SPE 107331

On Equation of State
Tarek Ahmed, Anadarko Petroleum Corp.

Summary
To predict the phase and volumetric behavior of hydrocarbon mixtures by using an Equation of State; e.g. the Peng and Robinson Equation of State "PREOS", the critical properties in terms of the critical pressure "p_c" and critical temperature "T_c" as well as the acentric factor "ω" must be given for each component present in the mixture including the plus-fraction. For pure compounds, the required properties are well-defined, but nearly all naturally occurring gas and crude oil fluids contain some heavy fractions that are not well defined and are not mixtures of discretely identified components. These heavy fractions often are lumped and called the "plus-fraction" (e.g. C_{7+} fraction). Adequately characterizing these undefined plus fractions in terms of their critical properties and acentric factors has long been a problem. Changing the characterization of the plus fraction can have a significant effect on the volumetric and phase behavior of a mixture predicted by the PREOS. The inaccuracy of any the cubic equation of state results from the following two apparent limitations:
1.   improper procedure of determining coefficients a, b, and α for the plus fraction
2.   Equations of state treatment of hydrocarbon components with critical temperatures less than the system temperature (i.e. methane and nitrogen).

Numerous authors have suggested that the EOS is generally not predictive and extensive splitting of the C_{7+} fraction is often required when matching laboratory data.

This paper presents a practical approach for calculating the coefficients a, b, and α of the plus-fraction from **its readily available measured physical properties in terms of molecular weight "M" and specific gravity "γ"** with the objective of improving the predictive capability of equation of state. The predictive capability of the relationship is displayed by matching a set of laboratory data on several crude oil and gas-condensate systems. In addition; the performance of the proposed method was also compared with predictive PVT results as generated by using PVTSim[TM] software of Calsep. Additional comparisons are made by comparing the proposed modified PR EOS results with those of Coats and Smart[4] regression methodology with PR EOS.

This study concludes that when the coefficients of the plus-fraction, i.e. a, b, and α, are determined based on the proposed methodology; <u>splitting of the C_{7+} into a number of pseudo-components is essentially unnecessary</u>.

Introduction
An equation of state (EOS) is an analytical expression relating the pressure to the volume and temperature. The expression is used to describe the volumetric behavior, the vapor/liquid equilibria (VLE), and the thermal properties of pure substances and mixtures. Numerous EOS's have been proposed since van der Waals[1] introduced his expression in 1873. These equations were generally developed for pure fluids and then extended to mixtures through the use of mixing rules. The mixing rules are simply a means of calculating mixture parameters equivalent to those of a pure substance. The PREOS[2] is perhaps the most popular and widely used EOS. In terms of the molar volume V_m, Peng and Robinson proposed the following two-constant cubic EOS:

$$p = \left[\frac{RT}{(V_m - b)}\right] - \frac{a(T)}{[V_m(V_m + b) + b(V_m - b)]}$$

$\qquad$ 1

van der Waals observed that for a pure component, the first and second isothermal derivatives of pressure with respect to volume are equal to zero at the critical point of the substance. This observation can be expressed mathematically as

$$\left(\frac{\partial p}{\partial V_m}\right)_{T_C} = 0 \qquad\qquad 2$$

and

$$\left(\frac{\partial^2 p}{\partial V_m^2}\right)_{T_C} = 0 \qquad\qquad 3$$

Peng and Robinson imposed the above derivative constraints on Equation 1 and solved the resulting two expressions for the parameters a(T_c) and b to give

$$a(T_c) = \Omega_a \frac{(RT_c)^2}{p_c} \qquad\qquad 4$$

and

$$b = \Omega_b \frac{(RT_c)}{p_c} \qquad\qquad 5$$

where the dimensionless parameters Ω_a and Ω_b are 0.45724 and 0.07780, respectively. At temperatures other than the T_c, Peng and Robinson adopted Soave's[3] approach for evaluating *a(T)*. The generalized expression for the temperature-dependent parameter is given by

$$a(T) = a(T_c)\alpha(T) \qquad\qquad 6$$

where

$$\alpha(T) = \left\{ 1 + m\left[1 - \sqrt{\frac{T}{T_c}}\right]\right\}^2 \qquad\qquad 7$$

with

$$m = 0.3746 + 1.5423\omega - 0.2699\omega^2 \qquad\qquad 8$$

Introducing the compressibility factor 'Z' into Equation 1 gives

$$Z^3 + (B-1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad\qquad 9$$

where

$$A = \frac{a(T)p}{(RT)^2} \qquad\qquad 10$$

and

$$B = \frac{bp}{(RT)} \qquad\qquad 11$$

To use Equation 9 for mixtures with its coefficients as expressed by Equations 10 and 11, Peng and Robinson recommend the following classic mixing rules:

$$[a(T)]_{mix} = \sum_i \sum_j [\sqrt{x_i x_j}[a(T_{ci})a(T_{cj})\alpha_i(T)\alpha_j(T)](1 - k_{ij})] \qquad\qquad 12$$

and

$$(b)_{mix} = \sum_i (x_i b_i) \qquad\qquad 13$$

In the application of Equations 12 and 13 to a hydrocarbon mixture, *a(T)* and *b* are calculated for each component in the mixture with Equations 4 through 8. Questionable assumptions are made in the application of these equations to the plus fraction and to

hydrocarbon components with critical temperatures less than the system temperature. These assumptions (outlined below) provide the reasoning for the proposed modification of the popular EOS.

Assumption 1 – In the derivation of expressions for $a(T)$ and b, as represented by Equations 4 and 5, the critical isotherm of a component is assumed to have a slope of zero and an inflection point at the critical point. The assumption, described mathematically by Equations 2 and 3, is valid only for a pure component. Because the plus fraction lumps millions of compounds that are making up the fraction, it is unlikely that Equations 4 and 5 would provide an accurate representation of the attraction parameter $a(T)$ and the co-volume b.

Assumption 2 – The coefficients of Equation 7 were developed by regressing vapor-pressure data from the normal boiling point to the critical point for several pure components. Again, it is unlikely that this equation will suffice for the higher-molecular-weight plus fractions.

Assumption 3 – As pointed out previously, the theoretical Ω_a and Ω_b values in the PREOS arise from imposing the van der Waals critical-point conditions, as expressed by Equations 2 and 3, on Equation 1. These values essentially reflect satisfaction of pure-component density and vapor-pressure data below critical temperature. At reservoir conditions, methane and nitrogen in particular are well above their critical points. Coats and Smart[4] pointed out that no theory or clear-cut guide exists to selection or alternation of the Ω for components well above their critical temperatures.

Wilson et al.[5] showed the distinct effect of the plus fraction's characterization procedure on all the PVT relationships predicted by an EOS. A number of studies[4, 6-10] reported comparisons of EOS and laboratory PVT results for a wide variety of reservoir fluids and conditions; most of these studies emphasize the plus-fraction characterization as the key element in attaining agreement between EOS and laboratory results.

Coats and Smart[4] presented numerous examples of matching the measured and calculated data for nine reservoir fluids of various degrees of complexity. They observed that without regression or significant adjustment of EOS parameters, the PREOS will not adequately predict observed fluid PVT behavior. Coats and Smart indicated that the adjustment of five parameters in the PREOS is frequently necessary and sufficient for good data match. These parameters are:
- Ω_a and Ω_b of methane,
- Ω_a and Ω_b of the plus fraction, and
- binary interaction coefficient between methane and the C_{7+} plus fraction k_{C1-C7+}

Whitson[9] observed that the method of adjusting the EOS constants Ω_a and Ω_b for the plus fraction is essentially the same as altering the critical properties of the heavy fraction.

Several authors[9, 11-15] showed that the ability of the EOS to predict the phase behavior of complex hydrocarbon mixtures can be substantially improved by splitting or breaking down the plus fraction into a manageable number of pseudo-components for EOS calculations.

Description of the Proposed Modification of the PREOS
Because the inadequacy of the predictive capability of the PREOS lies with the three assumptions outlined above, an approach was devised in this study to remove these assumptions. The approach is based on the fact that the acentric factor and critical properties of the C_{7+} are not well defined and never measure in the laboratory; however; there are measurements that routinely performed and readily available on the plus fraction that include: the molecular-weight "M", the boiling point "T_b", and specific gravity "γ" . Over the years; many reliable correlations that have developed to cross correlate these parameters from numerous measurements. Therefore; in the eliminating the first two assumptions, 49 hypothetical heavy petroleum fractions (i.e. plus fractions) with physical properties (density, molecular weight, and boiling point) governed by the applicability range of Riazi and Daubert[16] equation were generated. Riazi and Daubert developed a simple two-parameter equation for predicting the physical properties of pure compounds and undefined petroleum fractions. The proposed correlation; as shown by Equation 14, is applicable in the molecular-weight rage of 70 to 300 and normal boiling point range of 80 to 650°F. The expression correlates the molecular-weight "M" with the boiling point "T_b" and specific gravity "γ" of the substance; it takes the form:

$$M = a(T_b)^b \, \gamma^c \, \exp(dT_b + e\gamma + fT_b\gamma) \qquad\qquad 14$$

where

$a = 581.960$ $b = 0.97476$
$c = 5.43076 \times 10^{-4}$ $e = 9.53384$
$f = 1.11056 \times 10^{-3}$

The specific steps of the proposed modification are outlined below.

Step 1 – Each hypothetical heavy fraction with a specified molecular weight, boiling point, and density (specific gravity) is subjected to 10 temperature and 10
pressure values in the range of 60 to 300°F and 14.7 to 7,000 psia. The specified density is then adjusted to account for the temperature and pressure increases. A total of 100 density values are generated for each hypothetical heavy fraction.

Step 2 – Equation 9 is rearranged and expressed in terms of the density to give

$$[a(T_c)\alpha(T)b - RTb^2 - pb^3]\rho^3 - M[a(T_c)\alpha(T) - 3pb^2 - 2RTb]\rho^2$$
$$-M^2(pb - RT)\rho - pM^3 = 0 \qquad\qquad 15$$

Step 3 – Equation 15 is incorporated into a nonlinear regression model that uses $a(T_c)$, b, and $\alpha(T)$ as regression variables. For each hypothetical heavy fraction under consideration, Equation 15 is solved for the density by optimizing the regression variables to match the fraction generated density data.

