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TRANSPORT AND PHASE EQUILIBRIA PROPERTIES FOR STEAM
FLOODING OF HEAVY OILS

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Transport and Phase Equilibria Properties for
Steam Flooding of Heavy Oils

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TABLE OF CONTENTS

1. TABLE OF CONTENTS	
2. DISCLAIMER	v
3. ABSTRACT	vii
4. STATEMENT OF WORK	ix
5. GENERAL INTRODUCTION	1
6. THEORETICAL WORK	1
7. PHASE EQUILIBRIUM CALCULATIONS	1
Introduction	1
8. OIL CHARACTERIZATION	9
9. EXPERIMENTAL PART	15
10. NOMENCLATURE	19
11. REFERENCES	21

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TRANSPORT AND PHASE EQUILIBRIA PROPERTIES FOR STEAM FLOODING OF HEAVY OILS

ABSTRACT

Hydrocarbon/water and CO₂ systems are frequently found in petroleum recovery processes, petroleum refining, and gasification of coals, lignites and tar sands. Techniques to estimate the phase volume and phase composition are indispensable to design and improve oil recovery processes such as steam, hot water, or CO₂/steam combinations of flooding techniques typically used for heavy oils.

An interdisciplinary research program to quantify transport, PVT, and equilibrium properties of selected oil/ CO₂/water mixtures at pressures up to 10,000 psia and at temperatures up to 500 °F has been put in place.

The objectives of this research include experimental determination and rigorous modeling and computation of phase equilibrium diagrams, volumetric, and transport properties of hydrocarbon/CO₂/water mixtures at pressures and temperatures typical of steam injection processes for thermal recovery of heavy oils.

The project is divided in an experimental and a theoretical part. For the experimental part, we have measured bubble points and pressure-volume relations for four different oil samples. For the theoretical part a computer program to implement the technique to calculate phase equilibrium diagrams known as the area method was developed. This method though correct to predict binary mixtures equilibrium data has proved too cumbersome for multi-component calculations. A new method to compute multi-component phase equilibrium diagrams based on an improved version of the Peng-Robinson equation has been developed. This new version of the Peng-Robinson equation uses a new volume translation scheme and new mixing rules to improve the accuracy of the calculations. Calculations involving binary and ternary mixtures of CO₂/water and hydrocarbons are reported. A scheme to characterize multi-component materials such as, oils into a small set of "pseudo-components" has been implemented. The final goal is to be able to duplicate the predicted phase behavior diagrams for mixtures of CO₂/water and real oils at high pressures and temperatures.

TRANSPORT AND PHASE EQUILIBRIA PROPERTIES FOR STEAM FLOODING OF HEAVY OILS

STATEMENT OF WORK (SOW)

Under this Statement of Work (SOW), Dr. Jorge Gabitto from the Chemical Engineering Department at Prairie View A&M University (PVAMU), Dr. Maria Barrufet from the Petroleum Engineering Department at Texas A&M University (TAMU) and Dr. Rebecca Bryant from Bio-Engineering Inc. (B-E) will conduct research and training in the area of transport and thermodynamic properties determination for heavy oils. A research project is proposed to develop theoretical models, develop computer algorithms, and measure experimentally transport and thermodynamic properties of heavy oils.

Training of graduate and undergraduate students will be part of the project. Technology transfer of the results generated by the project will be achieved through BDM PT and publications in referred journals.

Dr. Gabitto will act as coordinator of the research team. Drs. Barrufet and Bryant will act as subcontractors to Dr. Gabitto.

GENERAL INTRODUCTION

This report is divided in three parts, theoretical work, experimental work and academic activities. The theoretical work part has two subparts, development of an improved Peng-Robinson equation of state with volume translation term and development of a procedure to characterize heavy oil mixtures.

THEORETICAL WORK

PHASE EQUILIBRIUM CALCULATIONS

Introduction

Water and CO₂ are used extensively in enhanced oil recovery processes such as steam flooding and CO₂ flooding. These methods are the most important thermal/miscible oil recovery processes (Wu, 1977 [1]; Harding et al., 1983 [2]; Turek et al., 1984 [3], Boberg, 1988 [4]). Steam and/or CO₂ are injected into reservoirs where hydrocarbons and brines coexist. Intermolecular interactions of CO₂ with water and hydrocarbons will affect the species partitioning into the coexisting equilibrium phases, i.e., the hydrocarbon K-values (K_i's) will likely be different from those obtained at the same pressure and temperature, but in the absence of water or of CO₂.

Many investigators have recognized the effect of water presence on phase equilibrium. It has not been taken into account in most engineering calculations due to lack of sufficient experimental data. This omission can result in serious errors in the design and simulation of the recovery and separation processes.

In steam-thermal recovery processes, steam is either injected into or generated within a reservoir where the hydrocarbons and water may coexist in three phases, vapor and two liquid phases, hydrocarbon and water. While steam distillation is considered one of the most important thermal oil recovery mechanisms, simulation of steam injection processes often neglects the effect of the aqueous phase upon the hydrocarbon equilibrium separation. In miscible enhanced oil recovery processes using CO₂ as a displacing

medium, the aqueous effects on the hydrocarbon/ CO₂ phase behavior have not been fully investigated. Because of the aqueous phase vapor pressure and the mutual solubility of water and hydrocarbon/ CO₂ in the liquid phases, neglecting the aqueous effects can induce serious error in the representation of hydrocarbon/ CO₂ phase behavior. Hornbrook et al., 1991 [4], reported the use of CO₂ in steam flooding showing many beneficial effects on oil recovery and economics.

Phase equilibrium diagrams and volumetric properties are important in the design, development and operation of chemical processes and reservoir simulations. In order to estimate these properties, cubic equations of state (EOS) are commonly used. Since the development of van der Waals equation of state [5], more accurate equations of state have been developed which can describe thermodynamic properties and phase equilibria of a wide range of substances with varying degrees of successes (for example, see [6-13]).

Among the simple two-parameter cubic equations of state, the Peng-Robinson equation of state (PR EOS) [14] is commonly used to model phase behavior and volumetric properties of fluid mixtures encountered in natural gas refinery, petrochemical and chemical applications. The Peng-Robinson equation of state for a pure fluid can be written as

$$P = RT / (v - b) - a / (v^2 + ubv + wb^2) \quad (1).$$

Where, P is the pressure, v is the molar volume, R is the gas constant, b is the excluded-volume parameter, and a, is the attraction energy parameter. For PR EOS, u = 2 and w = -1, and b and a are defined as,

$$b = b_c \text{ and } a = a_c \alpha(\omega, T_r) \quad (2).$$

Where, critical parameters b_c and a_c are given by

$$b_c = 0.07779607 (RT_c)/P_c \quad (3)$$

$$a_c = 0.45723553 (RT_c)^2/P_c \quad (4)$$

and $\alpha(\omega, T_r)$ is defined as

$$\alpha(\omega, T_r) = \left[1 + m(\omega) (1 - T_r^X) \right]^2 \quad (5).$$

Where, ω is the acentric factor, and T_r is the reduced temperature, $T_r = T/T_c$, with T the absolute temperature and T_c the critical temperature. In the original PR EOS, X =

