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Critical Properties Estimation From an Equation of State

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ABSTRACT

This paper describes a new method for calculating critical properties of petroleum fractions used as input to a cubic equation of state (EOS). The method differs from existing methods in that it forces the EOS to match measured values of boiling point and molar volume (molecular weight divided by specific gravity) for each petroleum fraction.

PVT predictions are made with the proposed method using the Peng/Robinson EOS for selected reservoir fluids reported in the literature. Saturation pressure and saturated density are calculated with the EOS and compared with experimentally determined values. Heptanes-plus (C_{7+}) fractions are characterized using the proposed method and results indicate that both volumetric and phase behavior are improved. Reservoir fluids used in the study represent a wide range of compositions with PVT properties reported at temperatures ranging from 38-120 °C.

A new method is suggested for matching experimental saturation pressure with an EOS. Using the proposed method for calculating critical properties, the boiling point of the heaviest petroleum fraction is adjusted until mixture saturation pressure is matched. A near-linear relation exists between boiling point of the heaviest fraction and saturation pressure. It is suggested that this method has more physical meaning than the common practice of adjusting methane binary interaction coefficients.

Proposed methods can be used with any cubic EOS. Critical properties are presented graphically for the Peng/Robinson and Soave/Redlich/Kwong equations. A generalized form of the two-constant cubic EOS is proposed, and necessary expressions for phase and volumetric calculations are given. The critical-property method is diagrammed schematically to facilitate programming. It can be easily incorporated into existing PVT software already based on an EOS.

References and illustrations at end of paper.

INTRODUCTION

Cubic equations of state are used to calculate volumetric and phase behavior of petroleum reservoir fluids. Input data required by an equation of state (EOS) usually includes critical pressure, critical temperature, and acentric factor of each component in the mixture. For pure compounds these properties are known. Critical properties must be estimated for the petroleum fractions making up heptanes-plus. Having defined critical properties for all the components in a mixture the EOS can be used to predict PVT properties.

This paper proposes a new method for calculating critical properties of petroleum fractions. The method requires normal boiling point and molar volume for each petroleum fraction. The EOS chosen is forced to fit the boiling point and molar volume by adjusting critical pressure and critical temperature. Acentric factor is estimated by an empirical correlation using boiling point and molar volume; this correlation is general and does not depend on the EOS.

¹⁶ Whitson reviews the most common empirical correlations used for estimating critical properties of petroleum fractions. He studies the effect of C_{7+} characterization on EOS predictions and concludes that none of the existing correlations gives consistently better PVT predictions. Observations from this earlier work led to the idea that an alternative approach could be used for defining critical properties of individual petroleum fractions based on the EOS used for mixture calculations.

In this work EOS predictions are compared with experimental PVT data and results indicate that the proposed method gives improved VLE and phase densities. PVT data for reservoir fluids have been taken from the literature (Refs. 3,8,9). They include fluid compositions and detailed C₇₊ description, saturation pressures and phase densities. The fluids have a wide range in compositions and measured PVT data are reported at several temperatures. Neither composition or temperature variation appear to affect the reliability of the proposed method. Also, the traditional method of adjusting binary interaction coefficients to fit saturation pressure is replaced by a new method of adjusting the boiling point of the C₇₊ residue (heaviest petroleum fraction).

The Peng/Robinson¹⁰ (PR) EOS has been used exclusively in this study, though the method is equally applicable to other two-constant¹³ cubic equations such as the Soave-Redlich-Kwong EOS. The method is not recommended for the modified Redlich-Kwong EOS proposed by Zudkevich and Joffe (see also Yarborough).

Since the critical property method is based on manipulation of a cubic EOS, the first section reviews the basic calculation procedures for solving an EOS for a single component. A generalized form of the two-constant cubic equation is given to make the method readily applicable to any EOS. By specifying a numerical constant, λ , and the universal critical compressibility factor, Z_c , the general EOS reduces to any two-constant cubic equation.

Equation of State Theory

Martin shows that almost all cubic equations can be generalized by a four-constant EOS. The pressure-explicit form of the equation is written,

$$p = \frac{RT}{(v-b)} - \frac{a}{(v-b+c)(v-b+d)} \quad \dots\dots\dots (1)$$

where p = pressure, T = temperature, v = molar volume, and R = universal gas constant. Constants a , b , c , and d define the EOS and they can be determined by (1) defining thermodynamic conditions or (2) fitting the equation to experimental data. Eq. 1 states that pressure results from the interaction of repulsive forces, $RT/(v-b)$, and attractive forces, $a/(v-b+c)(v-b+d)$.

The first cubic equation of state was proposed by van der Waals in 1873² and results from Eq. 1 if $b=c=d$, or $p=RT/(v-b)-a/v$. van der Waals chose two thermodynamic criteria for defining EOS constants. They have since been named van der Waals (VDW) critical criteria which, stated mathematically, require that first and second derivatives of pressure with respect to volume equal zero: $(\partial p/\partial v) = (\partial^2 p/\partial v^2) = 0$ at T_c and p_c .

In Fig. 1 pressure is plotted versus volume for a pure compound at several temperatures. On the critical temperature isotherm the slope equals zero at (v_c, p_c) and it does not change sign at the inflection point. These two graphical observations are equivalent to the VDW's criteria stated mathematically above.

Expressing an EOS in terms of pressure is awkward for practical purposes because volume is usually the unknown, while pressure and temperature are measured quantities defining the state of the system. To solve an EOS in terms of volume the compressibility factor, Z , is usually introduced as a shorthand for $p v/RT$ - i.e.,

$$Z = p v/RT$$

$$v = ZRT/p \quad \dots\dots\dots (2)$$

$$\rho = pM/ZRT$$

where ρ is density expressed as mass per unit volume (e.g., kg/m³).

