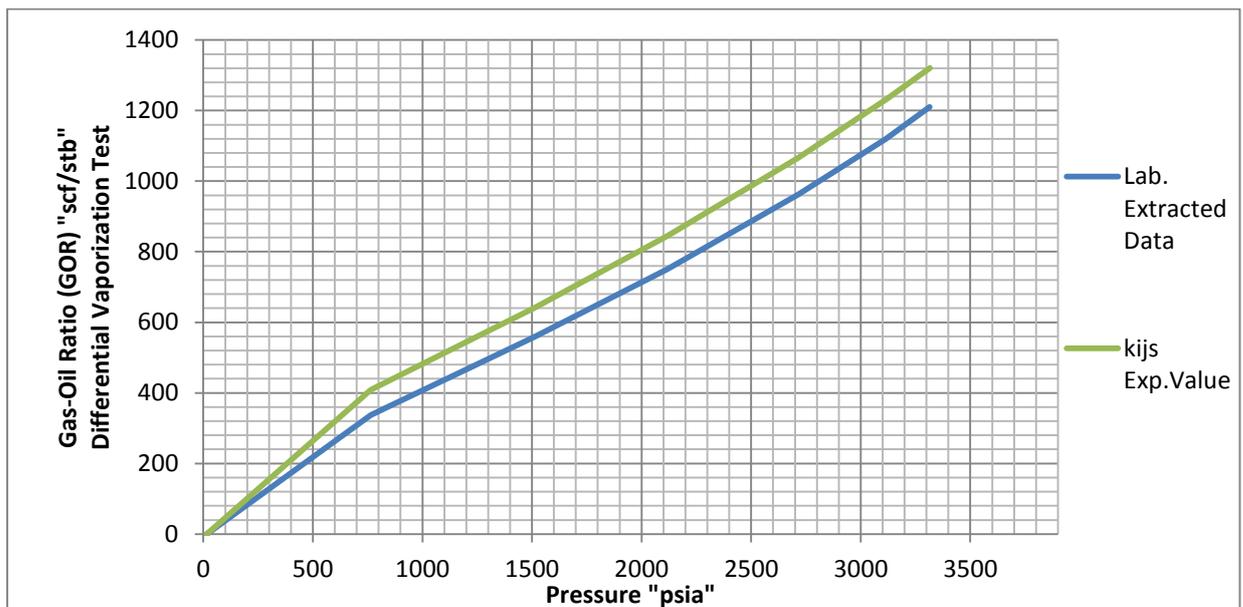
Figure 17: Gas-Oil Ratio (GOR) - Differential Vaporization Test_Oil Sample IV.

➢ *Procedure B:*

In this procedure the following tuning steps were followed:

1- The volume shift of the plus fraction C12+ was used as a regression parameter to tune the oil density at atmospheric conditions. This step is exactly the same with the step that was followed in procedure A.

2- After that the saturation pressure was tuned by using as a regression parameter the binary interaction coefficients between the hydrocarbon pairs. This is exactly the same as the one in procedure A.

3- The next step was by using a zero value for the binary interaction coefficients between the hydrocarbon pairs.

4- After that, the critical temperature of the plus fraction C12+ was used in the regression process, as both the oil volume factor (Bo) and the gas-oil ratio (GOR) that were predicted from the differential vaporization test were higher than those that were measured in the laboratory. The critical temperature of C12+ after the regression got a value of 904.06876 K, which means it had a 10.477% deviation from its original value.

5- Then the saturation pressure was to be tuned, and to do so, Omega A for components (NC5, FC6, FC7, FC8, FC9, FC10, FC11 and C12+) were given a value of 0.49 instead of 0.45723553. In other words Omega A had a deviation of about 7.166% from its initial value.

6- After that, the molecular weight of the plus fraction was used as a regression parameter in order to predict a closer API gravity measured from separator test to the laboratory measured one, and a closer oil density and residual oil density predicted from the differential vaporization test to the laboratory ones. The molecular weight of C12+ after the regression got a value of 302 g/mol instead of 284.41 with about 6.18% deviation.

The values of the fundamental properties after the tuning is shown in Table 61 and in figures (18-21).

Table 61: Fundamental properties values after tuning using procedure B_Oil Sample IV.

Property	Lab. Extracted Data	Predicted by Winprop "no tuning"	Final Tuning
ZL(atm)	0.008631951	0.0087	0.00903
ZL(sat)	0.961359067	0.7827	0.9688
MWL(atm)"g/mol"	166.05	164.3954	169.8426
MWL(sat)"g/mol"	76.3	75.22	77.55
Sep. ng-GOR	0.625200966	0.625150146	0.621660917
Sep. ng-Bo	0.622799587	0.626071254	0.622539918
ρo (atm) "lb/ft3"	50.69138808	49.78147	49.53949
ρo (sat) "lb/ft3"	39.95380341	38.9873	40.2523
ng'-DL Test	0.668494562	0.694626165	0.682467114
Patm"psi"	14.7	14.7	14.7
Psat"psia"	3315	2671.708	3311.585
Tatm"K"	288.706	288.706	288.706
Tsat"K"	340.9	340.9	340.9
GOR " sm3/sm3"	193.2467532	191.6936549	181.9636364
Sep. Bo	1.546	1.5631	1.4898

ρo (atm) "kg/m3"	812	797.4244772	793.5483206
ρo (sat)"kg/m3"	640	624.5180651	644.7814676
Sep.GOR "scf/stb"	1085	1076.28	1021.65
DL-GOR	1210	1360.39	1231.93
Residual oil density	824	813.1	805.1
DL-MW (1.1*residual)"kg/mol"	0.182655	0.18083494	0.18682686
Z'L atm - DL	0.009356867	0.009387815	0.009795252
Error% (ZL&ZL')	-8.398058252	-7.905915398	-8.474550296
Lab (ng'/1-ng') Error%	2.016541768	2.27467479	2.1492801
Lab (ng/1-ng) Error%	1.668096524	1.667734798	1.643131636

Table 62: Oil volume factor (Bo) - Constant Mass Study results_Procedure B_Oil Sample IV.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"
5015	0.9745	5015	0.958978	5015	0.978025
4515	0.981	4515	0.966146	4515	0.983819
4265	0.9848	4265	0.969993	4265	0.986902
4015	0.9885	4015	0.974036	4015	0.99012
3765	0.9925	3765	0.978293	3765	0.993484
3515	0.9966	3515	0.982784	3515	0.997007
3315	1	3315	0.986561	3315	0.999949
3300	1.0018	3300	0.986851	3311.58	1
3252	1.006	3252	0.987787	3300	1.00108
3165	1.0145	3165	0.98951	3252	1.00569
3004	1.0319	3004	0.992794	3165	1.01456
2745	1.0668	2745	0.998358	3004	1.03298
2398	1.1337	2671.71	1	2745	1.06935
1938	1.2787	2398	1.05445	2398	1.13629
1453	1.5723	1938	1.19547	1938	1.27811
972	2.173	1453	1.47503	1453	1.55859
615	3.2866	972	2.09494	972	2.1794
		615	3.27778	615	3.36233

Table 63: Oil volume factor (Bo) – Differential Vaporization results_Procedure B_Oil Sample IV.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"	Pressure"psia"	Bo"vol/svol"
3315	1.634	3115	1.73843	3311.58	1.62412
3115	1.589	2715	1.75336	3115	1.58866
2715	1.515	2671.71	1.75507	2715	1.52178
2115	1.423	2115	1.6081	2115	1.4312
1515	1.342	1515	1.47634	1515	1.34859
765	1.247	765	1.33408	765	1.25087

15	1.047	15	1.0315	15	1.02566

Table 64: Gas-Oil Ratio (GOR) – Differential Vaporization results_Procedure B_Oil Sample IV.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure"psia"	GOR"scf/stb"	Pressure"psia"	GOR"scf/stb"	Pressure"psia"	GOR"scf/stb"
3315	1210	3115	1360.39	3311.58	1231.93
3115	1120	2715	1360.39	3115	1150.02
2715	962	2671.71	1360.39	2715	994.828
2115	750	2115	1047.68	2115	784.055
1515	560	1515	766.355	1515	592.674
765	337	765	466.184	765	370.934
15	0	15	0	15	0

Table 65: Oil density – Differential Vaporization results_Procedure B_Oil Sample IV.