0.5, and $m(\omega)$ is expressed in terms of a simple polynomial in ω , specific to a particular fluid. In order to calculate volume from PR EOS, Eq.(1) can be expressed in terms of the compressibility factor Z as

$$Z^3 + (B - 1) Z^2 + (A - 3B^2 - 2B) Z + (B^3 + B^2 - AB) = 0 \quad (6), \text{ with}$$

$$A = aP / R^2 T^2, \quad B = bP / RT \quad \text{and} \quad Z = vP / RT \quad (7).$$

Note that Eqn.(6) is used to calculate volume and can yield one to three roots depending on the number of phases in the system. For the vapor/liquid phase equilibria in pure fluids, the largest positive root of Z corresponds to the vapor phase, while the smallest positive root of Z corresponds to the liquid phase. The fugacity coefficient ϕ of PR EOS can be given by

$$\ln \phi = (Z - 1) - \ln(Z - B) + \frac{A}{2\sqrt{2}B} \ln \frac{Z + (1 - \sqrt{2}) B}{Z + (1 + \sqrt{2}) B} \quad (8)$$

Since the original PR EOS (a) cannot describe saturated vapor pressures of fluids at low temperatures, (b) becomes unreliable for fluids with large acentric factors ($\omega > 0.5$), and (c) cannot describe accurately the saturated volumes of liquid and vapor phases, numerous attempts have been made in the past to modify PR EOS. Stryjek and Vera [15] were the first to modify PR EOS by representing m of α -term (Eq.(5)) as a function of both acentric factor and reduced temperature, $m(\omega, T_r)$, for $X = 0.5$. They fitted m to saturated vapor pressures of several fluids and expressed it in terms of a simple polynomial in ω and T_r . Their modification is known as PRSV EOS. Several other modifications of α -term in PR EOS can be found in the literature (for example, see [8, 16]). In these modifications of PR EOS, the common practice has been to represent saturated vapor pressure data as accurately as possible by manipulating m as a function of ω and T_r for $X=0.5$. Later, Twu *et al.* [17] presented a different approach for determining the α -term by expressing Eqn.(5) in an exponential form (without considering m) and were able to correlate saturated vapor pressures of a number of hydrocarbon fluids ranging from methane (C₁) to eicosane (C₂₀), here referred to as PRT EOS. Their α -term is a function of temperature only and contains three parameters. Twu *et al.* [17] found that the results obtained from PRT EOS for the saturated vapor pressures were more accurate than those obtained either from PR EOS or PRSV EOS. Since the above modifications of α -term (or m) are based on the experimental data of saturated vapor pressures for some selected systems having $\omega < 1$, these equations of state can be applied reliably only to the limited ranges of the acentric factor, ($\omega < 1$).

Keeping the form of α -term to be the same as given by Eqn.(5), we presented an improved form of PR EOS, called MPR EOS [10]. In MPR EOS $m(\omega)$ no longer depends on the properties of a particular fluid. Following the suggestion of Leibovici, [18], $m(\omega)$ was determined by satisfying the isofugacity condition at $T_r = 0.7$ for $X = 0.5$ using Eqn.(5) and Eqn.(1) and was represented in a polynomial form. So long as u and w of Eqn.(1) are temperature independent parameters, the proposed $m(\omega)$ can be applied to any cubic equation of state and to much larger values of ω ($\omega < 2$). For the well-defined value of $m(\omega)$ the X parameter of α -term (Eqn.(5)) did not yield an universal value of $X=0.5$ (a values adopted for the PR EOS of Eqn.(1)) as will also be shown in this work below. Therefore, we represented X in terms of a simple polynomial in reduced temperature containing four parameters, which were obtained by comparing calculated results with experimental data of the saturated vapor pressures of several fluids over a range of temperatures and pressures. In this work also we represent X in terms of a polynomial in T_r . Unlike the previous work, however, now X contains only three parameters.

In order to improve the prediction of saturated liquid densities using the two-parameter cubic equations of state, Peneloux *et al.* [19] introduced a temperature independent volume translation term in the Soave-Redlich-Kwong equation of state. The volume translation term is a constant volume term added to the actual molar volume to match the experimental molar volume at the fixed temperature and pressure. Their method did not change the vapor/liquid equilibrium conditions determined by the non-translated equation of state, but modified the phase volumes. Although this procedure works well at temperatures away from the critical point, deviation increases substantially beyond a reduced temperature of about 0.7-0.8. Jhaveri and Younger [20] used the method of Peneloux *et al.* [19] in PR EOS for the prediction of saturated liquid volumes of several fluids and found that the method was reliable up to the reduced temperature $T_r = 0.8$ for fluids with small values of the acentric factor. As the temperature and the acentric factor increase, their method becomes inaccurate. Following Jhaveri and Younger [20], Magoulas and Tassios [21] and Voros *et al.* [22] presented a temperature and acentric factor dependent volume translation term with a modified form of PR EOS for n-alkanes and several other nonpolar fluids. However, their method involves several complicated equations and parameters. Taking the advantage of the approach of Voros *et al.* [22], one of us [10] presented equations of Voros *et al.* [22] in simpler forms, still containing six parameters. In a more recent study Monnery *et al.* [23] presented a Gaussian-like volume translation term which models the temperature dependency of the

volume shift providing a small, constant correction for temperatures away from the critical point but an enhanced, continuous correction in the critical region. However, for high pressures and high temperatures this method predicts a relatively large value of the volume translation correction.

It may be noted that the temperature dependency of the volume translation parameters may result in physically unrealistic negative predictions for heat capacities depending on how the volume shift is incorporated [24]. This led Mathias et al [25] to propose a modification in the method of Peneloux et al. [19] by increasing the volume shift near the critical point. They added a temperature independent term in the volume translation, which is a function of the inverse isothermal compressibility. The isothermal compressibility was calculated from the equation of state. In order for the method to predict the critical shift, it required the critical volume. The method was found remarkably good for predicting the saturated volumes of some selected fluids of low molecular weight hydrocarbons, nitrogen and water for the entire temperature range from the triple point up to the critical point.

The purpose of this work is to develop an improved form of the Peng-Robinson equation of state following Fotouh and Shukla [10] and predict simultaneously the phase equilibria and volumetric properties of fluids of industrial interest over a wide range of acentric factor values and the entire temperature range along the saturation line. This is accomplished by (1) defining X as a function of temperature with three parameters only, (2) using our polynomial of $m(\omega)$, which can describe fluids with large acentric factors of practical interest ($\omega \leq 2$ and above) and is independent of temperature and a particular fluid, and (3) incorporating the temperature independent volume translation term of Mathias et al [25] with a simple modification. In this way, we further simplify our earlier modifications of α -term and introduce a new version of the volume translation term, which is more accurate close to the critical point. We also extend calculations to more systems of practical interest.

