

TITLE PAGE

UNIVERSITI TEKNOLOGI PETRONAS

**Simulation of Phase Behavior of Crude Oil using Different
Equations of State (EOS)**

By

Kang Hooi Yee

Dissertation submitted in a partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

Petroleum Engineering

MAY, 2011

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

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Perak Darul Ridzuan

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment for the requirement for the
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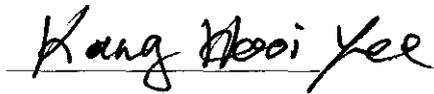
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TRONOH, PERAK

May, 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

A handwritten signature in black ink that reads "Kang Hooi Yee". The signature is written in a cursive style and is positioned above a horizontal line.

(KANG HOOI YEE)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May, 2011

ABSTRACT

The knowledge and understanding of the phase behavior of crude oil is essential in order to know the changes of fluid behavior with respect to changes of temperature and pressure. Phase behavior of hydrocarbon mixture can be modeled using equation of state (EOS). It offers the advantage of an improved fluid property prediction over conventional black oil model and can be used to predict behavior of the entire composition path and pressure range of the process. The purpose of this study is to investigate the modeling of crude oil phase behavior using four different EOS which are Peng-Robinson (PR), Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), and Zudkevitch-Joffe-Redlich-Kwong (ZJRK). The phase behavior of crude oil are examined and compared among three commercial softwares which are PVTi (ECLIPSE), PVTx (TEMPEST) and PVTp (Petroleum Expert). This work investigated the equation that best simulated the experimental Pressure, Volume and Temperature (PVT) data and described the phase behavior of crude oil accurately. Adjustment on the parameters of the chosen EOS, known as tuning or regression, is made to improve the prediction of chosen EOS model to match a variety of experimental fluid data. The work focused on the comparison using different EOS cross checked using three commercial PVT simulation softwares to test for the accuracy. Statistical error analysis along are used to evaluate the accuracy and applicability of the result generated. The results indicated PR EOS is the most accurate EOS in describing the phase behavior of crude oil. It fitted good and provided good representation of PVT experimental data. The tuning of the equation further resulted in greater accuracy. An efficient way of tuning strategy has been developed in this work which emphasis on the critical importance of sequence. It is concluded that the sequence of tuning which started with critical properties followed by BIC and omega properties resulted in greater accuracy.

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At the end, I wish to dedicate this dissertation to my father who is currently health unwell. He and my mother are a source of my constant encouragement. Also to my sisters who continuously be with me. This is as much their accomplishment as mine.

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NOMENCLATURES

δ_{ij}	Binary interaction coefficient
ω	Pitzer Acentric Factor
Ω_a	Constant Omega a
Ω_b	Constant Omega b
a	“Attraction” parameter
a_T	Constant A as a function of temperature
b	“Repulsion” Parameter
m	Moles
P	Absolute Pressure
P_c	Critical Pressure, psia
P_w	Reduced Vapor Pressure
R	Universal Gas Constant, $10.73 \text{ psi} - \text{ft}^3 / \text{lb} - \text{mole}, ^\circ R$
T	Absolute Temperature, $^\circ R$
T_c	Critical Temperature, $^\circ R$
T_R	Reduced Temperature, T/T_c
V	Volume
V_M	Volume, $\text{ft}^3 / \text{mole}$
y_i	mole fraction for phase i
y_j	mole fraction for phase j

CHAPTER ONE

1.0 Introduction

Equations-of-state (EOS) have been widely used to model phase behavior of fluid particularly in petroleum industry. It is capable in performing pressure, volume and temperature (PVT) calculations at various conditions and also to describe the phase behavior of reservoir fluids throughout the entire reservoir life cycle with correct characterization. The volumetric behavior and composition phase behavior of reservoir fluid are always concerns of petroleum engineers. Phase behavior of crude oil and the associated PVT properties are essentially important as it is not only restrained in the initial stages of reservoir development but also for the future planning and operations. Accurate estimation of Pressure, Volume and Temperature (PVT) properties of reservoir crude oil are paramount in all work of petroleum engineering as they are needed in reservoir simulation, reserves estimation, material balance calculation, production forecasts and enhanced oil recovery (EOR) schemes which sometimes involve the change of composition in the field of reservoir engineering; well completion, surface facility design and production optimization methods in the field of production sides. Basically obtaining an accurate fluid property is essentially critical as the effect covers the entire cycle of reservoir management and ensures consistency in reservoir processes. Knowing the importance, application of EOS has been gaining increasing popularity in recent years particularly after the introduction of the EOS-based composition simulation.

The phase behavior of crude oil mixture is dictated by the system pressure, temperature, fluid composition and component of non-hydrocarbon present. It can be modeled through EOS in modern compositional simulators, generally in cubic form, as one of the most important input data for reservoir simulation study. Since the calculation of reserves in an oil reservoir, production operations and design, determination of its performance and economics depends significantly on crude oil physical properties particularly in PVT data properties, a precise prediction of the PVT properties is necessary. The phase behavior, as the key element of crude oil, is vital as it forms the basis for reservoir simulation and evaluation of reservoir.

Nonetheless, the multi-component reservoir fluid is a complex mixture which its properties depend significantly upon the interaction of various chemical components. In the existing petroleum literature, two most commonly methods used to calculate PVT properties are EOS and conventional empirical PVT correlations. The EOS is considered highly complex and it requires detailed compositions of reservoir fluids in large comprehensive extent. EOS is available in cubic form and polynomial form. For the purpose of this study, only cubic EOS will be reviewed. Despite of the complexity and requirement of tuning which will be discussed in Chapter four, it has widely been used in the last few decades. It is even being predicted that this approach eventually is expected to replace the conventional black oil empirical correlations that currently being used. On the other hand, the empirical correlations do not require tuning or the detail composition data of fluid. It involves just the simple mathematical computation (Adel, 2006); require only the reservoir data such as reservoir pressure, temperature and specific gravity of reservoir fluids.

1.1 Background Study

As it is a well-known fact, reservoir fluid is highly complex by its nature in term of the composition, of hydrocarbons and non-hydrocarbons. The mixture of multi-component reservoir fluid has properties which depend significantly on the interaction of various components (Wu and Fish, 1989). Depending upon the types of fluid and each of its own unique composition, the physical properties of reservoir fluids may be greatly vary from one to the other. PVT data are necessary for fluid characterization and is usually determined from laboratory studies performed on samples of actual reservoir fluids collected from the bottom of wellbore or from the surface. However, comprehensive PVT studies are often cost and time consuming or samples collected are not reliable. The procedures involved somehow are tedious. Engineers hence seek for other viable approaches for the prediction of PVT properties in case of the absence of experimentally measured properties. In most cases, laboratory measurements of PVT are made up only on limited portion of the composition path. It is impractical to conduct laboratory for

such a wide range of conditions. In such cases, EOS can be used to make prediction of the change of behavior for the entire composition path and pressure range of the process especially in the case where it involves injection of miscible fluid in reservoirs (Wang and Gary, 2001). One of the winning points of using EOS is its wide ranges of tolerances over temperature and pressure to mixtures. It can also serve as a quality check measure against the laboratory results and the accuracy of fluid sampling procedures.

Nonetheless, uncertainties do exist associated with the use of an EOS to model the reservoir crude oil due to the complicated nature of the reservoir fluids. The last three decades have seen a great improvement in modeling phase behavior using EOS model. Numerous of works have been done on EOS comparison. Many articles in the literature discussed the use of EOS models for prediction of PVT reservoir fluid properties (Yarborough, 1979; Firoozabadi, 1988; Peng and Gary, 2001) and this included the prediction of the complex reservoir crude (Sarkar and Danesh, 1991) dealing with gas-condensate fluid. Experiences revealed that an EOS would outperform others for certain reservoir fluid types while some would be advantageous for only particular properties. The outcomes of all the findings pointed out that no one EOS that will accurately predict all kind of reservoir fluids. EOS usually needs adjustment or tuning according to Coats (Coats and Smart, 1986). Even if reasonable prediction accuracy can be obtained, the EOS parameters still need to be tuned to improve the agreement between the measured properties and the calculated results. However, literature revealed that the accuracy of any of the EOS model much likely depend on the qualitative measurement of the laboratory analysis PVT data. Also, it is affected by the consistency and accuracy of fluid sampling procedure (Wu and Rosenegger, 1997). To build a realistic equation of state model, therefore it is necessary to obtain reliable experimental PVT information.

Limitations of commonly used EOS have been revised and necessary modification of the adjustable EOS parameters have been carried out. This work will focus on simulation of phase behavior using different EOS, which are Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Zudkevitch-Joffe-Redlich-Kwong (ZJRK) - cubic equation with two empirical constants.

The correct description of phase behavior by EOS will give an accurate estimation of crude oil PVT properties such as Bubble Point Pressure (P_b), Solution gas-oil ratio (GOR) and oil formation volume factor (B_o) at bubble point. The essence of the PVT data analysis is to simulate the changes of crude oil in the reservoir and at the surface during production. These data properties will then be used in reservoir simulations as well as of many thermodynamics properties, predicting the reservoir future performance, calculation of oil and gas recovery, in material balance calculation, design of future EOR, practically all aspects from a field initial development to the subsequent operations (Adel *et al.*, 2006).

1.2 Problem Statement

Crude oil properties at varying thermodynamic conditions of pressure and temperature are required in a reliable quantification of fluid phase behavior. Therefore EOS is used to predict these properties. The use of different EOS directly for the estimation of phase behavior and PVT properties for crude oil will create erroneous owing to the equations are mostly applicable to fluids having similar nature to those from which the equations were derived. They have the limitations in which they were originally developed for a certain types of reservoir fluid characteristics with similar fluid compositions. The application of EOS to predict PVT parameters of reservoir fluids having distinct nature will result in inaccuracies mostly due to the characterization of the plus fraction; depends on the composition. Thus, it is difficult if not impossible to obtain the same accurate predictions through the EOS for different crude oil without tuning. The use of EOS will have to be addressed and tested. As a result extensive consideration will be needed in choosing and evaluating the suitability of the EOS being used since the crude oil behaves differently. Thus, this study will be conducted in selecting the EOS which best describe the phase behavior of crude oil and adjustment on the chosen EOS constant, or known as tuning, will be made to improve the prediction.

Physical properties of crude oil such as Bubble Point pressure (Pb), Solution gas-oil ratio (GOR) and oil formation volume factor at Bubble Point (Bo) are necessary for any reservoir studies. Understanding the physical changes and phase behavior of crude oil under different operating conditions will prove beneficial. However, incomplete data always cause a handful problem. There are many of EOS available and being used in reservoir engineering calculations; but there is no single one which can be used across different type of crude oil. Hence, the equation best applied with minimum errors under each specific condition needed to be investigated.

1.2.1 Problem Identification

Problem of using EOS in modeling of fluid behavior is the difficulty in matching the predicted data by EOS model to the experiment observed data. Even if the matching of the lighter component is good, the performance of EOS is questionable in their predictive work when apply to crude oil mixtures, especially the heavier ends. Furthermore, of which EOS to be used to build the model, each of the EOS has to be investigated and tested for the suitability in describing the phase behavior of crude oil.

As what has been reported in the existing literature. Some of the parameters of EOS will have to be adjusted in order for the calculations to reproduce experimental data of a reservoir fluid. Coats and Smart (1986) were first suggested that EOS parameters required tuning to better match experimental PVT behavior. Tuning of the adjustable parameters of EOS to match the measured PVT data of crude oil allows improvement of the representation of PVT and physical properties of crude oil. The modeling of the EOS will only be meaningful if the satisfactory agreement between EOS results and laboratory PVT test data achieved.

1.2.2 Significant of the Project

This project is certainly needed as it forms the basis of input data for reservoir simulation and evaluation of reservoir development strategy to be used in practical field application. It emphasizes that accurate phase behavior of fluid is required in any simulation. PVT phase behavior of crude oil and the use of EOS are the keys in developing the

fundamental understanding of all. This work will discuss on the comparison of the EOS and cross check among three commercially used softwares which will pinpoint the profound differences in spite of the similarity in their way of execution. It also stands to check on the accuracy of fluid sampling procedures and laboratory fluid property measurement.

The results generated will be compared among three commercial PVT Simulation softwares which are PVTi of ECLIPSE, PVTx of TEMPEST and PVTp of Petroleum Expert for same EOS being used.

1.3 Objectives

This project besides investigating the general characters and differences of EOS model that commonly being used, the ultimate goals of this study are as follows:

1. To evaluate the most widely used EOS against a set of data and to recommend the best EOS in describing the crude oil sample.
2. To compare the results generated by three commercial softwares which are widely been used in the industry in predicting crude oil behavior and PVT parameters and to examine if they could attain to a same result.
3. To improve performance of the EOS chosen by modification or tuning of the adjustable EOS parameters.

1.4 Scope of Study

The study is bifurcated in two phases where the first is aimed at reviewing the cubic equation of EOS that exist in petroleum literature and evaluating the significant of

equations for Oil Formation Volume Factor (B_o), Bubble Point Pressure (P_b) and solution gas-oil ratio (GOR). Only the cubic EOS is discussed in this work.

The second phase deals with the synthesis of improving or modifying those equations to predict the PVT properties of the crude oil. Through the mathematical expressions and graphical relationship generated by each of the EOS, the well-established equation which best describing the characterization of crude oil will be determined. For the comparative study, comparison of the equations with the observed data will be performed to signify the effectiveness of the new or modified equation. A comprehensive error analysis will be performed which is based upon the difference among the predicted, the laboratory measurement data and the improved or tuned prediction data.

CHAPTER TWO

2.0 LITERATURE REVIEW

Because of the interest in reservoir fluid systems, the review of literature will include the development of EOS and the used of each equation in estimating phase behavior of the systems.

2.1 DEVELOPMENT OF EQUATIONS-OF-STATE (EOS)

Many equations of state have been proposed in the literature. Comprehensive reviews were found in the works of Martin (1979), Tsonopoulos and Heidman (1985). The very first equation to predict vapor-liquid coexistence was first developed by the van der Waals (VDW). It is in simple cubic form and has only two constants. The basic parameters required are the critical properties and the normal boiling point or the vapor pressure. To account for the applicability of VDW to mixture which was at first developed over pure component, the interaction coefficients between primary constituents is included for compatibility (Firoozabadi, 1988).

Since the introduction, many cubic EOS's have been proposed. First was by Redlich and Kwong (Redlich and Kwong, 1949) who made a remarkable improvement of the VDW equation by adding a better description of temperature dependence of the molecular attraction. By far, the Redlich-Kwong EOS has been the most popular basis for developing new EOS model and can be used for mixtures by applying mixing rules to the equation. Later, Soave (1972) and Peng and Robinson (1976) proposed additional modifications for Redlich-Kwong equation to predict the vapor pressure, liquid density, and equilibrium ratios for greater accuracy. The success of the equation led to many further empirical improvements.

Soave (1972) suggested a new dependence to replace the temperature dependence by Redlich and Kwong. This prompted the development of equation of Soave-Redlich-Kwong (SRK) equation. To test the accuracy of it, Soave calculated and compared the vapor pressures of a series of hydrocarbon. It is proven that with that modification, the

experimental curve fitted well and was able to predict the phase behavior mixtures in the critical region in contrast to the original Redlich-Kwong equation with the addition of mixing rules. Peneloux *et al.* (1982) later introduced volume shift or translation to improve the accuracy of SRK EOS. In 1976, Peng and Robinson (1976) proposed a slightly different form of molecular attraction term and redefined it to improve the prediction of liquid volumes and critical compressibility. The Peng-Robinson (PR) EOS performed as well as the Soave-Redlich-Kwong equation. In 1984, Jhaveri and Youngren (1984) introduced a third parameter to calculate volume shift for plus fraction in PR EOS. The introduction of the binary interaction coefficients (BIC) described by Chueh and Prausnitz (1967) later on considerably improved the EOS prediction. Also, they provided set of correlation to calculate BICs from critical volumes.

Several aspects in petroleum engineering applications greatly rely on the Peng-Robinson EOS and Soave-Redlich-Kwong equation. The advantages of these equations are on the accuracy and representatives of the relation among temperature, pressure and phase compositions in binary and multi-component systems. However, the usage of the modifications is restricted to the estimation of vapor pressure and Soave-Redlich-Kwong equation yields poor liquid densities. Although many equations have been developed later, the Peng-Robinson EOS and Soave-Redlich-Kwong equations remained the most widely used in PVT simulation packages due to the simplicity and yield a more accurate representation (Palenchar *et al.*, 1986). The two-constant cubic EOS's have been proven to be useful in the computation of highly complex fluid mixtures which contains various molecular families. Firoozabadi pointed out that interaction coefficients between primary constituents should be included to account for the degree of compatibility (Keshawa and Firoozabadi, 1998).

In 1970, Zudkevitch and Joffe *et al.* further modified the Redlich-Kwong EOS and developed the equation of Zudkevitch-Joffe-Redlich-Kwong equation, based on the basis of works by Chueh and Prausnitz (Zudkevitch and Joffe, 1970; Chueh and Prausnitz, 1976). They proposed that the two constant in RK EOS should be a function of temperature. Value for each constant for propane at different temperatures is given. In 1979, a generalized form of Zudkevitch-Joffe-Redlich-Kwong EOS equation was

proposed by Yarborough (Yarborough, 1979). Generalized correlation of saturated liquid density and saturated liquid fugacity in place pure-component data was used in his works and compared the measured and computed mixtures densities which did not cover by Zudkevitch and Josse. He brought in the nonlinear correction term of constant A and B. Above the critical temperature, same constant values of 0.4278 and 0.0867 suggested by Zudkevitch and Josse is being applied. For mixtures, he further determined binary interaction coefficient in a manner more or less the same as described by Zudkevitch and Josse.