The Z-explicit form of Eq. 1 is

$$\begin{aligned} Z^3 + Z^2\{-3B + (C+D-1)\} \\ + Z\{3B^2 - 2B(C+D-1) + (A+CD-C-D)\} \\ + \{-B^3 + B^2(C+D-1) - B(A+CD-C-D) - CD\} = 0 \end{aligned} \quad \dots\dots\dots (3)$$

where a new set of EOS constants A , B , C , and D are expressed as

$$A = a \cdot p/R^2 T^2 = \alpha \cdot \Omega_a \cdot p_r/T_r^2 \quad \dots\dots\dots (4a)$$

$$B = b \cdot p/RT = \Omega_b \cdot p_r/T_r \quad \dots\dots\dots (4b)$$

$$C = c \cdot p/RT = \Omega_c \cdot p_r/T_r \quad \dots\dots\dots (4c)$$

$$D = d \cdot p/RT = \Omega_d \cdot p_r/T_r \quad \dots\dots\dots (4d)$$

where $T_r = T/T_c$ and $p_r = p/p_c$. Eqs. 4 are definitions which ease the mathematics used to develop an EOS.

In Eq. 1 the undefined EOS constants were a , b , c , and d . For Eqs. 4 the EOS constants are now Ω_a , Ω_b , Ω_c , and Ω_d , numerical constants which will be defined using the VDW critical criteria and the assumption that Ω_c is proportional to Ω_b , i.e., $\Omega_c = \lambda \cdot \Omega_b$, where λ is a numerical constant.

The conditions defining Ω constants are then

$$\partial p / \partial v = 0 \quad \dots\dots\dots (5a)$$

$$\partial^2 p / \partial v^2 = 0 \quad \dots\dots\dots (5b)$$

$$Z = Z_c = \text{constant} \quad \dots\dots\dots (5c)$$

$$\Omega_c = \lambda \cdot \Omega_b \quad \text{where } \lambda = \text{constant} \quad \dots\dots\dots (5d)$$

Eqs. 5a-5c apply at the critical point defined by T_c and p_c , and can be written in shorthand as $(Z - Z_c) = 0$. The last constraint, Eq. 5d, is chosen so that the general EOS can be easily simplified to the most common two- and three-constant equations. Results of algebraic manipulation shows that Ω constants are defined by:

$$\begin{aligned} \Omega_b^3 - \Omega_b^2(\lambda^2 - 3\lambda + 3Z_c) + \Omega_b(\lambda - 3\lambda Z_c + 3Z_c^2) \\ - Z_c^3 = 0 \quad \dots\dots\dots (6a) \end{aligned}$$

$$\Omega_d = \Omega_b(3 - \lambda) - 3Z_c + 1 \quad \dots\dots\dots (6b)$$

$$\begin{aligned} \Omega_a = \Omega_b^2(\lambda^2 - 3\lambda + 3) + \Omega_b(3\lambda Z_c - \lambda - 6Z_c + 3) \\ + (3Z_c^2 - 3Z_c + 1) \quad \dots\dots\dots (6c) \end{aligned}$$

The smallest root of Eq. 6a is chosen for Ω_b . Ω_d and Ω_a follow from Eqs. 6b and 6c, while Ω_c is defined by Eq. 5d. Z_c is the universal critical compressibility factor which is assumed to be the same for all compounds. By specifying λ and Z_c the EOS is defined, for example the RK and PR equations,

$$\text{RK EOS : } \lambda = 1 \text{ or } 2 \text{ and } Z_c = 1/3 \quad (7)$$

$$\text{PR EOS : } \lambda = 2 \mp \sqrt{2} \text{ and } Z_c = 0.307401\dots$$

Returning to Eq. 4a, the term α is a correction to EOS constant Ω_a to ensure accurate VLE predictions of pure compounds. α is temperature dependent and acentric factor, ω , is typically used to correlate variation in temperature dependence for compounds of varying species. Both the SRK and PR EOS's use the correction factor for Ω_a , resulting in the complete definitions of their respective equations:

Soave/Redlich/Kwong (SRK)

$$\lambda = 1 \text{ (or } 2)$$

$$Z_c = 1/3$$

$$\sqrt{\alpha} = 1 + m(1 - \sqrt{T_r})$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad \dots\dots\dots (8)$$

Peng/Robinson (PR)

$$\lambda = 2 - \sqrt{2} \text{ (or } 2 + \sqrt{2})$$

$$Z_c = 0.307401 \dots$$

$$\sqrt{\alpha} = 1 + m(1 - \sqrt{T_r})$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad \dots\dots\dots (9)$$

To complete the development of Eq. 1 it is necessary to express fugacity, f , for single and multicomponent systems. Without introducing the formal definition of fugacity it can be visualized by referring to Fig. 1. The subcritical isotherm labeled T_b has a cubic form. The pressure which divides the loop into two sections with equal area (shaded) is the vapor pressure for the temperature defining the isotherm. This equilibrium condition is also satisfied when component fugacities for vapor and liquid equal one another - i.e., $f_v = f_L$. At equilibrium conditions the vapor (which is represented by the volume solution at the right) is as content being a vapor as the liquid (which is represented by the volume at the left) is content being a liquid.