In Section 1, we present a brief account of the modified form of PR equation of state (MPR EOS). The accuracy of MPR EOS is tested in Section 2 by presenting comparisons of calculated results with experimental data for the saturated vapor pressures and volumes. Section 3 presents our conclusions.

1. Modified Peng -Robinson Equation of State (MPR EOS)

The general form of MPR EOS for a pure fluid is given by Eqn.(1) along with Eqns.(2-8). The important parameters of MPR EOS are m and X of the α -term (Eqn.(5)). As mentioned above, in this modification m depends on ω only and is given by [10]

$$m(\omega) = \sum_{j=0}^4 \sum_{k=0}^4 A_{jk} u_o^j \omega^k \quad (9).$$

Here $u_o = 2$ for PR EOS. Coefficients A_{jk} of the above polynomial are reported elsewhere [6].

For correlating the saturated vapor pressures accurately, we express X in term of a simple polynomial given by

$$X = B_0 + B_1 T_r + B_2 T_r^2 + B_3 T_r^3, \text{ with } B_0 = 0.5 \quad (10)$$

In this work, the three parameters B_1 , B_2 and B_3 are determined by regression of saturated vapor pressures of the pure fluids. For $B_1 = B_2 = B_3 = 0$, PR EOS is recovered.

Following the approach of Mathias et al. [25], the volume correction term is given by

$$v^{corr} = v + S_1 + F_c \left(\frac{S_2}{S_2 + \delta} \right) \quad (11).$$

Here δ is a dimensionless quantity related to the inverse isothermal compressibility given by

$$v^{corr} = v + S_1 + F_c \left(\frac{S_2}{S_2 + \delta} \right) \quad (12), \text{ and}$$

$$F_c = v_c^{Exp} - (v_c + S_1) \quad (13)$$

We note that F_c is the additional volume correction term to match the critical volume by equation of state determined using experimental data. In the work of Mathias et al. [25], a universal value of S_2 , $S_2=0.41$, was adopted and S_1 was considered as an independent parameter for each fluid. However, our calculations show that the above set of the S_1 and S_2 parameters is unable to correlate accurately the saturated volumes of all the 44 fluids investigated here. Therefore, we considered both S_1 and S_2 as independent variables. Also, we found that the above temperature independent volume correction was not adequate for some systems and for heavy hydrocarbons at low temperatures. In order to improve the results for volumes at low temperatures, we redefine Eqn.(11) as follows

$$v^{corr} = v + S_1 + F_c \left(\frac{S_2}{S_2 + \delta} \right) + S_3 T_r \quad (14).$$

Here Eqn.(14) is now temperature dependent and contains a third parameter, S_3 .

Based on the combinations of Eqn.(10) and Eqn.(11) and those of Eqn.(10) and Eqn.(14), there are two sets of calculations reported in this work. The results obtained from the first set of calculations (i.e., results are based on Eqn.(10) and Eqn.(11)) are referred to as MPR EOS. In this case, five parameters (B_1 , B_2 , B_3 , S_1 and S_2) were determined simultaneously from the regression of the saturated vapor pressures and liquid volumes of each fluid using the following objective function

$$ADPV\% = \sum_{i=1}^{n_p} ABS(\Delta P\%)_i + \sum_{j=1}^{n_v} ABS(\Delta V^L\%)_j \quad (15), \text{ with}$$

$$b = b_c \quad (16), \text{ and}$$

$$\Delta V^L\% = (V_{exp}^L - V_{cal}^L) / V_{exp}^L \times 100 \quad (17)$$

In the above equations, P_{exp} is the experimental vapor pressure, P_{cal} is the calculated vapor pressure, V_{exp}^L is the experimental liquid volume, V_{cal}^L is the calculated liquid volume, and n_p and n_v are numbers of the vapor pressure and the liquid volume data along the saturation line, respectively. When experimental data for liquid volume were not available, only B_1 , B_2 and B_3 were fitted to the saturated vapor pressures using the first term of Eqn.(15).

The results based on the second set of calculations (i.e., results were obtained using Eqn.(10) and Eqn.(14)), are referred to as MPR EOS (S_3). However, in this set only S_1 , S_2 and S_3 were optimized simultaneously for the determined values of B_1 , B_2 and B_3 of the first set of calculations.

2. Results and Discussion

In this work we have studied 61 systems consisting of non-polar, polar and associated fluids. Their critical temperature, critical pressure, critical volume and acentric factor are given in Table 1 [26, 27]. Table 1 also contains the values of B_1 , B_2 and B_3 , which describe the saturated vapor pressures of the fluids accurately. Table 2 contains results for the saturated vapor pressures. Before presenting the comparison between calculated and experimental results for the saturated vapor pressures and volumes, however, we first show the importance of X and the behavior of α with T_r for a few selected systems.

Since the general behavior of α as a function of ω and T_r has already been presented in [10], those results are not repeated here.

It may be noted that values of the acentric factor for fluids are generally determined at $T_r = 0.7$, and so the values of $m(\omega)$ in PR EOS are obtained for a particular fluid at $T_r = 0.7$, using $X = 0.5$ [14, 15]. The same fixed value of X , $X = 0.5$, is then used at all other temperatures. However, our results show that for the well defined $m(\omega)$ of Eqn.(9), the estimated X varies with the reduced temperature. For example, Fig. 1 shows the variation of X with T_r along the saturation curve for four hydrocarbon fluids, namely, methane, pentane, decane and eicosane, with the acentric factor lying in the range $0.01 \leq \omega \leq 0.91$. The figure shows that X is not fixed at $X=0.5$, rather it varies with T_r . Among the four fluids considered in the figure, $X = 0.5$ holds only for methane at $T_r = 0.7$, while X deviates significantly from $X = 0.5$ for eicosane even at $T_r = 0.7$. These results suggest that the choice of making X to be temperature dependent in MPR EOS is reasonable and important for describing the saturated vapor pressures accurately.

Fig. 2 shows the variation of α with T_r for the fluids of Fig.1. In this figure, α decreases as T_r increases, and α reduces to unity at the critical point temperature, $T_r = 1$. This behavior of α is in agreement with our earlier observation [10], suggesting again that α of MPR EOS gives a correct asymptotic behavior and can be used reliably for extrapolation to even heavier systems with larger values of the acentric factor. Consequently, MPR EOS avoids the introduction of any spurious effect in the temperature dependence of the energy and specific heat.

Table 2 contains the average absolute deviation (AAD%) between calculated and experimental values of the saturated vapor pressure for 61 fluids. In general, MPR EOS describes the vapor pressures accurately for all the systems investigated here. Also included in the table are results based on PR EOS and PRT EOS for some selected fluids only. The PR EOS results reported here are based on $m(\omega)$ of Eqn.(9), while the PRT EOS results were obtained using the α -term of Twu *et al.* [17]. The comparisons of the average absolute deviations of Table 2 show that MPR EOS offers a significant improvement over PR EOS for all the fluids investigated here. The results of MPR EOS and PRT EOS for 20 hydrocarbons, benzene, cyclohexane and argon are almost similar, the former results being slightly more accurate than those of the latter. The comparison of total average absolute deviations for the first 20 hydrocarbons for all the three equations of state shows that the results of MPR EOS (total AAD% = 0.46) and PRT EOS (total AAD% = 0.78) are more accurate than those of PR EOS (total AAD% =

1.79). Since MPR EOS results appear to be similar to or slightly better than PRT EOS results and the latter EOS has been shown to be more accurate than PRSV EOS [17], calculations based on PRSV EOS are not reported here.