In the late two decades, great emphasis has been put on the improvement of liquid volumetric predictions and treating the heavier hydrocarbon components such as heptanes-plus fraction.

2.1.1 EQUATIONS-OF-STATE (EOS)

An EOS which is cubic in volume and gives pressure in terms of volume and temperature is known as cubic EOS. EOS can be used to describe the relationship between pressure, volume and temperature for both pure mixture and diverse mixtures of hydrocarbon components in crude oil. It describes the interconnection between various macroscopically measurable properties of a system. It is applicable to different states including gas, liquid and solid states such as in the case of wax or bitumen. EOS is completely compositional and is capable of tracing effect of composition on the fluid properties and phase behavior unlike the black oil correlations.

In mathematical form, the EOS is in the form of $V=f(p,T)$. This form indicates that the volume is a dependent of pressure and temperature. Very often, the EOS refers to the relationship of the properties pressure (p), volume (V), and temperature (T) of a gas. Modifications are necessary to represent the behavior of fluid in liquids form as EOS becomes increasingly inaccurate at higher pressures and lower temperature. Most of the cases, EOS are developed based on pure substances. Mixing rules are required to extend the equation to mixtures.

2.1.1.1 Equation of state – Van der Waals

The van der Waals equation of state, proposed in 1873 can represent vapor-liquid coexistence.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (1)$$

where R is universal gas constant, $10.73 \text{ psi} - \text{ft}^3 / \text{lb} - \text{mole}, ^\circ\text{R}$

The different of the equation compared to the ideal gas equation, $PV = zRT$ are the terms of a/V^2 and b. The term of a/V^2 is added to pressure represents the forces of attraction between the molecules. While the constant b is subtracted from molar volume, represents the correction in subtraction of the volume occupied by the molecules. The constant a and b can be obtained from the critical properties of the fluid.

$$a = \Omega_a \frac{R^2 T_c^2}{P_c}, \text{ where } \Omega_a = 0.421875 \quad (2)$$

$$b = \Omega_b \frac{RT_c}{P_c}, \text{ where } \Omega_b = 0.125 \quad (3)$$

The equations improved the description of gas behavior and the passage of gas to the liquid phase as being compressed. However, it is limited at low pressures. Besides, it is insufficient in critical properties and phase equilibrium calculations.

2.1.1.2 Redlich-Kwong Equations

RK equation is the modification of the van der Waals EOS. It retains the equation and added a temperature-dependent attractive term as showed in equation (4). This modification improved the prediction of the volumetric and physical properties of the vapor phase.

$$P = \frac{RT}{V_M - b} - \frac{a}{V_M(V_M + b)\sqrt{T}} \quad (4)$$

Rearranged the equation,

$$\left[P + \frac{a}{\sqrt{T}V_M(V_M + b)} \right] (V_M - b) = RT \quad (5)$$

Where

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c}, \quad \Omega_a = 0.42747 \quad (6)$$

$$b = \Omega_b \frac{RT_c}{P_c}, \quad \Omega_b = 0.08664 \quad (7)$$

Different values of omega constants are used in RK EOS. The equation can be used in multi-component mixtures by applying mixing rules to the EOS parameters.

2.1.1.3 Soave-Redlich-Kwong Equations

Several attempts were made to improve the RK equation. SRK Equations as one of the most representative cubic EOS, It can accurately describe both the liquid and vapor phase. In 1972, Soave proposed a third parameter, the acentric factor, and a temperature dependency into the cohesive energy term to account for the effect of nonsphericity on fluid PVT properties. The modified EOS is given by:

$$P = \frac{RT}{(v-b)} - \frac{\alpha a}{v(v+b)} \quad (8)$$

The a and b in the equations are the energy parameter and the covolume parameter of the SRK, respectively. In Soave's work, the interaction parameter for the SRK EOS was fitted. This equation suggested that the parameter in the equation should be defined in terms of critical properties and acentric factor, α , which is developed of individual components,

where $\alpha = f\left(\frac{T}{T_c}, \omega\right)$.

ω is known as Pitzer acentric factor, it is defined as $\omega = -(\log p_{vr} + 1)$ at $T_r = 0.7$ where P_{vr} is the reduced vapor pressure. Thus the ω is constant for each pure substance. The term proposed by Soave replaced $a/T^{1/2}$ enable the equation to represent vapor pressure of a wide class of substance. The a and b is given:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c}, \quad \Omega_a = 0.42747 \quad (9)$$

$$b = \Omega_b \frac{RT_c}{P_c}, \quad \Omega_b = 0.08664 \quad (10)$$

To test the accuracy of the equation, the vapor pressures of a number of hydrocarbons and several binary systems were calculated and compared with experimental data (Soave, 1972). The curve fitted well and was able to predict the phase behavior mixtures in critical region. The EOS was later on extended to mixtures using the combinations:

$$a = \sum_i \sum_j x_i x_j (1 - \delta_{ij}) a_i^{1/2} \quad (11)$$

$$b = \sum_i x_i b_i \quad (12)$$

Where δ_{ij} is the interaction coefficient as described by Chueh and Prausnitz (1967). It corrects for the effect of deviation from geometric mean combination rule from a where it has to be corrected for the binary mixture data.

The interaction coefficients through empirical adjustment are used to model the intermolecular interaction and depend on the molecular size of components in a binary system. With the presence of the interaction coefficient, volumetric and phase behavior predictions of the mixture by the SRK equations were greatly improved.

The SRK equation is the most widely used RK EOS proposed to date that it is more accurately in predicting the vapor pressure, liquid density and equilibrium ratios in contrast to the original equation.

2.1.1.4 Zudkevitch-Joffe-Redlich-Kwong Equations

Majority of EOS assumed that saturation data of pure components are also applicable at conditions above the critical temperature. Zudkevitch and Joffe, however, made the assumption that the two parameters of Ω_a and Ω_b in RK equation remain constant above the critical point as the equation explicitly includes the square root of temperature in the attraction term (Sarkar, Danesh and Todd, 1991). Constant values of 0.4278 and 0.0867 are assigned, respectively. They concluded that at temperature below critical temperatures, Ω_a and Ω_b are temperature dependent and when reach supercritical temperatures, they tend to be temperature independent and equal to the values at $T_r=1$. This gives improvement in the ZJRK equation by the way of obtaining EOS parameters by some other methods for the super critical components.

Besides of the suggestion of constants a and b should be function of temperature, Zudkevitch and Joffe in their works showed that vapor fugacity and fugacities ratio (K values) remained unaffected and that the procedure does not greatly affect vapor densities. No longer after the modification, Joffe *et al.*, (1970) pointed out that liquid fugacities should not be used but vapor pressures. This form the equation known as Zudkevitch-Joffe-Redlich-Kwong EOS, which contains additional temperature factors multiplying the usual RK temperature dependence.

$$P = \frac{RT}{V-b} - \frac{a(T)/\sqrt{T}}{V[V+b(T)]} \quad (13)$$

$$a = \Omega_a^o \frac{R^2 T_c^2}{P_c} T_r^{-0.5} \alpha(T_r, \omega) \quad (14)$$

$$\text{and } b = \Omega_b^o \frac{R^2 T_c^2}{P_c} T_r^{-0.5} \beta(T_r, \omega) \quad (15)$$

$$\Omega_a^o = 0.4278 \text{ and } \Omega_b^o = 0.0867$$

Due to the complexity of the equation, other authors suggested that a table of α and β correction factor should be provided when referring to Zudkevitch-Joffe-Redlich-Kwong EOS (Whitson and Brule, 2000).

2.1.1.5 Peng-Robinson Equations

Four years after Soave's modification of the RK EOS, Peng and Robinson proposed a two constant equation in 1976 that greatly enhanced EOS prediction and improvement in liquid-density in particular in failure of the SRK EOS to predict liquid densities correctly (Firoozabadi, 1988).

$$P = \frac{RT}{V-b} - \frac{a_r}{V(V+b)+b(V-b)} \quad (16)$$

By applying the equation above at the critical point and fitting the experimental vapour pressures, the EOS parameters of a and b can be evaluated from the critical temperature, the critical pressure and acentric factor of the pure components as follow:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \quad (17)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (18)$$

where $\Omega_a^o = 0.45724$ and $\Omega_b^o = 0.077796$

The equation for a_T is: $a_T = a_c \alpha$ where a_T is the value of a at the critical temperature and α is a non-dimensional temperature-dependent term which has a value of 1.0 at the critical temperature.

$$\text{Where } \alpha^{1/2} = 1 + m(1 - T_r^{1/2}) \quad (19)$$

$$\text{And } m = 0.37464 + 1.5422\omega - 0.26992\omega^2 \quad (20)$$

For $\omega \leq 0.49$,

$$m = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.01666\omega^3 \quad (21)$$

For $\omega > 0.49$

This EOS originally developed for pure substances and was being extended for mixture fluid behavior prediction by using of mixing rules. The following mixing rules are recommended to use with Peng-Robinson EOS:

$$a_T = \sum_i \sum_j y_i y_j (a_{Ti} a_{Tj})^{1/2} (1 - \delta_{ij}) \quad (22)$$

$$b = \sum_j y_j b_j \quad (23)$$

where y_j is the gas or liquid mole fraction and δ_{ij} is binary interaction coefficient, which can be determined from available correlation.

In developing the equation, a different volume dependence was developed when recognizing the critical compressibility factor by Redlich and Kwong is overestimated. The new modified equation achieved a reasonable accuracy near the critical point, particularly the calculations of the compressibility factor and liquid density. Examples of using the equation to predict the vapor pressure and volumetric behavior of single-component system were given by Peng and Robinson too (Williams, 1980).

Peng-Robinson (1978) recommended a modification to the acentric factor and the resulting equation was described as modified PR EOS. The accuracy of the phase

behavior calculations is dependent on entering optimal values for the critical parameters and interaction parameters, particularly for the heavy fractions. This EOS provides the means of obtaining such optimal parameters by specifying specific gravity and molecular weight.

2.2 SUMMARY OF LITERATURE REVIEW

Since van der Waals EOS has been introduced, many EOS have been developed – e.g., the RK EOS in 1949, the modified RK EOS and the PR EOS in 1976. Most of the equations, however, retained the repulsive term of VDW EOS, $RT/(V-b)$, by modification done only on the denominator in the attractive term. Most of the petroleum engineering applications rely on the PR EOS or the modified RK EOS, of which SRK EOS has found wide acceptance. ZJRK EOS, which corrected by temperature dependant function has greatly improved in volumetric prediction. PR EOS predicts liquid densities more accurate than SRK EOS. Among the EOS proposed in literature, SRK and PR EOS are the most widely used in petroleum engineering.

2.3 THEORY

Despite of the large volume of publication of different EOS's, they need tuning to reproduce experimental data of crude oil when come to practical application. This is simply because the existing EOS are only a generalization of multi-component system. Parameters like bubble point pressure, gas-oil ratio, liquid phase densities and equilibrium compositions may differ by several percent from the experimental value. The inconsistencies in EOS predictions are from insufficient characterization of the plus fraction, inadequate binary interaction coefficients or incorrect composition overall. There are two approaches normally being used when come to tuning. The first approach is by keeping the theoretical parameters of the equation and performing the match on the critical properties of the heavier component which has been grouped up, critical pressure

(P_c) and critical temperature (T_c) and accentric factor ω for pseudocomponent. Second approach involves calculation of the critical properties and accentric factor of the heavier component from existing correlation and to modify the parameter constant A and B and also the binary interaction coefficient.

The heavy end fraction (also known as plus fraction) is composed of hundreds of hydrocarbon components and has some uncertainty in its molecular weight and critical properties. The plus fraction has to be split into carbon number fractions and parameters of EOS (T_c, P_c, ω) will have to be determined for each carbon number fraction. Also, the plus components have to be lumped into a manageable number of pseudocomponents (Krejbjerg and Pedersen, 2006). Generally, EOS are not predictive without the tuning of its parameters to match experimental data, as mentioned earlier. Wide publications found in the literature that tuning of the EOS is one of the best methods to improve the predictions of the fluid behavior (Meshari and William, 2005). Extensive works have also been made in the characterization of the plus fraction. Pedersen et al. (1989) had showed that a proper characterization of the heavy fraction will reduce for extensive tuning (Pedersen *et al.*, 1989). The physical constants of heavier end fraction (T_c, P_c, ω) may be considered as tuning parameters. Many of the publications in the existing literature reported that a proper characterization of the heavier end fraction will reduce the need for extensive tuning of EOS (Reyadh A., 2000).

2.3.1 PVT MODELING

Besides the development of the EOS, a review of literature pertinent to this study is presented as well. In this section, the PVT properties of interest will be reviewed. This will include crude oil PVT properties, PVT phase behavior experiments and phase behavior modeling.

2.3.1.1 Crude Oil PVT Properties

Crude oil physical properties are required for the reservoir engineering calculation especially in material balance calculations. The properties of interest are bubble point pressure (P_b), oil formation volume factor (B_o) at P_b and GOR. These properties are defined in this section and the physical processes involved in the way crude oil properties change as reservoir pressure is reduced at constant temperature are explained. (William McCain, 1990)

- **Bubble Point Pressure**

Bubble point is the pressure at which the first bubble of gas evolves.³⁰ Bubble point is related to a function of solution GOR, oil density and temperature. When a reservoir pressure is at its bubble point and, it is said to be saturated. The oil contains the highest dissolved gas that it can hold. Any reduction in pressure will release gas to form gas phase.

- **Oil Formation Volume Factor (B_o) at P_b**

Oil formation volume factor at bubble point is the volume at reservoir conditions occupied by one stock tank barrel of oil plus its solution gas. This factor is used to estimate the shrinkage of oil liquid volume as oil is produced from reservoir up to the surface. Oil B_o at bubble point has been estimated as a function of GOR, gas density, oil density, and also reservoir temperature.

- **Solution Gas-Oil Ratio**

The quantity of gas dissolved in oil at reservoir conditions is called solution gas-oil ratio. The dissolved gas will evolve from the oil as the oil is transported from the reservoir to surface conditions. Also, solution gas-oil ratio is also called as dissolved gas-oil ratio or gas solubility. It could be defined in terms of quantities of gas and oil which appear at the surface during production.

2.3.2 CONVENTIONAL PVT PHASE BEHAVIOR EXPERIMENTS

Some appropriate PVT experiments which closely related to the field operation are being carried out. This is due to the fact that reliable quantification of fluid phase behavior requires measurement of fluid properties at varying thermodynamic conditions of pressure and temperature. The primary objective of conducting the PVT experiments is to generate reliable fluid properties for the evaluation of the fluid properties and to be used in reservoir simulation. An experimental phase behavior study includes measuring volumetric properties as a function of pressure and temperature. The generally conducted experiments are constant composition expansion (CCE), Differential Liberation Expansion (DLE) and separator test.

2.3.2.1 Constant Composition Expansion (CCE)

Usually in any PVT fluid reports show data of the CCE at reservoir temperature. The data usually contains relative volume at different pressures for a fixed temperature. In order to plot the phase diagram for a crude oil with the quality lines, the CCE experiment has to be conducted at different temperatures. With today advance simulation software, this can be done with little input data required. Nonetheless, the simulated EOS has to compare to the laboratory measurement for accuracy. In laboratory, the crude oil at reservoir pressure and temperature conditions is expanded and the change in volume is measured at isothermal conditions. This enables the computation of the bubble point pressure which is taken as a point at which the slope of volume vs. pressure plot changes abruptly.

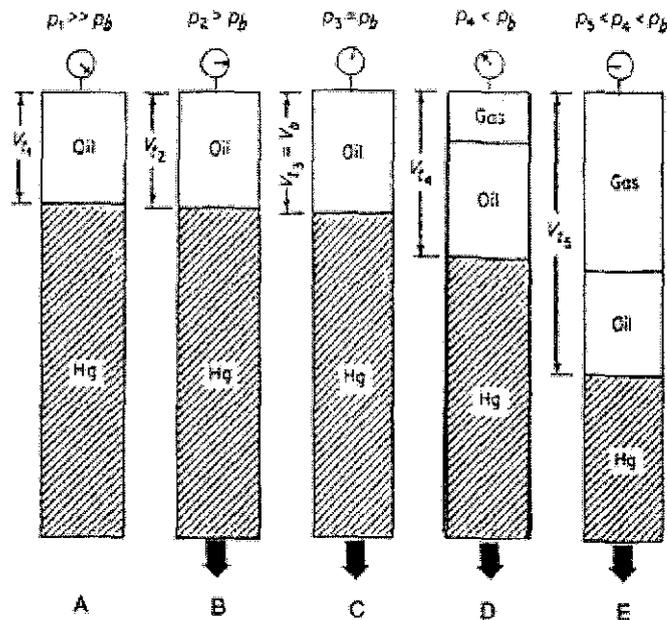


Figure 2.1: Schematic of Constant Composition Expansion (Tarek Ahmad, 2007)

2.3.2.2 Differential Liberation Experiment (DLE)

This experiment is an approximation of fluid property changes with pressure for oil during a natural depletion. The reservoir fluid is kept in a PVT cell at reservoir pressure and temperature conditions. The pressure in the cell is reduced and liberated gas is collected in stock tank conditions of 14.7 psia pressure and 60 °F under constant temperature. Once equilibrium has been reached, the gas and liquid volumes are measured. The test is conducted until the pressure of 14.7 psia and final residual oil volume measurement allows for the computation of solution gas oil ratio and formation volume factor at every step of differential liberation. Figure below shows a schematic of DLE experiment.