Lab. Extracted Data		Predicted by Winprop "no tuning"		Final Tuning	
Pressure"psia"	ρ_o "kg/m3"	Pressure"psia"	ρ_o "kg/m3"	Pressure"psia"	ρ_o "kg/m3"
3315	640	3115	630.496	3311.58	644.779
3115	649	2715	625.125	3115	651.128
2715	665	2671.71	624.517	2715	664.136
2115	687	2115	652.309	2115	684.135
1515	707	1515	682.135	1515	705.002
765	734	765	720.316	765	732.935
15	787	15	788.294	15	784.968
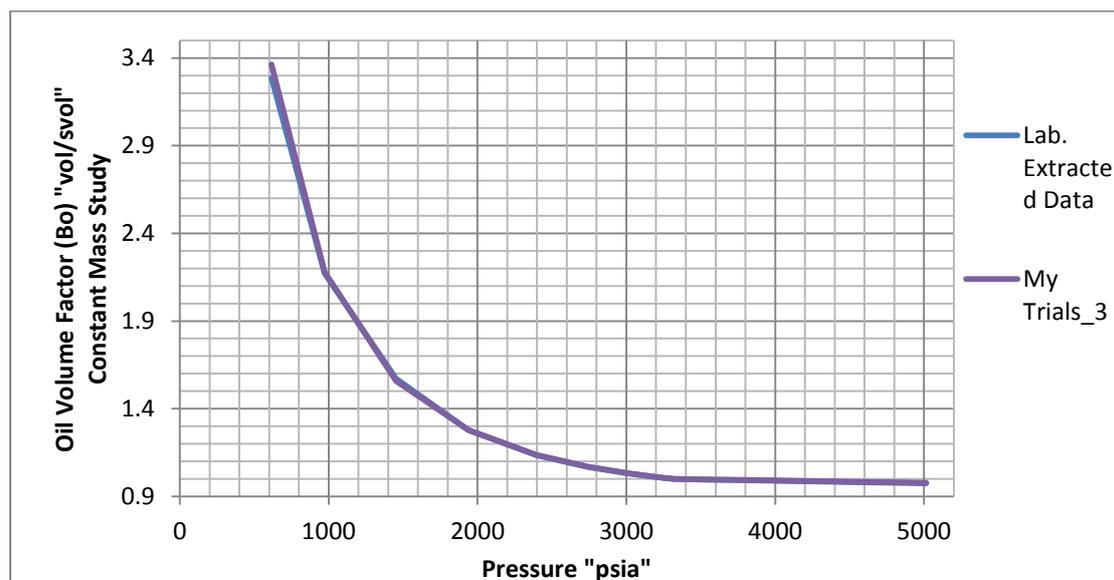
**Figure 18: Oil Volume Factor (Bo) - Constant Mass Study_Procedure B_Oil sample IV.**
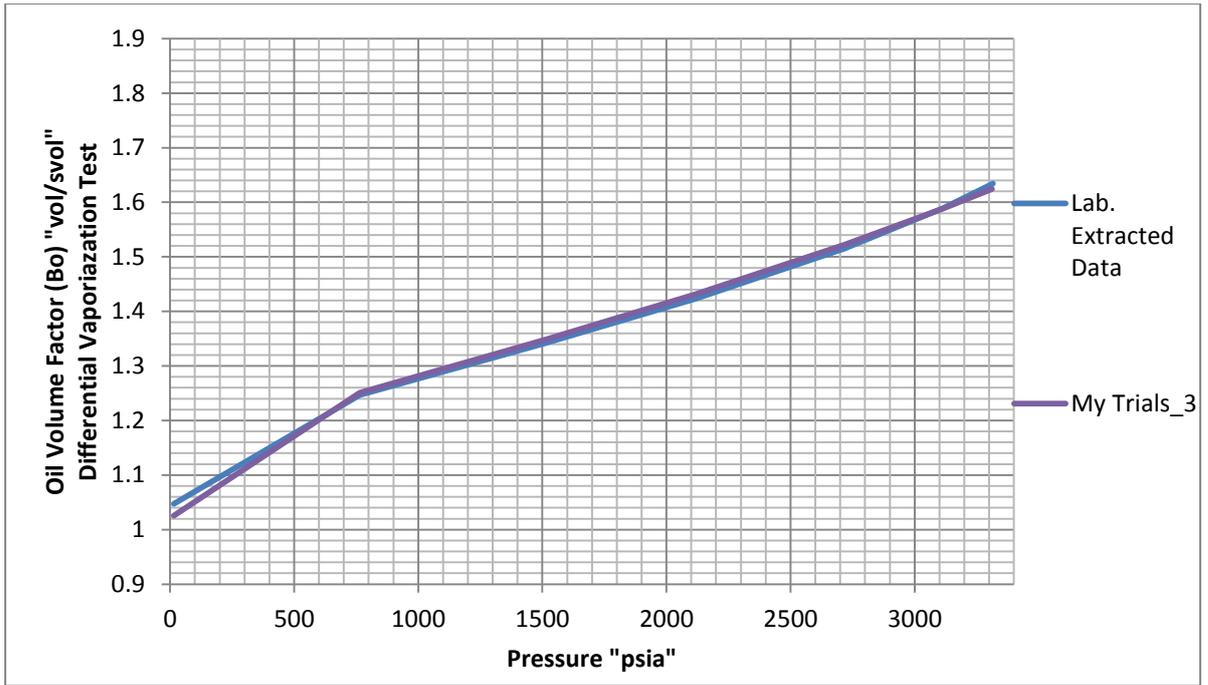
Figure 19: Oil Volume Factor (Bo) – Differential Vaporization_Procedure B_Oil sample IV.
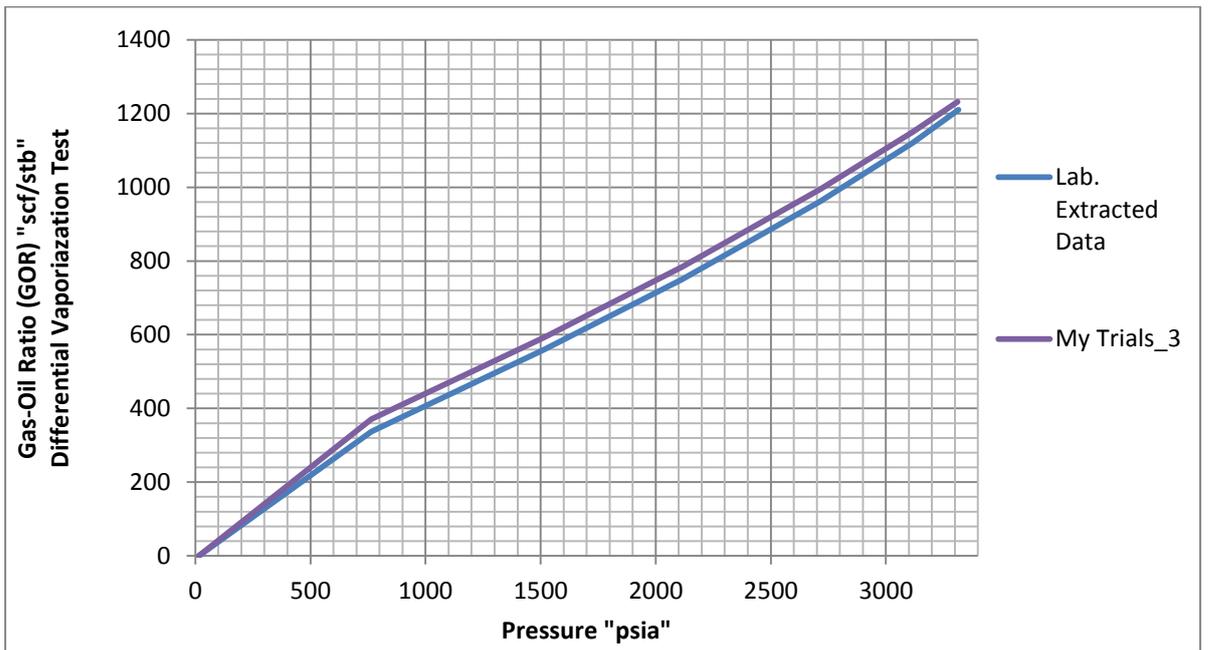
Figure 20: Gas-Oil Ratio (GOR) – Differential Vaporization_Procedure B_Oil sample IV.
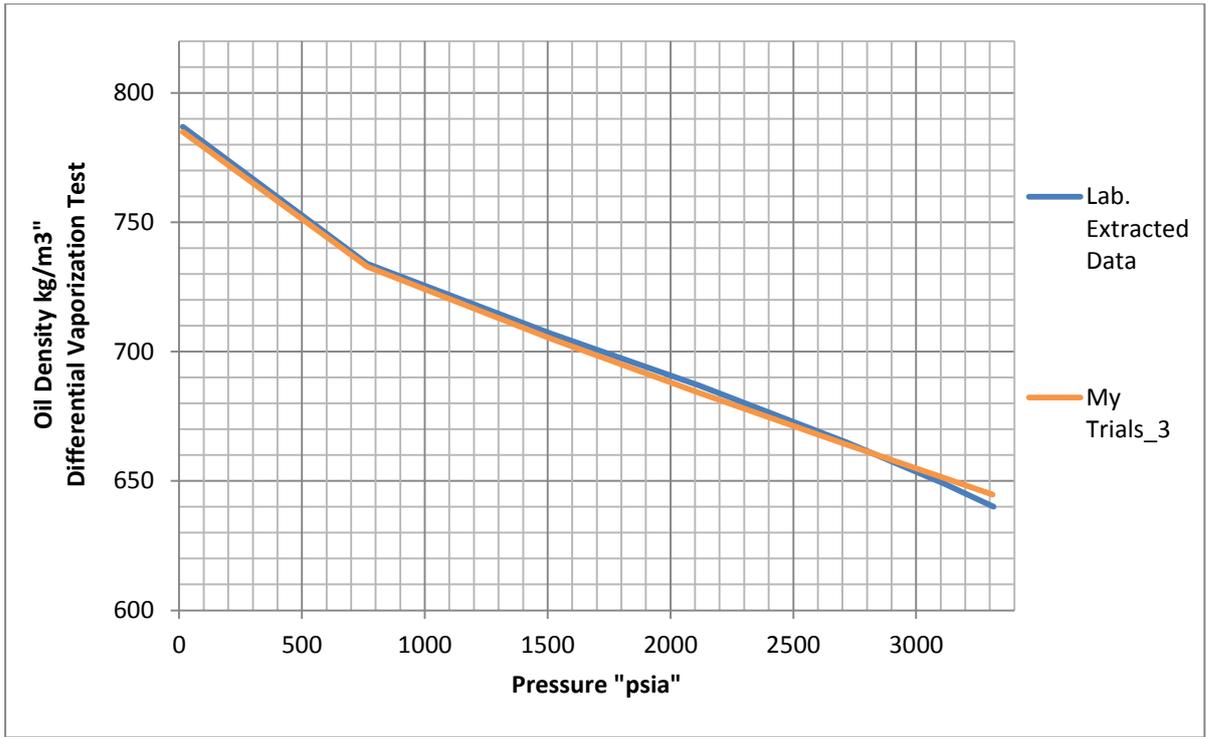
Figure 21: Oil density – Differential Vaporization _ Procedure B _ Oil sample IV.