In order to illustrate the accuracy of MPR EOS in the whole range of the saturation temperature, Figs. 3-6 present results for the saturated vapor pressures of four selected fluids of Table 1, namely, eicosane, benzene, carbon dioxide, and water, respectively. These fluids differ significantly in their acentric factor and polarity. Comparisons of calculated results with experimental data show that MPR EOS is in excellent agreement with experiment over the entire range of the saturation temperature. Since the superiority of MPR EOS over PR EOS has already been illustrated in Table 2 we do not repeat those comparisons in the figures. These comparisons show that MPR EOS is very successful in representing the vapor pressures of even associated fluids such as Water (Fig. 6) reasonably well. To illustrate the accuracy of MPR EOS in describing the saturated vapor pressures of heavy hydrocarbons, Fig. 7 shows comparisons between MPR EOS and experiment for four heavy hydrocarbon systems, C_{22} , C_{32} , C_{40} and C_{60} , exhibiting the large values of acentric factor ($0.95 < \omega < 2.6$). Even in these cases, the agreement between calculated and experimental results is excellent.

Now, we turn to the comparison of calculated results with experimental data of the saturated liquid and vapor volumes. Again we present results based on MPR EOS only, for the comparisons with PR EOS and PRT EOS have already been presented in our previous work [10], although a different approach for the volume translation was adopted before. Table 3 contains the volume translation parameters and AAD% between experiment and MPR EOS for 44 fluids of Table 2 for which reliable saturated liquid volumes are available. Results show that the liquid volumes estimated from MPR EOS are in very good agreement with experimental data. The saturated vapor volumes are also predicted well, but they are not as accurate as the liquid volumes because of the inherent problem in the volume translation approach.

In order to check the accuracy of MPR EOS in predicting the saturated volumes over the entire range of saturation temperatures, Figs.8-11 show the comparisons for densities obtained from MPR EOS and experiment for the same fluids as of Figs. 3-6. MPR EOS results (shown by solid line) are obtained using the temperature independent volume translation term containing two parameters only (Eqn.(11)). As can be seen from the figures, the agreement between calculated and experimental results for the densities is very good. However, a slight discrepancy between calculated and experimental liquid

density is seen at low temperatures indicating a temperature dependency of the density. In order to improve the accuracy of the densities at low temperatures, we used instead Eq.(14) (MPR EOS (S_3)) for estimating both the liquid and vapor densities. Now MPR EOS (S_3) results for the liquid density are in excellent agreement with experimental data for all the systems of Figs.8-11. The densities of the associated systems like water are also explained very well. The values of S_1 , S_2 and S_3 parameters and AAD% between experimental and calculated results for 44 systems are given in Table 4. It may be noted that the temperature dependence of the volume translation presented in this work is rather small and limited to the low temperatures only. Therefore the use of Eqn.(11) is sufficient for many practical applications unless a very high accuracy is desired in liquid densities. In the latter situations, one can use Eqn.(14) with confidence.

3. Conclusions

We have presented a modified form of the Peng-Robinson equation of state (MPR EOS) by introducing a temperature dependent parameter in the exponent of α -term and by properly defining $m(\omega)$ so that m is a function of ω only. This modification leads to a significant improvement in PR EOS, and MPR EOS can be used to predict accurately the saturation properties of even heavy hydrocarbons exhibiting sufficiently large values of the acentric factor. The temperature independent volume translation term is sufficient enough to estimate the densities, in particular the liquid densities, reliably. The incorporation of a temperature dependent volume translation term offers an improvement in liquid densities at low temperatures, thereby minimizing the slight discrepancy between MPR EOS and experimental results for the liquid density of some fluids at low temperatures. In general, comparisons of calculated results with experimental data for the vapor pressures of 61 systems and for the densities of 44 systems show a very good performance of MPR EOS over the entire range of the saturation temperature. Also, MPR EOS offers a significant improvement over PR EOS and is slightly more accurate than PRT EOS.

In our future studies we will extend MPR EOS to mixtures using theoretically consistent mixing rules and examine its accuracy in describing phase equilibrium diagrams and volumetric properties of multi-component mixtures of industrial interest.

OIL CHARACTERIZATION

The oil composition is determined experimentally by distillation (TBP Tests) and gas chromatography. The thermodynamic properties are calculated from the experimental information provided by the tests. A description is provided below.

True Boiling Point Tests (TBP Tests). They are used to characterize the oil with respect to the boiling points of its components. In these tests, the oil is distilled and the temperature of the condensing vapor and the volume of liquid formed are recorded. This information is then used to construct a distillation curve of liquid volume percent distilled versus condensing temperature. The condensing temperature of the vapor at any point in the test will be close to the boiling of the material condensing at that point. For a pure substance, the boiling and condensing temperature are exactly the same. For a crude oil the distilled cut will be a mixture of components and average properties for the cut will be determined. Table 5 shows typical results of a TBP test.

In the distillation process, the hydrocarbon plus fraction is subjected to a standardized analytical distillation, first at atmospheric pressure, and then in a vacuum at a pressure of 40 mm Hg using a fifteen theoretical plates column and a reflux ratio of five. The equipment and procedure is described in the ASTM 2892-84 book [28]. It is also common to use distillation equipment with up to ninety theoretical plates. Usually the temperature is taken when the first droplet distills over. The different fractions are generally grouped between the boiling points of two consecutive n-hydrocarbons, for example: C_{n-1} and C_n . The fraction receives the name of the n-hydrocarbon. The fractions are called hence, single carbon number (SCN). Every fraction is a combination of hydrocarbons with similar boiling points. . For each distillation cut, the volume, specific gravity, and molecular weight, among other measurements, are determined. Other physical properties such as molecular weight and specific gravity may also be measured for the entire fraction or various cuts of it. The density is measured by picnometry or by an oscillating tube densitometer. The average molecular weight of every fraction is determined by measuring the freezing point depression of a solution of the fractions and a suitable solvent, e.g., benzene.

If the distillate is accumulated in the receiver, instead of collected as isolated fractions, the properties of each SCN group cannot be determined directly. In such cases, material balance methods, using the density and molecular weight of the whole distillate and the TBP distillation curve, may be used to estimate the concentration and properties of the SCN groups [29]. A typical true boiling point curve is depicted in Figure 12. The

boiling point is plotted versus the collected volume. There are several ways of calculating each fraction boiling point

Gas Chromatography (GC). The composition of oil samples can be determined by gas chromatography. Whilst an extended oil analysis by distillation takes many days and requires a relative large volume of sample, GC analysis can identify components as heavy as C_{80} in a matter of hours using only a small fluid sample [30]. Individual peaks in the chromatogram are identified by comparing their retention times inside the column with those on known compounds previously analyzed at the same GC conditions. The intermediate and heavy compounds are eluted as a continuous stream of overlapping compounds. This is very similar to the fractionation behavior and treated similarly. All the components detected by the GC between two normal neighboring n-paraffins are commonly grouped together, measured and reported as a SCN equal to that of the higher normal paraffin. A major drawback of GC analysis is the lack of information, such as the molecular weight and density of the different identified SCN groups. The very high boiling point constituents of an oil sample cannot be eluted, hence, they can not be analyzed by GC methods.