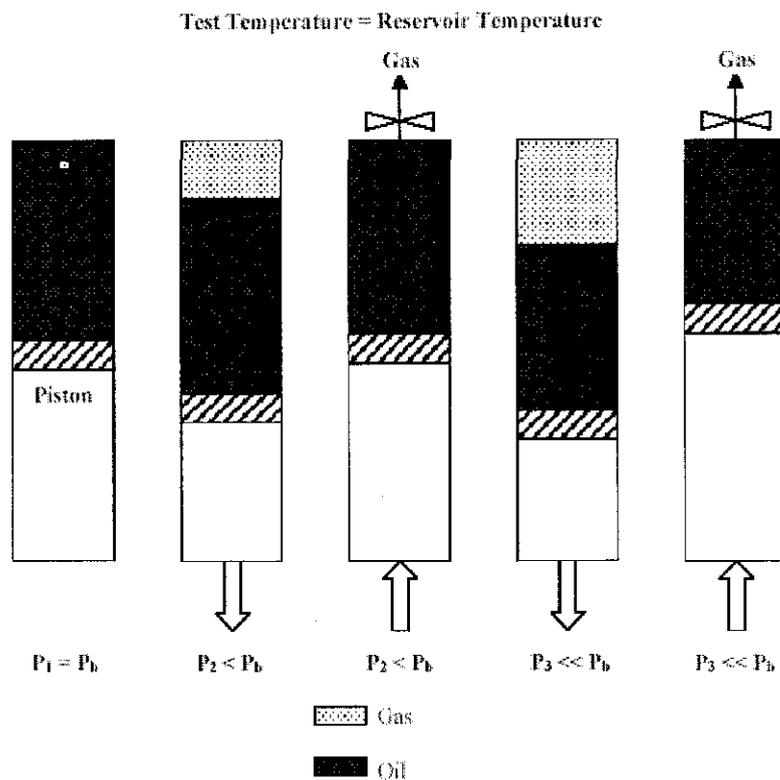


Figure 2.2: Schematic of Differential Liberation Experiment (Dandekar, 2005)

2.3.2.3 Separator Test

Separator test is a series of flashes with the liquid from one flash becoming the feed for the next flash at different conditions. The reservoir fluid at reservoir temperature and pressure conditions is flashed to atmospheric conditions in two or three stages in series. Figure 2.2 provided a schematic of the separator test. The primary objective of the separator test is to determine the optimum separator conditions that will give a minimum of the total gas oil ratio and a minimum in formation volume factor of oil at bubble point conditions.

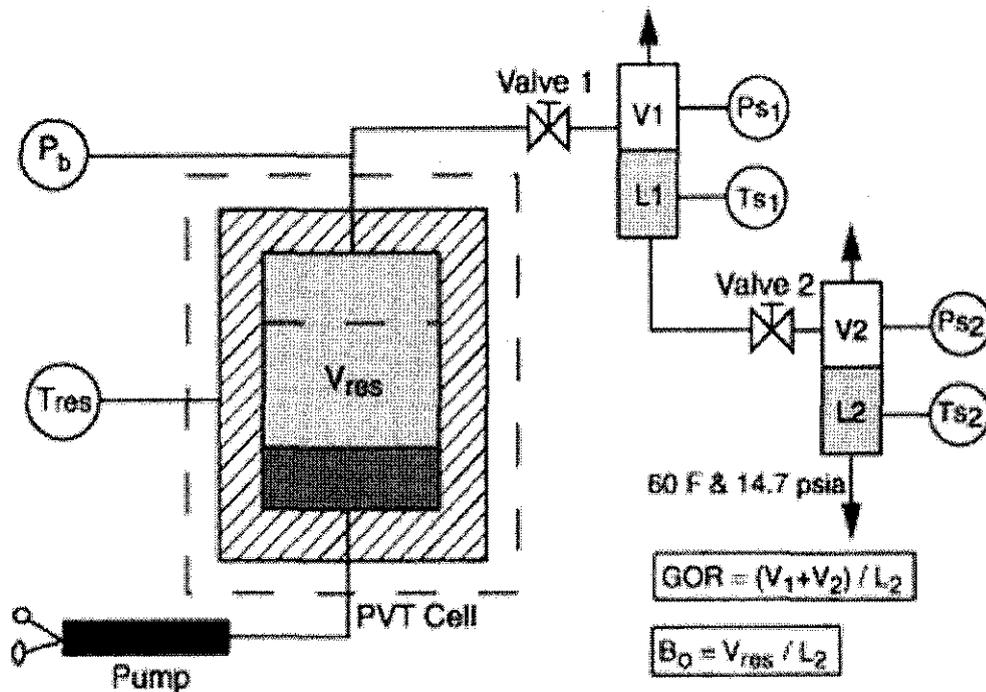


Figure 2.3: Schematic of Separator Tests

2.3.3 EOS MODELING AND TUNING

To date, there is no any single standard method for tuning being adopted. There are many publications in the literature which have discussed on how to minimize the difference between the predicted data and the measured laboratory data and lead to the procedure known as “tuning”. Different approaches have been proposed for tuning of EOS, the types and the numbers of EOS parameters to be modified are different from approach to approach. Tuning by regression so far is the most common method and this involves modification of the adjustable EOS parameters so as to obtain the best match between experimental data and prediction.

2.3.3.1 Tuning of EOS parameters

As mentioned earlier, EOS requires properties for each component such as T_c , P_c and acentric factor. These properties are well defined for pure components; however,

determination of these properties for mixtures which rely on correlations and the use of mixing rules inevitably create uncertainties and errors in EOS prediction. Tuning hence is needed to adjust the parameters of the selected EOS to achieve a satisfactory match between the laboratory fluid PVT data and the EOS calculation results. Manual adjustment through trial and error or by an automatic nonlinear regression approach has been reported in the literature (Coats and Smart, 1986). Experimental data available for regression typically is comprised of saturation pressures, liquid phase densities, gas-oil ratio and formation volume factors from DLE. For the parameters which could be the options for tuning, generally the ones with less confidence in their estimated value. Coats and Smart (1986) recommended modifying the following regression variables, EOS parameters:

- Binary Interaction Coefficient (BIC)
- Critical pressure (P_c), critical temperature (T_c) of the plus fraction or the pseudocomponents
- acentric factor (ω)
- Omega A and Omega B

2.3.3.2 Characterization of the Plus Fraction

As the crude oil nature can get very complicated, it further complicates the estimation of plus fraction properties like specific gravity and molecular weight, which are used in computation of critical properties. Most studies emphasize that the C7+ characterization as the key element in attaining good agreement. Many correlations for calculating critical properties of SCN groups have been proposed, such as Kesler-Lee (1976), Katz and Firoozabadi (1977), Whitson (1982) and more.

2.3.3.3 Binary Interaction Coefficients

Apart from modifying the combination of EOS parameters chosen for regression, different property correlation and the binary interaction coefficient (BIC) are also being considered. Appropriate values of empirical parameters, BIC, most often are required in using the cubic EOS. Few methods have been suggested in the literature to determine the

binary interaction parameters, but the interaction parameters calculated using those methods may not be able to predict the complex phase behavior at high pressures (Shaw *et al.*, 2002). Theoretically, the BIC is introduced to account for the molecular interaction between dissimilar molecules (Danesh, A. 1998). Their values are usually obtained by fitting predicted saturation pressure curves to the experimental data for binary systems. The BIC is the parameter for mixing rules, representing the difference of energy level between molecules to count for the interaction of molecules from the mixture composed of hydrocarbons, CO₂, N₂ and H₂S. It is more of a fitting parameter than a physical property (Danesh, A. 1998). Different values for different groups are needed.

2.3.3.4 Critical Properties

EOS requires critical pressure, critical temperature for each of the component presence. Many correlations have been developed for calculating the critical properties of hydrocarbon components based on the physical properties of specific gravity and normal boiling point temperature, as they are believed as the most inaccurate data, eg. Kesler Lee (Ahmad, T. 1989). A correct critical properties and acentric factor will well define the components. Together with molecular weight, it is sufficient for a simple prediction model.

2.3.3.5 Omega Properties

The constant value of Omega a and b are parameters accounted for pure component and they are dimensionless. Tuning the parameters of omega was proposed by Coats and Smart. This method has been widely used in the petroleum industry. The tuning of omega was found to be similar as the tuning of the critical properties (Whitson, 1984) as they are related to each other by the formula of:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \quad (24)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (25)$$

2.3.3.6 Acentric Factor

The acentric factor of the heptanes plus fraction has been chosen as one of the adjustable EOS parameter. The acentric factor will honor the relationship between the critical properties of the heptanes plus group.

2.3.4 Regression

The non-linear regression in the PVT simulation software minimizes the deviation between the measured experimental data set and the simulated EOS models of the PVT experiments. For each iteration by the regression, a selection of parameter is varied from the set of parameters simultaneously. The progress can be tracked as the objective function, which is a measure for the deviation, is displayed during the regression. The goal of tuning is to find a value out of the tuning group to achieve minimum number of the objective function, which is as below:

$$F = \sum_i^N \left[\frac{w_i (x_{i,calc} - x_{i,exp})}{x_{i,exp}} \right]^2 \quad (26)$$

where w_i is the weight factor with internally set default or subjected to overwrite values. and $x_{i,meas} = f(\Omega_a, \Omega_b, \dots, etc)$. N denotes the total number of experimental data points available in the regression.

The regression parameter was limited by the upper bound and lower bound for each of the corresponding parameter so that consistency of unity is obtained or the monotonically trend of data is reserved. Subjected to the limits, the regression determines the values of corresponding parameter that minimize the objective function F .

CHAPTER THREE

3.1 Project Methodology

The first part of this chapter describes the simulation work conducted in this work, which consist of fives divisions:

- 3.1 Data gathering and analysis
- 3.2 Fluid definition and fluid characterization
- 3.3 Experiment simulation
- 3.4 EOS evaluation using statistical mean
- 3.5 Tuning by regression

The second part of this chapter reviewed on the project activities and the milestone as included in the Gantt charts I and II. Third part of the chapter reviewed on the software tools which were used throughout the whole project work.

3.1.1 Data Gathering and Analysis

Project work started with data analysis to gather and/or extract necessary data of crude oil sample. It is followed by physical recombination of separator liquid using stock tank oil and stock tank gas; as well as physical recombination of reservoir fluid using known composition from separator liquid and separator gas.

Each composition obtained from each condition is different from each other. The surface liquid and gases must be recombined in order to determine the properties of crude oil in the reservoir. The recombination using a series of calculation as suggested by Mccain in which the compositions of the surface fluids are known.

3.1.2 Fluid definition and Fluid Characterization

Three commercial softwares, PVTi, PVTx and PVTp are used in this part of work including the work of generating saturation pressure of the fluid sample and were compared for performance and accuracy of the EOS model prediction.

Simulation work started first with fluid definition to specify each of the components presence that comprises the crude oil system. The reservoir fluids are composed of a lot of different hydrocarbon and non-hydrocarbon components. The PVT program needs to identify each of the component presence to relate to the properties store in the library.

Fluid characterization involves determination of the properties to each of the components presence which involves the measured molecular weight (MW) and specific gravity specification. This is aimed to generate properties of plus fraction.

3.1.3 Experiment Simulation

The simulation of experiment is started after the characterization. This work aimed to simulate the physical properties of crude oil which do not obtained through direct measurement from laboratory. Experiment simulated includes differential liberation (DL) and constant composition expansion (CCE).

3.1.4 EOS Evaluation Using Statistical Mean

Statistical error analysis is used as the criteria for the evaluation in this study based on a comparison of the predicted value calculated by with the observed laboratory value. Statistical means in term of error analysis is used to determine the accuracy of result developed in this study. Four of the EOS utilized in the study are analyzed from the results generated by the softwares. The best EOS that gives the most accurate fluid description is chosen and will be proceed with tuning. The following statistical mean is used to determine the accuracy of the results evaluated.

Absolute Relative Error (ARE):

$$RE = \frac{(x_{obs.} - x_{calc.})}{x_{obs.}} \times 100 \quad (27)$$

where $x_{obs.}$ and $x_{calc.}$ represent the measured and calculated variables, respectively.

3.1.5 Tuning by Regression

In this project work, the nonlinear regression was used for tuning. Basically, the regression would try to fit the calculated data from computation of PR to the data which has been measured in laboratory. Supposed if there is any discrepancy between the two sets of data, regression analysis will be performed to fit one set of data to the other. Tuning of EOS by means of improving the prediction will utilize as much as PVT experiment from the laboratory data. The procedure of tuning was carried out in a systematical way aiming to match the experimental observed data as closely as possible manipulating the EOS parameters. The EOS parameters are user-specified and may be any subset of the EOS variables. Experimental data are matched by mean of normal. An appraisal and sensitivity analysis is performed to determine which parameter has the highest sensitivity before started the work of regression.

3.2 SOFTWARES TOOL

The PVT simulation software is programmed uses generalized cubic EOS to perform phase-equilibrium and property calculations. These programs can be used to calculate fluid behavior solely on the basis of the predictive capabilities if any of the equations. More important, however, is the capability to use a nonlinear regression calculation that performs an automatic adjustment of EOS parameters to match a variety of input laboratory PVT measurements.

3.2.1 PVTi by ECLIPSE

PVTi is a PVT package of Schlumberger Simulation Software, Eclipse, a compositional PVT EOS based program used for characterizing a set of fluid samples. It is basically an interactive Equation of State (EOS) package used for the analysis of laboratory measurements performed to determine the phase behavior of reservoir fluids.

3.2.2 TEMPEST™ PVTx

TEMPEST PVTx is one of the modules of TEMPEST Suite. It is an equation of state PVT analysis tool which facilitates characterization of black oil or compositional fluids. TEMPEST-PVTx includes all the commonly used cubic Equations of State, including the Peng-Robinson and Soave-Redlich-Kwong.

3.2.3 PVTP by Petroleum Experts

PVTP is one of the suite tools in Integrated Production Modeling (IPM) software. It is an analytical tool which is able to manipulate and predict compositional changes using two distinct methodologies which are the black oil model and the EOS model.

3.3 Gantt chart FYPI

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic selection/confirmation	█													
2	Preliminary Research Work			█	█										
3	Submission of Preliminary Report														
4	Literature Review on Equations of State				█	█	█	█							
5	Submission of Progress Report														
6	FYP 1 Seminar														
7	Project Work Continues									█	█	█	█	█	
8	Analysis of Result and Discussion										█	█	█	█	
9	Report Preparation												█	█	
10	Submission of Interim Report														
11	Oral Presentation (Study week)														

█ Project Activities

□ Milestone

3.4 Gantt chart FYPII

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Data Analysis and Gathering	■													
2	Work of Simulation			■	■										
3	Analysis of simulation result														
4	Submission of Progress Report				■	■	■	■							
5	Paper Writing														
6	FYP II Seminar														
7	Project Work Continues									■	■	■	■	■	
8	Analysis of Result and Discussion									■	■	■	■	■	
9	Report Preparation												■	■	
10	Submission of Interim Report														
11	Oral Presentation (Study week)														

■ Project Activities

□ Milestone

CHAPTER FOUR

4.0 Result Discussion

This chapter discusses results from the simulation and the statistical analysis of the predictions made by EOS. The discussion bifurcated into two parts which the first part will discuss on the determination of suitable EOS which accurately described the phase behavior of crude oil. The later part of the discussion will focus on the tuning, or known by regression, on the EOS chosen.

4.1 Data Gathering and Data Analysis

For a proper description of phase behavior of crude oil, it was necessary to obtain the composition of the crude oil. In this work, provided was the data analysis of retention time (RT) and the peak area of each component in the crude oil samples collected from stock tank oil and stock tank gas. Analysis was conducted based on the simulated distillation of gas chromatography as shown from the chromatogram in Figure 4.1. More than 50 components were identified through the true boiling point distillation. Calculation was made in obtaining the weight percent (weight %) of each of the components.

Each of the area of the components is read from graph. Formulas being used in the hydrocarbon analysis are:

$$\text{Area \%} = \frac{\text{Peak Area of each components}}{\text{Total of Area}} \quad (28)$$

$$\text{Weight \%} = \frac{\text{Area \% of each components}}{\text{Total of Area \%}} \quad (29)$$

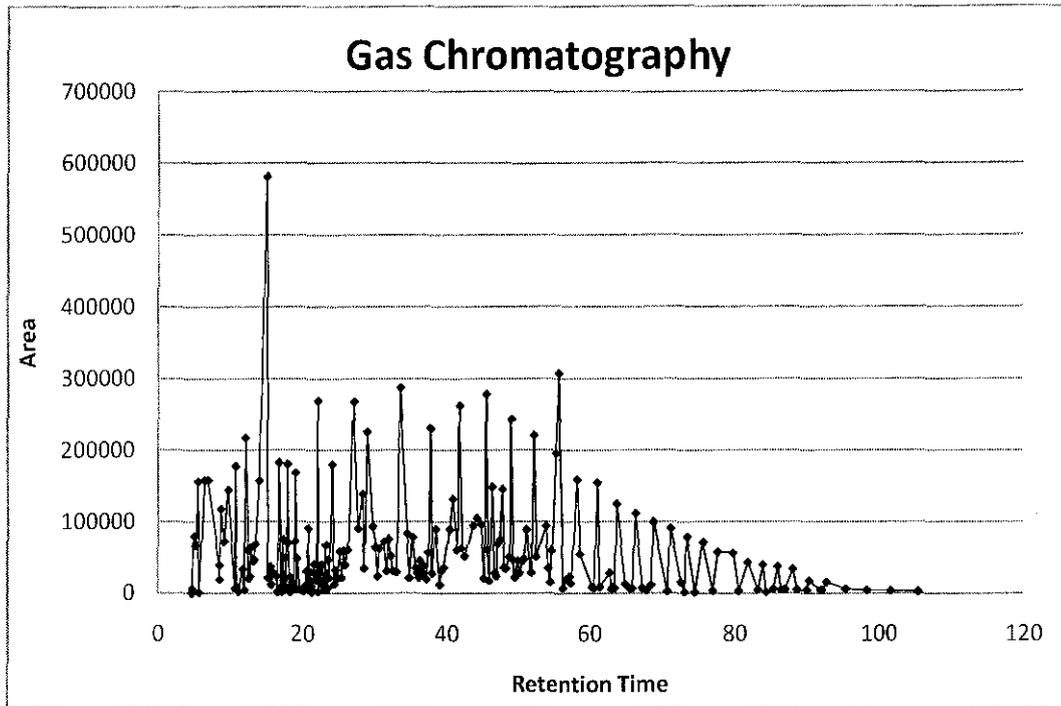


Figure 4.1: Gas Chromatography Analysis

The compositional results, in weight % were transformed into mole %, in Tables 4.1 using molecular weights listed for single carbon number (SCN) fractions in the generalized property table as shown in Appendix (Table A1). The SCN at this context refers to the specific hydrocarbon components at which each of the components having different number of isomers. Each of the components at small carbon number identified as Methane, Ethane, Propane, and the iso- and the normal- isomers of Butane and Pentane and the list goes on. As the number of isomers increases rapidly and so is generally switch to the SCNs description where each of the components presence are generally referred to.

$$\text{Number of Moles} = \frac{\text{Weight percent of each component}}{\text{Molecular Weight of each component}} \quad (30)$$

$$\text{Moles \%} = \frac{\text{Number of Moles}}{\text{Total Number of Moles}} \quad (31)$$

Result is showed in Table 4.1. No gas composition was observed from the stock tank oil sample.