For a single-component system the fugacity of a given phase is,

$$\ln(f/p) = -\ln(Z-B) + \frac{B}{Z-B} + \frac{A}{D-C} \left\{ \frac{B-D}{Z-B+D} + \frac{C-B}{Z-B+C} \right\}$$

$$+ \frac{A}{C-D} \ln\left(\frac{Z-B+D}{Z-B+C}\right) \quad \dots\dots\dots (10)$$

Fugacity of a single component system is calculated by first specifying the critical pressure, critical temperature, and acentric factor. Defining the state with pressure and temperature, Eqs. 4 are used to calculate A , B , C , and D , and Eq. 3 is solved for Z . If only one solution exists then fugacity is not of interest. If three solutions are found then the smallest Z is defined as liquid and the largest Z is defined as vapor. Eq. 10 is solved for fugacity of each phase and if $f_v = f_L$ then the pressure and temperature define an equilibrium point on the vapor pressure curve.

For a single component in a mixture the fugacity is given by,

$$\ln(f_i/z_{ip}) = -\ln(Z-B) + \frac{B_i}{Z-B} + \frac{A}{D-C} \left\{ \frac{B_i-D_i}{Z-B+D} + \frac{C_i-B_i}{Z-B+C} \right\} \\ + \left\{ \frac{2 \sum_j z_j A_{ij}}{(C-D)} + \frac{A(D_i-C_i)}{(C-D)^2} \right\} \ln \left(\frac{Z-B+D}{Z-B+C} \right) \quad \dots (11)$$

where $A_{ij} = \sqrt{A_i A_j}$. A, B, C, and D represent mixture averages calculated using the following mixing rules:

$$A = \sum_i \sum_j z_i z_j A_{ij} (1-k_{ij}) \quad \dots (12a)$$

$$B = \sum_i z_i B_i \quad \dots (12b)$$

$$C = \sum_i z_i C_i \quad \dots (12c)$$

$$D = \sum_i z_i D_i \quad \dots (12d)$$

where z_i is mole fraction of the phase and k_{ij} are binary interaction coefficients. Fugacity calculations for mixtures are complicated and they will not be covered here since the method for determining critical properties based on an EOS only requires fugacity calculation for single-component systems.

EOS Critical Property Estimation

The traditional method for estimating critical properties of petroleum fractions is illustrated in Fig. 2A. The first step is to determine or estimate normal boiling point, T_b , specific gravity, γ , and molecular weight, M , of each fraction. Empirical correlations are chosen to estimate critical temperature, T_c , critical pressure, p_c , and acentric factor, ω . Usually it is sufficient to specify T_b and γ for such correlations. Estimated values T_c , p_c , and ω for petroleum fractions are input into the EOS together with known values for pure compounds. Mixture phase behavior and volumetric calculations are performed as necessary. Composition, temperature, and pressure are usually the data defining the state of the system.

One might ask why the EOS is not used to check, for an individual petroleum fraction, if the EOS-calculated boiling point and specific gravity (i.e., molar volume, M/γ) match the measured values. It seems reasonable that if the EOS does in fact match measured T_b and M/γ data then mixture behavior also will be predicted with reasonable accuracy. The proposed method requires the selected EOS to match T_b and M/γ by adjusting T_c and p_c . Acentric factor is estimated by an empirical correlation.

Fig. 3 shows acentric factor plotted versus normal boiling point for paraffins and aromatics. Approximate linear relations can be written

$$\omega_P = -0.477 + 0.00218 \cdot T_b(K) \quad \dots (13a)$$

$$\omega_A = -0.587 + 0.00218 \cdot T_b(K) \quad \dots (13b)$$

Assuming an average Watson characterization factor, K_w , of 12.7 for paraffins and 10.0 for aromatics, the following approximate relation for ω can be derived,

$$\omega = -1.0 + 0.042 K_w + 0.00218 T_b(K) \quad \dots (14)$$

If T_b is given in Rankine then constant 0.00218 becomes 0.000983.

Since the measured data for petroleum fractions are T_b and M/γ it would be helpful to express ω in terms of these two data. Using the Riazi-Daubert correlation for molecular weight as a function of T_b and γ it has been possible to derive the following relation,

$$K_w = 91.127 (M/\gamma)^{0.49593} T_b(K)^{-0.75584} \quad (15)$$

If T_b is given in Rankine, constant 91.127 becomes 142.1.

Combined, Eqs. 14 and 15 estimate acentric factor knowing only T_b and M/γ . It is assumed that the estimate of ω is sufficient for the proposed method since normal boiling point itself is matched exactly by the EOS.

Having defined ω it is now necessary to use the EOS to match measured values of T_b and M/γ . This is done by adjusting T_c and p_c until a satisfactory match is achieved. The procedure is outlined in Figs. 2B and 2C. The trial and error procedure is begun by first guessing values of T_c and p_c . Reasonable estimates are given by the simple correlations of Riazi and Daubert¹² (see Whitson¹⁶).

To calculate T_b with an EOS it is necessary to specify T_c , p_c , ω , and pressure, which by definition is atmospheric (i.e., normal) pressure, p_{sc} . Temperature is assumed, EOS constants A, B, C, and D are calculated, and Eq. 3 is solved for Z. If only one Z solution is found then the temperature is not equal to T_b . If three solutions are found then the lowest value is designated as liquid and the largest value as vapor. Fugacities are calculated for each phase and if they are equal then the assumed temperature equals T_b . If fugacities do not equal then a new temperature is assumed.

Instead of using this procedure to solve for T_b it is sufficient to check if vapor and liquid fugacities are equal at the specified T_b (and p_{sc}). If they are not equal then an error function is calculated, $E(T_b)$, defined as the difference in fugacities of vapor and liquid phases. Holding p_c constant, T_c is varied until $E(T_b) = 0$. A simple Newton or chord method is sufficient to determine T_c .

Having matched T_b , M/γ is calculated with the EOS using T_c (from previous step), p_c (held constant in the previous step), ω (defined by Eqs. 14 and 15), pressure, p_{sc} , (equal to standard pressure), and temperature, T_{sc} , (equal to standard temperature). Constants A, B, C, and D are calculated and Eq. 3 is solved for the smallest Z factor. M/γ equals molar volume (i.e., ZRT/p).

