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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

By
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November 2002

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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.

Highlighting the importance of phase behavior, researchers ([1], and [2]) insist on obtaining truly representative reservoir fluids samples for experimental analysis. The prevailing sampling technique used for compositional analysis of the fluids is potentially a large source of error. These techniques bring the sample to atmospheric conditions and collect the liquid and vapor portion of the samples for further analysis. We developed a new experimental technique to determine phase volumes, compositions and equilibrium K-values at reservoir conditions. The new methodology would be able to measure phase volume and composition at reservoir like temperatures and pressures. We use a mercury free PVT system in conjunction with a Hewlett Packard gas chromatograph capable of measuring compositions on line at high pressures and temperatures. This is made possible by an essentially negligible disturbance of the temperature and pressure equilibrium during phase volume and composition measurements. In addition, not many samples are withdrawn for compositional analysis because a negligible volume (0.1 µl to 0.5 µl) is sent directly to the gas chromatograph through sampling valves. These amounts are less than 1×10^{-5} % of total volume and do not affect the overall composition or equilibrium of the system.

A new method to compute multi-component phase equilibrium diagrams based on an improved version of the Peng-Robinson equation has been developed [3]. 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 multi-component mixtures of CO₂/water and hydrocarbons are currently underway. A scheme to lump multi-component materials such as, oils into a small set of "pseudo-components" according to the technique outlined by Whitson [4] has been implemented. In order to successfully complete the project an extension of one year has been awarded. The final report will present the results of our experimental and 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 B-E 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 two parts, experimental work and theoretical part. 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.

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, [5]; Mehra et al., [6]; Shibata et al., [7]; Langasan and Smith, [8]). In more recent times (Weng and Lee, [9]; Barrufet and Rahman, [10]) 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 previous Annual Reports. 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 (7.062×10^{-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 book 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 sample 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.

$$P = a - bV \quad (1)$$

$$C_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{bV} \quad (2).$$

EXPERIMENTAL RESULTS

Aromatic/Water Quaternary System

We have tested a quaternary system of propane, pentane, benzene and water. The experimental setup was tested by charging a quaternary system of pre-determined composition. A previously tested quaternary system of propane, pentane, octane, and water was selected for compositional match. One component was changed from this quaternary system, benzene was selected instead of octane to introduce an aromatic component in the hydrocarbon/water systems.

First the hydrocarbon mixture was prepared using the normalized compositions and ascending volatility order. Both cell of the PVT systems were used for this preparation. The composition and density of the system was checked using gas chromatograph sampling. A measured amount of this hydrocarbon mixture was entrapped in the piston cell. Appropriate amount of water was put in the float piston cell to prepare the hydrocarbon/water quaternary system. Table I shows the amounts and mole % of the old and new quaternary systems.

The new quaternary system was tested at five temperatures ranging from 104° F to 300° F. The total volume for the system was fixed at 386.84 and the pressure range obtained for the tested temperature range was 130 psia to 608 psia. Vapor and oleic phases for all the temperatures were sampled for compositional analysis and volumes of all three phases were measured. Table II shows weight in centigram/cc for all the components. The total weights of all the components in vapor and oleic phase were

calculated by multiplying the Table II weights with the phase volumes. The aqueous phase weights for all the components were calculated from material balance.

$$W_a = W_t - W_v - W_o \quad (3).$$

Where, W_a = weight of a component in aqueous phase (gm)

W_t = total weight of a component initially charged (gm)

W_v = weight of a component in vapor phase (gm)

W_o = weight of a component in oleic phase (gm)

These weights are tabulated in Table III. The mole fraction for all three phases was calculated based on the information available in Table III. The moles % are tabulated in Table IV. Table III data along with the phase molecular weight and total moles charged was used to calculate the phase fractions. These phase fractions are tabulated in Table V. The data in Table II. can be converted to g. mole/cc, and molar volumes can also be calculated. These molar volumes are tabulated in Table VI.

THEORETICAL WORK

We present here some results corresponding to vapor-liquid equilibrium calculations for multi-component systems and results from our calculations for heavy oil fraction characterization based on the method proposed by Whitson [4]. For the sake of explanation a description of the main concepts behind the methods used is included.

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 [11]; Harding et al., 1983 [1]; Turek et al., 1984 [2], Boberg, 1988 [12]). 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 CO_2 .