Tables 4.1: Moles % of components in the crude oil sample from stock tank oil

Component	Weight %	No. of Moles	Moles %
Nitrogen	0.0000	0.0000	0.0000
Carbon Dioxide	0.0000	0.0000	0.0000
Methane	0.0000	0.0000	0.0000
Ethane	0.0510	0.0017	0.2362
Propane	0.6420	0.0146	2.0308
Iso-Butane	0.5350	0.0092	1.2834
N-Butane	1.2510	0.0215	3.0034
neo-pentane	0.0070	0.0001	0.0137
Iso-Pentane	1.2640	0.0175	2.4442
N-Pentane	1.2700	0.0176	2.4550
Hexanes	3.1489	0.0365	5.0970
Methylcyclopentane	1.4786	0.0176	2.4508
Benzene	0.3638	0.0047	0.6496
Cyclohexane	1.7726	0.0211	2.9381
Heptanes	3.8807	0.0387	5.4025
Methylcyclohexane	4.6540	0.0474	6.6117
Toluene	0.1910	0.0021	0.2887
Octanes	8.0890	0.0708	9.8786
Ethylbenzene	0.8500	0.0080	1.1168
m+p xylene	0.4340	0.0041	0.5698
o xylene	0.4940	0.0047	0.6495
Nonanes	6.9822	0.0544	7.5937
1,2,4 Trimethylbenzene	2.1440	0.0178	2.4876
Decanes	6.3733	0.0448	6.2481
Undecanes	6.5940	0.0422	5.8846
Dodecanes	5.4500	0.0320	4.4631
C13	5.9448	0.0338	4.7117
C14	5.6988	0.0300	4.1840
C15	7.4763	0.0366	5.1123
C16	4.6049	0.0211	2.9466
C17	3.6121	0.0156	2.1718
C18	4.2483	0.0173	2.4090
C19	1.8153	0.0070	0.9739
C20	1.4721	0.0054	0.7495
C21	1.1661	0.0040	0.5648
C22	0.9864	0.0033	0.4556
C23	0.7482	0.0024	0.3303
C24	0.7764	0.0024	0.3282
C25	0.5878	0.0017	0.2383
C26	0.4997	0.0014	0.1947
C27	0.4527	0.0012	0.1697
C28	0.3736	0.0010	0.1350
C29	0.3592	0.0009	0.1253
C30	0.3577	0.0009	0.1205
C31	0.3517	0.0008	0.1146
C32	0.2169	0.0005	0.0685
C33	0.1983	0.0004	0.0607
C34	0.0489	0.0001	0.0145
C35	0.0345	0.0001	0.0099
C36	0.0279	0.0001	0.0078
C37+	0.0214	0.0000	0.0057
Total	100.0000	0.7169	100.0000

In calculating the moles percentage of the samples, normalization was included to correct the total of moles percentage to 100%. Tasks performed under this study included the recombination of stock tank oil and stock tank gas in order to determine the composition of separator liquid. Since both the compositions of surface stock tank oil and stock tank gas are known, this recombination is done by the calculation based on the recorded ratio of produced gas rate to oil rate which defines the separator gas-oil ratio of 750 scf/stb. The final physical recombination involved the determination of recombined hydrocarbon composition in stock tank and separator recombination. Works of the recombination are shown in the Appendix Table A1 to A5. The summary of the results are showed as below.

Table 4.2 : Stock Tank Liquid Properties

Stock Tank Liquid Properties	
Molecular Weight Ib/Ib Mole	132.35
Density of Stock Tank Liquid (60°F and 14.7 psia) g/cc	0.726

Table 4.3 : Separator Gas Properties

Separator Gas Properties	
Molecular Weight Ib/Ib Mole	22.73
Density of Stock Tank Liquid (60°F and 14.7 psia) g/cc	0.346

Table 4.4 : Reservoir Fluid Properties

Reservoir Fluid Properties	
Molecular Weight Ib/Ib Mole	139.50
Density of Stock Tank Liquid (60°F and 14.7 psia) g/cc	0.749

4.2 Modeling/Simulation

The fluid properties data provided is input to the software as input data. The input data consists of composition of crude oil in molar percent, molecular weight and specific gravity of heptanes plus. Also, input data including reservoir properties such as reservoir temperature at 204°F and bubble point pressure at 2650 psig. Molecular weight of 153.1 and specific gravity of 0.776 is input to characterize the heptanes plus component.

The experimental observed data used for carrying out the EOS modeling consisted of the following:

- Compositional analysis of the reservoir fluid
- Saturation pressure at the reservoir temperature of 204°F
- Pressure-Volume-Temperature experimental data, mainly DL and CCE

The SCN fractions from C₇₊ to C₃₇₊ identified from the chromatogram were calibrated through n-paraffins belonging to the corresponding SCN group up to C₇₊ only as input data for EOS tuning as shown in the Table 4.5 below.

Table 4.5 : Composition of Crude Oil as input data for simulation.

Component Name	Component	Moles %
Nitrogen	N2	0.2166
Carbon Dioxide	CO2	0.4429
Methane	C1	40.2844
Ethane	C2	4.8319
Propane	C3	5.7328
Iso-Butane	IC4	1.5393
N-Butane	C4	2.7604
Iso-Pentane	IC5	1.5401
N-Pentane	C5	1.4350
Hexanes	C6	2.5866
Heptanes	C7+	38.6301

The experimental observed data from CCE and DL test carried out in laboratory are provided in Table 4.6 and Table 4.7. Graph in Figure 4.2 showed the relationship of crude oil relative volume and Y-function with respect to pressure.

Table 4.6: Provided crude oil data of relative volume and Y-Function from Constant Composition Expansion experiment at reservoir temperature, 204°F.

Pressure(psig)	Rel Volume (V/Vsat)	Y-Function
5000	0.976	
4500	0.980	
4000	0.984	
3500	0.988	
3200	0.990	
3000	0.992	
2900	0.993	
2800	0.993	
2700	0.994	
2650	1.000	
2600	1.004	4.362
2550	1.009	4.316
2500	1.014	4.271
2450	1.019	4.226
2400	1.025	4.180
2300	1.037	4.090
2200	1.051	3.999
2000	1.084	3.818
1800	1.129	3.636
1600	1.188	3.455
1400	1.270	3.274
1200	1.386	3.093
1000	1.558	2.911
800	1.832	2.730
0		2.005

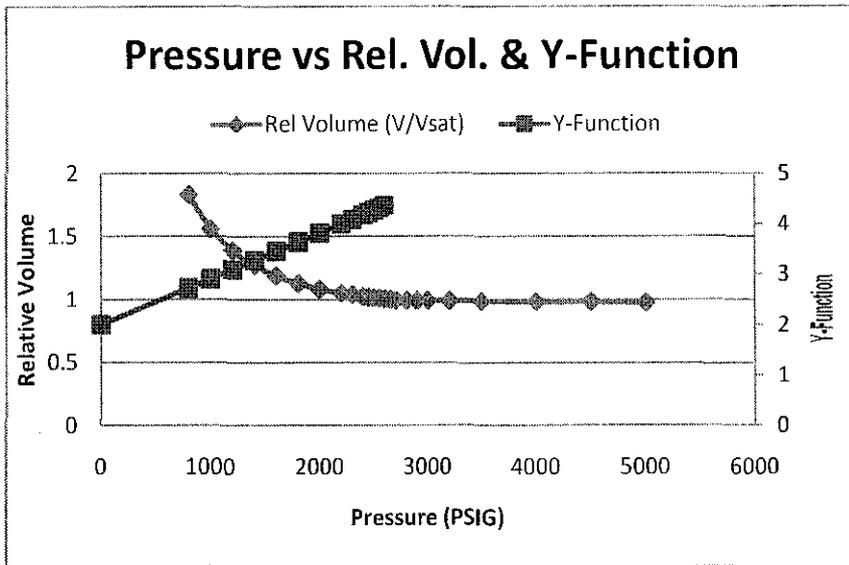


Figure 4.2: A plot of pressure versus relative volume and Y-function.

Table 4.7: Provided crude oil data from Differential Vaporization Experiment at reservoir temperature, 204°F

Pressure (psig)	Oil BO (bbl/stb)	Rs (scf/stb)	Oil Density (g/cc)	Z factor	Gas BO (cf/scf)	Cum Gas Gravity
2650	1.508	1060	0.657			
2400	1.488	1022	0.662	0.879	0.0129	0.67
2300	1.467	981	0.668	0.876	0.0135	0.66
2000	1.424	885	0.678	0.877	0.0115	0.669
1600	1.376	733	0.686	0.89	0.0107	0.675
1200	1.328	595	0.695	0.911	0.0146	0.672
800	1.28	451	0.704	0.931	0.0222	0.709
400	1.232	324	0.71	0.958	0.0445	0.767
200	1.201	217	0.714	0.969	0.0582	0.949
100	1.179	177	0.719	0.981	0.1456	1.037
0	1.064	0	0.775			

API Gravity of the Residual oil @ 60°F = 40.14

Density of the residual oil @ 60°F = 0.824

1. Barrel of oil at indicated pressure and temperature per standard barrel of residual oil at 60°F.
2. Cubic feet of gas at 14.73 psia and 60°F per standard barrel of residual oil at 60°F.
3. Cubic Feet of gas at indicated pressure and temperature per cubic feet at 14.73 psia and 60°F.

Having the fluid oil sample defined, the model was then tested out across three PVT simulation softwares to examine the predictive capability of each of the EOS. Tests are performed on the fluid sample purely based on simulated saturation pressures experiment. Results are shown in the tables below.

Comparison of Calculated Saturation Pressure Results

In this study, the matching results of EOS using all or selected data are discussed. Then the comparison results of three commercial softwares for generating EOS parameters are presented. This study by no means includes various cubic equations that have appeared in literature and the comparison was emphasis on saturation pressure which heavily affects the density calculations and Bo to make sure reasonably match was met. The saturation pressure is the key of comparison in this case.

Table 4.8 : Calculated Saturation Pressure, PSIG and Absolute Relative Error (ARE), % from three compare to observed Saturation Pressure at 2650 PSIG.

EOS	PVT _x	%ARE	PVT _i	%ARE	PVT _p	%ARE
Peng – Robinson	2249.59	15.1098	2392.34	9.722	2025.255	22.8206
Soave-Redlich-Kwong	2095.90	20.9094	2348.41	11.381	2038.601	23.0717
Redlich-Kwong	2034.45	23.2283	1597.63	39.712	-	-
Zudkevich-Joffe	-	-	2350.33	11.308	-	-

The performances of the calculation of four EOS from three softwares are compared in computing the crude oil saturation pressure. Distinct discrepancy was observed from the Table 4.8. However the three programmes gave quite similar results that the saturation pressure computed by Peng-Robinson has the closet value of 2392.34 psig to the laboratory measured value of 2650 psig. The PVT_i calculated saturation pressure shows good results as opposed to PVT_x and PVT_p in which the computed saturation pressure have less error except for Redlich-Kwong EOS. Result showed Soave-Redlich-Kwong has better predictability than Redlich-Kwong (Soave, 1972). It reveals also the improvement resulted from modification of Soave who introduced the parameter of acentric factor which is temperature dependent (Soave, 1972). As for Zudkevich-Joffe EOS, the saturation pressure calculated is much closer to the experimental observed

pressure which is at 2650 psig, although it is not as close as the Peng-Robinson calculation.

Additionally, evaluation on the Bo was studied although it may not be as significant as the saturation pressures. Matching of the bubble point pressure is utmost important to ensure that it is a single phase liquid at reservoir temperature and pressure. Matching of the Bo could be optional unless needed for process facilities and configuration. As shown in the Table 4.9, the Bo calculated are off from the experimental observed data with prediction errors. Such difference could be expected in flowing applications where the EOS model is utilized for providing predictions of the volumetric conversion factors for the phases in flowing conditions.

Table 4.9 : Calculated Oil Formation Volume Factor (Bo), rb/STB from three simulation softwares compare to observed Bo at 1.508 rb/stb

EOS	PVTb	%ARE	PVTj	%ARE	PVTp	%ARE
Peng – Robinson	1.7681	17.248	1.7189	12.269	1.306	13.3952
Soave-Redlich-Kwong	1.80881	19.9476	1.4366	4.970	1.367	9.3501
Redlich-Kwong	1.7895	18.6671	1.5611	3.401	-	-
Zudkevich-Joffe	-	-	1.5219	0.913	-	-

The resulted EOS predicted is followed by a comprehensive error analysis based on the comparison of the predicted value with the observed value.

A lower value of ARE% obtained implies a better prediction is obtained. Having the lowest error as observed from the error analysis, the difference in the performance is very pronounced that Peng Robinson EOS is chosen. The validation is due to the EOS model matches properly to the most significant PVT properties which is the saturation bubble point pressure.

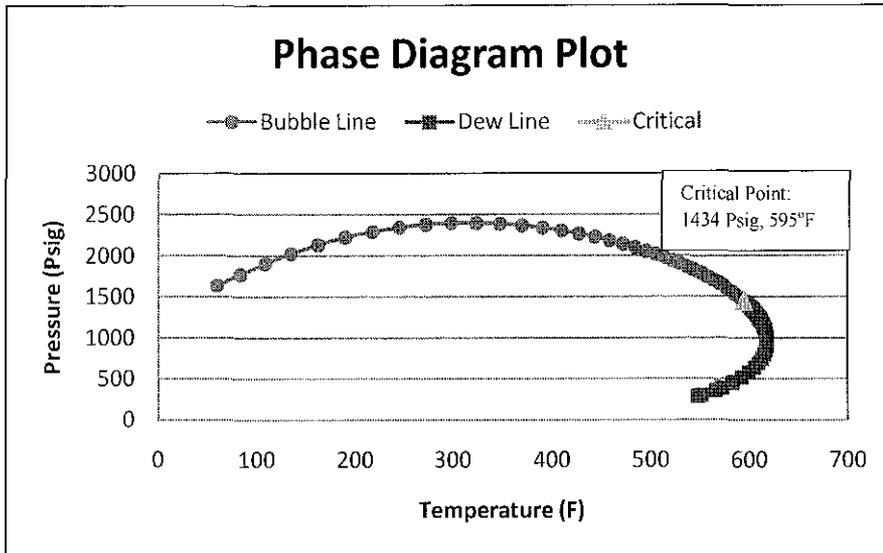


Figure 4.3 : Phase Diagram Plot with critical properties at 1434 Psig and 595°F.

As shown in the figure above, the upper part of the phase enveloped, down to the critical point, represents the bubble-point curve. The phase diagram of the crude oil sample is bounded on one side by a bubble-point line and the other side by a dew-point line. The two lines join at the critical point of 1434 psig and 595°F. The saturation pressure value predicted by the un-tuned EOS was 2392.34 psig. The percentage difference was 9.722%, indicating a significant error in the prediction of saturation pressure.

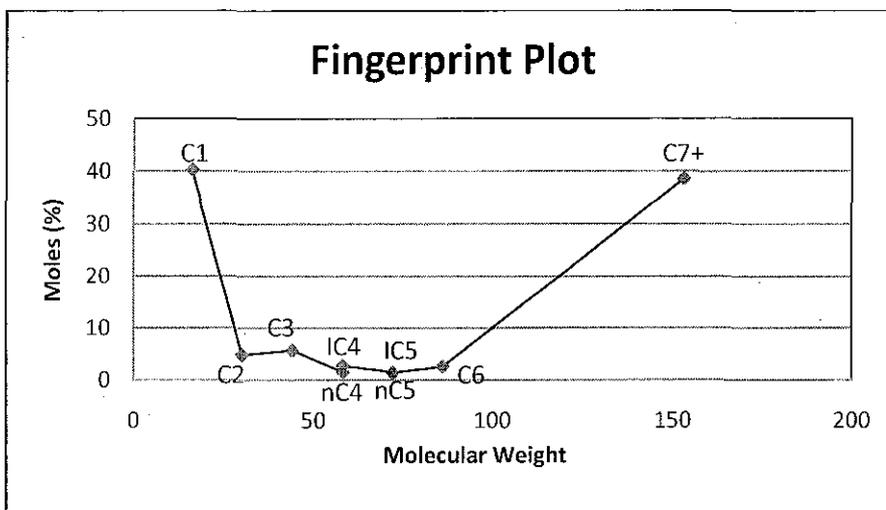


Figure 4.4: The fingerprint plot of mole fraction vs. Molecular weight

The fingerprint plot in Figure 4.4 describes the nature of the crude oil sample, which is of light oil sample. The heavy end fraction of C7+ resulted in an up-turning slope at the end part of the plot. It is sweet light oil being produced in the absence of hydrogen sulfide. Mole fraction of heptanes plus group for this sample is greater than 38%.