Thermodynamic Properties Prediction. To use any of the thermodynamic property-prediction models, e.g., equation of state, to predict the phase and volumetric behavior of complex hydrocarbon mixtures, one must be able to provide: the critical properties, temperature (T_c), pressure (P_c), acentric (ω) and molecular weight (M_w).

Petroleum engineers are usually interested in the behavior of hydrocarbon mixtures rather than pure components. However, the above characteristic constants of the pure and of the hypothetical components are used to define and predict the physical properties and the phase behavior of mixtures at any reservoir state. The properties more easily measured are normal boiling points, specific gravities, and/or molecular weights. Therefore existing correlations target these as the variables used to back up the parameters needed for EOS simulations. (T_c , P_c , ω , MW).

Many correlations of the critical properties of each pseudo-component as a function of experimentally determined variables such as; boiling point, specific gravity, average molecular weight, have been published in literature. Whitson [31] provides an excellent review. For the sake of brevity only a brief list is include here.

Riazi and Daubert [32] developed a simple two-parameter equation for predicting the physical properties of pure compounds and undefined hydrocarbon mixtures. The

proposed generalized empirical equation is based on the use of the normal boiling point and the specific gravity (γ) as correlating parameters. The basic equation is:

$$\psi = aT_b^b \gamma^c \quad (18),$$

where T_b is the normal boiling point temperature expressed in R and the constants a , b , c , depend upon the physical property indicated by ψ . The values to calculate the pseudo-components critical properties are shown in Table 6.

Riazi and Daubert [33] modified their equation while maintaining its simplicity while significantly improving its accuracy:

$$\psi = aT_b^b \gamma^c \exp[dT_b + e\gamma + fT_b\gamma] \quad (19)$$

$$\psi = aM_w^b \gamma^c \exp[dM_w + e\gamma + fM_w\gamma] \quad (20).$$

The constants a to f for the two different functional forms of the correlation are presented in Table 7, and depend upon the correlated property.

Cavett [34] proposed correlations for estimating the critical pressure and temperature of hydrocarbon fractions. The correlations have received a wide acceptance in the petroleum industry due to their reliability in extrapolating at conditions beyond those of the data used in developing the correlations. The proposed correlations were expressed analytically as functions of the normal boiling point (T_b) and API gravity (γ).

Lee and Kesler [35] proposed a set of equations to estimate the critical temperature, critical pressure, acentric factor, and molecular weight of petroleum fractions. The equations use specific gravity and boiling point in °R as input parameters. They also proposed an equation to calculate molecular weight (M_w),

$$M_w = -12,272.6 + 9,486.4\gamma + (4.6523 - 3.3287\gamma)T_b + (1 - 0.77084\gamma - 0.02058\gamma^2) \times \left(1.3437 - \frac{720.79}{T_b}\right) \times \frac{10^{-7}}{T_b} + (1 - 0.80882\gamma + 0.02226\gamma^2) \left(1.8828 - \frac{181.98}{T_b}\right) \times \frac{10^{12}}{T_b^3} \quad (21)$$

Lee and Kesler [35] stated that their equations for P_c and T_c provide values are nearly identical with those from the API Data Book up to a boiling point of 1,200°F.

Katz and Firoozabadi [36] presented a generalized set of physical properties for the petroleum fractions C_6 through C_{45} . The tabulated properties include the average boiling point, specific gravity; and molecular weight. The authors proposed tabulated properties

are based on the analysis of the physical properties of 26 condensates and naturally occurring liquid hydrocarbons. Figure 13 shows the relationship between molecular weight and either on the normal boiling point (T_b) and API gravity (γ) according to Katz and Firoozabadi [36].

Schou Pedersen et al. [37] used extensive experimental data for seventeen North Sea oil samples obtained using high temperature chromatography. They used experimental data up to the C_{80+} fraction. They checked the validity of the equation,

$$z_n = \exp[A + B C_n] \quad (22),$$

proposed by Pedersen et al. [38]. A and B are empirical constants determined by fitting the experimental data, z_n is the total molar fraction of components belonging to the fraction with n carbon number. The study found that the experimental data are well represented by Eqn. (22). Schou Pedersen et al. [37] also reported that a good representation of the heavy fraction is given by using compositional analysis up to C_{20+} . There is no advantage increasing the accuracy of the analysis from C_{20+} to C_{80+} .

EXPERIMENTAL PART

INTRODUCTION.

Good understanding of volumetric and phase behavior of petroleum reservoir fluids is required for accurate prediction of reservoir performance and production forecasting. Phase behavior data have been obtained traditionally by experimental testing or by use of generalized correlations. It is very important to obtain truly representative reservoir fluids samples using experimental analysis. These data are used to validate theoretical models. Similar efforts have been done for accurate prediction of phase compositions especially for mixtures of hydrocarbons and water and/or CO₂ (McKetta and Katz, [39]; Mehra et al., [40]; Shibata et al., [41]; Langasan and Smith, [42]). In more recent times (Weng and Lee, [43]; Barrufet and Rahman, [44]) used very accurate gas chromatographs along with PVT apparatus for determination of phase compositions.

The objective of this part of the project is to determine bubble point and pressure-volume relationships for several heavy oil samples.

APPARATUS AND EXPERIMENTAL SET-UP

The experimental apparatus and operating procedures have been presented in the first Annual Report. A brief summary is included here for the sake of completion. The laboratory set-up consists of three main parts:

I - VACUUM SYSTEM

II- HYDRAULIC SYSTEM

III. RECOMBINATION APPARATUS

I –Vacuum System. The vacuum system consists of a vacuum pump, two traps to protect the vacuum pump from liquid, and tubing.

II- Hydraulic System Hydraulic System consists of a Ruska positive displacement pump, a pressure gauge, high-pressure valves and tubing. The purpose of this system is to charge the volume in the upper portion of the recombination cell.

The capacity of the pump is 500 cc (0.01765 cu. ft.).

The maximum working pressure is 340.25 ATM (5000 psia).

The displacement pump is equipped with a discharge volume scale. This is used to monitor the volume of the discharge and, indirectly, the volume of the recombination cell. This scale can be read within 0.02 cc (7.062 e -7 cu. ft.).

III- Recombination Apparatus.

a). The Temperature Controlled Air-Bath Oven with maximum operating temperature 200 C (392 F). The temperature can be set with an accuracy of 0.2 C. Uniform air bath temperature distribution +- 1 C.

b). The Recombination Cell

JEFFREY Recombination cell model No 1000-10-P-REC

Floating piston.