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. In miscible enhanced oil recovery processes using CO_2 as a displacing medium, the aqueous effects on the hydrocarbon/ CO_2 phase behavior have not been fully investigated. Because of the aqueous phase vapor pressure and the mutual solubility of water and hydrocarbon/ CO_2 in the liquid phases, neglecting the aqueous effects can induce serious error in the representation of hydrocarbon/ CO_2 phase behavior. Hornbrook et al., 1991 [13], reported the use of CO_2 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 [14], 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) [15] 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

$$P = RT / (v - b) - a / (v^2 + ubv + wb^2) \quad (4).$$

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,

$$b = b_c \text{ and } a = a_c \alpha(\omega, T_r) \quad (5).$$

Where, critical parameters b_c and a_c are given by

$$b_c = 0.07779607 (RT_c)/P_c \quad (6)$$

$$a_c = 0.45723553 (RT_c)^2 / P_c \quad (7)$$

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

$$\alpha(\omega, T_r) = \left[1 + m(\omega) (1 - T_r^X) \right]^2 \quad (8).$$

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, Eqn.(1) can be expressed in terms of the compressibility factor Z as

$$Z^3 + (B - 1)Z^2 + (A - 3B^2 - 2B)Z + (B^3 + B^2 - AB) = 0 \quad (9), \text{ with}$$

$$A = aP/R^2T^2, \quad B = bP/RT \quad \text{and} \quad Z = vP/RT \quad (10).$$

Note that Eqn.(9) 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

$$\ln \phi = (Z - 1) - \ln(Z - B) + \frac{A}{2\sqrt{2}B} \ln \frac{Z + (1 - \sqrt{2})B}{Z + (1 + \sqrt{2})B} \quad (11)$$

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.

Several authors ([16] to [22]) have modified PR EOS by representing m of α -term (Eqn.(5)) as a function of both acentric factor and reduced temperature, $m(\omega, T_r)$, for $X = 0.5$. 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.* [23] presented a different approach for determining the α -term by expressing Eqn.(8) 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.* [23] 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.(8), we presented an improved form of PR EOS, called MPR EOS [4]. In MPR EOS $m(\omega)$ no longer depends on the properties of a particular fluid. Following the suggestion of Leibovici, [24], $m(\omega)$ was determined by satisfying the isofugacity condition at $T_r = 0.7$ for $X = 0.5$ using Eqns.(8) and (4) and was represented in a polynomial form. So long as u and w of Eqn.(4) 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.(8)) did not yield an universal value of $X=0.5$ (a values adopted for the PR EOS of Eqn.(4)). 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.

The purpose of this work is to develop an improved form of the Peng-Robinson equation of state following Fotouh and Shukla [19] and predict simultaneously the phase behavior 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.

We have presented in the previous annual reports 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.

A brief account of the modified form of PR equation of state (MPR EOS) is presented below.

Modified Peng-Robinson Equation of State (MPR EOS)

The general form of MPR EOS for a pure fluid is given by Eqn.(4) along with Eqns.(5-11). The important parameters of MPR EOS are m and X of the α -term (Eqn.(8)). As mentioned above, in this modification m depends on ω only and is given by [17]

$$m(\omega) = \sum_{j=0}^4 \sum_{k=0}^4 A_{jk} u_o^j \omega^k \quad (12).$$

Here $u_o = 2$ for PR EOS. Coefficients A_{jk} of the above polynomial are reported elsewhere [19].

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

$$X = B_0 + B_1 T_r + B_2 T_r^2 + B_3 T_r^3, \text{ with } B_0 = 0.5 \quad (13)$$

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

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

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

$$\delta = -\frac{v^2}{RT} \left(\frac{\partial P}{\partial v} \right)_T \quad (15), \text{ and}$$

$$F_c = v_c^{\text{Exp}} - (v_c + S_1) \quad (16)$$

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 showed that the above set of the S_1 and S_2 parameters was unable to correlate accurately the saturated volumes of all 44 fluids used in this work. 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 redefined Eqn.(14) as follows

$$v^{\text{corr}} = v + S_1 + F_c \left(\frac{S_2}{S_2 + \delta} \right) + S_3 T_r \quad (17).$$

Here Eqn.(17) is now temperature dependent and contains a third parameter, S_3 .