Step 4 – The optimized regression variables [i.e. $a(T_c)$, b, and $\alpha(T)$] are correlated with M, γ or T by the following relationships. For $a(T_c)$ or b of the plus fraction,

$$a(T_c)\,\text{or}\,b = \left[\sum_{i=0}^{3}\left(C_i D^i\right)\right] + \frac{C_4}{D} + \left[\sum_{i=5}^{6}\left(C_i \gamma^{i-4}\right)\right] + \frac{C_7}{\gamma} \qquad\qquad 16$$

with

$$D = \left(\frac{M}{\gamma}\right)_{c+}$$

Table 1 gives values of C_0 through C_7 (for $a(T_c)$ and b) of the above expression. For $\alpha(T)$, Peng and Robinson $\alpha(T)$ function as expressed by Equation 7 is modified according to

$$\alpha(T) = \left\{1 + m\left[1 - \left(\frac{520}{T}\right)^{0.5}\right]\right\}^2 \qquad\qquad 17$$

with

$$m = \left[\frac{D}{(C_0 + C_1 D)}\right] + C_2 M + C_3 M^2 \frac{C_4}{M} + C_5\gamma + C_6\gamma^2 + \frac{C_7}{\gamma} \qquad 18$$

Table 1 includes the values C_0 through C_7 for Equation 18.

Table 1 – Coefficients of Eqs. 16 and 18

Coefficient	$a(T_c)$		b	m
C_0	-2.433525	x 10^7	-6.8453198	-36.91776
C_1	8.3201587	x 10^3	1.730243 x 10^{-2}	-5.2393763 x 10^{-2}
C_2	-0.18444102	x 10^2	-6.2055064 x 10^{-5}	1.7316235 x 10^{-2}
C_3	3.6003101	x 10^{-2}	9.0910383 x 10^{-9}	-1.3743308 x 10^{-5}
C_4	3.4992796	x 10^7	13.378898	12.718844
C_5	2.838756	x 10^7	7.9492922	10.246122
C_6	-1.1325365	x 10^7	-3.1779077	-7.6697942
C_7	6.418828	x 10^8	1.7190311	-2.6078099

In the elimination of the third assumption, the Peng and Robinson parameters (i.e. $a(T_c)$, b, and m) for methane and nitrogen are altered. For this approach, 100 z-factor values for each component were obtained from appropriate gas-compressibility-factor charts. $a(T_c)$, b and m (to be used in Equation 17) for methane and nitrogen were optimized by incorporating a regression model in solving Equation 9 and matching the z-factor data for each fraction. The optimized values are:

- For Nitrogen: $a(T_c)$ = 4,569.3589, b = 0.46825820, and m = -0.97962859
- For Methane: $a(T_c)$ = 7,709.7080, b = 0.46749727, and m = -0.54976500

Several computational schemes[7, 10, 17] for generating binary interaction coefficients were tested for the purpose of providing the modified PREOS with a systematic and consistent procedure for determining the k_{ij}. Petersen's[17] computational technique was adopted and appropriately modified to provide the proper EOS coefficients. The technique is described in the following steps.

Step 1 –   Set:
$$k_{CO2\text{-}N2} = 0.12,$$
$$k_{CO2\text{-hydrocarbons}} = 0.10, \text{ and}$$
$$k_{N2\text{-hydrocarbons}} = 0.10$$

Step 2 –   Estimate the binary interaction coefficient between methane and the heptanes-plus fraction, $k_{C1\text{-}C7+}$. To provide this estimate, the coefficient under consideration was adjusted to minimize the error in calculating the saturation pressures of 12 hydrocarbon mixtures. Results of the study indicate the strong dependency of the calculated optimum values of $k_{C1\text{-}C+}$ on system temperatures. The following linear relationship provides an appropriate estimate of the parameter:

$$k_{C1\text{-}C7+} = 0.00189(T\text{-}460) - 0.297659 \qquad\qquad 19$$

where:
T = system temperature, $^{\circ}$R

Step 3 –   Calculate the binary interaction coefficients between components heavier than methane (i.e. C_2, C_3....etc.) and the plus fraction according to the following expression[17]:

$$k_{Cn\text{-}C+} = 0.8\, k_{C(n\text{-}1)\text{-}C7+} \qquad\qquad 20$$

where:
n = number of carbon atoms

Step 4 –   Determine the remaining k_{ij} from [17]

$$k_{ij} = k_{i-C7+} \frac{\left[(M_j)^5 - (M_i)^5 \right]}{\left[(M_{C7+})^5 - (M_i)^5 \right]} \qquad\qquad 21$$

where:
M_i = molecular weight of component i
M_{C7+} = molecular weight of the heptanes-plus fraction

Application of the Modified EOS and Discussion of Results

To validate the proposed methodology of treating the plus fraction, the modified EOS and PVTSim software were used to simulate a variety of published laboratory PVT tests and compare their predicted results with actual data. The verification procedure is outlined below:

1. In applying the proposed modification, the measured physical properties of the C_{7+} in terms of molecular weight and specific gravity were maintained as reported and used to calculate the parameters $a(T_c)$, b, and $\alpha(T)$ of the plus-fraction. No splitting of the plus fraction is required in performing the PVT analysis when applying the proposed modification.
2. For all various hydrocarbon mixtures used in the study; PVTSim was allowed to split the C_{7+} fraction into the following 11 pseudo-components: C_7, C_8, C_9, C_{10}-C_{12}, C_{13}-C_{14}, C_{15}-C_{16}, C_{17}-C_{19}, C_{20}-C_{22}, C_{23}-C_{25}, C_{26}-C_{30}
3. The modified PR EOS model and PVTSim were both tuned to only match the saturation pressure. The PVTSim regressed on the saturation pressure by adjusting the molecular weight of the plus fraction; while the modified PR model used the binary interaction coefficient between C_1 and C_{7+} as the regression variable to match saturation pressure

For convenience and brevity of presenting and discussing results of the study, the following terms are used in the paper:

CCE	= Constant composition expansion
DE	= Differential expansion
CVE	= Constant composition expansion
C-S	= Coats-Smart tuned model
Mod. EOS	= Modified Peng-Robinson equation of state
PVTSim	= Results as predicted by PVTSim software
Exp.	= Experimental data
V/V_s	= relative volume from CCE test; i.e. total volume of hydrocarbon system at any given pressure and temperature divided by the volume at saturation pressure

Density Predictions – To test the modified PREOS for its ability to predict the density of complex hydrocarbon mixtures under a wide range of pressures and temperatures, the equation was applied to predict densities of the 15 hydrocarbon mixtures used by Standing and Katz[18] to develop their popular correlation and the densities of 11 crude oil systems reported by Coats and Smart[4]

Table 2 and Figure 1 summarize results of the model and compare the predicted densities with those calculated from the Standing-Katz[18] (*S-K*) and Alani-Kennedy[19] (*A-K*) density correlations. In terms of the overall average absolute deviation, the modified EOS predicted the density of the 26 mixtures with the lowest deviation of 5.58%, which compares favorably with the two density correlations.

Table 2 – Comparison of Predicted Oil Densities with Experimental Data

Density (g/cm^3)

|	*p* (psia)	*T* (°F)	*Exp.*	*S-K*	*A-K*	*Mod. EOS*
S-K Data						
A-1	3,185	120	0.696	0.729	0.720	0.718
A-2	5,270	120	0.745	0.759	0.736	0.745
A-3	8,220	120	0.814	0.817	0.773	0.802
A-4	1,600	120	0.702	0.712	0.701	0.718
B-1	2,915	250	0.697	0.702	0.688	0.663
C-1	2,880	120	0.652	0.655	0.642	0.663
C-2	1,010	120	0.716	0.724	0.712	0.732
C-3	5,330	120	0.712	0.685	0.672	0.712
A-K Data						
D-1	4,330	120	0.731	0.729	0.714	0.726
E-1	4,195	120	0.753	0.744	0.728	0.748
F-1	3,185	250	0.654	0.670	0.658	0.638
F-2	4,315	250	0.657	0.664	0.656	0.628
F-3	5,330	250	0.677	0.684	0.672	0.648
G-2	3,485	35	0.679	0.675	0.667	0.701
G-3	4,970	35	0.766	0.764	0.748	0.764
C-S Data						
.Oil 1	2,520	180	0.768	0.784	0.762	0.764
Oil 2	4,460	176	0.530	0.509	0.537	0.544
Oil 3	2,2115	140	0.736	0.807	0.809	0.752
Oil 3	2,362	160	0.722	0.804	0.796	0.726
Oil 3	2,597	180	0.708	0.795	0.785	0.701
Oil 3	2,792	200	0.695	0.788	0.772	0.683
Oil 4	2,547	250	0.646	0.647	0.651	0.615
Oil 4	2,283	180	0.679	0.679	0.682	0.672
Oil 4	1,958	110	0.711	0.709	0.712	0.719
Oil 6	2,746	234	0.609	0.620	0.623	0.599
Oil7	1,694	131	0.713	0.717	0.735	0.722
Average absolute error, %				6.58	6.69	5.58
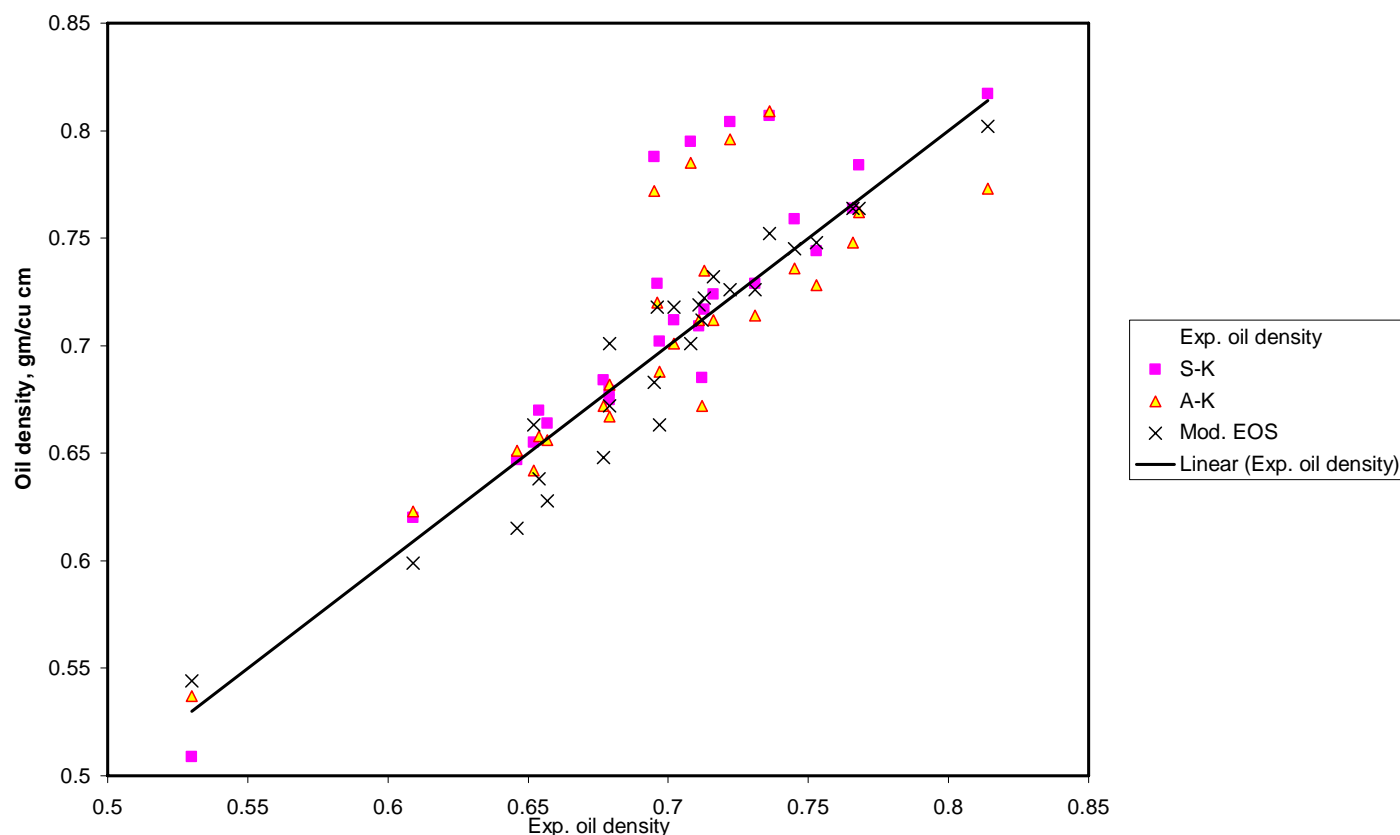
Figure 1. Comparison Of Predicted Densities