15.   Discussion of the Results

1- The sensitivity analysis tables were made in order to understand how every property is being affected after changing a certain parameter. These tables give us a clue of which direction each property will move if we change a certain parameter, the plus sign indicates an increasing in the property, while the minus sign indicates a decreasing in the value of the property.

2- A comparison was made between the three sensitivity tables to check the trend of each fundamental property with respect to the change of each property, and it was noticed that the fundamental properties of the fluids follow the same trend. This means that these sensitivity tables can be used as a general table for oil samples, and could be used in every oil sample.

3- In order to have a good tune and a good match for, the sequence of tuning and the parameters that are going to be used play a very important role. In this study, two different procedures were followed to tune oil sample IV, by using almost the same parameters in the tuning. A huge difference between the final values for each property was noticed.

4- Weight factors play a significant role in tuning, as it can be considered as one of the major parameters that affect the tuning process. In other words, using appropriate weight factors can lead to a significant better tuning than using the same weight factor for all the tests and all the properties of the fluid.

5- From this study, the fundamental properties of the fluid were to be tuned first, because the closer the predicted values of fundamental properties are to the laboratory values, the more realistic EOS model is going to be modeled. This could be done in ideal samples, but in real samples this is difficult to achieve, which means that sometimes, we should sacrify some of the fundamental properties values in order to get a better match on the overall properties of the sample.

6- In order to calculate the ng' from the differential vaporization test, a molecular weight with a value higher by 10% of the residual oil molecular weight was used.

7- The ng' measured from the differential vaporization test is higher than that measured from the separator test (ng), and this is due to the fact that the differential vaporization test is done on a much higher temperature, which means mole moles are going to be vaporized at higher temperature.

8- From the fundamental tables that were made for each sample, it was noticed that the differences in ng is not so important, but because it enters into the calculations of GOR with the following function [ng/(1-ng)], the errors becomes very significant.

9- The difference between ZL (measured form the separator test) and ZL' (measured from the differential vaporization test) is due to the fact that the composition that is calculated from the residual oil is not the same, which means that each flash step that is done, we produce a different gas composition, so we don't end up with the same composition as that measured in the lab, and this explains why there is a different value of ZL' and ZL.

16.   Conclusions

In this study, the fundamental properties were tuned first and then the compositional properties of the fluid were to be tuned, such as gas-oil ratio (GOR) and oil-volume factor (Bo).

Before starting the tuning process, one should first look at the composition of the fluid sample he/she got, and this is due to the fact that the composition of the sample tells which components affects more the tuning process and which affects less. In other words, the higher the concentration of a component in the fluid is, the more it affects the tuning process and it has greater effects on the sample itself.

The next step is to check how far the predicted fundamental properties are from the laboratory extracted data. This will give us a clue on how far the EOS model that is predicted by WinProp is from the real EOS model that suits the specific sample.

Then, if the predicted molecular weight of oil at the atmospheric conditions is far from the laboratory extracted, we should start tuning this property first. Sometimes it is hard to tune this property by simply using the molecular weight of the plus fraction, as we may reach to the bounds of this property and without having a great effect on the predicted molecular weight. So, I suggest modifying the weight factor of gas-oil ratio and oil-volume factor measured from the differential vaporization test and the weight factor of the saturation pressure and the oil density calculated at the saturation conditions.

 After that, the oil density at atmospheric conditions should be tuned by using the volume shift of the plus fraction as a regression parameter.

In order to tune the gas-oil ratio and the oil-volume factor for the differential vaporization test, the parameters that should be used in the regression is the critical temperature of the plus fraction and the critical temperature of methane (CH4).

Adjusting the critical temperature of the heavy components will affect the GOR and Bo curves at high pressures, in other words, they will shift these curves in an upward or downward movement mainly the mid of these curves. Whereas, the light components will shift GOR and Bo curves in the beginning of these curves, and will bring the predicted values at low pressures closer to the laboratory values. Also, adjusting the critical temperature of methane will shift in an upward or downward movement of the tail of GOR curve, and will affect a lot the Bo curve measured from constant mass study.

Adjusting the molecular weight of the plus fraction affects the API gravity measured from the separator test, the oil density and the residual oil density measured from the differential vaporization test, but it doesn't affect the oil-volume factor and the gas-oil ratio measured from the separator test.

Sometimes we might need to change the values of some properties in the fluid without making any regression processes, this can help a lot the tuning process, because CMG WinProp software doesn't give you the flexibility to tune against some fundamental

properties directly, for instance, if we want to tune ng from the separator test, or the molecular weight of oil at atmospheric conditions,…etc. This is because these properties are not included as regression parameter that could be tuned, which means that we can't do it using the regression option, so instead of that, we can chose the most appropriate parameter to adjust its value using the sensitivity table and then we can proceed with the tuning process.

