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Applications of Equations of State in the Oil and Gas Industry

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1. Introduction

Reservoir fluids contain a variety of substances of diverse chemical nature that include hydrocarbons and nonhydrocarbons. Hydrocarbons range from methane to substances that may contain 100 carbon atoms. The chemistry of hydrocarbon reservoir fluids is very complex. In spite of the complexity of hydrocarbon fluids found in underground reservoirs, equations of state have shown surprising performance in the phase-behavior calculations of these complex fluids. An equation of state (EOS) is an analytical expression relating 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 have been proposed since Van der Waals introduced his expression in 1873. Currently, a number of EOS are used in reservoir engineering which have shown more reliability in reservoir fluids calculations. In this chapter, a review over the most commonly used EOS in the oil and gas industry has been provided. We explore their strengths and weaknesses and to examine the predictive capability of these equations. A brief introduction to Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Patel-Teja (PT), Schmit-Wenzel (SW), and Esmaeilzadeh-Roshanfekr (ER) equations of state has been provided with intention to compare their efficiency in predicting different reservoir fluids properties. The Progress in developing EOS for the calculation of thermodynamic data and phase behavior is also reviewed. Effect of characterization on VLE predictions as well as advances in application of equations of state for heavy hydrocarbons has been considered in this work. Finally, as a case-study, phase behavior of a typical Omani crude oil as well as application of EOS with proper characterization method for this real oil sample has been examined.

2. Overview of EOS

Consider the plot of pressure versus total volume of a pure substance shown in Fig.1. An equation of state (EOS) is desired to represent the volumetric behavior of the pure substance in the entire range of volume both in the liquid and in the gaseous state.

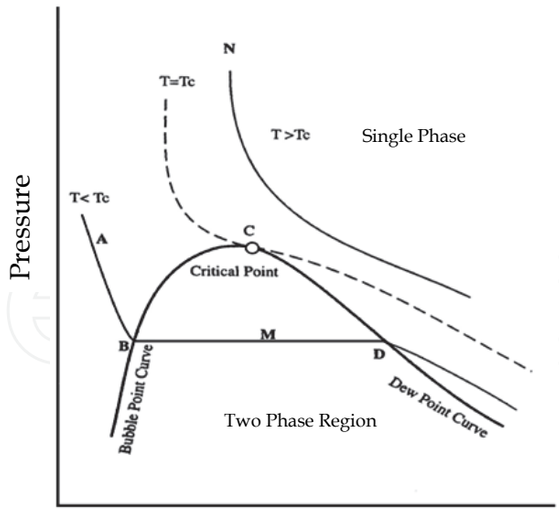


Fig. 1. Pressure volume diagram of a pure component

An EOS can represent the phase behavior of the fluid, both in the two-phase envelope (i.e., inside the binodal curve), on the two-phase envelope, and outside the binodal curve. Numerous EOS have been proposed to represent the phase behavior of pure substances and mixtures in the gas and liquid states since Van der Waals 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 calculation mixture parameters equivalent to those of a pure substance. The equations of state are divided into two main groups: cubic and noncubic. Noncubic equations can better describe the volumetric behavior of pure substances but may not be suitable for complex hydrocarbon mixtures (Firoozabadi, 1989). For instance, the modified Benedict-Webb-Rubin equation (Starling, K.E. 1973) is admittedly more accurate than the cubic EOS (such as the Peng-Robinson EOS) for the PVT description of pure substances, but it may be less accurate than the two-constant cubic equations for VLE computation of complex reservoir fluid systems (Katz and Firoozabadi, 1978). The application of BWRS type equations demands a high computational time and effort, due to their high powers in volume and large number of parameters, hence, unsuitable for reservoir fluid studies where many sequential equilibrium calculations are required. More importantly, for multi-component systems each parameter must be determined using a mixing rule, which at best is quite arbitrary (Danesh, 1998). Although acceptable phase behavior results can be obtained by BWRS (Starling, 1966), it has been surpassed by the simpler, yet more reliable van der Waals type cubic equation of state. There are many examples in the literature where EOS are compared (Sing, 2005; Ahmed, 2004). The findings all highlight the fact that there is currently no "all in one" EOS that will give the best prediction of all thermodynamic properties of different types of reservoir fluids. It seems that some EOS can do better than the others only for certain reservoir fluid types and some EOS are advantageous for particular properties. For example, the PR-EOS for superior phase transitions (O'Reilly, 2009). This may also lead to entire PVT experiments being better represented by a particular EOS. The objective is to review literature for a number of common cubic EOS used in reservoir engineering calculations and compare their strengths and weaknesses.

2.1 Commonly used EOS in reservoir engineering calculations

Since 1949 when Redlich and Kwong (RK) formulated their two-parameter cubic equation of state (EOS), many investigators have introduced various modifications to improve ability of RK-EOS. Two other well-known cubic equations are Soave (SRK) (1972) and Peng-Robinson (PR) (1976) equations. Although many modified forms of RK-EOS are reported in the literature, but at least for hydrocarbon systems and their mixtures, only SRK and PR equations have been widely accepted. Both SRK and PR equations use Pitzer acentric factor as the third parameter to obtain parameter a in their equations. Acentric factors are calculated through critical properties; therefore, for heavy compounds where critical properties should be estimated, errors in critical properties will be contributed to acentric factor. Probably, the most successful cubic EOS for vapor liquid equilibria (VLE) calculations have been those proposed by Soave, Redlich and Kwong and Robinson and Peng (Esmaeilzadeh et al., 2005). Both of these EOS assumed a fixed value of the critical compressibility factor for all substances and as a result the predicted values for saturated liquid density differs considerably from their experimental values.