In the next part of work, results from laboratory experiments are being input for comparison with the chosen EOS model. Since the model should also be able to predict other experimental data that are dependent on the phase behavior and volumetric prediction, the chosen PR EOS was used next to simulate the DL and CCE. The simulation software performs a number of calculations on the basis of the current fluid-system definition as determined by the EOS.

It can be readily seen from Figure 4.5 to Figure 4.8, the calculated data from PR EOS model off slightly from the experiment observed data. Comparisons of these results, using default PR EOS parameters, were not very satisfying. The maximum error equals to 15.53% and it occurs for the prediction of the GOR. The rest of the PVT properties calculated using PR EOS off the experimental observed data of relative volume, Bo and liquid density by prediction errors 5.56%, 8.60% and 10.50%, respectively.

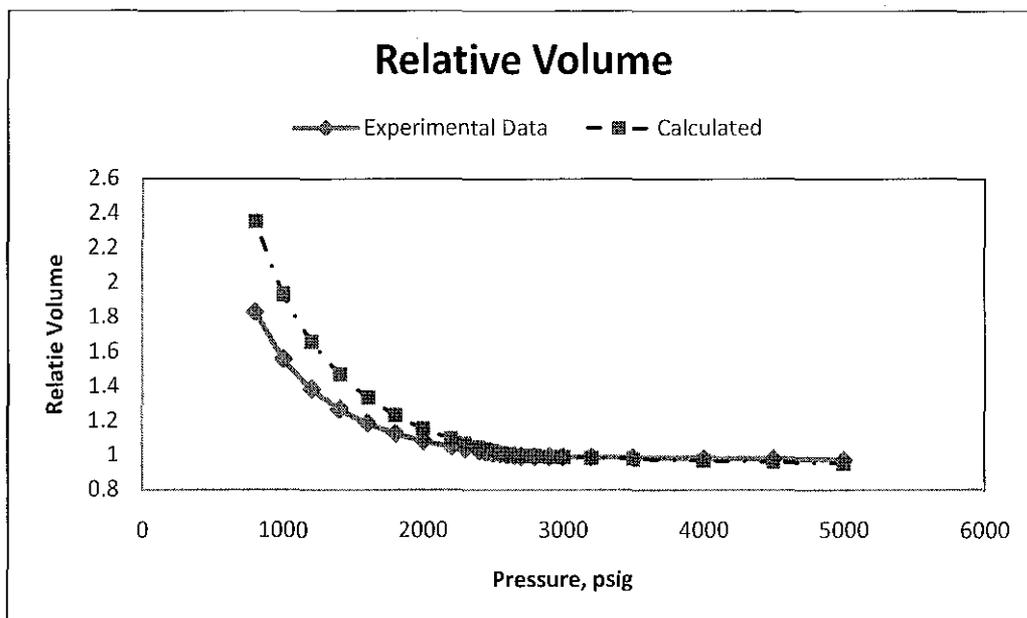


Figure 4.5: Liquid Relative Volume as a function of pressures in the CCE test at 204°F.

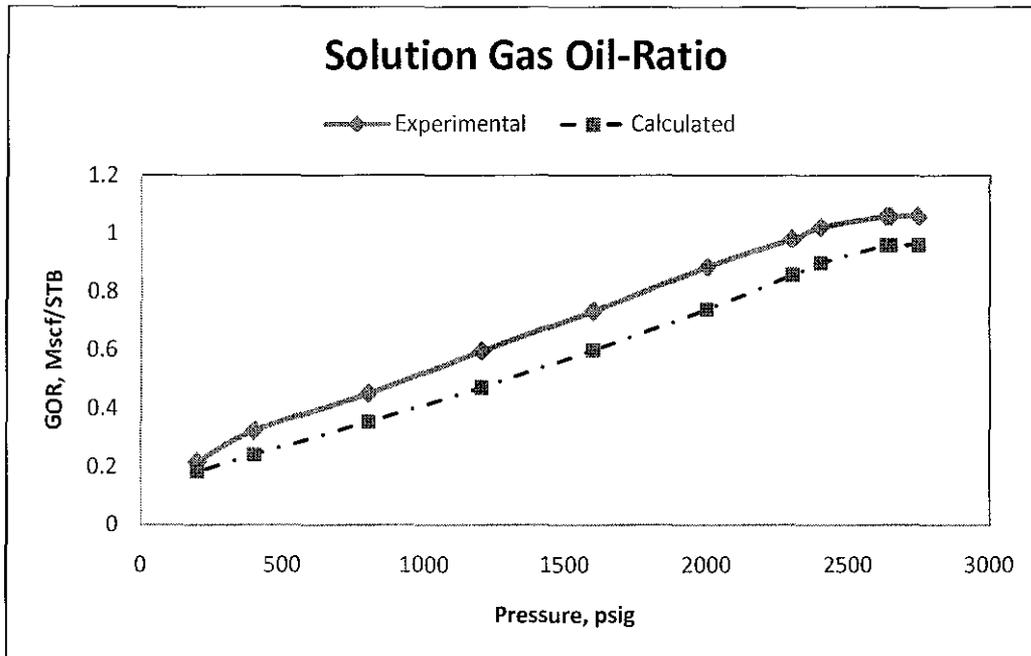


Figure 4.6 : Solution GOR as a function of Pressure in the DLE test at 204°F.

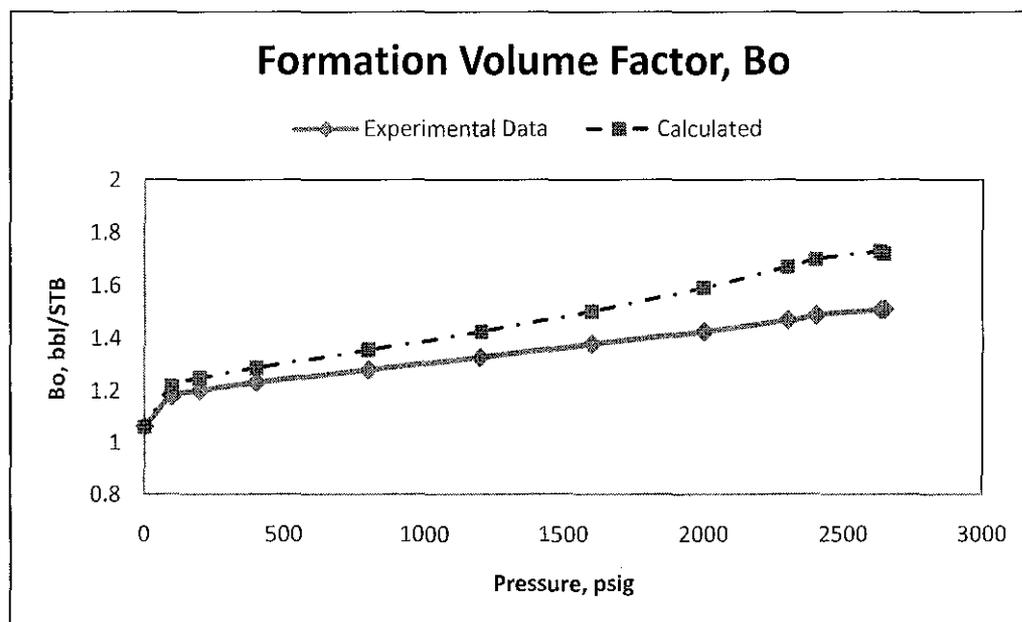


Figure 4.7: Oil Formation Volume Factor as a function of Pressure in the DLE test at 204°F.

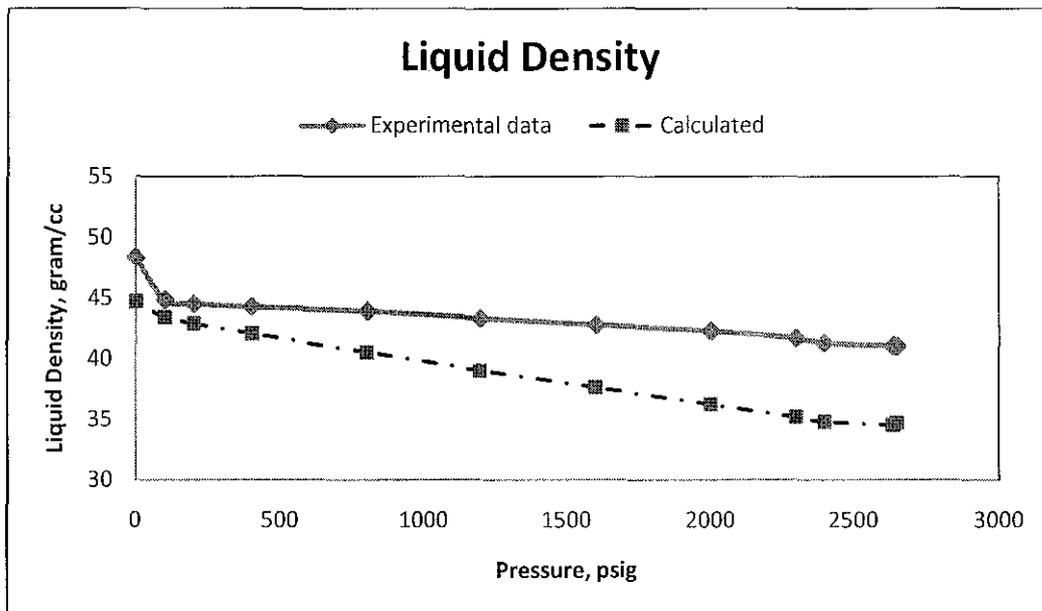


Figure 4.8: Liquid Density as a function of Pressure in the DLE test at 204°F.

4.3 Tuning

The percentage error from the previous results as discussed, indicating the need for tuning the EOS. The sensitivity tests eligible significant parameter to be selected from the global set of parameters supplied by the simulation software during the trial in regression. This includes Omega A, Omega B, P_c , T_c , acentric factor and BIC as shown in sensitivity plot in Figure 4.9.

The result of sensitivity tests are sorted in the descending order. Method employed in this tuning scheme was started from the most sensitive parameters. Literature indicated that for most regression problems involving BIC, Omega properties and critical properties of the data, which is proven correct in this work (Meshari Ali and William McCain, 2005).

The potential regression parameters are shortlisted into groups as follow:

Set I : CO₂/hydrocarbon BIC of heptanes plus group

Set II : Critical pressure (P_c) and critical temperature (T_c) of the heptanes plus group

Set III : Acentric Factor, Omega Ω_a and Omega Ω_b of the heptanes plus group

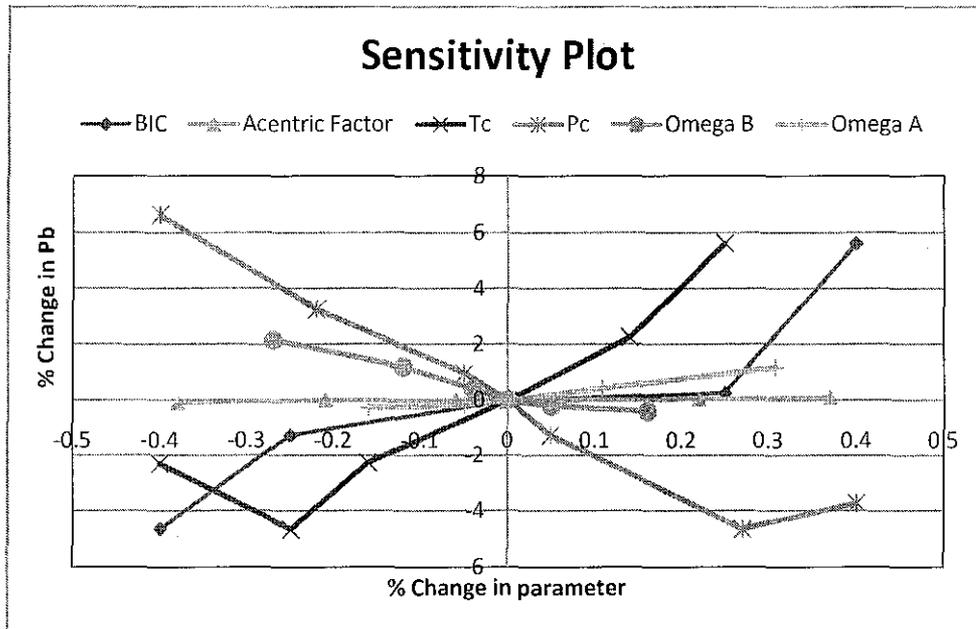


Figure 4.9: Sensitivity of the EOS parameters

From the analysis of the test also, it was found that among the BIC of all components, the BIC between CO₂ and heptanes plus has the most impact compare to other and hence it was chosen as tuning parameter. The BIC was found to be sensitive of the change of saturation pressures and it is common to tune them to fit to the data (Peng W. and Gary A., 2001). The grouping of the acentric factor with omega properties results in fewer regression variables but still allows the heptanes plus fraction to contribute to the parameter adjustment process. This practice might effective, but it is not always good (Pedersan et al., 1989). Therefore, there are only three groups of parameters being selected for the tuning in this work so that in matching of the experimental data, the consistency among the parameters is still maintained. The weight factors given for experimental data set were kept default at 1 except weight factor of 10 was specified to the bubble point pressure expressing the importance.

4.3.1 Evaluating the different tunings

As mentioned previously, in order to describe the phase behavior of a crude oil and calculate its volumetric properties precisely, the PR EOS chosen needs the values of critical pressures, critical temperature and acentric factor for each of the component

particularly at the end component. Table 4.10 are the library data extracted from PVT simulation software which uses Kesler-Lee correlation (Kesler and Lee, 1976) for calculating critical properties and acentric factor for each SCN group. With the molecular weight measure from laboratory at 151.3, the calculated specific gravity is 0.776 from the correlation, as shown in Figure 4.10.

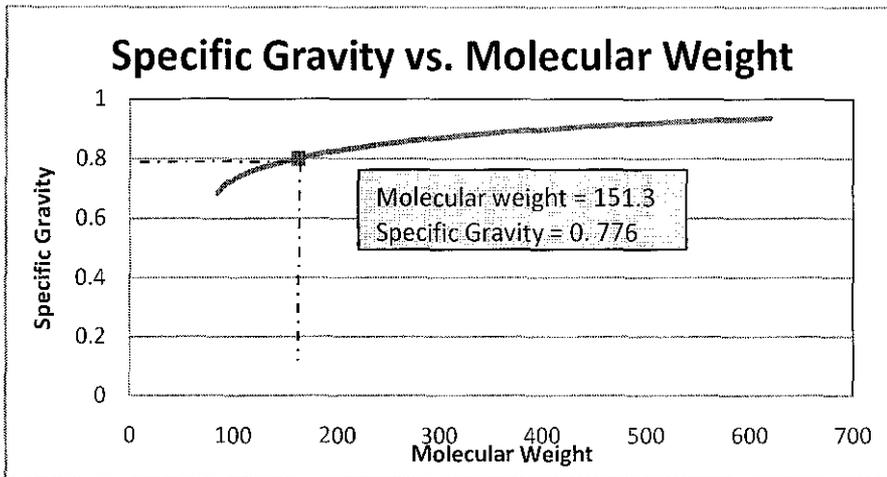


Figure 4.10: Kesler-Lee Correlation in calculating specific gravity by known molecular weight.

Tables 4.10: Properties of the crude oil components

Components	Molecular Weight	Critical Pressure (psig)	Critical Temperature (F)	Omega A	Omega B	Acentric Factor
N2	28.013	477.62	-232.51	0.45724	0.077796	0.04
CO2	44.01	1056.6	88.79	0.45724	0.077796	0.225
C1	16.043	653.09	-116.59	0.45724	0.077796	0.013
C2	30.07	693.65	90.104	0.45724	0.077796	0.0986
C3	44.097	601.06	205.97	0.45724	0.077796	0.1524
IC4	58.124	514.36	274.91	0.45724	0.077796	0.1848
NC4	58.124	535.96	305.69	0.45724	0.077796	0.201
IC5	72.151	476.88	369.05	0.45724	0.077796	0.227
NC5	72.151	474.09	385.61	0.45724	0.077796	0.251
C6	84	421.92	453.83	0.45724	0.077796	0.299
C7+	153.1	315.38	732.44	0.45724	0.077796	0.52472

All components presence in Table 4.10 is contained in the internal library table except for C7+ which is interpolated on the basis of molecular weight. The BIC of the various

component defined as showed in Table 4.11 closely resemble values given by Yarborough (Yarborough, 1979).

Table 4.11: Binary interaction coefficients (BIC) between each of the component

Component	N2	CO2	C1	C2	C3	IC4	NC4	IC5	NC5	C6	C7+
N2	0	-0.012	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
CO2	-0.012	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C1	0.1	0.1	0	0	0	0	0	0	0	0.0279	0.04064
C2	0.1	0.1	0	0	0	0	0	0	0	0.01	0.01
C3	0.1	0.1	0	0	0	0	0	0	0	0.01	0.01
IC4	0.1	0.1	0	0	0	0	0	0	0	0	0
NC4	0.1	0.1	0	0	0	0	0	0	0	0	0
IC5	0.1	0.1	0	0	0	0	0	0	0	0	0
NC5	0.1	0.1	0	0	0	0	0	0	0	0	0
C6	0.1	0.1	0.0279	0.01	0.01	0	0	0	0	0	0
C7+	0.1	0.1	0.04064	0.01	0.01	0	0	0	0	0	0

In this case, the BIC between the methane and heptanes plus group is less influential as what have been proposed by most of the researchers (McCain, 1989, Raffie H. and Tennyson J., 2003). The heptanes plus properties, however, has the highest level of uncertainty (Wu and Fish, 1989). To improve the phase equilibrium and volumetric calculations predicted by the PR EOS, a number of tuning by regression schemes were carried out. Six different sequences of tuning were carried out based on the three groups of parameters. The details of each sequence are tabulated in the Table 4.12 below. For each of the tuning made, five iterations of run are allowed until no convergence has been made.