Coats-Smart Hydrocarbon Systems – Coats and Smart[4] reported a detailed experimental description of several hydrocarbon systems. Nine of the hydrocarbon systems, with the compositions given in Table 3, were used in the study. Coats and Smarts "C-S" used a regression-based PVT program to match the laboratory by tuning parameters of equation of state. Most of their calculations were performed by splitting the heptanes-plus into four fractions.

Table 3 – Coats and Smart Compositional Data

	Gas 2[*]	Gas 2[**]	Gas 5	Oil 1	Oil 2	Oil 3	Oil 4	Oil 6	Oil 7
CO_2	0.00690	0.00610	0.02170	0.00440	0.00900	0.60310	0.02350	0.01030	0.0008
N_2		0.00420	0.00340	0.00450	0.00300	0.00930	0.00110	0.00550	0.0164
H_2S	0.00040	0.00040							
C_1	0.58320	0.57490	0.70640	0.35050	0.53470	0.07050	0.35210	0.36470	0.2840
C_2	0.13550	0.13450	0.10760	0.04640	0.11460	0.01570	0.06720	0.09330	0.0716
C_3	0.07610	0.07520	0.04940	0.02480	0.08790	0.03060	0.06240	0.08850	0.1048
C_4	0.04030	0.04150	0.03020	0.01660	0.04560	0.03310	0.05070	0.06000	0.0840
C_5	0.02410	0.02330	0.01350	0.01600	0.02090	0.02680	0.05230	0.03780	0.0382
C_6	0.01900	0.01790	0.00900	0.05460	0.01510	0.02580	0.04100	0.03560	0.0405
C_{7+}	0.11450	0.12200	0.05880	0.48240	0.16920	0.18510	0.34970	0.30430	0.3597
M_+	193	193	153	225	173	189	213	200	252
γ_+	0.8135	0.8115	0.8100	0.9000	0.8364	0.8275	0.8406	0.8366	0.8429
T, °F	190	190	267	180	176	179	250	234	131
P, psig	4,450	4,415	4,842	2,520	4,460	2,597	2,547	2,746	1,694

The proposed modification of the Peng-Robinson EOS was tested extensively using the above hydrocarbon system as well as a larger number of unreported fluid studies. Results of the some of applications of the modified PREOS to a selected number of hydrocarbon systems are presented below.

Near-Critical Gas Systems – Gas 2 is a near-critical gas-condensate fluid at a reservoir temperature of 190°F. Coats and Smart stated that because of the possibility of a small error in gas measurement during well testing, two slightly different separator gas/liquid ratios are used to obtain the two reservoir fluid compositions given in Table 3. The first sample (Gas 2[*]) exhibited a saturation pressure and density of 4,465 psia and 28.85 lb_m/ft^3 and was labeled a dewpoint gas. The second sample (Gas 2[**]) displayed a bubblepoint of 4,430 psia and a density of 29.54 lb_m/ft^3 and consequently was labeled a bubblepoint gas. In applying the modified expression to simulate the volumetric behavior of the two systems, Equations 19 through 21 initially were used to determine the binary interaction coefficients for each system. Table 4 lists these values for Gas 2[*]. The modified equation predicts a dewpoint pressure of 3,890 psia (compared with 3,680 psia for the original PREOS) and a saturation density of 28.45 lb_m/ft^3. For the bubblepoint gas, the equation predicts a saturation pressure of 3,824 psia (the original PREOS predicts 3,664 psia) and a saturation density of 28.86 lbm/ft^3.

Table 4 – Binary Interaction Coefficients for Gas 2[*]

Component i	Component j										
	CO_2	N_2	C_1	C_2	C_3	$i-C_4$	$n-C_4$	$i-C_5$	$n-C_5$	C_6	C_{7+}
CO_2	0.000	0.012	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
N_2		0.000	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
C_1			0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.061
C_2				0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.049
C_3					0.000	0.000	0.000	0.000	0.000	0.001	0.039
$i-C_4$						0.000	0.000	0.000	0.000	0.000	0.031
$n-C_4$							0.000	0.000	0.000	0.000	0.25
$i-C_5$								0.000	0.000	0.000	0.020
$n-C_5$									0.000	0.000	0.016
C_6										0.000	0.013
C_{7+}											0.000

Figure 2 compares experimental CCE data of the dew-point gas in terms of liquid relative volume with those as predicted by PVTSim and the modified PR model. Both models overestimated the liquid volume just below the dew point pressure. However; PVTSim predicted a bubblepoint system when the fluid was flashed below the saturation pressure. A constant volume depletion "CVE " test was also performed on the dew-point gas as shown in Table 5. Results from simulating the test by applying the modified PR EOS are compared with predicted values from experimental and PVTSim as documented graphically in terms of liquid dropout in Figure 3. Table 5 and Figure 3 show that PVTSim failed to recognize the system as a dewpoint gas and predicted a 100% liquid at saturation pressure. The match between the observed data and the modified PR model prediction in terms of liquid dropout is excellent with an average absolute error of 1.05%. A more detailed documentation of results of the proposed EOS for simulating CCE tests is given in Reference 20.
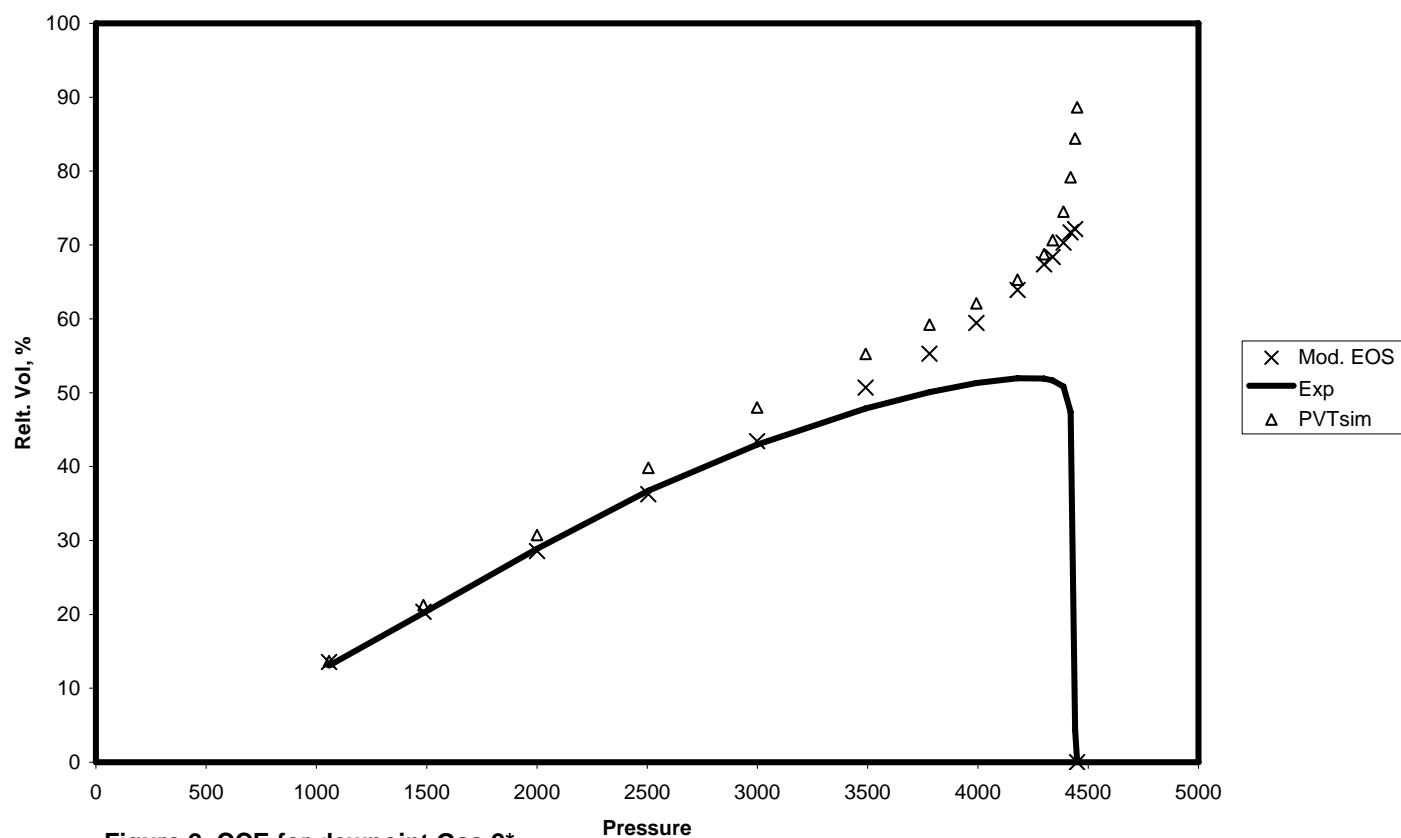
Figure 2. CCE for dewpoint Gas 2*