An error function, $E(M/\gamma)$, is defined as the difference in measured and calculated M/γ . The critical pressure, p_c , is adjusted and the procedure for matching T_b is repeated. When both $E(T_b)$ and $E(M/\gamma)$ equal zero then the T_c and p_c values have been determined. The double trial-and-error procedure is relatively simple to program. With the generalized EOS presented in this paper it is easy to determine critical properties of petroleum fractions for any two- or three-constant EOS.

Tables of PR and SRK critical properties for extended ranges of T_b and M/γ can be obtained from the author. Figs. 4a - 4d present the results graphically. Instead of reporting critical temperature directly, it is given as the ratio of T_c to T_b , i.e., T_c/T_b . Critical pressure is reported in MPa and the conversion to psia is $p_c(\text{psia}) = 145.0377 \cdot p_c(\text{MPa})$.

PVT Predictions using EOS Critical Properties

Hoffman, Crump, and Hocott³ present compositional and PVT data for a reservoir oil and its gas cap fluid. Extended analysis of heptanes-plus is given to C_{35} for the oil, including mole fractions, molecular weights, and specific gravities (corresponding to cuts with boiling points of normal paraffins). Methane content is 52 mol-% and C_{7+} is 36.84 mol-%, with an average C_{7+} molecular weight of 198.7 and specific gravity of 0.8409. Reported bubble point pressure is 3840 psia (26.47 MPa) at 201 °F (93.89 °C).

Using critical properties based on the PR EOS a bubble point is predicted at 3829 psia, or 0.3% lower than the measured pressure. Interaction coefficients have not been used. Predicted saturated oil density is 0.6867 g/cc, compared with the experimental value of 0.6672, or 2.9% high.

Katz and Firoozabadi match the measured bubble point using the PR EOS with increasing interaction coefficients between methane and C_{7+} fractions, and a methane binary of 0.17 for the heaviest fraction, C_{35} . The methane- C_{35} binary was used to match the measured bubble point pressure. Cavett's correlations are used for T_c and p_c while it is assumed that the Edmister correlation is used for ω . Estimated bubble-point oil density is not reported by Katz and Firoozabadi.

The gas-cap fluid reported by Hoffman, et al. is analyzed in SCN fractions up to C_{22} . SCN properties are similar, but not the same for the reservoir oil and equilibrium gas. Methane content of the gas cap fluid is 91.35 mol-% and heptanes-plus constitutes 1.54 mol-% with an average molecular weight of 141.25 and specific gravity of 0.7867.

Using the gas compositions reported by Hoffman, et al. and critical properties calculated with the proposed method the PR EOS predicts a dew point at 201 °F of 4044 psia, some 5.3% high. This is worse than the prediction given by Katz and Firoozabadi (+0.8%) using methane binaries for C_{7+} fractions calculated from an empirical correlation.

Table 1 illustrates how critical properties calculated from different correlations affect predicted dew point pressure. It is obvious that dew point pressure is dependent on the properties used to describe the petroleum fractions.

Predicted equilibrium gas composition from the bubble point VLE calculation using EOS critical properties resulted in methane content of 91.70 mol-%, C_{7+} having 1.318 mol-% with an average molecular weight of 128.00 and specific gravity of 0.7854. C_{7+} specific gravity is in good agreement with the experimental value but molecular weight shows more deviation, possibly suggesting that the use of paraffin molecular weights by Hoffman, et al. is not correct.

If equilibrium vapor composition resulting from the bubble point flash is used to represent the gas cap fluid, retaining only components to C_{22} , a dew point is predicted at 3706 psia. If the exact composition to C_{35} is used, then dew point is predicted exactly (equal to the bubble point, 3865 psia). This shows the sensitivity in dew point prediction due to a round-off error in composition of less than 0.001 mol-%.

Calculated liquid densities and yields are compared with experimental data in Table 2. Peng/Robinson predictions correspond to those listed in Table 1, where PR-2, PR-3, and PR-4 use methane binaries suggested by Katz and Firoozabadi. Binaries are not used when EOS-based critical properties are used (PR-1).

Results indicate that the Cavett/Edmister (PR-3) combination performs best, though the proposed method gives excellent results as well. Interestingly, liquid yields for predictions based on calculated gas composition from the bubble-point calculation are very poor, despite good prediction of liquid densities.

Next we consider the data presented by Olds, Sage, and Lacey in 1945. Extensive experimental results are given for six recombined systems, each measured at three temperatures (100, 190, and 250 °F). Hexanes-plus is fractionated into seven cuts with approximately equal weight fractions (~10%). Properties of the separator gas and liquid are given in the original work and recombined reservoir mixtures have been calculated using reported gas/oil ratios.

Critical properties of the petroleum fractions are calculated using the PR EOS. EOS predictions are presented in Table 3 for saturation pressure, vapor and liquid densities. Binary interaction coefficients are set equal to zero in all cases.

Absolute average deviation for saturation pressure is 4.57% not including the leanest mixture (GOR=14440 scf/stb), and 5.45% including the leanest mixture. Maximum error is 10%. Dew points for very lean condensates are difficult to measure experimentally and therefore it is reasonable to question measurements of the 14440-GOR mixture. Considering the range of temperatures and compositions, and lack of any adjustment or use of binary interaction coefficients, the predictions are very good. The transition from bubble- to dew-point is also predicted correctly.

Saturated liquid and vapor densities are overpredicted. Absolute average deviation is 5.14% with maximum error of 8.1%. Saturated liquid densities are predicted more accurately than vapor densities. The general trend of overprediction is opposite of that which is usually observed with the PR EOS (using empirical property correlations).