Table 4.12: The sequences of tuning using the grouped parameters

Trial	Parameter I	Parameter II	Parameter III
1	BIC (CO ₂ : C ₇₊)	T _c & P _c	Omega A and Omega B
2	BIC	Omega A and Omega B	T _c & P _c
3	Omega A and Omega B	T _c & P _c	BIC
4	Omega A and Omega B	BIC	T _c & P _c
5	T _c & P _c	BIC	Omega A and Omega B
6	T _c & P _c	Omega A and Omega B	BIC

From the grouping of the adjustable parameter based on the sensitivity, steps below are taken. First the default value of critical properties and Omega are kept unchanged while BIC was tuned to match the saturation pressure of the mixture through regression. In second step, critical properties are being tuned fitted to the experimental PVT data as continuation after the tuning of critical properties. Third step of tuning involved the tuning of omega properties to further enhance the agreement between the data. The steps of tuning go as indicated in the Table 4.12. The Peng-Robinson EOS model of the PVTi was tuned against the bubble point pressure and the Bo, GOR and oil density at its bubble point. To make sure the parameters remained within acceptable range, the limit for the upper and lower bounds for each of the regression variable was set to maximum 20% of changes from the original value.

Result from the different sequences of tuning showed that sequence started with critical properties followed by BIC and omega gives the best result. This tuning resulted in subsequent improving matching of saturation pressure as the tuning goes.

4.3.2 Tuning by Regression

In the work of tuning, the program allows the definition of a single regression variable to represent the average of a range of EOS parameters. The resulting values for the regression parameters can be found in Table.13 according to the most efficient sequence found as discussed in the previous section.

Table 4.13: Adjustment of EOS Parameters selected for regression and percentage of saturation pressure match.

Tuning Parameters	Initial Value	Adjusted value	Psat initial (Calculated), psig	Psat Regressed, psig	% variation	% match Psat
Tc	732.44	653.117	2392.344	2409.733	0.7268	9.0667
Pc	315.38	358.282	2392.344			
BIC (CO ₂ :C ₇₊)	-0.012	0.048	2392.344	2649.001	10.728	0.0376
Omega A	0.45724	0.32043	2392.344			
Omega B	0.077796	0.0656	2392.344			
Acentric Factor	0.52472	0.63607	2392.344			

Modifiers for each of the regression variable are shown in the Table A6 in appendix, including the default lower and upper regression limits.

Table 4.14 is a summary of the comparison between the calculated crude oil properties before and after regression done in terms of relative volume, GOR, Bo and liquid density. Since the tuned model should also be able to predict more accurate PVT properties that are dependent on phase behavior, the tuned EOS result was examined. The result shows the improvement in absolute relative error after regression has made according to the sequence selected among all the trials.

Table 4.14: Comparison of crude oil properties before and after regression

Properties	Experimental Data	Before Regression	% ARE	After Regression	% ARE
Relative Volume	1	0.9997	0.03	0.9999	0.01
GOR	1.06	0.96	9.433962	1.0944	3.245283
Bo	1.508	1.7189	13.98541	1.5216	0.901857
Liquid Density	41.0152	36.7169	10.47977	41.0151	0.000244

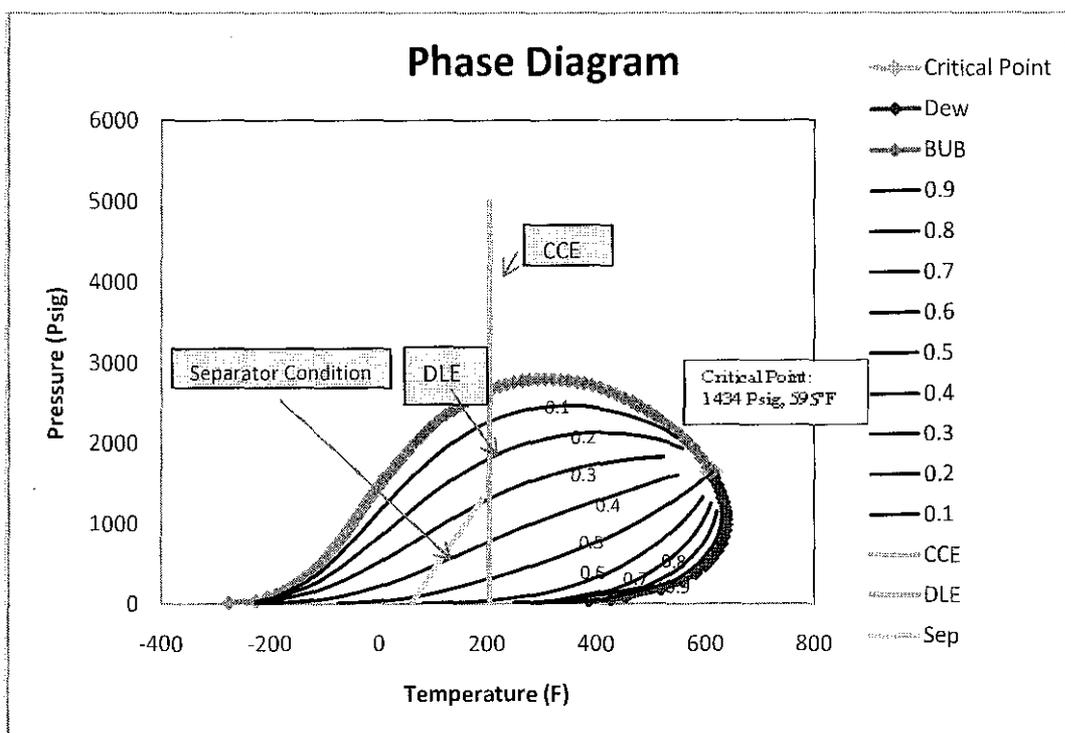


Figure 4.11: Phase diagram plot as the result of the regression

The tuned model is validated by plotting the phase diagram to achieve a satisfactory confirmation of the properties estimation. A reliable EOS heavily depends on the phase diagram which related to the phase volumes and phase mole percentage. Precaution was taken so that the critical point is not shifted during the regression as the critical point is maintained as the same prior to regression which is on 1434 psig and 595°F as shown in Figure 4.11.

The result calculation from the regression was plotted in the graphs in Figure 4.12 until Figure 4.15 where the error is minimized compare to the prior regression calculation for both DL and CCE. Each of the figures shows one of the crude oil properties vs. pressure. The tuned EOS simulates typical experiments and provides analysis of the fluid with comparison to the full laboratory experiment.

Figure 4.12 shows the plot of relative volume of crude oil with respect to pressure where the average error was minimized from 5.56% before tuning to 4.48% after regression. Graph of GOR with respect to pressure in Figure 4.13 which has the highest error percentage of error 15.53% in previous work was improved to 3.13% only. It is clear that there is a significant improvement in the simulated EOS values after regression. As for the Bo in Figure 4.14, improvement has made from 8.60% to 2.94% in error calculation. Lastly the liquid density which has error of 10.50% initially has minimized to 3.76%. Oil formation volume factor decreases steeply to match experimental data set after tuning while liquid density match extremely well with the experimental data.

All the results showed in the graphs apparently indicates the significance of adjusting the previously mentioned parameters and proven that the parameters chosen for tuning are valid.

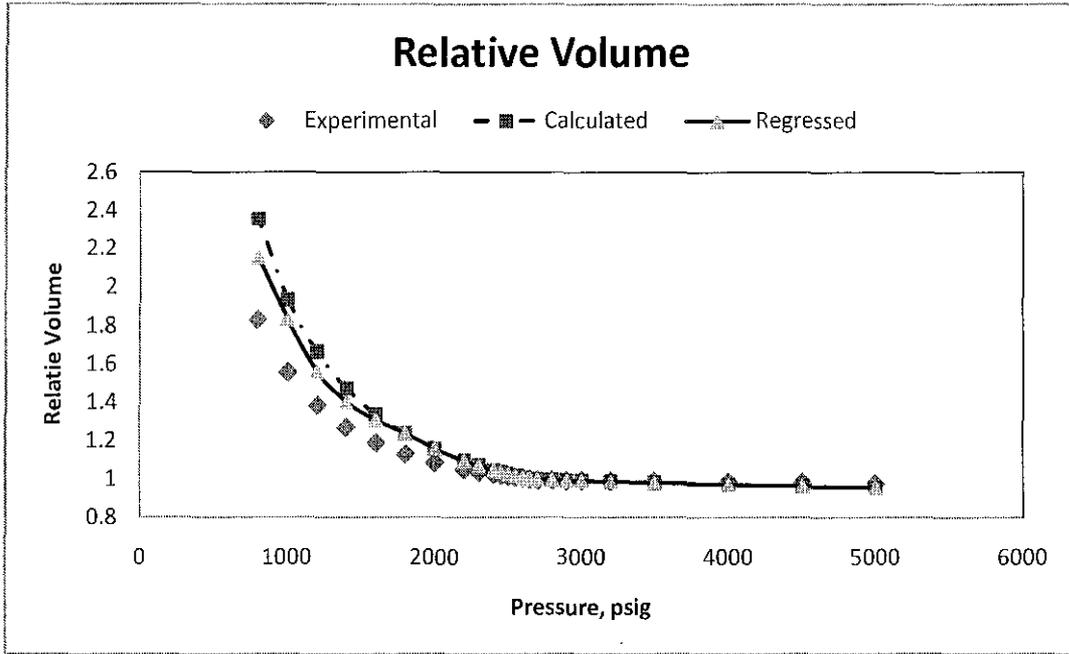


Figure 4.12: Liquid Relative Volume as a function of pressures in the CCE test at 204°F

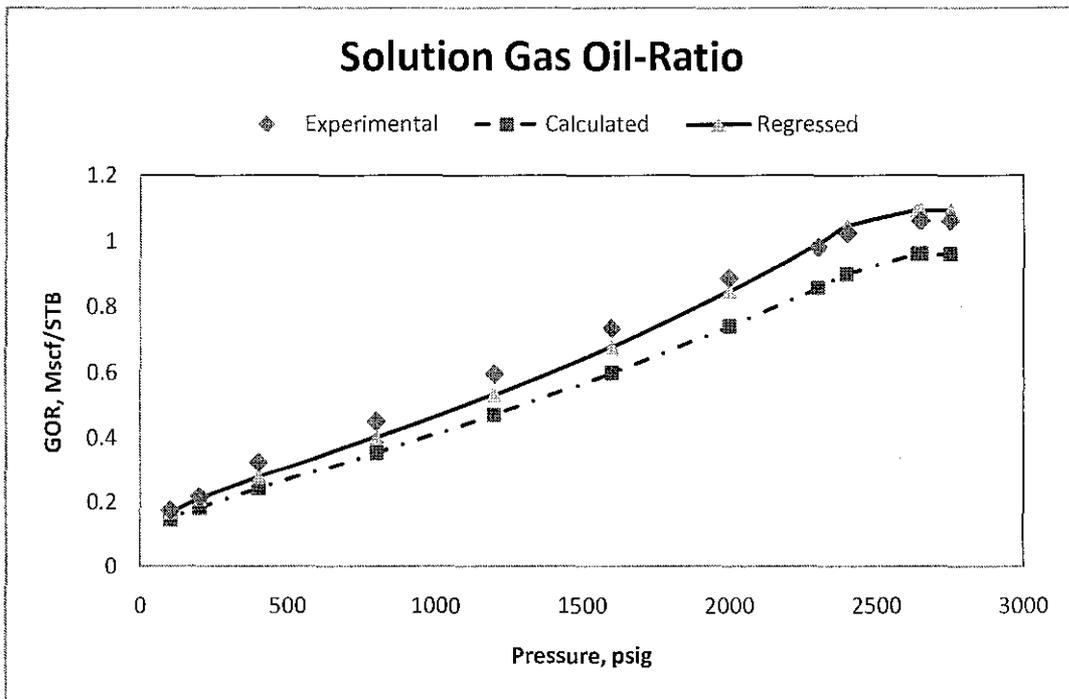


Figure 4.13: Solution GOR as a function of Pressure in the DLE test at 204°F.

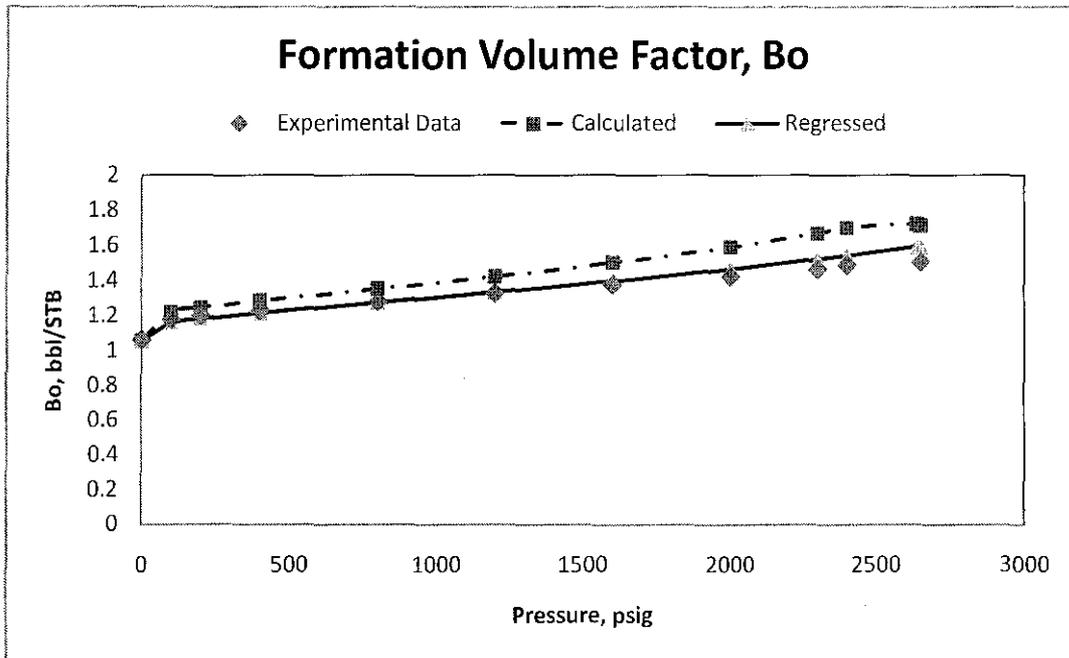


Figure 4.14: Oil Formation Volume Factor as a function of Pressure in the DLE test at 204°F.

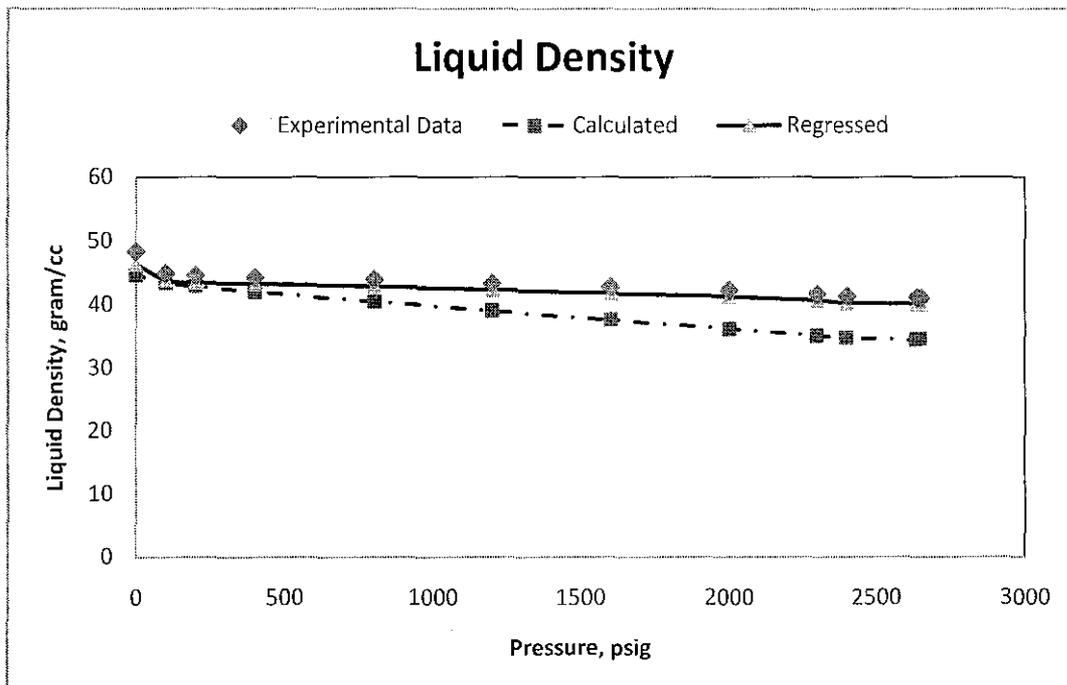


Figure 4.15: Liquid Density as a function of Pressure in the DLE test at 204°F.