17.   Appendix C

PVT Data for oil sample number III.

17.1 Separator Liquid Analysis:

1- Composition (mole percent)

Component	Flashed Liquid	Flashed Gas	Separator Liquid
N2	0.00	0.00	0.00
CO2	0.01	0.39	0.04
H2S	0.00	0.00	0.00
CH4	0.19	45.78	3.92
C2H6	0.47	19.5	2.03
C3H8	2.07	18.78	3.43
iC4H10	0.92	3.53	1.13
nC4H10	2.6	7.07	2.97
iC5H12	1.36	1.76	1.40
nC5H12	1.95	1.72	1.94
Pseudo C6	4.87	0.89	4.54
Pseudo C7	11.19	0.5	10.32
Pseudo C8	13.35	0.08	12.27
Pseudo C9	9.7	0.00	8.9
Pseudo C10	8.44	0.00	7.75
Pseudo C11	6.31	0.00	5.8
C12+	36.56	0.00	33.57
Total	100	0.00	100.00
Molar ratio	0.9182	100	1.0000

2- Phase properties

	Flashed Liquid		Flashed Gas		Separator Liquid	
Molar Mass:	lb/mol	g/mol	lb/mol	g/mol	lb/mol	g/mol
C7+	0.385	174.5	0.2252	102.14	0.385	174.4
C12+	0.534	242.0			0.534	242.0
fluid	0.351	159.0	0.0699	31.69	0.328	148.6

Density:	g/cm3	kg//m3	g/cm3	kg//m3	g/cm3	kg//m3
C7+	0.826	826				
C12+	0.852	852				
fluid	0.809	809	1.338E-3	1.338		

rel. density			1.094			

17.2 Reservoir Fluid Analysis:

1- Composition (mole percent)

Component	Separator Liquid	Separator Gas	Reservoir Fluid
N2	0.00	0.03	0.01
CO2	0.04	0.53	0.24
H2S	0.00	0.00	0.00
CH4	3.92	82.22	35.78
C2H6	2.03	8.69	4.74
C3H8	3.43	4.72	3.96
iC4H10	1.13	0.76	0.98
nC4H10	2.97	1.51	2.38
iC5H12	1.4	0.40	0.99
nC5H12	1.94	0.42	1.32
Pseudo C6	4.54	0.29	2.81
Pseudo C7	10.32	0.31	6.25
Pseudo C8	12.27	0.10	7.32
Pseudo C9	8.90	0.02	5.29
Pseudo C10	7.75	0.00	4.60
Pseudo C11	5.80	0.00	3.44
C12+	33.57	0.00	19.91
Total	100.00	100.00	100.00
Molar ratio	0.5932	0.4068	1.0000

2- Phase properties

Molar Mass:	Separator Liquid		Separator Gas		Reservoir Liquid	
	lb/mol	g/mol	lb/mol	g/mol	lb/mol	g/mol
C7+	0.385	174.4	0.2310	104.77	0.384	174.2
C12+	0.534	242.0			0.534	242.0
fluid	0.351	148.6	0.0457	20.74	0.213	96.6

Density:	g/cm3	kg//m3	g/cm3	kg//m3	g/cm3	kg//m3
C7+						
C12+						
fluid			0.875E-3	0.875		

| rel. density | | | 0.716 | | | |

17.3 Constant Mass Study Fluid

at 160.0 F (344.3 K)

Pressure		Relative	Compressibility factor		Y-Function
psia	MPa	volume	1/psia	1/MPa	
5015	34.58	0.9668	9.09 E-6	1.318 E-3	
4515	31.13	0.9712	10.40 E-6	1.509 E-3	
4015	27.68	0.9763	10.76 E-6	1.560 E-3	
3765	25.96	0.9789	11.12 E-6	1.612 E-3	
3515	24.24	0.9817	11.47 E-6	1.663 E-3	
3265	22.51	0.9845	12.20 E-6	1.770 E-3	
3015	20.79	0.9875	12.55 E-6	1.820 E-3	
2765	19.06	0.9906	12.47 E-6	1.808 E-3	
2515	17.34	0.9937	12.85 E-6	1.864 E-3	
2258	15.57	0.9970	13.36 E-6	1.937 E-3	
Pb= 2034	14.02	1.0000	202.19 E-6	29.325 E-3	
2022	13.94	1.0023	204.7 E-6	29.691 E-3	2.440
2000	13.79	1.0069	213.59 E-6	30.979 E-3	2.440
1979	13.64	1.0114	219.19 E-6	31.791 E-3	2.415
1938	13.36	1.0206	232.48 E-6	33.718 E-3	2.395
1862	12.84	1.0389	262.75 E-6	38.109 E-3	2.366
1730	11.93	1.0763	319.00 E-6	46.267 E-3	2.301
1515	10.45	1.1555	423.29 E-6	61.393 E-3	2.201
1243	8.57	1.3059	603.82 E-6	87.577 E-3	2.079
931	6.42	1.6090	946.90 E-6	137.336 E-3	1.945
595	4.100	2.3598			1.778

Thermal expansion factor of reservoir fluid: 0.545 E-3 1/F (0.981 E-3 1/K)

Measured at:	5015	psia	34.58	MPa
From:	72.5	F	295.6	K
To:	160.0	F	344.3	K

17.4 Differential Vaporization of reservoir fluid

at 160.0 F (344.3 K)

1- Oil phase properties

Pressure		Oil volume factor, Bo	Solution Gas-Oil ratio, Rs		Reservoir Oil density	
Psia	MPa	vol/svol	scf/sbbl	sm^3/sm^3	g/cm^3	kg/m^3
5015	34.58	1.294			0.709	709
4515	31.13	1.300			0.706	706
4015	27.68	1.307			0.702	702
3765	25.96	1.310			0.700	700
3515	24.24	1.314			0.698	698
3265	22.51	1.318			0.696	696
3015	20.79	1.322			0.694	694
2765	19.06	1.326			0.692	692
2515	17.34	1.330			0.690	690
2258	15.57	1.335			0.687	687
Pb=2034	14.02	1.339	599	106.6	0.685	685
1982	13.67	1.328	584	104.1	0.689	689
1715	11.82	1.295	506	90.1	0.698	698
1315	9.07	1.249	396	70.5	0.712	712
915	6.31	1.205	291	51.9	0.726	726
465	3.21	1.156	177	31.5	0.741	741
15	0.10	1.051	0	0.0	0.773	773

Residual oil relative density at standard conditions: 0.813

API gravity: 42.5

2- Gas phase properties

Pressure		Gas volume factor, Bg	Z	Gas viscosity		Gas rel. density
Psia	MPa	vol/svol		cP	mPa.s	
1982	13.67	0.0077	0.868	0.0160	0.0160	0.632
1715	11.82	0.0090	0.877	0.0153	0.0153	0.637
1315	9.07	0.0120	0.899	0.0142	0.0142	0.641
915	6.31	0.0178	0.929	0.0131	0.0131	0.654
465	3.21	0.0363	0.963	0.0117	0.0117	0.698
15	0.10	1.1638	0.996	0.0078	0.0078	1.149

17.5 Separation test of reservoir fluid

Tank conditions: 70.0 F   (294.3 K)   15psia   (0.10 MPa)

Pressure		Temperature		Gas liquid ratio *					
				Separator		Tank		Total	
Psia	MPa	F	K	scf/sbbl	sm^3/sm^3	scf/sbbl	sm^3/sm^3	scf/sbbl	sm^3/sm^3
660	4.55	100.0	310.9	325	57.8				
250	1.72	100.0	310.9	118	21.1				
60	0.41	100.0	310.9	71	12.6	25	4.4	538	95.9

*Gas volume at standard conditions per volume of tank liquid at standard conditions.