Capacity of the Cell 1,000 cc (0.0353 Cu. ft.).

Maximum working pressure 689.48 bar (10,000 psia).

Maximum working temperature 200 C (392 F).

c). The Rocking Mechanism

Laboratory set-up. This rocking mechanism is provided to mix efficiently a multi component fluid such the desired equilibrium condition can rapidly be obtained.

The laboratory set-up was constructed according the standard set-up suggested in manual hook of the recombination apparatus. The recombination Cell is connected from the bottom with hydraulic system and with the Sample Cylinder from the top. The hydraulic system is connected with the bottom of both recombination cell and simple cylinder. The sample cylinder is connected with hydraulic system from the bottom and with the recombination cell from the top. The vacuum system is used with all the system depending of step of experiment.

Determination of Isothermal Compressibility from Pressure Volume Behavior. Pressure volume pairs were recorded for selected isotherms in the single and in the two-phase regions. The bubble-point pressure was determined from intersecting these two curves. The isothermal compressibility can be determined from the fitted equation.

$$P = a - bV \quad (23)$$

$$C_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{bV} \quad (24).$$

A representative plot of pressure versus volume is shown in Fig. 14. The work is currently underway and we expect to finish within the next four months. The experimental pressure-volume curves will be theoretically model using the Peng-Robinson algorithm described in the theoretical part. The heavy oil characterization algorithm will be used to represent the actual oil sample. The sample thermodynamic properties will be evaluated using the procedure described in the oil characterization section.

NOMENCLATURE

NOTATIONS

A	Energy parameter
b	Excluded-volume parameters
P	Pressure
R	Gas constant
v	Molar volume
Z	Compressibility factor

Greek Symbols

α	Constant in the equation of state, α -term
ω	Acentric factor

Abbreviations

EOS	Equation of state
MSRK EOS	Modified Soave-Redlich-Kwong EOS
SRK EOS	Soave-Redlich-Kwong EOS

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TABLES

Table 1. Critical parameters of fluids and coefficients of the polynomial⁺ of Eqn.(10).

Fluid	T _c , K	P _c , bar	ω	V _c ,cc/m	B ₁	B ₂	B ₃
Methane	190.58	46.04	0.0108	98.60	0.1270	-0.4346	0.3637
Ethane	305.42	48.80	0.0990	145.50	0.1569	-0.4387	0.3067
Propane	369.82	42.49	0.1517	200.00	0.1704	-0.4511	0.3001
Butane	425.17	37.97	0.1931	255.00	0.1974	-0.4657	0.2875
Pentane	469.65	33.69	0.2486	313.00	0.1816	-0.4634	0.3020
Hexane	507.85	30.31	0.3047	371.00	0.1596	-0.4576	0.3115
Heptane	540.26	27.36	0.3494	428.00	0.1709	-0.4558	0.3009
Octane	568.83	24.86	0.3962	486.00	0.1739	-0.4622	0.3085
Nonane	595.65	23.06	0.4368	544.00	0.1807	-0.4707	0.3096
Decane	618.45	21.23	0.4842	600.0	0.1732	-0.4615	0.3108
Undecane	638.76	19.66	0.5362	660.0	0.1533	-0.4445	0.3222
Dodecane	658.20	18.24	0.5752	717.0	0.1591	-0.4507	0.3198
Tridecane	675.80	17.23	0.6186	767.0	0.1539	-0.4496	0.3353
Tetradecane	692.40	16.21	0.6413	825.0	0.1777	-0.4623	0.3342
Pentadecane	706.80	15.20	0.7083	883.0	0.1352	-0.4367	0.3467
Hexadecane	720.60	14.19	0.7471	942.0	0.1351	-0.4324	0.3383
Heptadecane	733.37	13.17	0.7700	1000.0	0.1645	-0.4468	0.3011
Octadecane	745.26	12.14	0.7900	1058.0	0.1854	-0.4718	0.2896
Nonadecane	755.93	11.17	0.8270	1117.0	0.1814	-0.4611	0.2798
Eicosane	767.04	10.40	0.9070	1175.0	0.1440	-0.4433	0.2789
Propene	365.57	46.65	0.1408	190.0	0.1814	-0.4660	0.2966
Benzene	562.16	48.98	0.2120	259.0	0.2007	-0.4844	0.2741
Ethylbenzene	617.2	36.06	0.303	374.0	0.2004	-0.4971	0.2964
Cyclopentane	511.8	45.02	0.196	258.0	0.2132	-0.5107	0.2823
Cyclohexane	553.58	40.73	0.2130	308.0	0.2083	-0.5311	0.3220
Toluene	591.80	41.06	0.2632	316.0	0.2189	-0.5765	0.3663
Propylene	365.60	46.65	0.1400	188.4	0.2036	-0.5016	0.3021
O-xylene	630.30	37.34	0.31	369.0	0.1683	-0.4546	0.3042
M-xylene	617.10	35.36	0.326	376.0	0.1543	-0.4482	0.3178
P-xylene	616.2	35.1	0.320	379.0	0.1533	-0.4432	0.3150

Table 2. Deviations between experimental and calculated results for saturated vapor pressures

Fluid	T _r -range	n	AAD%	AAD%	AAD%
			PR	MPR	PRT
Methane ³⁰	0.51-0.99	23	0.71	0.09	0.17
Ethane ²⁹	0.36-0.99	19	0.49	0.20	0.24
Propane ²⁹	0.40-0.99	23	0.70	0.19	0.73
Butane ²⁹	0.37-0.99	27	1.47	0.57	0.41
Pentane ^{21,27}	0.40-0.99	29	0.75	0.52	0.75
Hexane ^{21,27}	0.40-0.99	29	0.74	0.38	0.78
Heptane ^{21,27}	0.42-0.99	31	0.45	0.31	0.32
Octane ^{21,27}	0.42-0.99	31	0.78	0.28	0.54
Nonane ^{21,27}	0.42-0.99	31	0.89	0.32	0.52
Decane ^{21,27}	0.42-0.99	20	0.99	0.28	0.27
Undecane ^{21,27}	0.45-0.99	20	1.19	0.37	0.44
Dodecane ^{21,27}	0.46-0.99	20	1.40	0.58	0.68
Tridecane ^{21,27}	0.50-0.99	20	2.39	0.41	1.18
Tetradecane ^{21,27}	0.49-0.99	20	4.41	0.70	0.72
Pentadecane ^{21,23}	0.50-0.99	19	3.59	0.57	0.92
Hexadecane ^{17,27}	0.49-0.99	21	3.09	0.35	0.60
Heptadecane ^{21,27}	0.50-0.99	19	2.32	0.39	1.30
Octadecane ^{21,27}	0.50-0.99	19	2.81	1.00	2.18
Nonadecane ^{21,27}	0.50-0.99	20	4.70	1.00	0.88
Eicosane ^{21,27}	0.50-0.99	19	1.87	1.4	1.89
i-Butane ³¹	0.1-36	22	-	0.3	-
i-Pentane ³¹	0.1-33	22	-	0.1	-
i-Octane ³¹	0.1-33	22	-	0.6	-
Propene ³⁰	0.54-0.99	23	0.50	0.13	-
Benzene ³¹	0.49-0.99	30	1.24	0.30	0.33
Ethylbenzene ³¹	0.41-0.80	17	-	1.50	-
Cyclopentane ³¹	0.38-0.96	33	-	1.10	-
Cyclohexane ³¹	0.51-0.99	27	1.43	0.60	0.44
Toluene ^{31,32}	0.40-0.99	28	4.30	1.50	-
Propylene ³¹	0.36-0.99	24	-	1.20	-