Table 5 – CVE at 190°F for Dewpoint Gas

Component	Pressure (psig)						
	4,450.0	3,500.0	2,700.0	1,900.0	1,100.0	500.0	500*
CO_2	0.00730	0.00767	0.00790	0.00824	0.00874	0.00922	0.00228
N_2	0.00000	0.00000	0.00000	0.00000	0.00000	0.0000	0.00000
C_1	0.58320	0.71198	0.72463	0.72791	0.71235	0.65973	0.07116
C_2	0.13550	0.13745	0.13945	0.14384	0.15417	0.17230	0.06429
C_3	0.07610	0.06804	0.06713	0.06782	0.07388	0.09265	0.07722
$i-C_4$	0.02015	0.01640	0.01568	0.01528	0.01625	0.02135	0.03199
$n-C_4$	0.02015	0.01538	0.01447	0.01387	0.01463	0.01961	0.03818
$i-C_5$	0.01205	0.00822	0.00738	0.00666	0.00658	0.00874	0.03124
$n-C_5$	0.01205	0.00783	0.00691	0.00611	0.00592	0.00781	0.03397
C_6	0.01900	0.01069	0.00885	0.00719	0.00631	0.00786	0.06607
C_{7+}	0.11450	0.01634	0.00762	0.00308	0.00117	0.00073	0.58360
Z-Factor							
Mod. EOS	0.9605	0.8359	0.8016	0.8031	0.8461	0.9061	
Experimental	0.9969	0.8402	0.7966	0.8140	0.8603	0.9108	
PVTSim	0.976	0.812	0.784	0.798	0.949	0.980	
G_p							
Mod. EOS	0.00000	12.89	25.411	41.007	58.989	73.304	
Experimental	0.00000	9.589	22.551	39.165	58.225	72.743	
PVTSim	0.0000	9.79	22.46	38.950	58.010	73.170	
Liquid Dropout (%)							
Mod. EOS	0.0	56.53	51.0	46.20	41.35	37.25	
Experimental	0.0	52.31	49.40	45.33	40.51	36.82	
PVTSim	100	61.37	54.91	48.4	41.87	36.69	

*Residual liquid composition

Figure 3. LDO for Dewpoint Gas-2*

Figure 4. CCE for Bubblepoint Gas2**
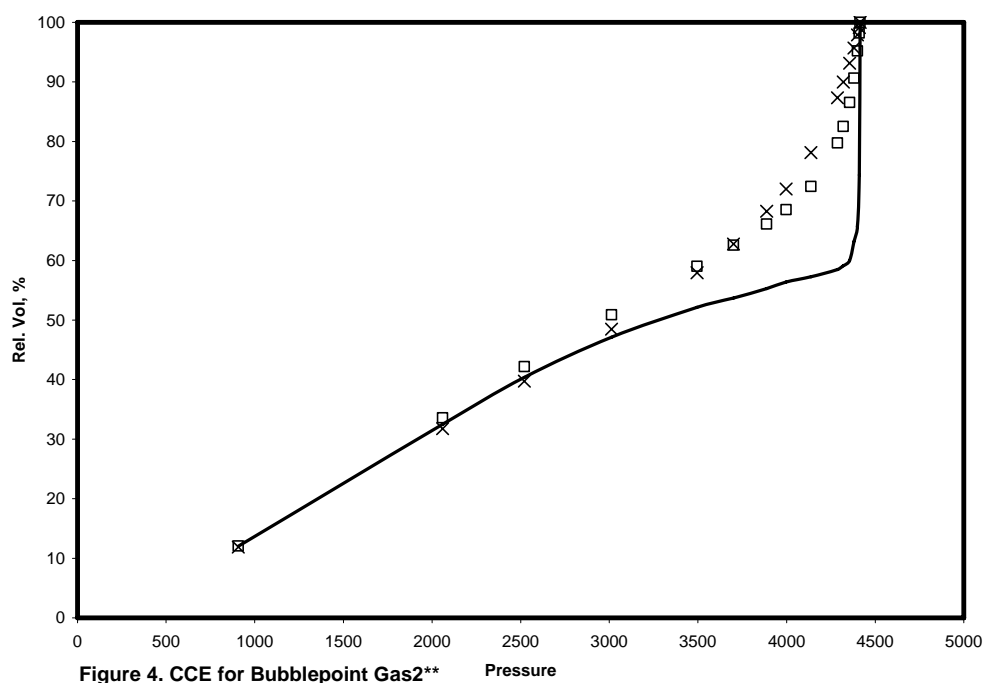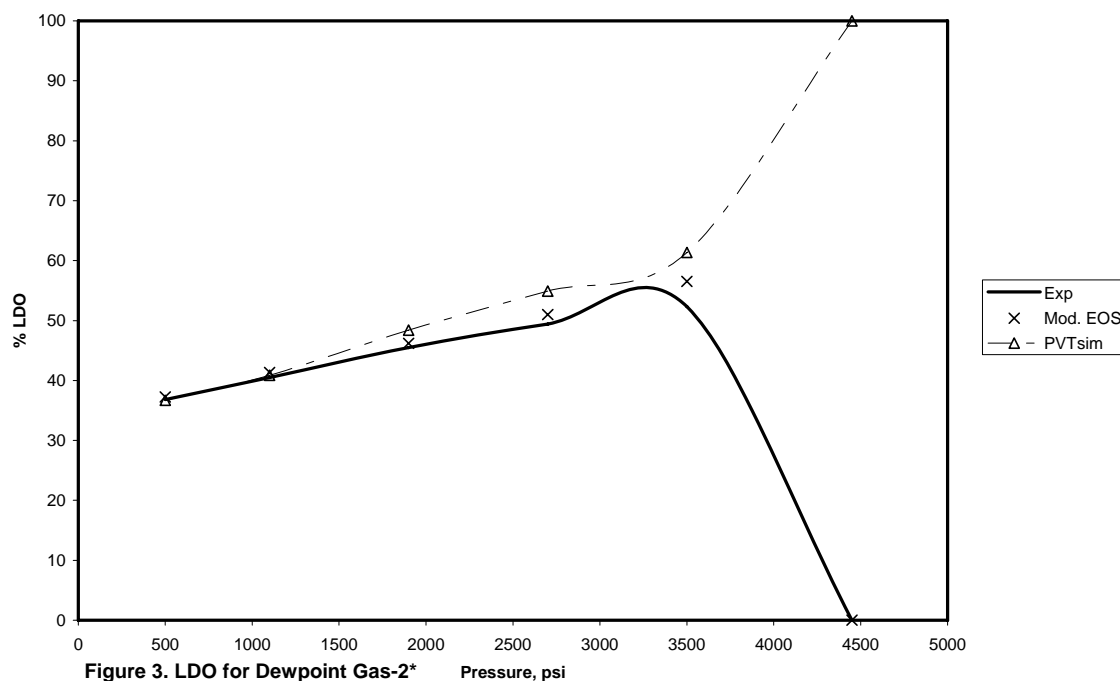
Gas-Condensate System 5 – Gas 5 is a retrograde gas with a reported upper dewpoint pressure of 4,857 psia at 276°F. The model predicts an excellent value of 4,805 psia for the dewpoint pressure. In simulating the CVE and CCE tests for the system, the modified equation and PVTSim show excellent predictive capabilities in reproducing the experimental data, as Table 6 illustrates. The tabulated results compare the observed data with both models in terms of Z factor, liquid dropout, G_p, and V/V_s. The modified expression gives average deviations of 1.6% for the Z-factor, 1.3% for G_p, and 1.9% for liquid dropout. The near-exact match of the modified PR EOS with reported liquid dropout data is documented graphically in Figure 5.

Table 6 – Expansion Data for Gas 5

	Pressure (psig)						
Component	4,642.0	3,900.0	3,000.0	2,100.0	1,200.0	700.0	700.0*
CO_2	0.02170	0.02185	0.02207	0.02237	0.02276	0.02302	0.00611
N_2	0.00340	0.00348	0.00355	0.00359	0.00360	0.00356	0.00032
C_1	0.70640	0.72207	0.73481	0.74357	0.74575	0.73990	0.08684
C_2	0.10760	0.10893	0.11010	0.11124	0.11256	0.11352	0.02989
C_3	0.04940	0.04957	0.04970	0.04997	0.05083	0.05216	0.02532
$I-C_4$	0.01510	0.01502	0.01493	0.01491	0.01518	0.01583	0.01246
$n-C_4$	0.01510	0.01490	0.01471	0.01460	0.01490	0.01574	0.01636
$I-C_5$	0.00675	0.00658	0.00639	0.00625	0.00633	0.00681	0.01184
$n-C_5$	0.00675	0.00653	0.00629	0.00610	0.00615	0.00668	0.01428
C_6	0.00900	0.00853	0.00802	0.00753	0.00741	0.00814	0.03040
C_{7+}	0.05880	0.04254	0.02942	0.01986	0.01452	0.01467	0.76619
	Z-Factor						
Mod. EOS	1.0085	0.9324	0.8870	0.8742	0.8990	0.9290	
Experimental	0.985	0.911	0.881	0.882	0.916	0.943	
PVTSim	0.990	0.912	0.873	0.870	0.900	0.929	
	G_p						
Mod. EOS	0.00000	13.373	29.34	48.29	69.02	80.561	
Experimental	0.00000	12.812	29.341	49.110	69.907	81.220	
PVTSim	0.00000	12.890	29.050	48.410	69.370	81.010	
	Liquid Dropout (%)						
Mod. EOS	0.0	6.37	9.24	10.19	9.84	9.20	
Experimental	0.0	6.10	9.10	10.40	9.80	9.10	
PVTSim	0.0	6.28	10.39	11.16	10.06	9.03	