Pressure		Temperature		Separator liquid density		Tank liquid density		Oil vol. factor *	Shrinkage factor **
Psia	MPa	F	K	g/cm^3	kg/m^3	g/cm^3	kg/m^3	vol/svol	vol/svol
660	4.55	100.0	310.9	0.751	751			1.298	0.887
250	1.72	100.0	310.9	0.765	765			1.298	0.924
60	0.41	100.0	310.9	0.776	776	0.807	807	1.298	0.954

*Volume of reservoir fluid at saturation conditions per volume of tank liquid at std. conditions.

**Volume of tank liquid at std. conditions per volume of separator liquid at separator conditions.

18. Appendix A

PVT Data for oil sample number I.

18.1 Semi-detailed composition (pseudo boiling point distribution)

Component		Mole %		Molar Mass (g/mol)		Density (15 deg.C) (g/cm^3)	
O_2		0.00		---			
N_2		0.00		---			
CO_2		0.02		44.01			
H_2S		0.15		34.08			
CH_4		0.00		---		---	
C_2H_6		0.08		30.07		0.356	
C_3H_8		0.38		44.10		0.508	
C4		0.96		58.12		0.579	
	N		0.74		58.12		0.584
	I		0.22		58.12		0.563
C5		2.38		72.15		0.627	
	N		1.49		72.15		0.631
	I		0.89		72.15		0.620
Pseudo C6		5.45		85.65		0.667	
	N		2.71		86.18		0.665
	I		2.56		86.18		0.664
	C		0.18		70.13		0.750
	A		0.00		---		---
Pseudo C7		9.32		92.84		0.727	
	N		2.81		100.20		0.688
	I		2.56		100.20		0.690
	C		3.09		84.16		0.781
	A		0.86		78.11		0.884
Pseudo C8		12.46		104.75		0.758	
	N		2.67		114.23		0.707
	I		3.24		114.23		0.718
	C		4.40		98.19		0.790
	A		2.15		92.14		0.871
Pseudo C9		11.46		117.24		0.780	
	N		2.44		128.26		0.722
	I		2.67		128.26		0.729
	C		2.32		112.21		0.788
	A		4.03		106.17		0.875
Pseudo C10		9.80		130.81		0.789	
	N		2.33		142.28		0.734
	I		2.03		142.28		0.734
	C		1.29		126.24		0.799
	A		4.15		120.19		0.866
Pseudo C11		7.57		146.45		0.786	
	N		1.59		156.31		0.744
	I		2.28		156.31		0.743
	C		1.25		140.27		0.811
	A		2.45		134.03		0.862
C12+		39.98		233.27			

Average molar mass = 159.49 g/mol

18.2 Constant mass study of reservoir fluid

At: 235.0 F   (385.9 K)

Pressure		Relative	Compressibility factor		Y-Function
Psia	MPa	volume	1/Psia	1/MPa	
6015	41.47	0.9240			
5535	38.16	0.9379	30.90E-6	4.481E-3	
5215	35.96	0.9477	32.42E-6	4.702E-3	
4833	33.32	0.9604	34.69E-6	5.031E-3	
4610	31.78	0.9682	36.16E-6	5.245E-3	
4415	30.44	0.9759	40.42E-6	5.863E-3	
Pi= 4211	29.03	0.9855	47.86E-6	6.941E-3	
4040	27.85	0.9945	52.62E-6	7.632E-3	
Pb= 3954	27.26	1.0000	63.72E-6	9.242E-3	
3873	26.70	1.0107	132.13E-6	19.163E-3	1.933
3821	26.34	1.0182	141.19E-6	20.477E-3	1.902
3766	25.97	1.0264	144.71E-6	20.988E-3	1.886
3720	25.65	1.0336	151.74E-6	22.008E-3	1.868
3669	25.30	1.0418	153.60E-6	22.278E-3	1.856
3578	24.67	1.0572	160.60E-6	23.293E-3	1.834
3354	23.13	1.0995	171.52E-6	24.877E-3	1.797
2971	20.48	1.1916	201.89E-6	29.282E-3	1.726
2437	16.80	1.3896	266.82E-6	38.699E-3	1.597
1890	13.03	1.7408	368.77E-6	53.486E-3	1.474
1604	11.06	2.0485	526.05E-6	76.297E-3	1.396

Thermal expansion factor of reservoir fluid: 0922E-3 1/F (1.660E-3 1/K)

Measured at:	6015	Psia	41.47	MPa
From :	72.0	F	295.4	K
To :	235.0	F	385.9	K

18.3 Differential vaporization of reservoir fluid

At: 235.0 F   (385.9 K)

1- Oil phase properties

Pressure		Oil volume factor, Bo	Solution Gas-Oil ratio, Rs		Reservoir Oil density	
Psia	MPa	vol/svol	scf/sbbl	sm^3/sm^3	g/cm^3	Kg/m^3
6015	41.47	3.156			0.556	556
5535	38.16	3.204			0.548	548
5215	35.96	3.237			0.542	542
4833	33.32	3.281			0.535	535
4610	31.78	3.307			0.530	530
4415	30.44	3.334			0.526	526
4211	29.03	3.366			0.521	521
4040	27.85	3.397			0.516	516
Pb= 3954	27.26	3.416	3999	712.3	0.514	514
3715	25.61	2.811	3054	543.9	0.545	545
3415	23.55	2.430	2429	432.6	0.573	573
2815	19.41	2.072	1779	316.8	0.608	608
2215	15.27	1.833	1339	238.5	0.640	640
1615	11.14	1.663	994	177.1	0.666	666
1015	7.00	1.516	691	123.2	0.689	689
515	3.55	1.391	438	78.1	0.711	711
15	0.10	1.088	0	0.0	0.765	765

Residual oil relative density at standard conditions: 0.833
API gravity: 38.3

2- Gas phase properties

Pressure		Gas volume factor, Bg	Z	Gas viscosity		Gas rel. density
Psia	MPa	vol/svol		cP	mPa.s	
3715	25.61	0.0042	0.794	0.0273	0.0273	1.083
3415	23.55	0.0045	0.782	0.0248	0.0248	1.015
2815	19.41	0.0054	0.779	0.0212	0.0212	0.941
2215	15.27	0.0070	0.786	0.0186	0.0186	0.898
1615	11.14	0.0098	0.805	0.0166	0.0166	0.886
1015	7.00	0.0161	0.834	0.0147	0.0147	0.935
515	3.55	0.0335	0.879	0.0129	0.0129	1.024
15	0.10	1.3039	0.996	0.0088	0.0088	1.639

18.4 Separation test of reservoir fluid:

Tank condition: 80.0 F (299.8 K) 15 psia (0.10 MPa)

Pressure		Temperature		Gas liquid ratio *					
				Separator		Tank		Total	
Psia	MPa	F	K	scf/sbbl	sm^3/sm^3	scf/sbbl	sm^3/sm^3	scf/sbbl	sm^3/sm^3
815	5.62	90.0	305.4	2030	361.5				
465	3.21	90.0	305.4	227	40.5				
265	1.83	90.0	305.4	132	23.5				
55	0.38	90.0	305.4	242	43.1	81	14.5	2712	483.1

*Gas volume at standard conditions per volume of tank liquid at standard conditions.

Pressure		Temperature		Separator liquid density		Tank liquid density		Oil vol. factor *	Shrinkage factor **
Psia	MPa	F	K	g/cm^3	Kg/m^3	g/cm^3	Kg/m^3	vol/svol	vol/svol
815	5.62	90.0	305.4	0.709	709			2.556	0.739
465	3.21	90.0	305.4	0.748	748			2.556	0.816
265	1.83	90.0	305.4	0.782	782			2.556	0.880
55	0.38	90.0	305.4	0.803	803	0.800	800	2.556	0.974

*Volume of reservoir fluid at saturation conditions per volume of tank liquid at std. conditions.