Extra work of tuning by regression was verified using PVTx (TEMPEST) PVT simulation software to test out the sequences as per proposed. Although the tuned result was slightly poorer compare to the performance of PVTi (ECLIPSE), the result indicate that consensus was reached between the two softwares. The tuning by regression on the critical properies followed by BIC and omega properties accordingly has found to give improved PVT prediction compared to prior tuning. The results of the tuning is included in Appendix B

CHAPTER FIVE

5.0 Conclusion

A comprehensive research study was undertaken to study the phase behavior of crude oil. It has been studied experimentally and modeled using cubic EOS. By virtue of this research conducted for the simulation of phase behavior of crude oil using different of EOS, some conclusions could be drawn from this work:

1. Among all the EOS, PR EOS is chosen as it gives the closet bubble point pressure compare to the observed laboratory measurement.
2. ECLIPSE PVTi has lower error compare to the other two simulation software, hence better accuracy in term of the performance.
3. Disparity between the calculated data and laboratory observed data and be resolved through tuning by regression.
4. The agreement between laboratory data and regressed PR EOS results is generally good to excellent. The tuning of the EOS resulted in a comparable model which describes almost exactly the crude oil phase behavior.
5. The result of this studies indicated that tuning by regression on the critical properties followed by BIC and omega properties accordingly has found to be the most efficient sequence in tuning.

This work has demonstrated the importance of tuning for model the PVT properties of crude oil correctly. The proposed strategy to tune EOS is very simple, systematic and can be applied to other type of crude oil.

5.1 Recommendation

The tuning based on the sequence is no doubt an efficient way of adjusting the EOS model to laboratory measurement, but this requires heavily on the familiarity with the PVT program used and experience associated with the difficulties that arise in the matching effort. Nonetheless, the auto regression offered in most of the PVT program

does allow rapid improvement on the EOS parameter sets and values, except that the results may not be promising most of the time.

On the other sides, it is also recommended that as much as PVT experiments should be conducted and utilized in the tuning of EOS. This has been discussed in the work of Hiroshi and Takeshi (Hiroshi and Takeshi, 2002) which they mentioned that the selected matching from PVT experiments may mislead the tuning of EOS, although the EOS seems to capture all the PVT experiments included. By having more experiments, this problem can be avoided.

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Appendix A

Table A1: Stock Tank Oil Composition Calculation from Gas Chromatogram

Component	MW	SG	Weight %	No. of Moles	Moles %	Weight	Density
Nitrogen	28.0100	0.8094	0.0000	0.0000	0.0000	0.0000	0.0000
Carbon Dioxide	44.0100	0.8180	0.0000	0.0000	0.0000	0.0000	0.0000
Methane	16.0400	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethane	30.0700	0.3562	0.0510	0.0017	0.2362	0.0710	0.0008
Propane	44.1000	0.5070	0.6420	0.0146	2.0308	0.8956	0.0103
Iso-Butane	58.1200	0.5629	0.5350	0.0092	1.2834	0.7459	0.0072
N-Butane	58.1200	0.5840	1.2510	0.0215	3.0034	1.7456	0.0175
neo-pentane	72.1500	0.5974	0.0070	0.0001	0.0137	0.0099	0.0001
Iso-Pentane	72.1500	0.6247	1.2640	0.0175	2.4442	1.7635	0.0153
N-Pentane	72.1500	0.6311	1.2700	0.0176	2.4550	1.7713	0.0155
Hexanes	86.1800	0.6638	3.1489	0.0365	5.0970	4.3926	0.0338
Methylcyclopentane	84.1600	0.7540	1.4786	0.0176	2.4508	2.0626	0.0185
Benzene	78.1100	0.8829	0.3638	0.0047	0.6496	0.5074	0.0057
Cyclohexane	84.1600	0.7835	1.7726	0.0211	2.9381	2.4727	0.0230
Heptanes	100.2000	0.6882	3.8807	0.0387	5.4025	5.4133	0.0372
Methylcyclohexane	98.1900	0.7748	4.6540	0.0474	6.6117	6.4920	0.0512
Toluene	92.1400	0.8743	0.1910	0.0021	0.2887	0.2661	0.0025
Octanes	114.2300	0.7070	8.0890	0.0708	9.8786	11.2843	0.0698
Ethylbenzene	106.1700	0.8744	0.8500	0.0080	1.1168	1.1857	0.0098
m+p xylene	106.1700	0.8666	0.4340	0.0041	0.5698	0.6049	0.0049
o xylene	106.1700	0.8849	0.4940	0.0047	0.6495	0.6896	0.0057
Nonanes	128.2600	0.7219	6.9822	0.0544	7.5937	9.7397	0.0548
1,2,4 Trimethylbenzene	120.2000	0.8797	2.1440	0.0178	2.4876	2.9901	0.0219
Decanes	142.2900	0.7342	6.3733	0.0448	6.2481	8.8904	0.0459
Undecanes	156.3100	0.7445	6.5940	0.0422	5.8846	9.1982	0.0438
Dodecanes	170.3400	0.7527	5.4500	0.0320	4.4631	7.6024	0.0336
C13	176.0000	0.8110	5.9448	0.0338	4.7117	8.2927	0.0382
C14	190.0000	0.8220	5.6988	0.0300	4.1840	7.9495	0.0344
C15	204.0000	0.8320	7.4763	0.0366	5.1123	10.4290	0.0425
C16	218.0000	0.8380	4.6049	0.0211	2.9466	6.4235	0.0247
C17	232.0000	0.8440	3.6121	0.0156	2.1718	5.0386	0.0183
C18	246.0000	0.8500	4.2483	0.0173	2.4090	5.9262	0.0205
C19	260.0000	0.8560	1.8153	0.0070	0.9739	2.5323	0.0083
C20	274.0000	0.8620	1.4721	0.0054	0.7495	2.0535	0.0065
C21	288.0000	0.8670	1.1661	0.0040	0.5648	1.6267	0.0049
C22	302.0000	0.8710	0.9864	0.0033	0.4556	1.3759	0.0040
C23	316.0000	0.8760	0.7482	0.0024	0.3303	1.0437	0.0029
C24	330.0000	0.8800	0.7764	0.0024	0.3282	1.0830	0.0029
C25	344.0000	0.8850	0.5878	0.0017	0.2383	0.8199	0.0021
C26	358.0000	0.8890	0.4997	0.0014	0.1947	0.6971	0.0017
C27	372.0000	0.8920	0.4527	0.0012	0.1697	0.6314	0.0015
C28	386.0000	0.8960	0.3736	0.0010	0.1350	0.5211	0.0012
C29	400.0000	0.8990	0.3592	0.0009	0.1253	0.5011	0.0011
C30	414.0000	0.9020	0.3577	0.0009	0.1205	0.4989	0.0011
C31	428.0000	0.9050	0.3517	0.0008	0.1146	0.4906	0.0010
C32	442.0000	0.9080	0.2169	0.0005	0.0685	0.3026	0.0006
C33	456.0000	0.9110	0.1983	0.0004	0.0607	0.2766	0.0006
C34	470.0000	0.9140	0.0489	0.0001	0.0145	0.0682	0.0001
C35	484.0000	0.9170	0.0345	0.0001	0.0099	0.0482	0.0001
C36	498.0000	0.9200	0.0279	0.0001	0.0078	0.0389	0.0001
C37+	521.0000	0.9220	0.0214	0.0000	0.0057	0.0298	0.0001
			100.0000	0.7169	100.0000	139.4939	0.7484

Table A2: Stock Tank Gas Composition given in STG mol%. The composition was renormalized to achieve the 100% of total composition.

Component	STG mol%	Normalized Moles %
Nitrogen	1.8300	1.8171
Carbon Dioxide	1.1400	1.1320
Methane	48.2900	47.9496
Ethane	13.5900	13.4942
Propane	20.3100	20.1668
Iso-Butane	4.3900	4.3591
N-Butane	6.2300	6.1861
neo-pentane	0.0400	0.0397
Iso-Pentane	1.6400	1.6284
N-Pentane	1.1400	1.1320
Hexanes	0.7500	0.7447
Methylcyclopentane	0.4000	0.3972
Benzene	0.0700	0.0695
Cyclohexane	0.3400	0.3376
Heptanes	0.0700	0.0695
Methylcyclohexane	0.3100	0.3078
Toluene	0.0400	0.0397
Octanes	0.1000	0.0993
EBz	0.0000	0.0000
M+P-Xylene	0.0000	0.0000
O-Xylene	0.0000	0.0000
Nonanes	0.0200	0.0199
1,2,4 TMBz	0.0000	0.0000
Decanes	0.0100	0.0099
Undecanes	0.0000	0.0000
Dodecanes plus	0.0000	0.0000
Total	100.7100	100.0000

Table A3: Separator Liquid composition in Moles percentage after recombination of stock tank oil and stock tank gas

Component	STO_Moles %	STG_Moles %	Separator Liquid(Moles %)
Nitrogen	0.0000	1.8171	0.1203
Carbon Dioxide	0.0000	1.1320	0.0750
Methane	0.0000	47.9496	3.1756
Ethane	0.2362	13.4942	1.1143
Propane	2.0308	20.1668	3.2319
Iso-Butane	1.2834	4.3591	1.4871
N-Butane	3.0034	6.1861	3.2142
neo-pentane	0.0137	0.0397	0.0154
Iso-Pentane	2.4442	1.6284	2.3902
N-Pentane	2.4550	1.1320	2.3674
Hexanes	5.0970	0.7447	4.8087
Methylcyclopentane	2.4508	0.3972	2.3148
Benzene	0.6496	0.0695	0.6112
Cyclohexane	2.9381	0.3376	2.7659
Heptanes	5.4025	0.0695	5.0493
Methylcyclohexane	6.6117	0.3078	6.1942
Toluene	0.2887	0.0397	0.2723
Octanes	9.8786	0.0993	9.2309
Ethylbenzene	1.1168	0.0000	1.0428
m+p xylene	0.5698	0.0000	0.5320
o xylene	0.6495	0.0000	0.6065
Nonanes	7.5937	0.0199	7.0921
1,2,4 Trimethylbenzene	2.4876	0.0000	2.3229
Decanes	6.2481	0.0099	5.8349
Undecanes	5.8846	0.0000	5.4948
Dodecanes	4.4630	0.0000	4.1675
C13	4.7117	0.0000	4.3997
C14	4.1840	0.0000	3.9069
C15	5.1123	0.0000	4.7737
C16	2.9466	0.0000	2.7514
C17	2.1718	0.0000	2.0280
C18	2.4090	0.0000	2.2495
C19	0.9739	0.0000	0.9094
C20	0.7495	0.0000	0.6998
C21	0.5648	0.0000	0.5274
C22	0.4556	0.0000	0.4254
C23	0.3303	0.0000	0.3084
C24	0.3282	0.0000	0.3064
C25	0.2383	0.0000	0.2226
C26	0.1947	0.0000	0.1818
C27	0.1697	0.0000	0.1585
C28	0.1350	0.0000	0.1261
C29	0.1253	0.0000	0.1170
C30	0.1205	0.0000	0.1125
C31	0.1146	0.0000	0.1070
C32	0.0685	0.0000	0.0639
C33	0.0607	0.0000	0.0566
C34	0.0145	0.0000	0.0135
C35	0.0099	0.0000	0.0093
C36	0.0078	0.0000	0.0073
C37+	0.0058	0.0000	0.0054
	100.0000	100.0000	100.0000

Table A4: Separator Gas composition given in moles percentage.

Component	Sep. Gas mol%	Molecular Weight	SG	Weight	Density
Nitrogen	0.3100	28.0100	0.8094	0.0868	0.2509
Carbon Dioxide	0.8000	44.0100	0.8180	0.3521	0.6544
Methane	76.3000	16.0400	0.3000	12.2385	22.8900
Ethane	8.4400	30.0700	0.3562	2.5379	3.0063
Propane	8.1600	44.1000	0.5070	3.5986	4.1371
Iso-Butane	1.5900	58.1200	0.5629	0.9241	0.8950
N-Butane	2.3200	58.1200	0.5840	1.3484	1.3549
neo-pentane	0.0000	72.1500	0.5974	0.0000	0.0000
Iso-Pentane	0.7000	72.1500	0.6247	0.5051	0.4373
N-Pentane	0.5300	72.1500	0.6311	0.3824	0.3345
Hexanes	0.4300	86.1800	0.6638	0.3706	0.2854
Methylcyclopentane	0.1200	84.1600	0.7540	0.1010	0.0905
Benzene	0.0200	78.1100	0.8829	0.0156	0.0177
Cyclohexane	0.1000	84.1600	0.7835	0.0842	0.0784
Heptanes	0.0200	100.2000	0.6882	0.0200	0.0138
Methylcyclohexane	0.0900	98.1900	0.7748	0.0884	0.0697
Toluene	0.0200	92.1400	0.8743	0.0184	0.0175
Octanes	0.0400	114.2300	0.7070	0.0457	0.0283
Ethylbenzene	0.0000	106.1700	0.8744	0.0000	0.0000
m+p xylene	0.0000	106.1700	0.8666	0.0000	0.0000
o xylene	0.0000	106.1700	0.8849	0.0000	0.0000
Nonanes	0.0100	128.2600	0.7219	0.0128	0.0072
1,2,4 Trimethylbenzene	0.0000	120.2000	0.8797	0.0000	0.0000
Decanes	0.0000	142.2900	0.7342	0.0000	0.0000
Undecanes	0.0000	156.3100	0.7445	0.0000	0.0000
Dodecanes	0.0000	170.3400	0.7527	0.0000	0.0000
	100.0000			22.7305	34.5688

Table A5: Reservoir Fluid in Moles percentage after calculation of physical recombination.

Component	Separator Liquid_Mol%	Separator Gas mol%	Reservoir Fluid mol%
Nitrogen	0.1203	0.3100	0.2166
Carbon Dioxide	0.0750	0.8000	0.4429
Methane	3.1756	76.3000	40.2844
Ethane	1.1143	8.4400	4.8319
Propane	3.2319	8.1600	5.7328
Iso-Butane	1.4871	1.5900	1.5393
N-Butane	3.2142	2.3200	2.7604
neo-pentane	0.0154	0.0000	0.0076
Iso-Pentane	2.3902	0.7000	1.5325
N-Pentane	2.3674	0.5300	1.4350
Hexanes	4.8087	0.4300	2.5866
Methylcyclopentane	2.3148	0.1200	1.2010
Benzene	0.6112	0.0200	0.3112
Cyclohexane	2.7659	0.1000	1.4130
Heptanes	5.0493	0.0200	2.4971
Methylcyclohexane	6.1942	0.0900	3.0965
Toluene	0.2723	0.0200	0.1442
Octanes	9.2309	0.0400	4.5668
Ethylbenzene	1.0428	0.0000	0.5136
m+p xylene	0.5320	0.0000	0.2620
o xylene	0.6065	0.0000	0.2987
Nonanes	7.0921	0.0100	3.4981
1,2,4 Trimethylbenzene	2.3229	0.0000	1.1441
Decanes	5.8349	0.0000	2.8739
Undecanes	5.4948	0.0000	2.7064
Dodecanes	4.1675	0.0000	2.0526
C13	4.3997	0.0000	2.1670
C14	3.9069	0.0000	1.9242
C15	4.7737	0.0000	2.3512
C16	2.7514	0.0000	1.3552
C17	2.0280	0.0000	0.9988
C18	2.2495	0.0000	1.1079
C19	0.9094	0.0000	0.4479
C20	0.6998	0.0000	0.3447
C21	0.5274	0.0000	0.2598
C22	0.4254	0.0000	0.2095
C23	0.3084	0.0000	0.1519
C24	0.3064	0.0000	0.1509
C25	0.2226	0.0000	0.1096
C26	0.1818	0.0000	0.0896
C27	0.1585	0.0000	0.0781
C28	0.1261	0.0000	0.0621
C29	0.1170	0.0000	0.0576
C30	0.1125	0.0000	0.0554
C31	0.1070	0.0000	0.0527
C32	0.0639	0.0000	0.0315
C33	0.0566	0.0000	0.0279
C34	0.0135	0.0000	0.0067
C35	0.0093	0.0000	0.0046
C36	0.0073	0.0000	0.0036
C37+	0.0054	0.0000	0.0027
	100.0000	100.0000	100.0000

Table A6: Percentage changes in values of modifiers of EOS parameters selected for regression.