EOS Predictions of the Olds, Sage, and Lacey data presented in 1949 are reviewed in Table 4. The PR EOS is used to calculate critical properties. Binary interaction coefficients are not used. All systems studied by Olds, et al. are oils with reported bubble point pressures and saturated oil densities. Measurements are made at three temperatures for each mixture of differing GOR.

Absolute average deviation for bubble-point pressure is 5.61%, with a maximum error of 13.7%. For all GOR mixtures deviation in bubble-point pressure increases with increasing temperature. Temperature dependence may result in part from incorrect extrapolation of correction factor, α , (see Eqs. 4a, 8, and 9) for methane at supercritical temperatures.

Saturated liquid densities are predicted with an absolute average deviation of 3.30% with a maximum error of 6.3%. Deviation also increases with temperature for all GOR mixtures.

From results presented in this section it can be concluded that the present method of defining critical properties based on an EOS is reasonably accurate for predictions of saturation pressure and mixture densities. It also appears that VLE predictions are good. The method is not inferior to empirical correlations and has the advantage of being consistent with the EOS used. For accurate predictions using the proposed method it is necessary to have detailed analysis of the C7+ fraction, preferably distillation data including boiling point, specific gravity, and molecular weight for each fraction.

Matching Experimental Saturation Pressure

Traditionally, experimental saturation pressure is matched by an EOS using binary interaction coefficients between methane and C7+ fractions. As can be seen from the mixing rules (Eqs. 12), binaries only affect EOS constant A. It can be shown that VLE calculations are dominated by A, as indicated by the choice to introduce α , a correction factor for modifying vapor pressures of pure compounds.

Practically, the use of binaries to match saturation pressures is very efficient. Interaction coefficients are, however, not easily given physical meaning and there is a tendency to overcompensate for bad input data (e.g., critical properties) by introducing large binaries. Whitson gives several examples indicating that interaction coefficients have a strong temperature dependence. This can be an important factor in thermal recovery and surface process applications.

The present method suggests that boiling point of the heaviest petroleum fraction is the most uncertain C7+ data and that it alone can be adjusted to match saturation pressure. A direct relation exists between T_b of the heaviest fraction and saturation pressure, as indicated for a North Sea fluid in Fig. 5. An increase in T_b results in an increase of saturation pressure. Physically, boiling point is easily defined and has obvious limits.

A first estimate of T_{b+} for the heaviest fraction can be made using molecular weight, M_+ , and specific gravity, γ_+ . The Watson characterization factor is estimated from

$$K_{w+} = 4.5579 M_+^{0.15178} \gamma_+^{-0.84573} \dots (16)$$

and boiling point is found directly from the definition of K_w - i.e., $T_{b+} = (K_{w+} \cdot \gamma_+)^{1.8}$ where T_b has units Kelvin.

CONCLUSIONS

1. A new method for calculating critical properties and acentric factor of petroleum fractions based on an EOS appear to give promising improvements in both volumetric and phase behavior predictions. The method requires molar volume (ratio of molecular weight to specific gravity) and boiling point. The acentric factor relation is empirical, accounting for oil type (i.e., paraffinicity) using the Watson characterization factor.

2. The method for calculating critical properties has been tested using the Peng/Robinson EOS. Results indicate that saturation pressure and saturated density predictions are reasonably accurate without using binary interaction coefficients to match experimental VLE data.

3. If experimental saturation pressure is not predicted accurately with the proposed method, a procedure is recommended whereby the boiling point of the heaviest C₇₊ fraction is adjusted to match measured saturation pressure of the mixture. This procedure has a more direct physical understanding than methods using binary interaction coefficients. It is felt that boiling point of the heaviest fraction is the greatest unknown of measurable C₇₊ properties and can therefore be adjusted within reasonable limits.

NOMENCLATURE

a, b, c, d = constants in the general form of the cubic EOS

A, B, C, D = EOS constants

E = error function

f = fugacity

K_w = Watson characterization factor
 $= T_b(^{\circ}R)^{1/3}/\gamma$

m = correlating parameter for α

M = molecular weight

p = absolute pressure

p_r = reduced pressure, $p_r = p/p_c$

p_c = critical pressure

p_v = vapor pressure

R = universal gas constant

T = absolute temperature

T_b = normal boiling point

T_c = critical temperature

T_r = reduced temperature, $T_r = T/T_c$

v = molar volume

V = volume

Z = compressibility factor, $Z = pv/RT$

Z_c = critical compressibility factor

α = correction factor for EOS constant A

λ = proportionality constant between EOS constants Ω_c and Ω_b , defining the proposed family of cubic equations

Δ = deviation, $\Delta = (\text{calc.} - \text{meas.})/\text{meas.}$

ρ = density

ω = acentric factor, $\omega = -\log(p_v/p_c) - 1.0$ at $T_r = 0.7$

Ω = numerical EOS constants

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TABLE 1 - EFFECT OF CRITICAL PROPERTIES USED WITH THE PENG/ROBINSON EOS TO PREDICT THE HOFFMAN ET AL. RESERVOIR GAS DEW POINT PRESSURE.

Correlation	Dew Point Pressure (psia)	
	Predicted without Methane Binaries	With Katz/Firoozabadi Methane Binaries
Experimental	3841	
1. EOS-Based (proposed)	4044 (+5.3) ²	
2. Riazi/Daubert + Edmister:	3322(-13.5)	3632 (-5.4)
3. Cavett + Edmister	3668 (-4.5)	3870 (+0.7)
4. Lee/Kesler	3523 (-8.3)	4049 (+5.4)

¹ Same as reported by Katz and Firoozabadi.