*Residual liquid composition
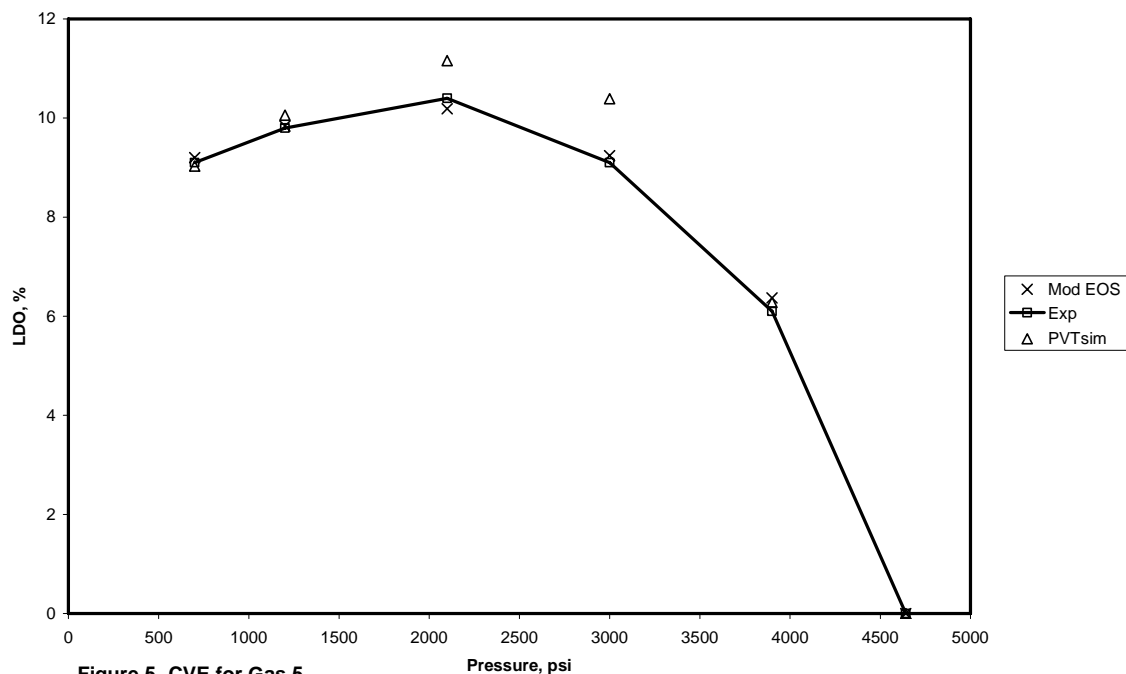
Figure 5- CVE for Gas 5

Crude Oil 1 – This oil, with the composition given in Table 3, exhibits a saturation pressure and density of 2,535 psia and 47.96 lb_m/ft^3 at 180°F. The modified model predicted excellent values for the bubblepoint pressure and saturation density of 2,501 psia and 47.68 lb_m/ft^3. The modified EOS is tested for its predictive ability by a simulating CCE test. Table 7 compares the predicted and adjusted liquid ratio V/V_s with the observed data. The observed average absolute deviation is 0.156%. Both models are in excellent agreement with the reported values

Table 7 – CCE for Oil 1 at 180°F

p	V/V_s		
(psig)	PVTSim	Mod. EOS	Experimental
5,000	0.9740	0.9739	0.9782
4,000	0.9832	0.9831	0.9662
3,000	0.9940	0.9940	0.9951
2,900	0.9952	0.9952	0.9961
2,800	0.9964	0.9964	0.9971
2,700	0.9977	0.9977	0.9982
2,600	0.9990	0.9990	0.9992
2,520	1.0000	1.0000	1.0000

Crude Oil 2 – This oil is characterized as volatile hydrocarbon system with a reported bubblepoint pressure, p_b, is 4,475 psia at 176°F. Table 8 compares the experimental differential values of R_{sbd}, B_{obd}, and oil density at the saturation pressure with those of the PVTSim and modified PR predicted values. PVTSim produced excellent match values at the saturation pressure as compared with the modified PR EOS. However; as shown in Table 9 and expressed graphically in Figures 6 and 7, the modified PR results compare extremely well with the DE test data. A further evaluation of the proposed modified EOS is presented in Table 10 for predicting CVE data on this volatile oil. Both models perform equally well in matching cumulative gas production G_P, however; both models failed reproduce acceptable match with the experimental gas deviation factor.

Table 8 – Observed and Predicted Data, Crude Oil 2

Approach	p_b (psia)	R_{sbd} (scf/STB)	B_{obd} (RB/STB)	ρ (lb_m/ft^3)
Experimental	4,475	3,377	2.921	33.10
PVTSim	3,344 (-25.3)	3345 (-0.95)	2.967 (-1.5)	31.10 (-6.0)
Modified EOS	4,502 (0.60)	3,019 (-7.9)	2.675 (-8.4)	33.99 (2.6)

*Numbers in parentheses represent percent error of predictions

Table 9- DE at 176°F for Oil 2

P	R_{sd} (scf/STB			B_{od} (RB/STB)		
(psig)	PVTSim	Mod. EOS	Experimental	PVTSim	Mod. EOS	Experimental
4,460.0	3345.1	3109	3,377	2.967	2.6736	2.921
4,000.0	2723.9	2401	2,351	2.605	2.3039	2.343
3,492.0	2085.4	1909	1,814	2.249	2.0563	2.059
3,003.0	1632.2	1540	1,471	2.004	1.8737	1.886
2,514.0	1265.2	1254	1,205	1.809	1.7351	1.756
2,004.0	985.7	1004	970	1.662	1.6145	1.645
1,534.0	711.4	805	775	1.516	1.5191	1.555
1,001.0	473.1	600	573	1.386	1.4201	1.464
505.0	313.5	409	383	1.291	1.3243	1.372
209.0	285	271	245	1.039	1.2490	1.298
0.0	0	0	000	1.000	1.0601	1.057
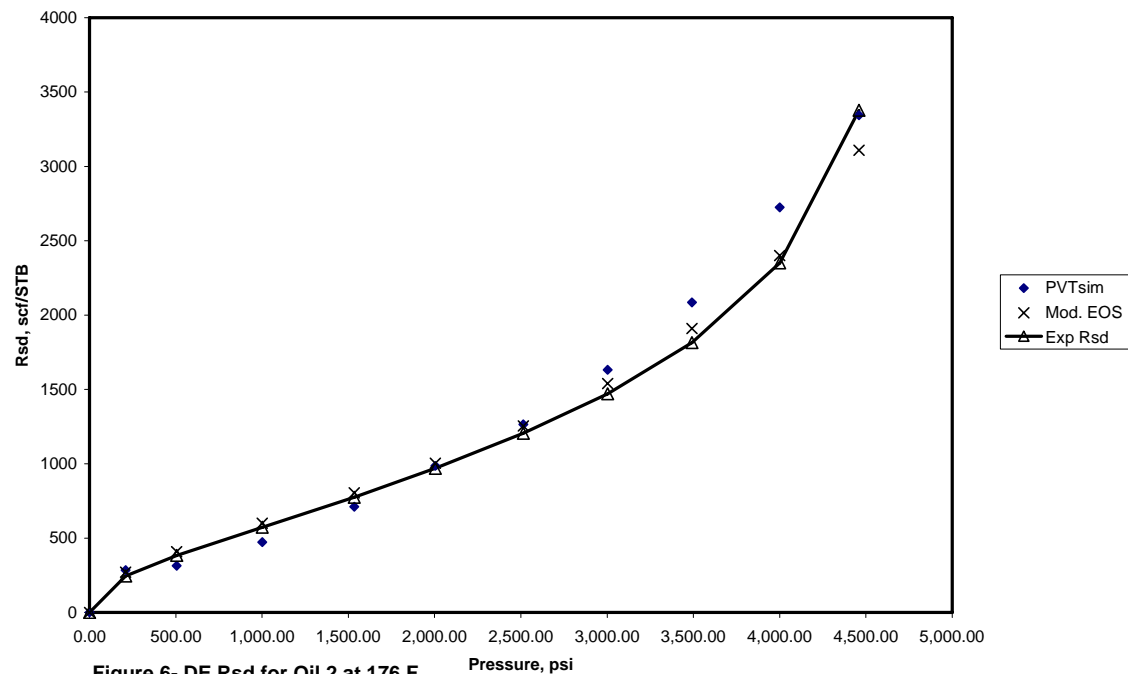
Figure 6- DE Rsd for Oil 2 at 176 F
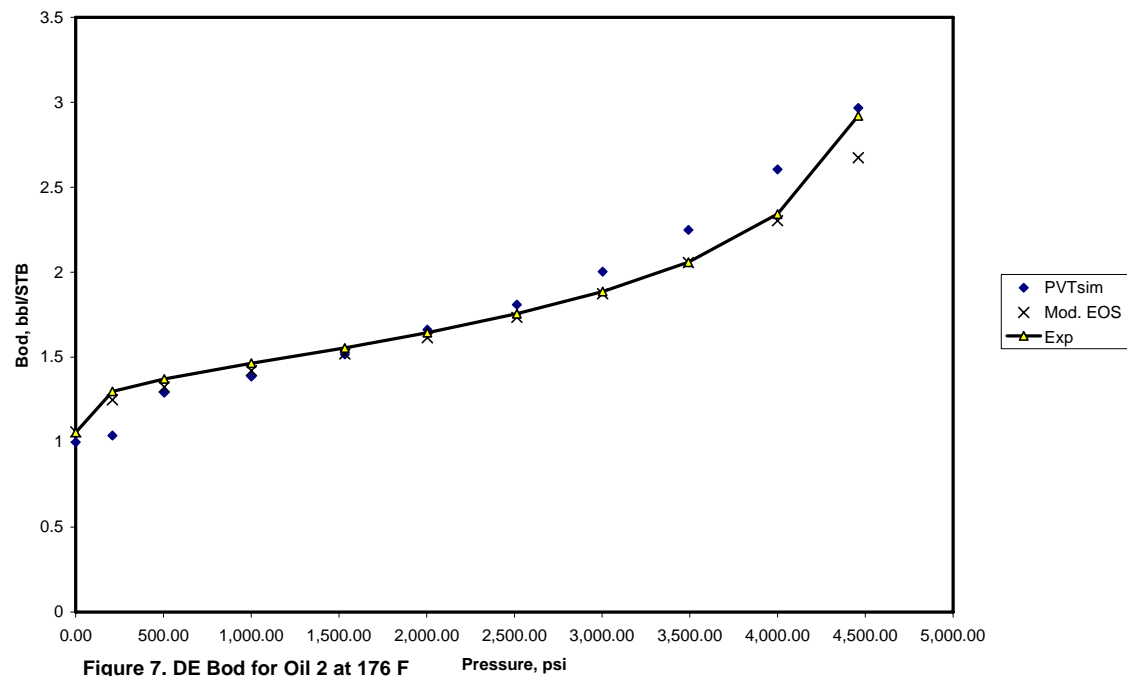
Figure 7. DE Bod for Oil 2 at 176 F