O-xylene ³¹	0.40-0.99	29	-	1.20	-
M-xylene ³¹	0.41-0.99	25	-	0.80	-
P-xylene ³¹	0.41-0.99	25	-	0.90	-
Naphthalene ³¹	0.47-0.86	16	-	1.40	-
H ₂ ³¹	0.42-0.99	19	4.45	1.20	-
Ar ³⁴	0.55-0.99	32	1.05	0.15	0.24
Kr ³¹	0.55-0.99	22	-	0.11	-
Xe ³¹	0.55-0.99	20	-	0.13	-
O ₂ ³⁵	0.36-0.99	31	1.30	0.28	-
N ₂ ³⁶	0.53-0.99	18	0.41	0.15	-
Cl ₂ ³¹	0.44-0.99	16	-	0.90	-
F ₂ ³¹	0.66-0.99	11	-	0.35	-
CF ₄ ³⁷	0.39-0.98	16	-	0.48	-
CCl ₄ ³¹	0.45-0.90	15	-	1.13	-
C ₂ H ₄ ^{38,39}	0.38-0.99	19	0.96	0.69	-
CH ₃ Cl ³¹	0.5-0.90	14	-	0.43	-
HCl ⁴⁰	0.48-0.74	11	0.84	0.19	-
CO ³¹	0.5-0.99	24	-	0.39	-
CO ₂ ⁴¹	0.71-0.99	45	0.84	0.12	-
H ₂ S	2-18	4	-	0.5	-
COS	1-11	4	-	0.6	-
SO ₂ ³¹	0.75-0.99	12	-	0.27	-
NH ₃ ⁴²	0.48-0.99	44	0.40	0.50	-
H ₂ O ³¹	0.42-0.99	24	1.59	0.22	-
Acetone ³¹	0.42-0.99	16	1.45	0.65	-
1-Octanol ^{32,33}	0.47-0.56	15	1.40	0.99	-
1-Decanol ^{32,33}	0.48-0.56	14	0.88	1.01	-
Methanol ^{32,43}	0.52-0.97	27	1.90	1.80	-
1-Pentanol ³¹	0.74-0.87	16	3.69	0.24	-
1-Butanol ³¹	0.63-0.99	22	7.26	0.80	-
1-Propanol ³¹	0.62-0.95	19	6.49	2.00	-
Ethanol ³¹	0.47-0.99	36	1.90	0.70	-
C ₂₂ ²¹	0.51-0.82	32	-	0.3	-
C ₃₂ ²¹	0.56-0.87	32	-	0.5	-

C_{40}^{21}	0.60-0.90	32	-	0.7	-
C_{60}^{21}	0.67-0.96	32	-	1.0	-

Table 3. Volume translation parameters and deviations between experimental and calculated (MPR EOS) results for saturated liquid (L) and vapor (V) densities.

Fluid	N_p	S_1	S_2	AAD% (L)	AAD% (V)
Methane	22	4.7664	0.3894	0.5	1.2
Ethane	19	4.7422	0.2939	0.5	1.0
Propane	23	5.1108	0.3166	1.0	1.3
Butane	25	5.1759	0.3187	1.3	1.8
Pentane	29	4.0299	0.3363	1.2	-
Hexane	29	2.4402	0.3527	1.0	-
Heptane	31	0.0547	0.3304	1.0	-
Octane	31	-2.3803	0.3479	1.0	-
Nonane	31	-4.2874	0.3003	1.0	-
Decane	20	-3.2076	0.2382	1.0	-
Undecane	20	-13.2168	0.1461	1.2	-
Dodecane	20	-19.0051	0.2455	1.0	-
Tridecane	20	-18.3242	0.1679	1.0	-
Tetradecane	20	-25.7874	0.2763	0.9	-
Pentadecane	19	-21.3261	0.1693	1.3	-
Hexadecane	21	-38.7336	0.1728	1.3	-
Heptadecane	19	-53.9240	0.2158	0.9	-
Octadecane	19	-80.7186	0.3158	0.8	-
Nonadecane	20	-99.3482	0.2381	0.9	-
Eicosane	19	-120.982	0.2504	1.0	-
Propene	23	6.6629	0.5715	0.9	0.9
Benzene	30	3.1922	0.4202	1.2	5.0
Toluene	28	-14.0125	-0.6703	0.5	-
H ₂	19	6.2555	0.6193	0.5	1.5
Ar	31	4.0712	0.3659	0.7	1.9
Kr	22	4.2832	0.4252	0.9	2.3
Xe	21	5.2633	0.4647	0.8	1.9
O ₂	31	3.5569	0.3209	0.9	1.2

N ₂	18	4.4466	0.3229	0.7	1.4
Cl ₂	16	3.0134	0.3992	1.3	3.5
F ₂	11	3.2399	0.3526	0.3	1.1
CF ₄	16	4.8159	0.2896	1.5	1.7
CCl ₄	15	4.4920	0.3069	0.8	-
C ₂ H ₄	19	4.3383	0.4093	1.6	2.0
CH ₃ Cl	14	0.7428	0.1289	0.4	1.9
HCl	11	-0.3791	-0.1568	0.8	1.5
CO	24	4.3709	0.4115	0.6	2.8
CO ₂	45	2.3946	0.4085	0.5	2.1
SO ₂	12	1.1311	0.3118	0.3	1.4
NH ₃	44	-2.8944	0.3321	0.3	2.5
H ₂ O	24	-3.3399	0.5659	1.0	1.2
Acetone	2	-9.3174	0.1472	0.0	-
Methanol	27	-6.5457	0.4306	0.6	-
Ethanol	17	-4.5176	0.5553	1.0	-

Table 4. Volume translation parameters and deviations between experimental and calculated (MPR EOS (S_3)) results for saturated liquid (L) and vapor (V) densities