Based on the combinations of Eqns.(13) and (14) and those of Eqns.(13) and (17), we performed two kind of calculations in this work. The results obtained from the first set of calculations (i.e., results based on Eqns.(13) and (14)) were 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,

$$ADPV\% = \sum_{i=1}^{n_p} ABS(\Delta P\%)_i + \sum_{j=1}^{n_v} ABS(\Delta V^L\%)_j \quad (18), \text{ with}$$

$$\Delta P\% = (P_{\text{exp}} - P_{\text{cal}}) / P_{\text{exp}} \times 100 \quad (19), \text{ and}$$

$$\Delta V^L\% = (V_{\text{exp}}^L - V_{\text{cal}}^L) / V_{\text{exp}}^L \times 100 \quad (20)$$

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.(18).

The calculations corresponding to vapor-liquid equilibrium data are reported in Tables VII and VIII. We used two systems containing ten hydrocarbons, from C_1 to C_8 , plus C_{10} and C_{14} . We added CO_2 in the first case and CO_2 plus N_2 in the second. Our algorithm also calculates the value of the pressure while temperature is held constant at the experimental value. Comparisons with experimental results reported by Turek et al. [2] showed very good agreement in both cases for the molar compositions reported in Tables VII and VIII. The values of calculated pressures also agreed well with the experimental results.

Heavy Oil Fraction Characterization

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 [4] provides an excellent review. For the sake of brevity only the method used in this work is included.

Riazi and Daubert [26] 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:

$$\psi = aT_b^b\gamma^c \quad (21), \text{ where:}$$

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 .

Riazi and Daubert [27] modified their equation while maintaining its simplicity and significantly improving its accuracy:

$$\psi = aT_b^b \gamma^c \exp[dT_b + e\gamma + fT_b\gamma] \quad (22)$$

$$\psi = aM_w^b \gamma^c \exp[dM_w + e\gamma + fM_w\gamma] \quad (23).$$

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

Whitson's Lumping Scheme

Whitson [4] proposed a regrouping scheme whereby the compositional distribution of Lumping is the reversed problem. The $C_7 +$ fraction is reduced to only a few Multiple-Carbon-Number (MCN) groups. Whitson suggested that the number of MCN groups necessary to describe the plus fraction is given by the following empirical rule:

$$N_g = \text{Int}[1 + 3.3 \log(N - n)] \quad (24), \text{ where:}$$

N_g = number of MCN groups

Int = Integer

N = number of carbon atoms of the last component in the hydrocarbon system

n = number of carbon atoms of the first component in the plus fraction

The integer function requires that the real expression evaluated inside the brackets be rounded to the nearest integer. The molecular weights separating each MCN group are calculated from the following expression:

$$Mw_I = Mw_n \left[\exp \left[\frac{1}{N_g} \right] \ln \left(\frac{Mw_N}{Mw_n} \right) \right]^I \quad (25), \text{ where:}$$

Mw_N = molecular weight of the last reported component in the extended analysis of the plus fraction.

Mw_n = molecular weight of the first hydrocarbon group in the extended analysis of the plus fraction.

$I = 1, 2, \dots, N_g$

Molecular weight of hydrocarbon groups (molecular weight of C_7 -group, C_8 -group, etc.) falling within the boundaries of these values are included in the I^{th} MCN group.

A sample calculation is shown in Table X. The molecular weight of fraction 1 is 96 while the molecular weight of fraction 45 is 539. The method predicted 6 pseudo-

fractions with the molecular weights shown in the Table. The components with molecular weights between pseudo-components k-1 and k are ascribed to pseudo-component k.

FUTURE WORK

A one year no cost extension has been awarded to this project. This extra time will be employed in completing the research project based on the following research plan:

- 1). Characterization of several heavy oil samples using the computer code based on the Whitson method [4].

- 2). Calculation of phase behavior for several mixtures of pseudo-components determined using the results of part 1). Some of the mixtures will also include CO₂ and water. The computer program developed to implement the modified Peng-Robinson EOS will be used on this calculations.

- 3). Comparison between predicted and experimental values. P-V behavior or critical P for mixtures at constant T are some of the possible comparisons.

- 4). Write-up of the final report.