Table 10- CVE at 176°F for Oil 2							
	Pressure (psig)						
Component	4,460.0	3,600.0	2,800.0	2,000.0	1,200.0	600.0	600.0[*]
CO_2	0.00900	0.00984	0.01020	0.01074	0.01158	0.01256	0.00352
N_2	0.00300	0.00491	0.00479	0.00454	0.00405	0.00333	0.00020
C_1	0.53470	0.73509	0.74529	0.74678	0.73019	0.67668	0.08654
C_2	0.11460	0.11526	0.11767	0.12251	0.13386	0.15557	0.06976
C_3	0.08790	0.07183	0.07101	0.07187	0.07858	0.10006	0.10309
$I-C_4$	0.02280	0.01624	0.01548	0.01498	0.01568	0.02010	0.03705
$n-C_4$	0.02280	0.01474	0.01381	0.01311	0.01351	0.01739	0.04213
$I-C_5$	0.01045	0.00578	0.00514	0.00457	0.00434	0.00533	0.02363
$n-C_5$	0.01045	0.00541	0.00473	0.00411	0.00381	0.00461	0.02492
C_6	0.01510	0.00643	0.00526	0.00419	0.00348	0.00388	0.04092
C_{7+}	0.16920	0.01447	0.00662	0.00260	0.00092	0.00050	0.56822
	Gas Deviation Factors						
PVTSim	0.8900	0.8130	0.7820	0.7910	0.8370		
Mod. EOS	0.8388	0.8051	0.8011	0.8361	0.8899		
Experimental	0.798	0.783	0.788	0.843	0.913		
	G_ρ , %						
PVTSim	0.00	2.12	13.42	28.84	47.57	63.09	
Mod. EOS	0.00000	8.954	19.827	33.422	49.638	63.172	
Experimental	0.00000	7.535	17.932	32.371	49.908	63.967	

*Residual liquid composition

Crude Oil 3 – This CO_2 rich system contains 60 mol% CO_2. The hydrocarbon system exhibits a saturation pressure and density of 2,612 psia and 44.17 lb_m/ft^3 at 180°F. Coats and Smart "C-S" presented the results of CCE tests on the system at four different temperatures. Coats and Smart used 12 components system to match the saturation pressure over the reported range of temperatures used in the laboratory. The authors predicted saturation pressure values that are approximately 500 psi lower the experimental values. The tabulated values shown below compare the observed saturation pressures and densities at these four temperatures with those of the modified EOS and Coats and Smart 12 components system. The modified EOS shows excellent match with the oil saturation at the bubble point pressure

Observed and Predicted Data for Crude Oil 3

	Temperature (°F)			
	140	160	180	200
Exp.				
p_b	2,144	2,392	2,627	2,821
ρ_{ob}, lb_m/ft^3	45.9	45.1	44.2	43.3
C-S				
p_b	1,776 (-17)	-2,000 (-16.5)	2,210 (-16)	2,403 (-14.9)
ρ_{ob}, lb_m/ft^3	43.1 (-6)	42.3 (-6.2)	41.5 (-6.1)	40.6 (-6.2)
Mod. EOS				
p_b	2,082 (-2)	2,210 (-7.0)	2,304 (-12)	2,375 (-15.3)
ρ_{ob}, lb_m/ft^3	46.9 (2.2)	45.3 (0.5)	43.7 (-1.1)	41.8 (-3.4)

Numbers in Parentheses represent percent error of predictions

Crude Oil 4 – The reported experimental data available on the system includes differential expansion results at 110 and 250°F and CCE data at 110, 180 and 250°F. The system is slightly volatile with $B_{obd} = 1.671$ and $R_{sbd} = 932$ scf/STB at 250°F. Table 11 lists the predicted values for selected PVT properties as compared with the reported values at saturation pressures. Table 12 gives detailed documentation of results of predicting the DE data at the specified temperatures. With adjustment and in terms of the average absolute error, the model predicts R_{sd} and B_{od} data at 110°F within 3.5 and 0.77%, respectively. At 250°F, the equation gives results within 6% for R_{sd} and 3% for B_{od}.

Table 11 – Observed and Predicted Data, Crude Oil 4

	Temperature (°F)		
	110	180	250
Exp.			
p_b	1,988	2,313	2,577
R_s	701		932
B_{obd}	1,341		1,671
ρ_{ob}, lb_m/ft^3	44.4	42.4	40.3
C-S			
p_b	1,694 (-14.8)	2,033 (-12.1)	2,274 (-11.76)
R_{sbd}	611 (-12.8)		756 (-18.9)
B_{obd}	1.294 (-3.5)		1.517 (-9.2)
ρ_{ob}, lb_m/ft^3	40.0 (-9.9)	38.4 (9.4)	36.8 (-8.7)
Mod. EOS			
p_b	1,695 (-14.7)	2,330 (0.7)	2,655 (3.0)
R_{sbd}	694 (-0.9)		949 (1.8)
B_{obd}	1,323 (-1.3)		1.769 (5.9)
ρ_{ob}, lb_m/ft^3	44.8 (1.1)	41.96 (-1.0)	38.35 (-4.8)

Numbers in Parentheses represent percent error of the predictions

Table 12 – Expansion Data for Oil 4

DE at 110°F						
p	R_{sd} (scf/STB)			B_{od} (RB/STB)		
(psig)	PVTSim	Mod. EOS	Experimental	PVTSim	Mod. EOS	Experimental
1,958.0	720.0	694	701	1.368	1.3243	1.341
1,753.0	714.7	629	633	1.366	1.2990	1.313
1,557.0	639.8	570	577	1.333	1.2762	1.291
1,354.0	565.1	509	510	1.301	1.2524	1.264
1,153.0	493.8	450	450	1.270	1.2293	1.240
949.0	423.8	391	389	1.239	1.2063	1.217
748.0	356.9	334	330	1.210	1.1839	1.193
548.0	291.5	278	270	1.181	1.1616	1.168
347.0	225.4	220	209	1.151	1.1382	1.144
157.0	155.4	158	143	1.117	1.1120	1.116
75.0	117.2	123	106	1.097	1.0963	1.097
0.0	0.0	000	000	1.015	1.0234	1.024

| DE at 250°F						
2,547.0	1010.2	948	943	1.724	1.7678	1.671
2,360.0	931.8	863	865	1.680	1.7168	1.636
2,143.0	846.6	784	788	1.633	1.6712	1.595
1,893.0	755.1	690	704	1.583	1.6157	1.553
1,645.0	670.3	604	625	1.536	1.5644	1.512
1,393.0	589.4	522	548	1.491	1.5160	1.473
1,150.0	515.5	450	477	1.450	1.4720	1.436
895.0	441.0	376	407	1.408	1.4275	1.401
647.0	370.2	307	338	1.367	1.3846	1.365
400.0	297.5	237	265	1.323	1.3387	1.326
182.0	219.5	163	190	1.270	1.2858	1.275
87.0	170.0	120	146	1.232	1.2504	1.243
0.0	0.0	000	000	1.054	1.124	1.094
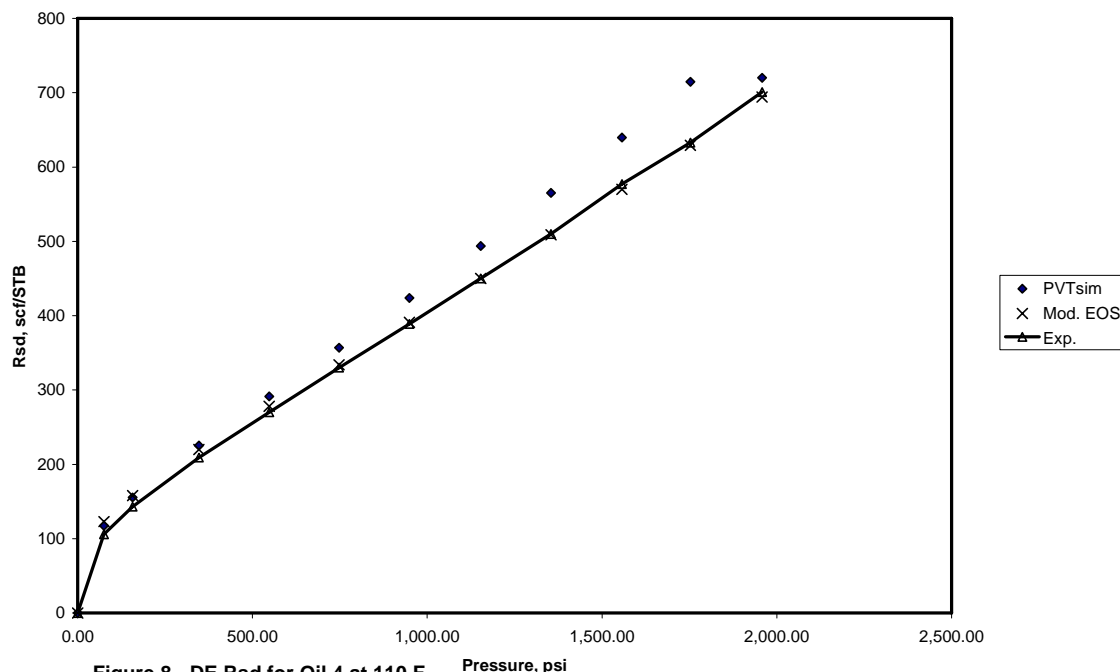
Figure 8- DE Rsd for Oil 4 at 110 F

Crude Oil 6 – This oil exhibits a saturation pressure of 2,746 psia at 234°F. Table 13 gives the reported R_s and B_o and ρ_o at the bubblepoint pressure compared with the predicted results. Table 14 shows DE data calculated by the EOS before and after adjustment. (For detailed results of CCE data, see Table 6 of Reference 20). In a prediction mode, the modified expression reproduced the entire solution GOR and relative oil volume data with average absolute errors of 6.3 and 1.7%, respectively. (See Table 7 of Reference 20 for CCE predicted data).