**Volume of tank liquid at std. conditions per volume of separator liquid at separator conditions.

18.5 Semi-detailed composition (pseudo boiling point distribution)

Component		Mole %		Molar Mass (g/mol)		Density (15 deg.C) (g/cm³)	
O₂		0.00		---			
N₂		0.16		28.01			
CO₂		4.61		44.01			
H₂S		14.43		34.08			
CH₄		46.06		16.04		0.300	
C₂H₆		6.97		30.07		0.356	
C₃H₈		4.55		44.10		0.508	
C4		3.31		58.12		0.577	
	N		2.31		58.12		0.584
	I		1.00		58.12		0.563
C5		2.24		72.15		0.626	
	N		1.21		72.15		0.631
	I		1.03		72.15		0.620
Pseudo C6		1.73		85.90		0.666	
	N		1.27		86.18		0.665
	I		0.43		86.18		0.664
	C		0.03		70.13		0.750
	A		0.00		---		----
Pseudo C7		2.06		94.96		0.715	
	N		1.01		100.20		0.688
	I		0.43		100.20		0.690
	C		0.48		84.16		0.781
	A		0.14		78.11		0.884
Pseudo C8		2.30		105.96		0.751	
	N		0.71		114.23		0.707
	I		0.54		114.23		0.718
	C		0.69		98.19		0.790
	A		0.36		92.14		0.871
Pseudo C9		1.95		117.51		0.779	
	N		0.45		128.26		0.722
	I		0.45		128.26		0.729
	C		0.37		112.21		0.788
	A		0.68		106.17		0.875
Pseudo C10		1.64		130.80		0.789	
	N		0.39		142.28		0.734
	I		0.34		142.28		0.734
	C		0.21		126.24		0.799
	A		0.70		120.19		0.866
Pseudo C11		1.26		146.51		0.786	
	N		0.27		156.31		0.744
	I		0.38		156.31		0.743
	C		0.20		140.27		0.811
	A		0.41		134.03		0.862
C12+		6.73		233.27			

Average molar mass = 50.02 g/ mol

19.   Appendix D

PVT Data for oil sample number IV

19.1 Reservoir fluid analysis

From mathematical recombination

Composition

Component	Separator liquid mol %	Separator gas mol %	Monophasic fluid mol %
N_2	0.02	0.33	0.20
CO_2	0.09	0.54	0.35
H_2S	0.00	0.00	0.00
CH_4	4.71	81.79	48.69
C_2H_6	2.88	8.65	6.17
C_3H_8	5.94	5.47	5.67
i-C_4H_{10}	1.75	0.70	1.15
n-C_4H_{10}	5.58	1.57	3.29
i-C_5H_{12}	2.51	0.30	1.25
n-C_5H_{12}	3.43	0.31	1.65
Pseudo C_6H_{14}	5.32	0.15	2.37
Pseudo C_7H_{16}	9.77	0.13	4.27
Pseudo C_8H_{18}	10.18	0.06	4.41
Pseudo C_9H_{20}	7.17	0.00	3.08
Pseudo $C_{10}H_{22}$	5.37	0.00	2.30
Pseudo $C_{11}H_{24}$	4.37	0.00	1.88
C12+	30.90	0.00	13.27
Total	100.00	100.00	100.00
Molar ratio	0.4294	0.5706	1.0000

Phase properties	Separator liquid		Separator gas		Monophasic fluid	
Molar mass	lbm/mol	g/mol	lbm/mol	g/mol	lbm/mol	g/mol
C_7+	0.4326	196.23	0.2307	104.63	0.4319	195.89
C_{12}+	0.6270	284.41			0.6270	284.41
Fluid	0.3316	150.39	0.0453	20.55	0.1682	76.30
Density	g/cm^3	Kg/m^3	g/cm^3	Kg/m^3	g/cm^3	Kg/m^3
C_7+						
C_{12}+						
Fluid			0.000868	0.858		
Relative density			0.710	0.710		

19.2 Constant Mass study   at 154°F

Pressure		Relative volume	Compressibility	
Psia	MPa		Psia^{-1}	MPa^{-1}
5015	34.58	0.9745	0.00001189	0.001725
4515	31.13	0.9810	0.00001439	0.002087
4265	29.41	0.9848	0.00001520	0.002205
4015	27.68	0.9885	0.00001583	0.002297
3765	25.96	0.9925	0.00001632	0.002368
3515	24.24	0.9966	0.00001671	0.002424
Pb= 3315	22.86	1.0000	0.00001696	0.002460
3300	22.75	1.0018	0.00008142	0.011810
3252	22.42	1.0060	0.00008631	0.012518
3165	21.82	1.0145	0.00009558	0.013863
3004	20.71	1.0319	0.00011446	0.016601
2745	18.93	1.0668	0.00015020	0.021785
2398	16.53	1.1337	0.00021121	0.030633
1938	13.36	1.2787	0.00032607	0.047293
1453	10.02	1.5723	0.00051854	0.075208
972	6.70	2.1730	0.00089114	0.129248
615	4.24	3.2866	0.00151120	0.219181

Thermal expansion coefficient	0.000625	F^{-1}	0.00113	K^{-1}
Measured at	5015	Psia	34.58	MPa
From	72.0	°F	295.4	K
to	154.0	°F	340.9	K

19.3 Differential vaporization at 154.0 °F (340.9 K)

1- Oil phase properties

Pressure		Oil volume factor		Solution gas oil ratio		Reservoir oil density	
Psia	MPa			ft^3/bbl	m^3/m^3	g/cm^3	kg/m^3
5015	34.58	1.592	1.593			0.657	657
4515	31.13	1.603	1.604			0.653	653
4265	29.41	1.609	1.610			0.650	650
4015	27.68	1.615	1.616			0.648	648
3765	25.96	1.622	1.623			0.645	645
3515	24.24	1.628	1.629			0.643	643
Pb=3315	22.86	1.634	1.635	1210	218.1	0.640	640
3115	21.48	1.589	1.590	1120	201.8	0.649	649
2715	18.72	1.515	1.516	962	173.3	0.665	665
2115	14.58	1.423	1.424	750	135.2	0.687	687
1515	10.45	1.342	1.342	560	100.9	0.707	707
765	5.27	1.247	1.247	337	60.8	0.734	734
15	0.10	1.047	1.047	0	0.0	0.787	787

Residual oil at standard conditions

Density	0.824	g/cm^3	824	kg/m^3
Relative density	0.825			
API gravity	40.1			

19.4 Separation test

Multi-stage separation

Pressure		Temperature		Gas liquid ratio					
				Separator		Tank		Total	
Psia	MPa	°F	K	ft³/bbl	m³/m³	ft³/bbl	m³/m³	ft³/bbl	m³/m³
865	5.96	90.0	305.4	711	128.1				
625	4.31	95.0	308.1	80	14.4				
270	1.86	135.0	330.4	142	25.6				
70	0.48	130.0	327.6	103	18.6				
15	0.10	95.0	308.1			49	8.9	1085	195.5

Pressure		Temperature		Separator liquid density		Tank liquid density		Tank liquid density at std. conditions	
Psia	MPa	°F	K	g/cm³	Kg/m³	g/cm³	Kg/m³	g/cm³	Kg/m³
865	5.96	90.0	305.4	0.740	740				
625	4.31	95.0	308.1	0.749	749				
270	1.86	135.0	330.4	0.745	745				
70	0.48	130.0	327.6	0.763	763				
15	0.10	95.0	308.1			0.800	800	0.814	814

Pressure		Temperature		Oil volume factor		Shrinkage factor	
Psia	MPa	°F	K				
865	5.96	90.0	305.4			0.830	0.829
625	4.31	95.0	308.1			0.851	0.850
270	1.86	135.0	330.4			0.872	0.871
70	0.48	130.0	327.6			0.920	0.920
15	0.10	95.0	308.1	1.546	1.547	0.983	0.982

19.5 Separator liquid analysis

From flash to ambient conditions

Composition

Component	Stock tank liquid mol %	Stock tank gas mol %	Separator liquid mol %
N_2	0.00	0.14	0.02
CO_2	0.02	0.61	0.09
H_2S	0.00	0.00	0.00
CH_4	0.05	39.72	4.71
C_2H_6	0.52	20.61	2.88
C_3H_8	3.55	23.86	5.94
$i\text{-}C_4H_{10}$	1.51	3.55	1.75
$n\text{-}C_4H_{10}$	5.27	7.88	5.58
$i\text{-}C5H_{12}$	2.66	1.37	2.51
$n\text{-}C_5H12$	3.72	1.32	3.43
Pseudo C_6H_{14}	5.96	0.53	5.32
Pseudo C_7H_{16}	11.03	0.34	9.77
Pseudo C_8H_{18}	11.53	0.07	10.18
Pseudo C_9H_{20}	8.12	0.00	7.17
Pseudo $C_{10}H_{22}$	6.08	0.00	5.37
Pseudo $C_{11}H_{24}$	4.95	0.00	4.37
C12+	35.02	0.00	30.90
Total	100.00	100.00	100.00
Molar ratio	0.8824	0.1176	1.0000