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TABLES

Component	WT./gms	MW	WT %	MOLE %
C3	28.93	44.10	19.13	12.92
C5	19.92	72.15	13.17	5.44
C8	32.90	114.23	21.75	5.67
H2O	69.49	18.02	45.95	75.96
TOTAL	151.24			
Old water, propane, pentane and octane quaternary system				
Component	WT./gms	MW	WT %	MOLE %
C3	28.28	44.10	20.51	12.91
C5	19.54	72.15	14.17	5.45
BENZENE	22.03	78.15	15.98	5.67
H2O	68.01	18.02	49.33	75.97
TOTAL	137.86			
New water, propane, pentane and benzene quaternary system				

Table I. Comparison of two quaternary systems

P (psia)	T (F)	PHASE	WEIGHT CG/CC			
			WATER	PROPANE	PENTANE	BENZENE
130	104	VAPOR	0.054817524	1.42384549	0.09198107	0.03085973
		OLEIC	0.113589546	22.7948235	17.4627313	19.7758563
		AQUEOUS				
190	149	VAPOR	0.047504726	2.47118688	0.21611928	0.09304652
		OLEIC	0.164824272	21.2642211	17.4109750	20.2408703
		AQUEOUS				
302	200	VAPOR	0.034815642	3.62560324	0.49474503	0.47671037
		OLEIC	0.26835774	19.1294882	16.0489745	17.2991232
		AQUEOUS				
473	250	VAPOR	0.120215603	4.53460386	0.86694113	0.61861040
		OLEIC	0.331645379	17.0497777	14.7814981	17.7841972
		AQUEOUS				
608	300	VAPOR	0.286065308	6.00520271	1.76106542	1.03739851
		OLEIC	0.657628879	13.7277546	13.7319591	16.3918564
		AQUEOUS				

Table II. Calculated amounts in vapor and oleic phases for water, propane, pentane and benzene quaternary system.

				TOTAL WEIGHTS (gm)			
P (psia)	T (F)	Phase	Vol (cc)	Water	Propane	Pentane	Benzene
130	104	VAPOR	207.98	0.1140	2.9613	0.1913	0.0642
		OLEIC	110.57	0.1256	25.2042	19.3085	21.8662
		AQUEOUS	68.29	67.7704	0.1144	0.0402	0.0997
		TOTAL	386.84	68.0100	28.2800	19.5400	22.0300
190	149	VAPOR	210.18	0.0998	5.1939	0.4542	0.1956
		OLEIC	107.64	0.1774	22.8888	18.7412	21.7873
		AQUEOUS	69.02	67.7327	0.1973	0.3446	0.0472
		TOTAL	386.84	68.0100	28.2800	19.5400	22.0300
302	200	VAPOR	210.4	0.0733	7.6283	1.0409	1.0030
		OLEIC	106.25	0.2851	20.3251	17.0520	18.3803
		AQUEOUS	70.19	67.6516	0.3266	1.4470	2.6467
		TOTAL	386.84	68.0100	28.2800	19.5400	22.0300
473	250	VAPOR	211.62	0.2544	9.5961	1.8346	1.3091
		OLEIC	103.86	0.3444	17.7079	15.3521	18.4707
		AQUEOUS	71.36	67.4112	0.9760	2.3533	2.2502
		TOTAL	386.84	68.0100	28.2800	19.5400	22.0300
608	300	VAPOR	214.58	0.6138	12.8860	3.7789	2.2260
		OLEIC	99.58	0.6549	13.6701	13.6743	16.3230
		AQUEOUS	72.68	66.7413	1.7239	2.0868	3.4809
		TOTAL	386.84	68.0100	28.2800	19.5400	22.0300

Table III. Measured and calculated amounts in three phases for water, propane, pentane and benzene quaternary system.

			Mole percentages			
P (psia)	T (F)	PHASE	WATER	PROPANE	PENTANE	BENZENE
130	104	VAPOR	8.22	87.26	3.45	1.07
		OLEIC	0.62	50.76	23.77	24.85
		AQUEOUS	99.88	0.07	0.01	0.03
190	149	VAPOR	4.19	89.15	4.77	1.89
		OLEIC	0.92	48.62	24.33	26.12
		AQUEOUS	99.74	0.12	0.13	0.02
302	200	VAPOR	1.99	84.67	7.06	6.28
		OLEIC	1.67	48.60	24.92	24.80
		AQUEOUS	98.39	0.19	0.53	0.89
473	250	VAPOR	5.15	79.45	9.28	6.12
		OLEIC	2.20	46.17	24.46	27.17
		AQUEOUS	97.82	0.58	0.85	0.75
608	300	VAPOR	8.37	71.77	12.86	7.00
		OLEIC	4.88	41.62	25.45	28.05
		AQUEOUS	97.05	1.02	0.76	1.17

Table IV. Three phase mole % for water, propane, pentane and benzene quaternary system.