Table 13 – Observed and Predicted Data, Crude Oil 6

Approach	p_b (psia)	R_{sbd} (scf/STB)	B_{obd} (RB/STB)	ρ (lb_m/ft^3)
Experimental	2,746	1.230	1,866	38.0
Coats-Smart	2,398 (-12.7)	1,002 (-19)	1,659 (-11.1)	35.6 (-6.3)
Modified EOS	2,916 (6.2)	1,233 (0)	1,909 (2.3)	37.40 (-1.6)

Table 14 – Expansion Data for Oil 6

p	R_{sbd} (scf/STB)			B_{obd} (RB/STB)		
(psig)	PVTSim	Mod. EOS	Experimental	PVTSim	Mod. EOS	Experimental
2,746.0	1,321.0	1,232	1,230	1.917	1.9053	1.866
2,598.0	1,288.0	1,142	1,151	1.898	1.8514	1.821
2,400.0	1,178.5	1,048	1,059	1.836	1.7981	1.771
2,200.0	1,076.1	947	972	1.778	1.7385	1.725
1,897.0	934.1	806	849	1.698	1.6562	1.658
1,600.0	807.3	686	737	1.627	1.5864	1.599
1,300.0	688.9	576	631	1.560	1.5222	1.543
1,000.0	577.7	474	529	1.497	1.4624	1.488
700.0	470.1	377	428	1.434	1.4032	1.433
394.0	355.4	273	321	1.363	1.3374	1.371
195.0	265.7	194	231	1.302	1.2826	1.313
112.0	215.9	152	178	1.265	1.2510	1.274
0.0	0.0	000	000	1.052	1.1079	1.086

The "DE at 234°F" header spans the entire table above the column structure.
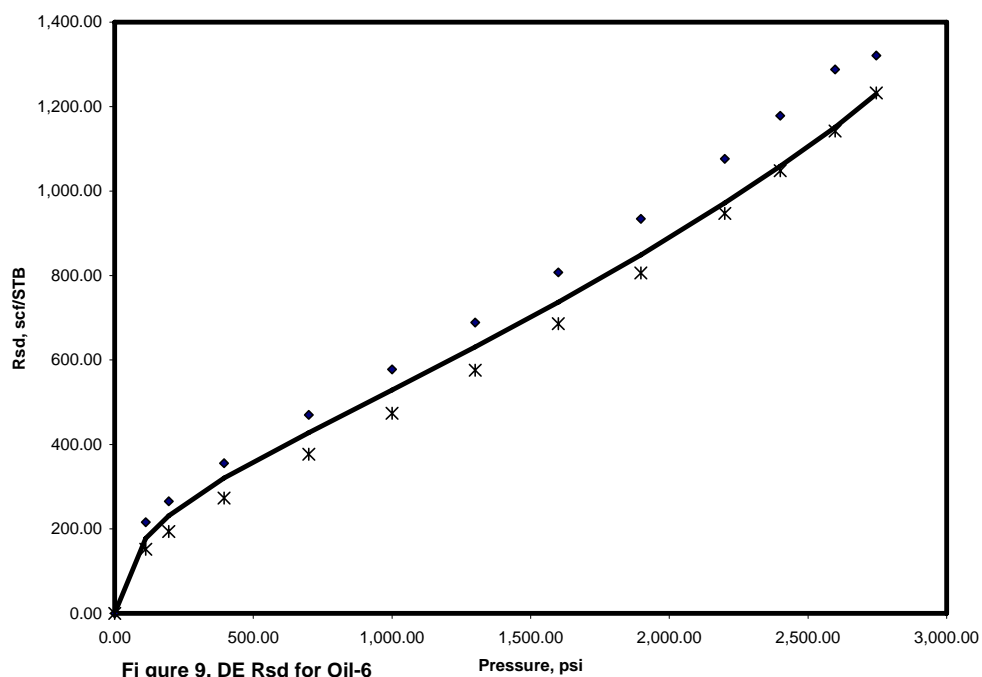
Fi gure 9. DE Rsd for Oil-6
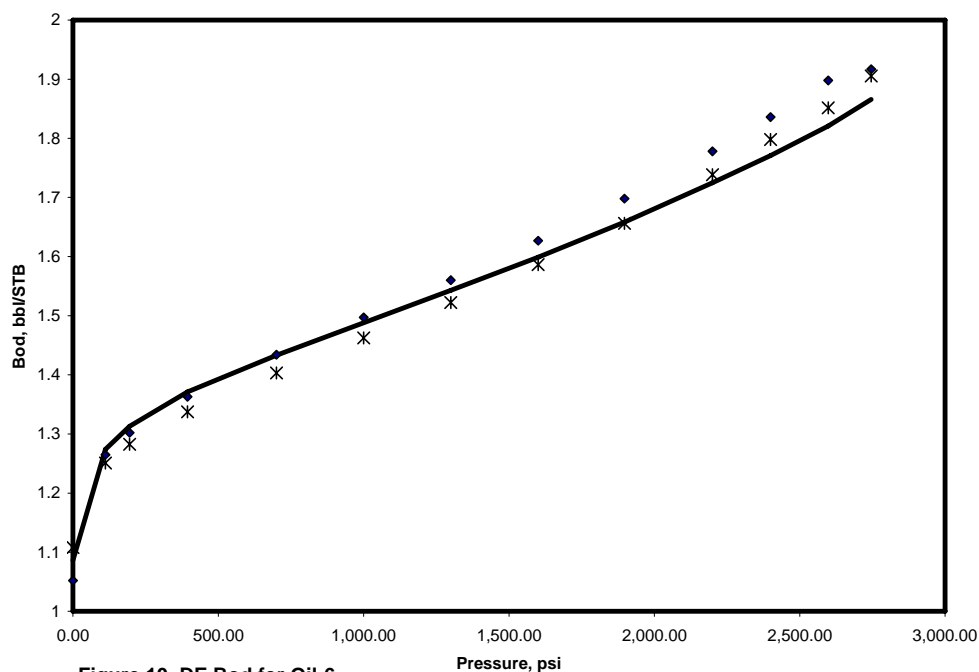
Figure 10. DE Bod for Oil-6

Crude Oil 7 – This hydrocarbon system is the least volatile of the oil samples in the Coats and Smart study. The oil shows a bubblepoint of 1,709 psia and a saturation density of 44.5 lb_m/ft^3 at 131°F. Table 15 shows the predicted PVT properties at saturation pressure compared with the experimental and Coats-Smart model data. Table 16 compares measures DE data with those simulated with both; the modified PREOS PVTSim model. The modified EOS reproduced the observed PVT with average deviations of 7.5% and 1.7% for R_{sd} and B_{od}, respectively.

Table 15 – Observed and Predicted Data, Crude Oil 7

Approach	p_b (psia)	R_{sbd} (scf/STB)	B_{obd} (RB/STB)	ρ (lb$_m$/ft^3)
Experimental	1,709	557	1,324	44.5
Coats-Smart	1,531 (-10.4)	542 (-2.7)	1,296 (-2.10)	40.7 (-8.5)
Modified EOS	1,572 (-8.0)	624 (12.0)	1,346 (1.7)	45.0 (1.1)

Numbers in parentheses represent percent error of predictions

Table 16 – Expansion data for Oil 7

DE at 131°F						
p	R_{sd} (scf/STB)			B_{od} (RB/STB)		
(psig)	PVTSim	Mod. EOS	Experimental	PVTSim	Mod. EOS	Experimental
1,694.0	641.2	624	557	1.369	1.3472	1.324
1,550.0	602.8	587	526	1.352	1.3321	1.311
1,400.0	562.9	550	493	1.334	1.3168	1.298
1,252.0	523.7	513	460	1.317	1.3013	1.285
1,100.0	483.3	475	423	1.299	1.2853	1.270
950.0	443.3	437	389	1.280	1.2694	1.256
798.0	402.3	398	349	1.262	1.2529	1.240
643.0	359.9	358	310	1.242	1.2357	1.224
500.0	319.8	320	273	1.223	1.2192	1.209
350.0	275.4	278	229	1.202	1.2005	1.188
200.0	224.2	230	179	1.175	1.1779	1.160
102.0	178.5	188	137	1.149	1.1562	1.136
0.0	000	000	000	1.017	1.0328	1.034

Red River Crude Oil System – The crude oil system of the Red River Field (Montana) is slightly volatile with B_{obd} = 1.706 and R_{sbd} = 921 at 250°F. The modified equation reproduced the observed B_{od} and R_{sd} with average deviations of 5.1 and 4.3%, respectively. The PVT properties of the crude oil system at saturation pressure were p_b = 2,392 psia, R_{sbd} = 921 scf/STB, B_{obd} = 1.706 RB/STB, and ρ = 38.13 lb$_m$/ft^3. Those predicted by the modified EOS were p_b = 2,497 psia, R_{sd} = 1,061 scf/STB, B_{obd} = 1.8973 RB/STB, and ρ = 36.2 lb$_m$/ft^3 for errors of 4.4, 15.2, 11.2 and -5.0% for p_b, R_{sd}, B_{od} and ρ, respectively. Table 17 gives detailed documentation of stimulated DE test for the system. PVTSim and modified give values for B_{od} that are considerably higher than the observed data, however; both models match with the CCE data equally well. In terms of R_{sd}, the modified EOS performed much better than PVTSim in the rang of all the pressures used in conducting the test.

Table 17 – Expansion Data for Red River Crude Oil

DE at 250°F						
p	R_{sd} (scf/STB)			B_{od} (RB/STB)		
(psig)	PVTSim	Mod. EOS	Experimental	PVTSim	Mod. EOS	Experimental
2,377.0	1,146.3	1,060	921	1.849	1.8947	1.706
2,250.0	1,081.5	982	872	1.811	1.8428	1.678
1,950.0	939.0	836	761	1.728	1.7509	1.614
1,650.0	809.5	698	657	1.653	1.6622	1.555
1,350.0	690.3	577	561	1.584	1.5843	1.501
1,050.0	578.5	469	467	1.518	1.5144	1.448
750.0	470.9	366	375	1.453	1.4470	1.395
450.0	360.9	266	274	1.384	1.3780	1.334
225.0	265.7	183	191	1.319	1.3170	1.279
125.0	212.0	139	140	1.279	1.2822	1.241
0.0	0.0	000	000	1.059	1.1341	1.102

Wyoming's Heavy Crude Oil, Teapot Dome Field – This heavy oil contains 9.61 mol% C_1 and 75.01 mol% C_{7+}. The plus fraction is characterized by a molecular weight of 223.5 and a specific gravity of 0.8429. The oil exhibits a bubblepoint of 505 psia at 162°F. The PVT properties were p_b = 505 psia, R_{sbd} = 110 scf/STB, B_{obd} = 1.1098 RB/STB, and ρ = 48.77 lb$_m$/ft^3. The model predicted p_b = 520 psia, R_{sbd} = 113 scf/STB, B_{obd} = 1.1060 RB/STB, and ρ = 48.77 lb$_m$/ft^3 with errors of 2.97, 2.7, 0.34, and 0% for p_b, R_{sbd}, B_{obd} and ρ, respectively. Table 18 shows the close match with the reported data.