Fluid	N_p	S_1	S_2	S_3	AAD%(L)	AAD%(V)
Methane	22	2.5973	0.5269	3.5327	0.2	1.2
Ethane	19	4.7422	0.2939	0.0	0.5	1.0
Propane	23	-0.8911	0.5262	10.5908	0.2	1.2
Butane	25	-2.5769	0.5339	13.7642	0.4	1.8
Pentane	29	-5.5924	0.5539	16.8898	0.3	-
Hexane	29	-8.9474	0.8117	19.4805	0.3	-
Heptane	31	-13.3855	0.4735	22.0711	0.2	-
Octane	31	-17.5655	0.4596	23.8092	0.2	-
Nonane	31	-23.2837	0.4224	30.2371	0.2	-
Decane	20	-26.4884	0.3085	36.2402	0.25	-
Undecane	20	-30.7422	0.1927	27.7639	1.0	-
Dodecane	20	-44.1526	0.3089	40.6326	0.3	-
Tridecane	20	-53.4431	0.2443	54.7098	0.6	-
Tetradecane	20	-48.1152	0.3275	33.4603	0.6	-
Pentadecane	19	-67.9893	0.2286	68.9859	0.4	-
Hexadecane	21	-81.5002	0.2236	65.6339	0.5	-
Heptadecane	19	-84.3385	0.2426	44.9089	0.5	-
Octadecane	19	-105.295	0.3726	38.2230	0.7	-
Nonadecane	20	-126.515	0.2659	39.3219	0.8	-
Eicosane	19	-147.024	0.2717	37.4636	0.9	-
Propene	23	6.6781	0.5318	0.0190	0.9	0.9
Benzene	30	-5.8136	0.6072	14.7355	0.6	5.0
Toluene	28	-15.9152	-0.6251	3.3318	0.3	-
H ₂	19	6.2004	0.5663	-0.0306	0.4	1.5
Ar	31	1.8636	0.5367	3.5699	0.3	1.9
Kr	22	1.5687	0.6542	4.5592	0.6	2.3
Xe	21	1.0816	0.7107	6.9621	0.5	1.9
O ₂	31	1.5744	0.5693	3.5923	0.2	1.2
N ₂	18	4.3911	0.3285	0.1022	0.7	1.4
Cl ₂	16	-1.1968	0.5485	7.0417	0.6	3.3

F ₂	11	1.6009	0.5067	2.6158	0.2	1.1
CF ₄	16	-0.1248	0.5556	9.0107	0.2	1.8
CCl ₄	15	-5.7359	0.7067	19.6986	0.0	-
C ₂ H ₄	19	0.0692	0.7089	7.8008	0.8	2.0
CH ₃ Cl	14	-4.2692	0.7333	9.5229	0.1	1.9
HCl	11	-0.4262	-0.1468	0.0999	0.8	1.5
CO	24	1.2764	0.7866	5.4475	0.3	2.6
CO ₂	45	-0.3486	0.4776	3.7309	0.3	2.0
SO ₂	12	1.0540	0.3123	0.1010	0.3	1.4
NH ₃	44	-2.9632	0.3333	0.1133	0.3	2.5
H ₂ O	24	-1.7528	0.3806	-3.0045	0.2	1.2
Acetone	2	-9.3690	0.1506	0.0992	0.0	-
Methanol	27	-5.0163	0.3819	-2.5138	0.5	-
Ethanol	17	-4.5594	0.5553	0.0421	1.0	-

Note: For the given values of B₁, B₂ and B₃ of Table 2, S₁, S₂, and S₃ were fitted simultaneously to the saturated liquid volumes.

Table 5. Typical TBP Analysis Results.

Component	Ti	Tf	T mean	ΔV (cm3)	$\Sigma(\Delta V)$	V % Off
Hypo1	99	220	159.5	5.1	5.1	5.3
Hypo2	214	323	268.5	8.0	13.1	13.5
Hypo3	323	432	377.5	7.9	21.0	21.7
Hypo4	432	526	479	8.1	29.1	30.1
Hypo5	526	612	569	7.9	37.0	38.2
Hypo6	612	693	652.5	7.9	44.9	46.4
Hypo7	693	765	729	7.9	52.8	54.5
Hypo8	765	821	793	7.8	60.6	62.6
Hypo9	821	908	864.5	8.1	68.7	71.0
Hypo10	908	1010	959	5.2	73.9	76.3
Residual			1261.1692	22.9	96.8	100.0
Whole Oil			729			
Residual Volume Left				22.9		

Table 6. Riazi and Daubert [32] Constants for Property Estimation.

				<i>Percent Deviation</i>	
ψ	a	b	c	<i>Average</i>	<i>Maximum</i>
M_w	4.5673×10^{-5}	2.1962	- 1.0164	2.6	11.8
$T_c, ^\circ R$	2.42787	0.58848	0.3596	1.3	10.6
P_c, psia	3.12281	- 2.3125	2.3201	3.1	9.3
$V_c \text{ ft}^3/\text{lbm}$	7.5214×10^{-3}	0.2896	- 0.7666	2.3	9.1

Table 7. Riazi and Dauberts [33] Constants for Property Estimation.

Form (1)				
Constant	M_w	$T_c (^{\circ}R)$	$P_c (psia)$	$V_c (ft^3 / lbm)$
a	581.96	10.6443	6.162×10^6	6.233×10^{-4}
b	0.97476	0.81067	-0.4844	0.7506
c	6.51274	0.53691	4.0846	-1.2028
d	5.43076×10^{-4}	-5.1747×10^{-4}	-4.725×10^{-3}	-1.4679×10^{-3}
e	9.53384	-0.54444	-4.8014	-0.26404
f	1.11056×10^{-3}	3.5995×10^{-4}	3.1939×10^{-3}	1.095×10^{-3}
Form (2)				
Constant	$T_c (^{\circ}R)$	$P_c (psia)$	$V_c (ft^3 / lbm)$	$T_b (^{\circ}R)$
a	544.4	4.5203×10^{-4}	1.206×10^{-2}	6.77857
b	0.2998	-0.8063	0.20378	0.401673
c	1.0555	1.6015	-1.3036	-1.58262
d	-1.3478×10^{-4}	-1.8078×10^{-4}	-2.657×10^{-3}	3.77409×10^{-3}
e	-0.61641	-0.3084	0.5287	2.984036
f	0.0	0.0	2.6012×10^{-3}	-4.25288×10^{-3}

FIGURES

Fig. 1. Variation of X with reduced temperature along the saturation curve.

Fig. 2. Variation of α with reduced temperature for systems of Fig.1.

Fig. 3. Comparison of calculated results with experimental data of saturated vapor pressure of eicosane .

Fig. 4. Comparison of calculated results with experimental data of saturated vapor pressure of benzene

Fig. 5. Comparison of calculated results with experimental data of saturated vapor pressure of carbon dioxide.

Fig. 6. Comparison of calculated results with experimental data of saturated vapor pressure of water.

Fig. 7. Comparison of calculated results with experimental data of saturated vapor pressure of long chain hydrocarbons.

Fig. 8. Comparison of calculated results with experimental data of saturated densities of eicosane.

Fig. 9. Comparison of calculated results with experimental data of saturated densities of benzene.

Fig. 10. Comparison of calculated results with experimental data of saturated densities of carbon dioxide.

Fig. 11. Comparison of calculated results with experimental data of saturated densities of water.

Fig. 12. True boiling point distillation curve for a standard oil.

Fig. 13. Molecular weight calculation from T_b or specific gravity (SG).

Fig 14. Pressure-Volume variation for Oil B at various temperatures.