P (psia)	T (F)	PHASE	Phase Fractions
130	104	VAPOR	0.01549
		OLEIC	0.22663
		AQUEOUS	0.75789
190	149	VAPOR	0.02659
		OLEIC	0.21485
		AQUEOUS	0.75856
302	200	VAPOR	0.04112
		OLEIC	0.19087
		AQUEOUS	0.76801
473	250	VAPOR	0.05513
		OLEIC	0.17507
		AQUEOUS	0.76980
608	300	VAPOR	0.08195
		OLEIC	0.14990
		AQUEOUS	0.76815

Table V. Phase fractions for water, propane, pentane and benzene quaternary system.

T (F)	P (psia)	Volumes (cc)			Molar Volumes (cc /g.moles)		
		V _a	V _o	V _v	Vapor	Oleic	Aqueous
104	130	68.29	110.57	207.98	2702.57	98.20	18.14
149	190	69.02	107.64	210.18	1591.04	100.84	18.31
200	302	70.19	106.25	210.40	1029.91	112.05	18.40
250	473	71.36	103.86	211.62	772.64	119.41	18.66
300	608	72.68	99.58	214.58	527.04	133.71	19.04

Table VI. Three phase molar volumes for water, propane, pentane, and benzene quarternary system.

Component	X _{experimental}	Y _{experimental}	Y _{calculated}
1	0.681580	0.883040	0.878025
2	0.0408020	0.084500	0.087702
3	0.004950	0.005190	0.005298
4	0.011060	0.006200	0.007482
5	0.017850	0.007030	0.007000
6	0.014320	0.003620	0.003546
7	0.012350	0.001950	0.001960
8	0.021680	0.002260	0.002371
9	0.023050	0.001540	0.001633
10	0.150230	0.004500	0.004831
11	0.022110	0.000170	0.000153

Table VII. Vapor-Liquid equilibrium data for the system CO₂-C₁-C₂-C₃-C₄-C₅-C₆-C₇-C₈-C₁₀-C₁₄. T (K) = 338.7, P_{exp} (Bar) = 103.7 and P_{cal} (Bar) = 101.52.

Component	X _{experimental}	Y _{experimental}	Y _{calculated}
1	0.000510	0.002610	0.002950
2	0.192750	0.284870	0.251429
3	0.256600	0.659520	0.689775
4	0.022530	0.020050	0.021821
5	0.031030	0.014200	0.015205
6	0.048530	0.010290	0.010478
7	0.033920	0.003710	0.003596
8	0.026180	0.001430	0.0014941
9	0.044560	0.001250	0.001359
10	0.045780	0.000678	0.000712
11	0.259670	0.001370	0.001164
12	0.037949	0.000026	0.000017

Table VIII. Vapor-Liquid equilibrium data for the system N₂- CO₂-C₁-C₂-C₃-C₄-C₅-C₆-C₇-C₈-C₁₀-C₁₄. T (K) = 322, P_{exp} (Bar) = 103.7 and P_{cal} (Bar) = 98.82.

Form (I)				
Constant	Mw	T_c (°R)	P_c (psia)	V_c (ft³ / lbm)
a	581.96	10.6443	6.162x10 ⁶	6.233x10 ⁻⁴
b	0.97476	0.81067	-0.4844	0.7506
c	6.51274	0.53691	4.0846	-1.2028
d	5.43076x10 ⁻⁴	-5.1747x10 ⁻⁴	-4.725x10 ⁻³	-1.4679x10 ⁻³
e	9.53384	-0.54444	-4.8014	-0.26404
f	1.11056x10 ⁻³	3.5995x10 ⁻⁴	3.1939x10 ⁻³	1.095x10 ⁻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}

Table IX. Riazi and Daubert [27] Constants for Property Estimation.

Group	Molecular Weight
1	127
2	170
3	227
4	303
5	404
6	539

Table X. Grouping data for characterization of fractions with up to 45 components.