Table 18 – Expansion Data for Teapot Dome Crude Oil

P, (psig)	Mod. EOS R_{sd}, scf/STB	Experimental R_{sd}, scf/STB	Mod. EOS B_{od}, RB/STB	Experimental B_{od}, RB/STB
490.3	113	110	1.1060	1.1098
385.3	97	94	1.0991	1.1025
285.3	80	77	1.0920	1.0962
185.3	63	58	1.0840	1.0886
85.3	42	36	1.0740	1.0782
35.3	28	23	1.0665	1.0701
0.0	00	00	1.0481	1.0491

North Sea Gas-Condensate System – The system is characterized by a dewpoint of 6.750 psia at 280°F. The gas contains 73.19 mol% C_1 and 8.21 mol% C_{7+}. The plus fraction is characterized by a molecular weight of 148 and a specific gravity of 0.16. The maximum liquid dropout with a value of 21.6% occurs at 3,100 psia. Whitson and Torp[10] gave a detailed compositional and experimental analysis of the system. The modified equation predicts a dewpoint pressure of 6,189 psia. Table 19 gives complete results of the CVE simulation. The tabulated values show that the EOS predicts the entire liquid dropout and Z-factor data with average absolute deviations of 4.7 and 1.8%, respectively. Results of the model are generally in excellent agreement with reported data.

Table 19 – CVE at 280°F for the North Sea Reservoir

Component	6,750.0	5,500.0	4,300.0	3,100.0	2,100.0	1,200.0	700.0	700.0*
	Pressure (psig)							
CO_2	0.02370	0.02379	0.02399	0.02438	0.02493	0.02568	0.02630	0.00748
N_2	0.00310	0.00320	0.00327	0.00334	0.00338	0.00337	0.00332	0.0037
C_1	0.73190	0.75710	0.77263	0.78619	0.79345	0.79296	0.78412	0.10353
C_2	0.07800	0.07950	0.08034	0.08126	0.08227	0.08376	0.08523	0.02357
C_3	0.03550	0.03574	0.03577	0.03585	0.03619	0.03730	0.03903	0.01904
$I-C_4$	0.00710	0.00706	0.00700	0.00694	0.00696	0.00721	0.00774	0.00600
$n-C_4$	0.01450	0.01426	0.01403	0.01381	0.01379	0.01438	0.01570	0.01572
$I-C_5$	0.00640	0.00620	0.00601	0.00580	0.00569	0.00590	0.00659	0.01079
$n-C_5$	0.00680	0.00652	0.00627	0.00600	0.00583	0.00604	0.00682	0.01355
C_6	0.01090	0.01023	0.00964	0.00893	0.00839	0.00847	0.00966	0.03245
C_{7+}	0.08210	0.05641	0.04105	0.02749	0.01912	0.01492	0.01549	0.76750
	Z- Factor							
PVTSim	1.225	1.068	0.966	0.913	0.904	0.922	0.943	
Mod. EOS	1.2380	1.0890	0.9720	0.9130	0.9140	0.9370	0.9600	
Experimental	1.2618	1.1105	0.9958	0.9239	0.9029	0.9182	0.9407	
	$G_{p\,(\%)}$							
PVTSim	0.00000	9.310	21.89	38.620	55.42	71.920	81.270	
Mod. EOS	0.00000	9.024	21.744	38.674	55.686	72.146	81.301	
Experimental	0.00000	9.512	21.782	38.093	54.800	71.473	80.940	
	Liquid Dropout (%)							
PVTSim	0.0	9.31	22.52	23.52	22.19	20.20	18.85	
Mod. EOS	0.0	14.10	19.70	21.60	21.30	20.20	19.30	
Experimental	0.0	12.89	19.07	20.92	20.56	19.23	18.13	

Conclusions

1. Improved correlations for calculating $a(T_c)$, b, and $\alpha(T)$ of the plus fraction, methane, and nitrogen are presented.
2. The modified PREOS gives hydrocarbon liquid density predictions that are compatible with or better than, the S-K and the A-K density correlations.
3. The proposed modifications eliminate the need for splitting the heptanes-plus fraction into pseudo-components.
4. The proposed modifications significantly improve the ability of the PREOS to predict the PVT properties of complex hydrocarbon mixtures.

5. With such significant improvement in the predictive capability of the modified EOS, the equation is recommended for calculating the volumetric behavior of crude oil and condensate systems

Nomenclature

a, b, A, B	= EOS constants
B_o	= oil FVF obtained from differential expansion, RB/STB
B_{ob}	= oil FVF at bubblepoint pressure, RB/STB
J_L	= volume fraction of liquid in expansion cell
G_p	= volume fraction of gas removed from a laboratory CVE cell
k_{ij}	= binary interaction coefficient between Components i and j
m	= characteristic constant
M	= molecular weight, lbm/lbm mol
p	= pressure, psi
p_b	= bubblepoint pressure, psi
p_c	= critical point, psi
p_s	= saturation pressure, psi
R	= universal gas constant, 10.73 psia ft^3/mol °R
R_s	= solution GOR obtained from differential expansion, scf/STB
T	= temperature, °R
T_c	= critical temperature, °R
V	= laboratory expansion cell total volume, ft^3
V_L	= volume of liquid in expansion cell, ft^3
V_m	= molar volume
V_s	= volume of expansion cell at saturation pressure, ft^3
x	= mole fraction
z	= compressibility factor
α	= correction factor for a
γ	= specific gravity
ρ	= density, lbm/ft^3
$ρ_{ob}$	= density at bubblepoint, lbm/ft^3
ω	= acentric factor
$Ω_a$, $Ω_b$	= EOS constants

Subscripts

c	= critical
i, j	= component number
mix	= mixture
o	= oil
ob	= bubblepoint

References

1. van der Waals, J.D.: "On the Continuity of the Liquid and Gaseous State," PhD dissertation, Sigthoff U. Leiden (1873)
2. Peng, D.Y. and Robinson, D.B.: "A New Two-Constant Equation of State," Ind. & Eng. Chem. (1976) 15, No. 1, 59-64
3. Soave, G.: "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," Chem. Eng. Sci. (1972) 27, 1197-1203
4. Coats, K.H. and Smart, G.T.: "Application of a Regression Based EOS PVT Program to Laboratory Data," SPERE (May 1986) 277-99.
5. Wilson, A., Maddox, R.N. and Erbar, J.H.: "C Fractions Affect Phase Behavior," Oil & Gas J. (Aug. 21, 1978) 76-81
6. Katz, D.L. and Firoozabadi, A.: "Predicting Phase Behavior of Condensates/Crude Oil Systems Using Methane Interaction Coefficients," JPT (Nov. 1978) 1649-55; Trans., AIME 265
7. Firoozabadi A., Hekim, Y., and Katz, D.L.: "Reservoir Depletion Calculations for Gas Condensates Using Extended Analyses in the Peng-Robinson Equation of State," Cdn. J. Chem. Eng. (1978) 56, 610-15
8. Yarborough, L.: "Application of a Generalized Equation of State to Petroleum Reservoir Fluids," Equations of State in Engineering, Advances in Chemistry Series, K.C. Choa and R.L. Robinson (eds.), American Chemical Soc., Washington DC (1979) 182, 385-435
9. Whitson, C.H.: "Characterizing Hydrocarbon Plus Fractions," SPEJ (Aug. 1983) 683-94
10. Whitson, C.H. and Torp, S.B.: "Evaluating Constant Volume Depletion Data: JPT (March 1983) 610-20

11. Lohrenz, J., Bray, B.G., and Clark, C.R.: "Calculating Viscosities of Reservoir Fluids From Their Compositions," JPT (Oct. 1964) 1171-76; Trans., AIME 231

12. Katz, D.L.: "Overview of Phase Behavior in Oil and Gas Production," JPT (June 1983) 1205-14

13. Ahmed, T., Cady, G., and Story, A.: "An Accurate Method of Extending the Analysis of C_{7+}," paper SPE 12916 presented at the 1984 SPE Rocky Mountain Regional Meeting, Casper, WY, May 21-23

14. Ahmed, T., Cady, G. and Story, A.: "A Generalized Correlation for Characterizing the Hydrocarbon Heavy Fractions," paper SPE 14266 presented at the 1985 SPE Annual Technical Conference and Exhibition, Las Vegas, Sept. 22-25

15. Kenyon, D. and Behie, G.: "Third SPE Comparative Solution Project: Gas Cycling of Retrograde Condensate Reservoirs," JPT (Aug. 1987) 981-97

16. Riazi, M.R. and Daubert, T.E.: "Characterization Parameter for Petroleum Fractions," Ind. & Eng. Chem. Res. (197) 26, No. 4

17. Petersen, C.S.: "A Systematic and Consistent Approach to Determine Binary Interaction Coefficients for the Peng-Robinson Equation of State," SPERE (Nov. 1989) 488-96

18. Standing, M.B. and Katz, D.L.: "Density of Crude Oils Saturated with Natural Gas," Trans., AIME (1942) 146, 150-65

19. Alani, G.H. and Kennedy, H.T.: "Volumes of Liquid Hydrocarbons at High Temperatures and Pressure," Trans., AIME (1960) 219, 288-92

20. Ahmed, T.: "Supplement to a Practical Equation of State," SPE 22219 available from SPE Book Order Dept., Richardson, TX.

SI Metric Conversion Factors

bbl	x	1.589 873	E^{-01}	$= m^3$
ft^3	x	2.831 685	E^{-02}	$= m^3$
°F	(°F-32)/1.8			=°C
lbm	x	4.535 924	E^{-01}	= kg
psi	x	6.894 757	E^{+00}	= kPa