Phase properties	Stock tank liquid		Stock tank gas		Separator liquid	
Molar mass	Ibm/mol	g/mol	Ibm/mol	g/mol	Ibm/mol	g/mol
C7+	0.4328	196.30	0.2262	102.60	0.4326	196.23
C12+	0.6270	284.41			0.6270	284.41
Fluid	0.3661	166.05	0.0724	32.86	0.3316	150.39
Density	g/cm^3	Kg/m^3	g/cm^3	Kg/m^3	g/cm^3	Kg/m^3
C7+	0.842	842				
C12+	0.874	873				
Fluid	0.813	812	0.001387	1.372		
Relative density			1.135	1.135		

20.   References

[1] Van der Waals, J.D., 1873. On the Continuity of the Liquid and Gaseous State. Sijthoff, Leiden, The Netherlands (Ph.D. dissertation).

[2] Redlich, O., Kwong, J., 1949. On the thermodynamics of solutions. An equation of state.Fugacities of gaseous solutions. Chem. Rev. 44, 233−247.

[3] Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state.Chem. Eng. Sci. 27, 1197−1203.

[4] Edmister, W., Lee, B., 1986. Applied Hydrocarbon Thermodynamics, In: second ed. vol. 1.Gulf, Houston, TX, p. pp. 52.

[5] Graboski, M.S., Daubert, T.E., 1978. A modified soave equation of state for phase equi- librium calculations, 1. Hydrocarbon system. Ind. Eng. Chem. Process. Des. Dev. 17, 443−448.

[6] Sim, W.J., Daubert, T.E., 1980. Prediction of vapor-liquid equilibria of undefined mix- tures. Ind. Eng. Chem. Process. Des. Dev. 19 (3), 380−393.

[7] Elliot, J., Daubert, T., 1985. Revised procedure for phase equilibrium calculations with soave equation of state. Ind. Eng. Chem. Process. Des. Dev. 23, 743−748.

[8] Peng, D., Robinson, D., 1976a. A new two constant equation of state. Ind. Eng. Chem.Fundam. 15 (1), 59−64.

[9] Peng, D., Robinson, D., 1978. The Characterization of the Heptanes and Their Fractions: Research Report 28. Gas Producers Association, Tulsa, OK.

[10] Ahmed,Tareq H-Equations of State and PVT Analysis, Second Edition_Applications for Improved Reservoir Modeling-Gulf Professional Publishing(2016).

[11] Nikos, V., et al., 1986. Phase behavior of systems comprising north sea reservoir fluids and injection gases. J. Pet. Technol. 38 (11), 1221−1233.

[12] Stryjek, R., Vera, J.H., 1986. PRSV: an improvement Peng-Robinson equation of state for pure compounds and mixtures. Can. J. Chem. Eng. 64, 323−333.

[13] Jhaveri, B.S., Youngren, G.K., 1984. Three-parameter modification of the Peng-Robinson equation of sate to improve volumetric predictions. In: Paper SPE 13118, presented at the SPE Annual Technical Conference, Houston, September 16−19, 1984.

[14] Whitson, C.H., Brule, M.R., 2000. Phase Behavior. SPE, Richardson, TX.

[15] Ahmed, T., 1991. A practical equation of state. (translation). SPE Reserv. Eng. 6 (1), 137−146.

[16] Pedersen, K., Thomassen, P., Fredenslund, A., 1989. Characterization of gas condensate mixtures. In: AdVances in Thermodynamics. Taylor and Francis, New York.

[17] Peneloux, A., Rauzy, E., Freze, R., 1982. A consistent correlation for Redlich-Kwong- Soave volumes. Fluid Phase Equilib. 8, 7−23.

[18] Katz, D.L., Firoozabadi, A., 1978. Predicting phase behavior of condensate/crude-oil sys- tems using methane interaction coefficients. J. Petrol. Tech. (November), 1649−1655.

[19] Ahmed, T., 1985. Composition modeling of Tyler and Mission canyon formation oils with CO_2 and lean gasses. Final report submitted to Montanans on a New Track for Science (MONTS), Montana National Science Foundation Grant Program.

[20] Riazi, M.R., Daubert, T.E., 1980. Simplify property predictions. Hydrocarb. Process. (March), 115−116.

[21] Riazi, M.R., Daubert, T.E., 1987. Characterization parameters for petroleum fractions. Ind.Eng. Chem. Fundam. 26 (24), 755−759.

[22] Cavett, R.H., 1962. Physical data for distillation calculations — vapor-liquid equilibrium.In: Proceedings of the 27th Meeting, API, San Francisco, pp. 351−366.

[23] Kesler, M.G., Lee, B.I., 1976. Improve prediction of enthalpy of fractions. Hydrocarb. Process. (March), 153−158.

[24] Edmister, W.C., 1958. Applied hydrocarbon thermodynamics, part 4, compressibility fac- tors and equations of state. Petroleum Refiner. 37 (April), 173−179.

[25] Standing, M.B., 1977. Volumetric and Phase Behavior of Oil Field Hydrocarbon Systems.Society of Petroleum Engineers, Dallas, TX.

[26] Matthews, T., Roland, C., Katz, D., 1942. High pressure gas measurement. In: Proceedings of the Natural Gas Association of America (NGAA).

[27] Hall, K.R., Yarborough, L., 1971. New simple correlation for predicting critical volume.Chem. Eng. (November), 76.

[28] Twu, C., 1984. An internally consistent correlation for predicting the critical properties and molecular weight of petroleum and coal-tar liquids. Fluid Phase Equilib. 16, 137.

[29] Soreide, I., 1989. Improved Phase Behavior Predictions of Petroleum Reservoir Fluids From a Cubic Equation of State. (Doctor of engineering dissertation). Norwegian Insti- tute of Technology, Trondheim.

[30] Graboski, M.S., Daubert, T.E., 1978. A modified soave equation of state for phase equilibrium calculations, 1. Hydrocarbon system. Ind. Eng. Chem. Process. Des. Dev. 17, 443−448.

[31] Vidal, J., Daubert, T., 1978. Equations of state—reworking the old forms. Chem. Eng. Sci.33, 787−791.

[32] Slot-Petersen, C., 1987. A systematic and consistent approach to determine binary inter- action coefficients for the Peng-Robinson equation of state. In: Paper SPE 16941, pre- sented at the 62nd Annual Technical Conference of the SPE, Dallas, September 27−30, 1987.

[33] Whiston, C., Brulé, M., 2000. "Phase Behavior." Monograph volume 20, Society of Petro- leum Engineers. Richardson, TX.

[34] Reid, R., Prausnitz, J.M., Sherwood, T., 1987. The Properties of Gases and Liquids, fourth ed. McGraw-Hill, New York.

[35] Lee, S., et al., 1979. Experimental and theoretical studies on the fluid properties required for simulation of thermal processes. Paper SPE 8393, In: Presented at the 54th Annual Technical Conference of the Society of Petroleum Engineers, Las Vegas, September 23−26.

[36] Hong, K.S., 1982. Lumped-component characterization of crude oils for compositional simulation. Paper SPE/DOE 10691, In: Presented at the 3rd Joint Symposium On EOR, Tulsa, OK, April 4−7.

[37] Katz, D., 1983. Overview of phase behavior of oil and gas production. J. Petrol. Tech. (June), 1205−1214.

[38] Lohrenz, J., Bray, B.G., Clark, C.R., 1964. Calculating viscosities of reservoir fluids from their compositions. J. Petrol. Tech. (October), 1171−1176.