² Deviation, Δ, %, given in parentheses.

TABLE 2 - COMPARISON OF MEASURED AND EXPERIMENTAL LIQUID DENSITIES FOR THE HOFFMAN, ET AL. RESERVOIR GAS

Press. (psia)	Liquid Density, g/cc				
	Exp.	PR-1	PR-2	PR-3	PR-4
2915	0.6565	0.6637	0.5921	0.6364	0.6300
2515	0.6536	0.6709	0.6020	0.6475	0.6392
2015	0.6538	0.6822	0.6159	0.6619	0.6520
1515	0.6753	0.6967	0.6315	0.6779	0.6665
1015	0.7160	0.7148	0.6486	0.6957	0.6834
515	0.7209	0.7390	0.6675	0.7164	0.7029
Δ(%)		2.32	2.80	1.50	2.48

Press. (psia)	Liquid Yield (bbl/MMscf)				
	Exp.	PR-1	PR-2	PR-3	PR-4
2915	9.07	9.31	8.37	9.75	10.21
2515	12.44	11.97	12.01	12.61	12.93
2015	15.56	14.53	15.33	15.23	15.48
1515	16.98	16.09	17.30	16.74	17.00
515	15.08	14.97	16.17	15.45	15.73
Δ(%)		3.65	4.46	2.54	3.93

TABLE 3 - COMPARISON OF SATURATED PROPERTIES FOR OLDS-SAGE-LACEY
RESERVOIR MIXTURES (1945) USING THE EOS-BASED CRITICAL
PROPERTY METHOD WITH THE PR EOS.

GOR (scf/bbl)	Temp- erature (F)	Saturation Pressure (psia)			Saturated Density (lb/ft ³)		
		Meas.	Calc.	Δ(%)	Exp.	Calc. ¹	Δ(%)
552	100	1112	1065	-4.2	42.55	43.34	+1.8
552	190	1410	1383	-1.9	39.68	40.52	+2.1
552	250	1675	1549	-7.5	37.52	38.50	+2.6
940	100	1870	1723	-7.9	39.65	40.88	+3.1
940	190	2210	2174	-1.6	36.13	37.78	+4.6
940	250	2380	2375	-0.2	33.66	35.44	+5.3
2205	100	3430	3102	-9.6	34.13	35.44	+3.8
2205	190	3542	3691	+4.2	29.61	31.52	+6.5
2205	250	3595	3880	+7.9	27.07	28.75	+6.2

5361	100	4490	4348	-3.2	27.01	28.54	+5.7
5361	190	4590	4836	+5.4	22.90	24.40	+6.6
5361	250	4630	4869	+5.2	20.37	21.85	+7.3
7393	100	4560	4615	+1.2	24.05	25.99	+8.1
7393	190	4730	4981	+5.3	20.46	22.02	+7.6
7393	250	4780	4933	+3.2	18.35	19.65	+7.1
14440	100	3835	4556	+18.8	19.08	20.05	+5.1
14440	190	4305	4709	+9.4	16.24	16.96	+4.4
14440	250	4440	4504	+1.4	14.49	15.15	+4.6

¹ Saturated densities are calculated at the experimental saturation pressure assuming a single phase mixture.

² Lower GOR's are bubble-point mixtures and higher GOR's are dew-point mixtures, as is correctly predicted by the PR EOS.

TABLE 4 - COMPARISON OF SATURATED PROPERTIES FOR OLDS-SAGE-LACEY
RESERVOIR MIXTURES (1949) USING THE EOS-BASED CRITICAL
PROPERTY METHOD WITH THE PR EOS.

GOR (scf/bbl)	Temp- erature (F)	Bubble-Point Pressure (psia)			Bubble-Point Density (lb/ft ³)		
		Meas.	Calc.	Δ(%)	Exp.	Calc. ¹	Δ(%)
274	100	817	796	-3.8	49.12	49.87	+1.5
274	190	1020	1067	+4.6	46.36	47.96	+3.5
274	250	1170	1236	+5.6	44.66	46.54	+4.2
460	100	1540	1361	-11.6	47.96	48.34	+0.8
460	190	1830	1805	-1.4	44.92	46.29	+3.0
460	250	2020	2051	+1.5	43.08	44.78	+3.9
620	100	2085	1799	-13.7	46.62	47.19	+1.2
620	190	2439	2360	-3.2	43.55	45.04	+3.4
620	250	2670	2656	-0.5	41.53	43.50	+4.7
811	100	2656	2273	-14.4	44.68	45.96	+2.9
811	190	3067	2944	-9.0	41.98	43.73	+4.2
811	250	3384	3284	-3.0	39.70	42.21	+6.3

¹ Saturated densities are calculated at the experimental saturation pressure assuming a single phase mixture.