Variable	Modifier	Minimum	Maximum	Change (%)	Total (Normalized) RMS fit
Pcrit:C7+	1.13630	0.5	1.5	13.635	0.24654
Tcrit:C7+	0.89170	0.5	1.5	-10.830	
Omega_A:C7+	0.70079	0.5	1.5	-29.921	0.25500
Omega_B:C7+	0.84354	0.5	1.5	-15.646	
Bic:CO ₂ -C7+	5	-5	5	400	0.25498

Appendix B

Table B1: Sequence Tuning by regression with Peng-Robinson in calculating PVT Properties of Formation Volume Factor (FVF) by Tempest™ PVTx

Experimental Observed Data		Critical Properties Tuning		BIC Tuning		Omega Properties Tuning	
P obs (Psig)	Oil FVF obs	P calc (Psig)	Oil FVF Calc	P calc (Psig)	Oil FVF Calc	P calc (Psig)	Oil FVF Calc
2650	1.508	2400	1.7857	2400	1.63357	2424.05	1.6539
2400	1.488	2300	1.7788	2300	1.63788	2400	1.64871
2300	1.467	2249.59	1.7681	2299.53	1.6379	2300	1.6276
2000	1.424	2000	1.6739	2000	1.5739	2000	1.56806
1600	1.376	1600	1.59645	1600	1.49645	1600	1.49585
1200	1.328	1200	1.52609	1200	1.42609	1200	1.42995
800	1.28	800	1.4603	800	1.3603	800	1.3679
400	1.232	400	1.39327	400	1.29327	400	1.30388
200	1.201	200	1.35483	200	1.25483	200	1.26652
100	1.179	100	1.32805	100	1.22805	100	1.2398
0	1.064	0	1.26514	0	1.06514	0	1.06986

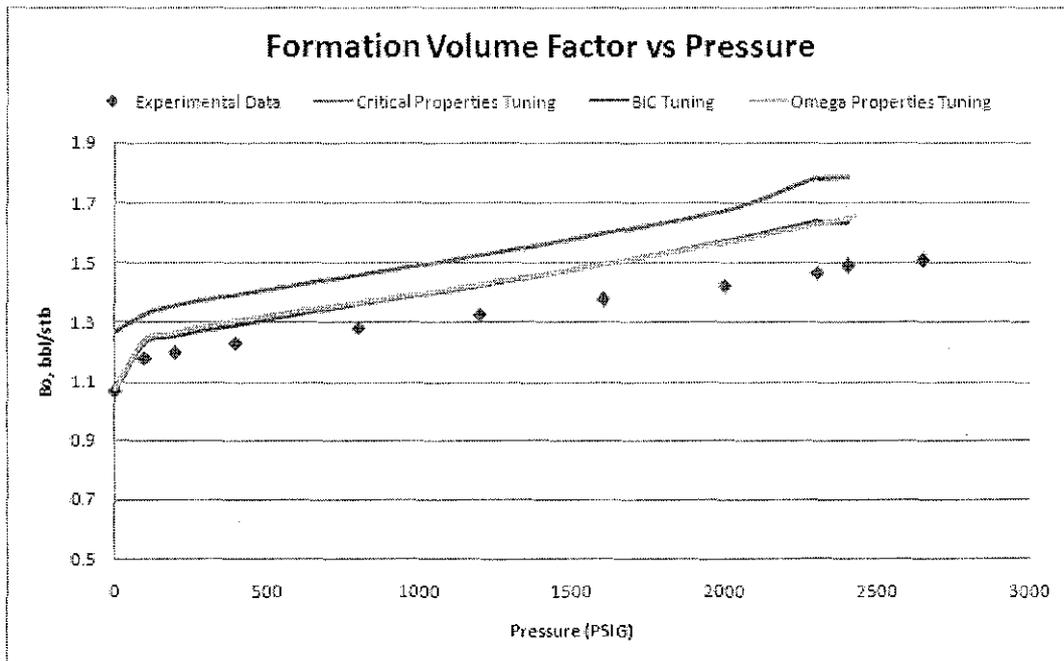


Figure B-1: Formation Volume Factor (FVF) versus Pressure plot per each step taken in tuning by regression in PVTx.

Table B2: Sequence Tuning by regression with Peng-Robinson in calculating PVT Properties of Solution Gas-Oil Ratio by Tempest™ PVTx

Experimental Observed Data		Critical Properties Tuning		BIC Tuning		Omega Properties Tuning	
P obs (Psig)	Rs obs(sc/stb)	P calc (Psig)	Rs Calc (sc/stb)	P calc (Psig)	Rs Calc (sc/stb)	P calc (Psig)	Rs Calc (sc/stb)
2650	1060	2400	1016.59	2400	1016.59	2424.05	1014.19
2400	1022	2300	1016.59	2300	1016.59	2400	1003.29
2300	981	2249.59	1016.59	2299.53	1016.59	2300	958.839
2000	885	2000	879.539	2000	879.539	2000	833.316
1600	733	1600	713.802	1600	713.802	1600	681.483
1200	595	1200	564.278	1200	564.278	1200	544.07
800	451	800	426.96	800	426.959	800	417.232
400	324	400	294.122	400	294.121	400	293.37
200	217	200	224.099	200	224.098	200	227.127
100	177	100	180.743	100	180.742	100	185.119
0	0	0	0	0	0	0	0

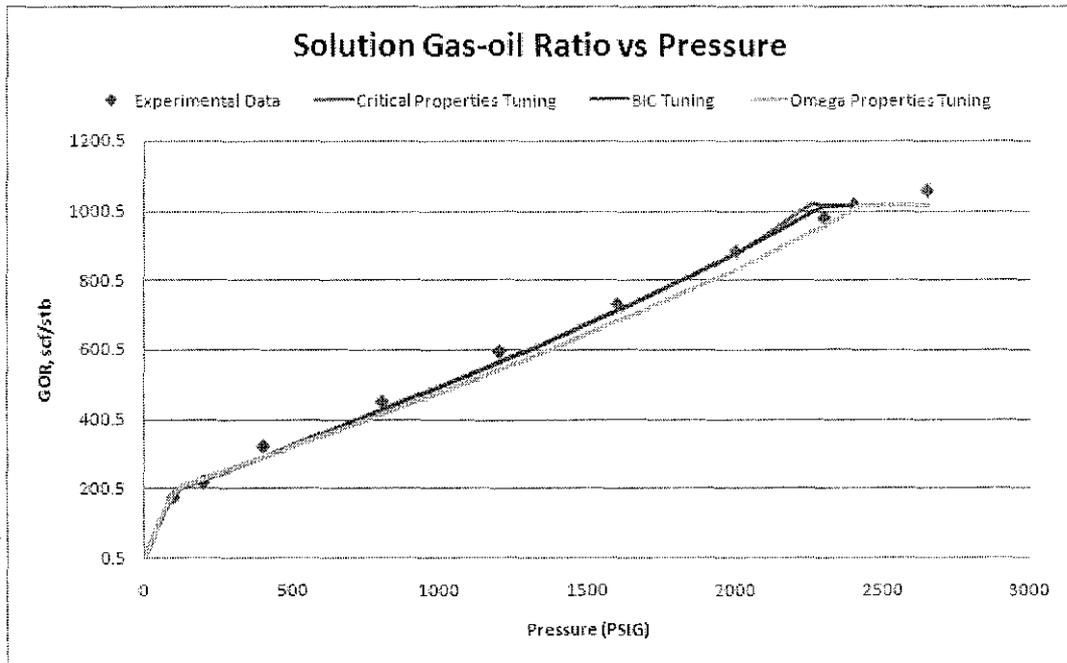


Figure B-2: Solution Gas-Oil Ratio versus Pressure plot per each step taken in tuning by regression in PVTx.

Table B3: Sequence Tuning by regression with Peng-Robinson in calculating PVT Properties of Oil Density by Tempest™ PVTx

Experimental Observed Data		Critical Properties Tuning		BIC Tuning		Omega Properties Tuning	
P obs (Psig)	Oil Density obs(g/cc)	P calc (Psig)	Oil Density calc(g/cc)	P calc (Psig)	Oil Density calc(g/cc)	P calc (Psig)	Oil Density calc(g/cc)
2650	0.657	2400	0.62956	2400	0.62956	2424.05	0.62009
2400	0.662	2300	0.6279	2300	0.6279	2400	0.621
2300	0.668	2249.59	0.62789	2299.53	0.62789	2300	0.62482
2000	0.678	2000	0.63982	2000	0.63982	2000	0.6362
1600	0.686	1600	0.65574	1600	0.65574	1600	0.65128
1200	0.695	1200	0.6717	1200	0.6717	1200	0.66634
800	0.704	800	0.68787	800	0.68787	800	0.68164
400	0.71	400	0.70513	400	0.70513	400	0.69809
200	0.714	200	0.71496	200	0.71496	200	0.70761
100	0.719	100	0.72134	100	0.72134	100	0.71396
0	0.775	0	0.74702	0	0.74702	0	0.74118

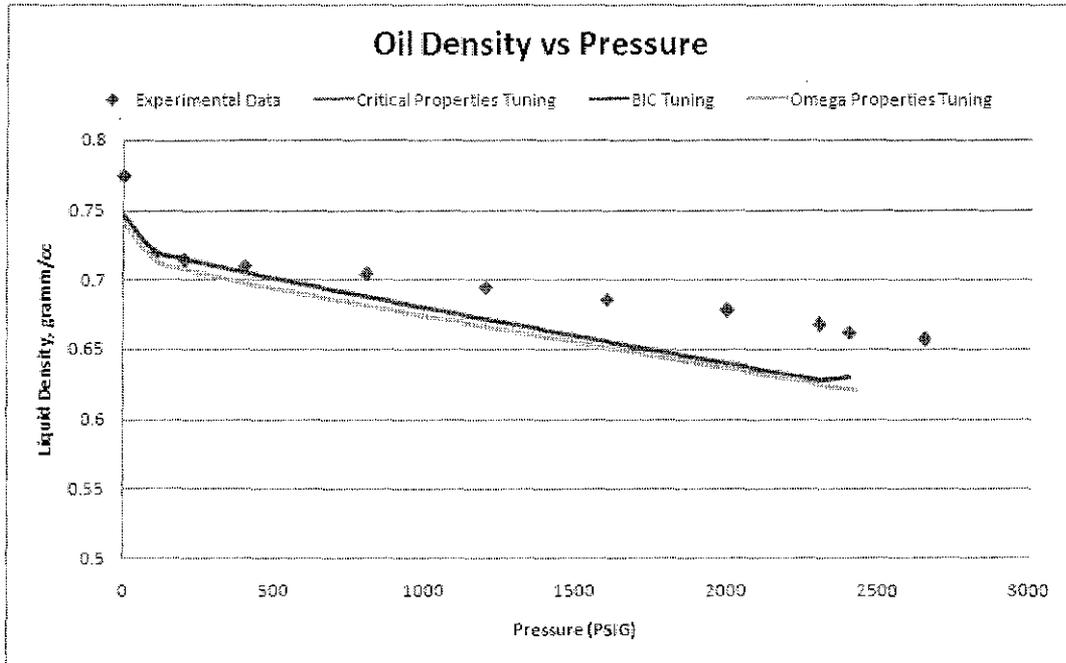


Figure B-3: Oil Density versus Pressure plot per each step taken in tuning by regression in PVTx.

Table B4: Sequence Tuning by regression with Peng-Robinson in calculating PVT Properties of Relative Volume by Tempest™ PVTx

Experimental Observed Data		Critical Properties Tuning		BIC Tuning		Omega Properties Tuning	
P obs (Psig)	Rel Vol obs	P calc (Psig)	Rel Vol Calc	P calc (Psig)	Rel Vol Calc	P calc (Psig)	Rel Vol Calc
5000	0.976	5000	0.94734	5000	0.94734	5000	0.94362
4500	0.98	4500	0.95491	4500	0.95491	4500	0.95208
4000	0.984	4000	0.96326	4000	0.96326	4000	0.96149
3500	0.988	3500	0.97255	3500	0.97255	3500	0.97204
3200	0.99	3200	0.97865	3200	0.97865	3200	0.97903
3000	0.992	3000	0.98297	3000	0.98297	3000	0.984
2900	0.993	2900	0.98522	2900	0.98522	2900	0.98659
2800	0.993	2800	0.98752	2800	0.98752	2800	0.98925
2700	0.994	2700	0.98988	2700	0.98988	2700	0.992
2650	1	2600	0.9923	2600	0.9923	2600	0.99482
2600	1.004	2550	0.99354	2550	0.99354	2550	0.99626
2550	1.009	2500	0.99479	2500	0.99479	2500	0.99773
2500	1.014	2450	0.99606	2450	0.99606	2450	0.99922
2450	1.019	2400	0.99735	2400	0.99735	2424.05	1
2400	1.025	2300	0.99999	2300	0.99999	2400	1.00496
2300	1.037	2249.59	1	2299.53	1	2300	1.02702
2200	1.051	2200	1.02344	2200	1.02344	2200	1.05161
2000	1.084	2000	1.08003	2000	1.08002	2000	1.10999
1800	1.129	1800	1.15287	1800	1.15286	1800	1.18417
1600	1.188	1600	1.24823	1600	1.24823	1600	1.28033
1400	1.27	1400	1.37606	1400	1.37606	1400	1.40823
1200	1.386	1200	1.55308	1200	1.55307	1200	1.58432
1000	1.558	1000	1.80969	1000	1.80969	1000	1.83853
800	1.832	800	2.20739	800	2.20739	800	2.23136

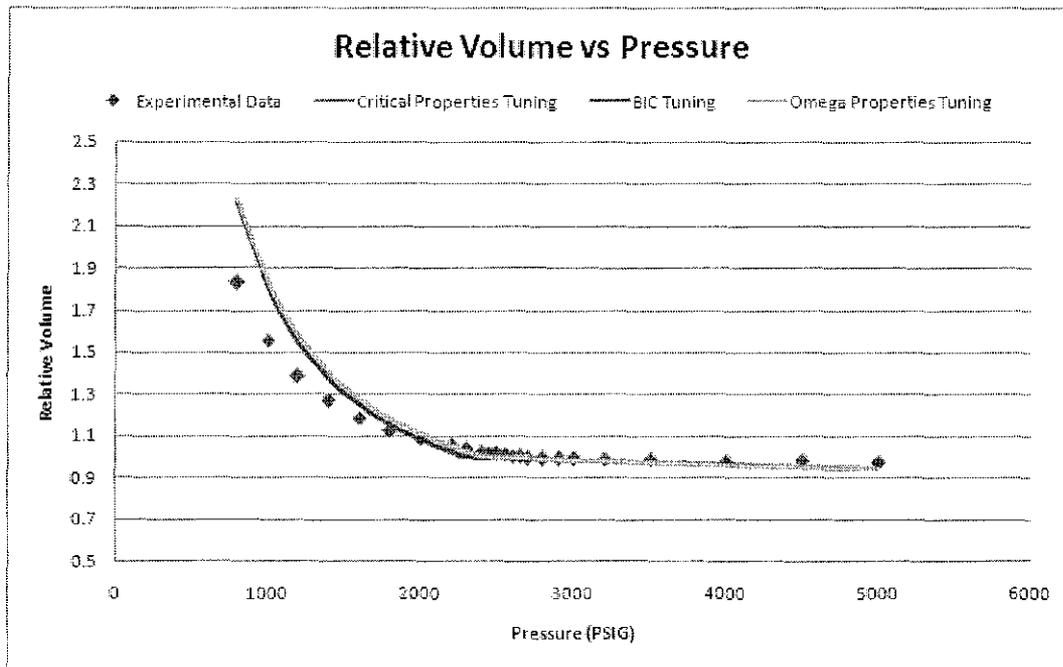


Figure B-4: Relative Volume versus Pressure plot per each step taken in tuning by regression in PVTx.

LOGBOOK

Name	Kang Hooi Yee	Week No	1
Supervisor	Mr. Ali F. Mangi Alta'ee		
Title	Simulation of Phase Behavior of Crude Oil using different Equations-of-State		
		ID	9917

Discussion (Complete Activities)

Data gathering & Analysis

- Received data of stock tank oil from Mr. Ali, required to calculate the composition of each components presence in stock tank from chromatogram.
- Provided also with stock tank gas composition and separator gas composition.
- Required to perform separator recombination to get a representative crude oil sample.

Literature Review

- Performing tuning.

Planned Activities (for next week)

- Done with separator fluid recombination.
- Start simulation.
- Data gathering of crude oil PVT experiment in laboratory.

Progress vs. Gantt Chart: On track

Problems encountered: Problem of fluid recombination was resolved under Mr. Ali guidance.

- Note:
- 1) Maximum 1 pages only
 - 2) Supervisor needs stamp on this log book



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Date: 30/Jan/2011

Note: Supervisors shall retain the forms for five consecutive years

LOGBOOK

Name	Kang Hooi Yee	Week No	3
Supervisor	Mr. Ali F. Mangi Alta'ee		
Title	Simulation of Phase Behavior of Crude Oil using different Equations-of-State		
		ID	9917

Discussion (Completed Activities)

Simulation/Modelling

- Done with fluid composition definition and fluid characterization.
- Simulating experiment of crude oil sample by using different EOS
- Compilation of data from all the four EOS using three different softwares.

Planned Activities (for next week)

Simulation/Modelling

- Finalize which EOS describe best the phase behavior of crude oil
- Determine which software has better performance

Progress vs. Gantt Chart: Ahead of schedule planned.

Problems encountered: RK EOS in PVTx not showing any result.

- Note:
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Date: 4/5/2011

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LOGBOOK

Name	Kang Hooi Yee	Week No	6
Supervisor	Mr. Ali F. Mangi Alta'ee		
Title	Simulation of Phase Behavior of Crude Oil using different Equations-of-State		
		ID	9917

Discussion (Completed Activities)

Simulation/Modelling

- Finalized PR EOS as the most accurate EOS in describe crude oil sample.
- Eclipse PVTi has been chosen and to be continue with tuning.
- Tabulate data and analysis

Planned Activities (for next week)

Simulation

- Proceed with tuning

Report writing

- Submission of progress report

Progress vs. Gantt Chart: /

Problems encountered: /

- Note:
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Date: 4/5/2011

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LOGBOOK

Name	Kang Hooi Yee	Week No	8
Supervisor	Mr. Ali F. Mangi Alta'ee		
Title	Simulation of Phase Behavior of Crude Oil using different Equations-of-State		
		ID	9917

Discussion (Completed Activities)

Simulation/Modelling

- Tuning of EOS to match the observed experimental data.

Review of progress report

- Insufficient of data discussion in result discussion in report.

Planned Activities (for next week)

Seminar

- Pre-seminar with Adonis, Irzie and Zahidah.

Progress vs. Gantt Chart: Goes well as planned.

Problems encountered: Slides preparation

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Date: 4/5/2011

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LOGBOOK

Name	Kang Hooi Yee	Week No	10
Supervisor	Mr. Ali F. Mangi Alta'ee		
Title	Simulation of Phase Behavior of Crude Oil using different Equations-of-State		
		ID	9917

Discussion (Complete Activities)

- Submission of poster for pre-EDX.
- Submission of first draft of final report.

Planned Activities (for next week)

- Poster designing.
- Drafting of final report, continuation from previous progress report.

Progress vs. Gantt Chart:

Problems encountered:

- Note:
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Date: 4/5/2024

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