[39] Pedersen, K., Thomassen, P., Fredenslund, A., 1982. Phase equilibria and separation pro- cess. Report SEP 8207. Institute for Kemiteknik, Denmark Tekniske Hojskole, July.

[40] Whitson, C.H., 1983. Characterizing hydrocarbon-plus fractions. Soc. Petrol. Eng. J.275 (August), 683. AIME, 275.

[41] Ahmed, T., 2014. Equations of State and PVT Analysis. Course Material.

[42] Whitson, C., 1980. Characterizing hydrocarbon-plus fractions. Paper EUR 183, In: Presented at the European Offshore Petroleum Conference, London, October 21−24.

[43] Lee, S., et al., 1979. Experimental and theoretical studies on the fluid properties required for simulation of thermal processes. Paper SPE 8393, In: Presented at the 54th Annual Technical Conference of the Society of Petroleum Engineers, Las Vegas, September 23−26.

[44] Behrens, R., Sandler, S., 1986. The use of semi-continuous description to model the C_{7+} fraction in equation-of-state calculation. Paper SPE/DOE 14925, In: Presented at the Fifth Annual Symposium on EOR, Held in Tulsa, OK, April 20−23.

[45] Agarwal, R.K., Li, Y.-K., Nghiem, L.X., and Coombe, D.-A., "Multi-Phase Multi-Component Isenthalpic Flash Calculations with a Cubic Equation of State," presented at the 39th Annual Technical Meeting of CIM, June 12-16, 1988, Calgary, Alberta.

[46] SPE (104631): Validation of splitting the hydrocarbon plus fraction: First step in tuning equation of state.

[47] Katz, D. L. and Firoozabadi, A.: "Prediction Phase Behavior of Condensate/Crude-Oil System Using Methane Interaction Coefficients," paper SPE 6721, presented at the SPE-AIME 52nd Annual Fall Technical Conference and Exhibition, Denver, 9-12 October, 1977.

[48] Whitson, C. H.: "Characterizing Hydrocarbon plus Fractions," SPE 12233, presented at the 1980 European Offshore Petroleum Conference and Exhibition, held in London, October 21-24.

[49] Pedersen, K. S., Thomassen, P., and Fredenslund, A.: *Properties of Oils and Natural Gases, Contributions in Petroleum Geology and Engineering*, Vol. 5, Gulf Publishing Co., Houston (1989).

[50] Ahmed, T., Cady, G. V., and Story, A. L.: "A Generalized Correlation for Characterizing the Hydrocarbon Heavy Fraction," paper SPE 14266 presented at the 60th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Las Vegas, 22-25 September, 1985.

[51] Ahmed, T., Cady, G. V., and Story, A. L.: "An Accurate Method for Extending the Analysis of C^+," paper SPE 12916 presented at the 1984 Rocky Mountain Regional Meeting, Casper, Wyoming 21-23 May.

[52] Katz, D. L., "Overview of Phase Behavior of Oil and Gas Production," *JPT* (June 1983) **228**, 1205-1214.

[53] SPE (96416): Tuning an equation of state – The critical importance of correctly grouping.

[54] Pedersen, K. S., Thomassen, P, and Fredenslund, A.: *Properties of Oils and Natural Gases, Contributions in Petroleum Geology and Engineering,* Gulf Publishing, Houston (1989) Vol. 5.

[55] Leibovici, C. F.: "A Consistent Procedure for the Estimation of Properties Associated to Lumped Systems," *Fluid Phase Equilibria* (1993) **87** 189-197.

[56] Twu, C. H. and Coon, J. E.: "An Internally Consistent Approach for Determining the Properties of Lumped Components Using a Cubic Equation of State," *Fluid Phase Equilibria* (1996) **117** 233-240.

[57] Aguilar, R. A. and McCain, W. D., Jr.: "An Efficient Tuning Strategy to Calibrate Cubic EOS for Compositional Simulation," paper SPE 77382 presented at the SPE Annual Technical Conference and Exhibition, San Antonio, 29 September-2 October 2002.

[58] SPE (28589): A Comparison of EOS Tuning Simulation.

[59] Hoffman, A. E., Crump, J. S. and Holcott, C. R. "Equilibrium Constants for a Gas Condensate System". Trans. AIME (1953) 198, 1-10.

[60] SPE (94211): Monitoring PVT Properties Derivatives Ensures Physically Sound Tuned EOS Behaviour over Entire Operating Conditions Range.

[61] Pedersen, K.S et al.: *Properties of Oils and Natural Gases*, Gulf Publishing Co., Houston, TX (1989).

[62] Wang, P. *et al.*: "Proper Use of Equations of State for Compositional Reservoir Simulation", *JPT* (July 2001) 74.

[63] Kesler, M.G. *et al*: "Improve Predictions of Enthalpy of Fractions", *Hydro. Proc.* (March 1976), 153.

[64] Twu, C.H : "An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal-Tar Liquids", *Fluid Phase Equil.* (1984) 16, 137.

[65] Oellrich, L. e*t al*: "Equation-of-State Methods for Computing Phase Equilibria and Enthalpies", *Int. Chem. Eng.* (January 1981) 21, 1.

[66] SPE (56744): Fully Automatic Procedure for Efficient Reservoir Fluid Characterization.

[67] Coats, K.H. and Smart, G.T.: "Application of a Regression-Based EOS PVT Program to Laboratory Data," *SPE Reservoir Engineering*, May 1986, 277.

[68] SPE (77382): An Efficient Tuning Strategy to Calibrate Cubic EOS.

[69] Whitson, C.H.: "Characterizing Hydrocarbon Plus Fractions," Soc. *Pet. Eng. J.* (August 1983), 683–693.

[70] Lee, B.I., and Kesler, M.G.: "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding State," *AIChE J.* (1975) Vol. 21, 510–515.

[71] Raizi, M.R., and Al-Hassaf, T.A.: "Physical Properties of Heavy Petroleum Fractions and Crude Oils," *Fluid Phase Equilibria* (1996), Vol. 117, 217–224.

[72] SPE (11197): Application of a Regression-Based EOS PVT program to Laboratory Data.

[73] Yarborough, Lyman: "Application of Generalized Equation of State to Petroleum Reservoir Fluids," Equations of State in Engineering, AdVances in Chemistry Series, K.C. Chao and R.L. Robinson (eds.), American Chemical Society, Washington, DC (1979) 182, 385-435.

[74] SPE (14487): On the Dangers of Tuning EOS Parameters.

[75] SPE (991352): Regression to Experimental PVT Data.

[76] SPE (37011): A simple and efficient approach for improving the prediction of reservoir fluid viscosity.

[77] Lohrenz, J., Bray, B.C. and Clark, C.R.: "Calculating Viscosities of Reservoir Fluids from Their Compositions". JPT, (October 1964), 1171-1176.

[78] Jossi, J. A., Stiel, L. I. and Thodos, G.: "The Viscosity of Pure Substances in the Dense Gaseous and Liquid Phases", AIChE J,8(1962). 59-63.

[79] Ely, J.E. and Hanley. H.J.M.: "Prediction of Transport Properties. I.Viscosity of Fluids and Mixtures". Ind. Eng. Chem. Fundam., 20(1981). 323-332,

[80] Pedesen, K. S. and Fredenslund, Aa.: "An Improved Corresponding States Models for the Prediction of Oil and Gas Viscosities and Thermal Conductivities". Chem. Eng. Sci. 42(1987), 182-186.

[81] Aasberg-Petersen, K., Knudsen, K. and Fredenslund, Aa.: "Prediction of Viscosities of Hydrocarbon Mixtures", Fluid Phase Equilibria, 70(1991), 293-308.

[82] Little, J. E. and Kennedy, H. T.: "A Correlation of the Viscosity of Hydrocarbon Systems With Pressure, Temperature and Composition.", SPE J, (June 1968), 157-162.

[83] Lawal, A. S.: "Prediction of Vapor and Liquid Viscosities From the Lawal-Lake-Silbergerg Equation of State", paper SPE/DOE Fifth Symposium on Enhanced Oil Recovery of the Society of Petroleum Engineers and the Department of Energy heldin Tulsa, OK, April 20-23.1986.