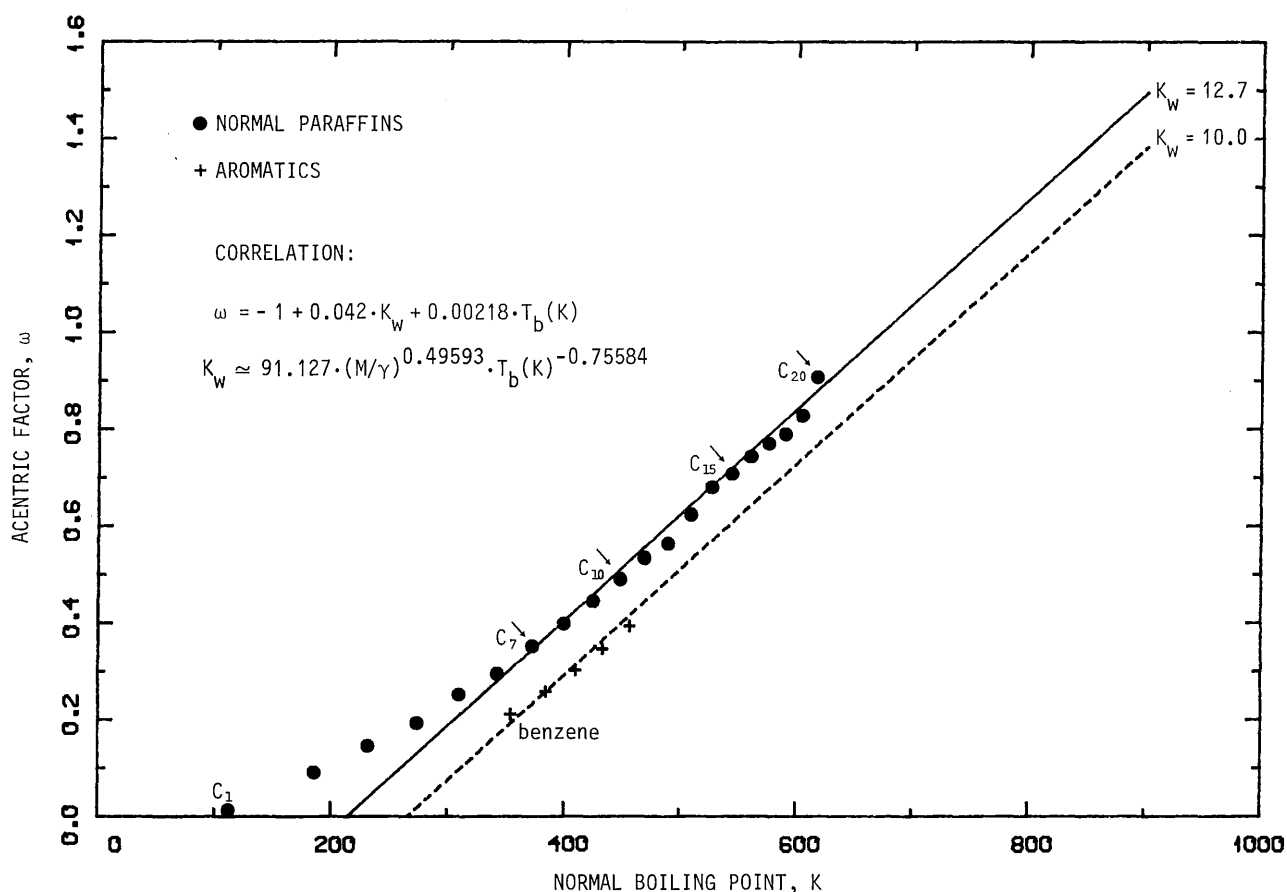


Fig. 3—Relation between acentric factor and normal boiling point for normal paraffins, aromatics, and the generalized correlation.

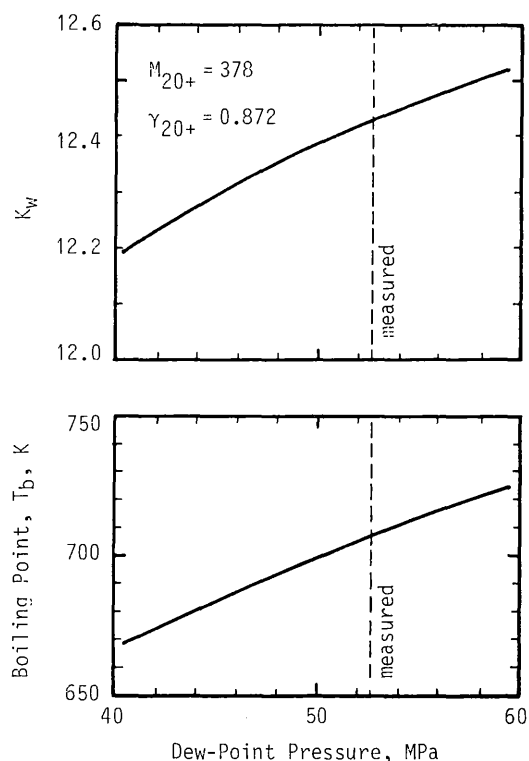


Fig. 5—Empirical relation between dewpoint pressure of a North Sea gas condensate and boiling point and Watson characterization factor of the heaviest petroleum fraction (C_{20+}).

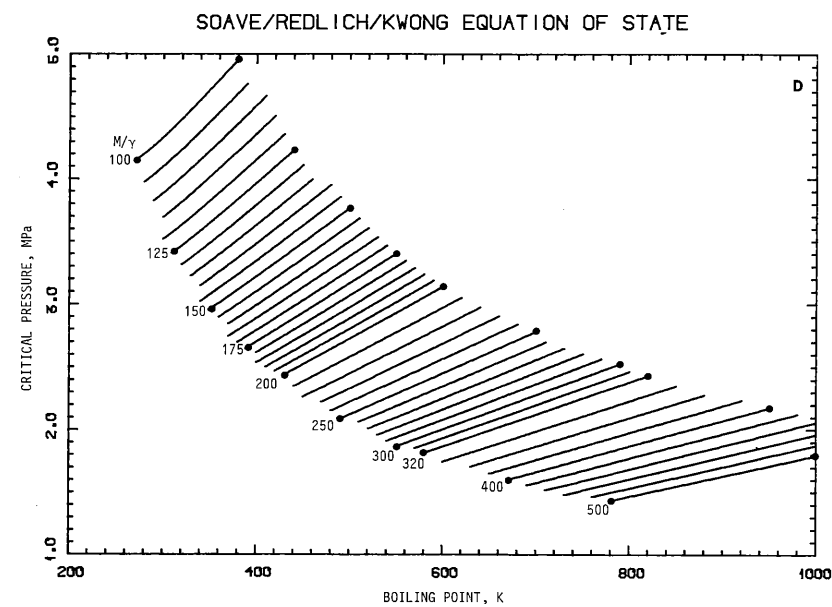
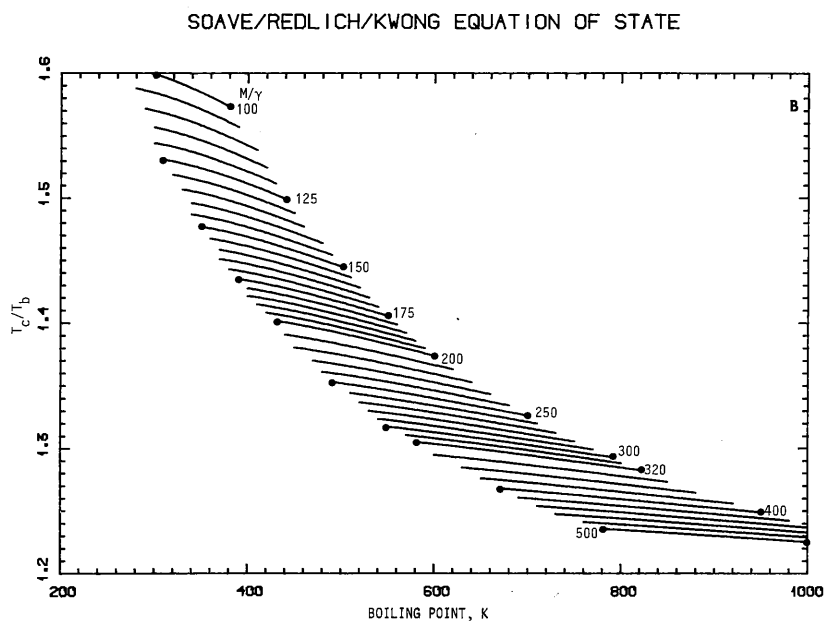
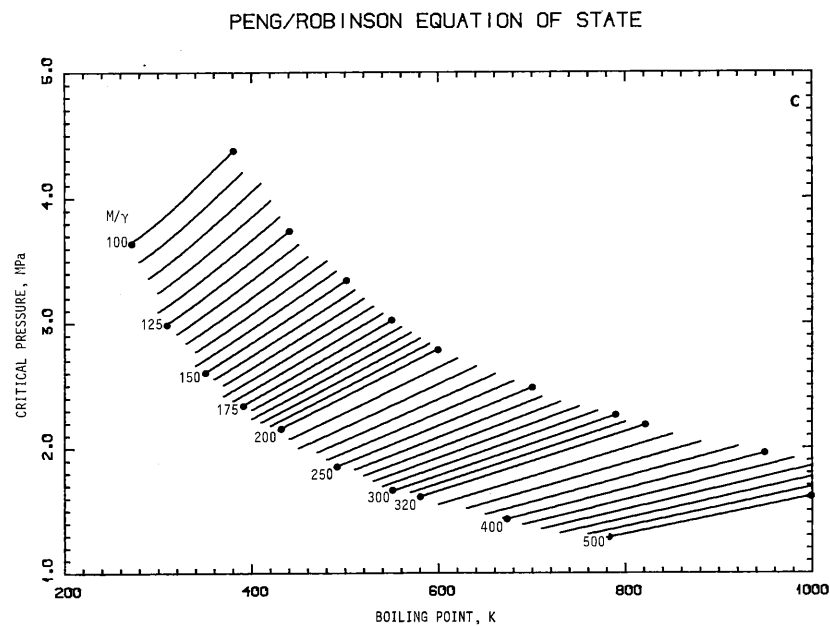
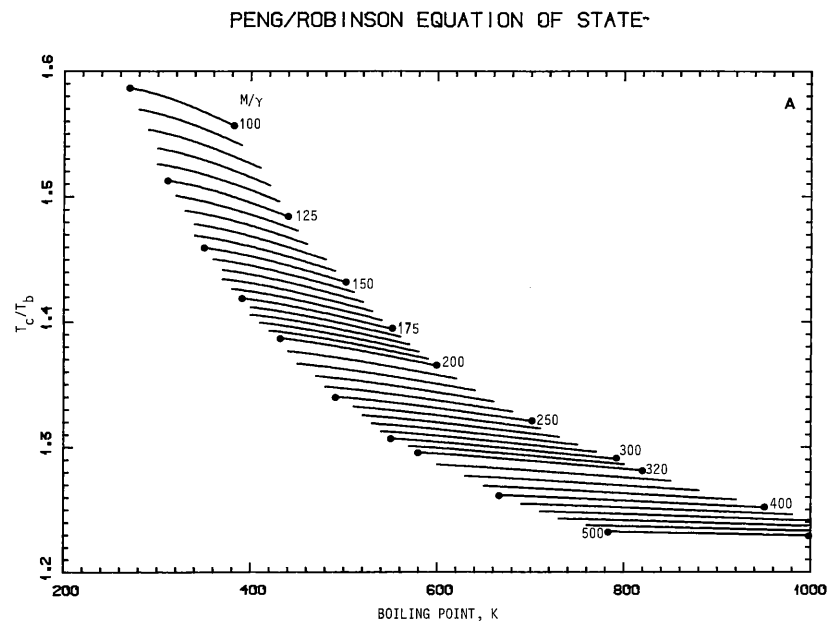


Fig. 4—Critical property correlations for petroleum fractions calculated using the proposed method with the Peng/Robinson and Soave/Redlich/Kwong EOS's.

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