2.1.1 Soave-Redlich-Kwong (SRK) EOS

In 1972, Soave improved on the RK-EOS which represents an attempt to take molecular geometry and polarity into account by replacing the term $\frac{\alpha}{T^{0.5}}$ in RK-EOS with a more general temperature-dependent term $\alpha(T)$. He showed that a simple expression for the temperature dependency of attraction parameter "a" enabled the equation to represent vapor pressure of a wide class of substances. The proposed equation known as SRK-EOS is as follows:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{1}$$

Where

$$a(T) = 0.42747 \frac{R^2 T_c^2}{P_c} \alpha(T) \tag{2}$$

$$b = 0.0867 \frac{RT_c}{P_c} \tag{3}$$

Soave proposed a simple form for $\alpha \equiv \alpha(T_r, \omega)$ for all pure substances, taking advantage of the concept of the acentric factor of Pitzer (Pitzer et al., 1955) . Soave compared the predicted vapor pressure from his modification and the original RK EOS for a number of substances, showing that his modification greatly improved vapor pressure predictions. In this modification α(T) is extrapolated for the supercritical temperatures. Soave compared only the measured and computed saturation pressures of several binary systems that showed good agreement. SRK is quite capable of predicting vapour-liquid equilibria, but it does not provide reliable liquid density. (Danesh, 1998)

2.1.2 Peng-Robinson (PR) EOS

Another important variation of the van der Waals EOS was introduced in 1976 by Peng and Robinson. SRK-EOS fails to predict liquid densities accurately. Improved density prediction

was the main motivation of the authors of PR-EOS which in general is superior in density predictions of reservoir fluid systems. Although this equation improves the liquid density prediction, it cannot describe volumetric behavior around the critical point. The PR-EOS 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:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \tag{4}$$

Where

$$a(T_c) = 0.45724\ \frac{(RT_c)^2}{P_c} \tag{5}$$

$$b = 0.07780 \frac{(RT_c)}{P_c} \tag{6}$$

The generalized expression for the temperature-dependant parameter is given by

$$a(T) = a(T_c)\alpha(T) \tag{7}$$

where

$$\alpha(T) = \left\{1 + m\left[1 - \sqrt{\frac{T}{T_C}}\right]\right\}^2 \tag{8}$$

With

$$m = 0.3746 + 1.5423\omega - 0.2699\omega^2 \tag{9}$$

Comparison of the vapor-pressure prediction of several substances by the SRK EOS and the PR EOS with experimental data shows that the error is small for both equations, although the PR EOS performs better by a small margin (Firoozabadi A., 1988). Peng and Robinson also compared enthalpy departures for five pure substances from both their proposed EOS and the SRK EOS. Both equations generate enthalpy values of about the same reliability. According to different researchers' experience, PR-EOS enjoys more simplicity and reliability than many other equations. However, both PR and SRK equations break-down at C10 – C11and heavier compounds. Peneloux and Rauzy (1982) introduced a constant for each substance to be subtracted from the volume obtained in the SRK equation. Their modification greatly improves liquid density predictions, but it requires a fourth parameter beside critical temperature, critical pressure and acentric factor required by SRK equation.

2.1.2.1 Volume shift

A comparison of the predicted liquid molar volume by leading two parameter EOS with experimental data of pure compounds generally shows a systematic deviation. The deviation is almost constant over a wide pressure range away from the critical point. Hence, subtracting the predicted molar volume by a constant correction term can improve the predicted liquid density. The effect on the predicted vapor volume is generally insignificant due to its large value relative to that of liquid away from the critical point. Peneloux et al.

[26] were the first who introduced the volume shift concept, i.e. shifting the volume axis, and applied it to SRK,

$$v^c = v\text{-}c \tag{10}$$

where v^c is the corrected molar volume, and c is the correction term determined by matching the measured and predicted saturated liquid volumes at $T_r = 0.7$. The volume shift generally improves the predicted liquid density, and has a minimal effect on the vapor density at low and moderate pressures as its molar volume is relatively large compared to the value of c. At high pressure condition, the inclusion of c parameter may not necessarily improve the predicted gas density as it is just a correction term for the liquid density. However, it is advisable to adjust the gas phase volume by the third parameter to maintain consistency, particularly near the critical point where properties of the two phases approach each other. Peneloux et al. correlated the volume translation parameter c as,

$$c = 0.40768(0.29441 - Z_{RA})\, RT_c/P_c \tag{11}$$

where ZRA is the Rackett compressibility factor. For a more detailed discussion, reader is suggested to refer to Peneloux et al. (1982).

2.2 Three-parameter EOS

A two-parameter EOS predicts the same critical compressibility factor, Z, for for all substances, i.e. 0.307 and 0.333 by PR and SRK respectively, whereas Z_c varies within a range of 0.2 to 0.3 for hydrocarbons. Although the inaccuracy of predicted volume at the critical point, not necessarily leads to unreliable volumetric data at all conditions, it demonstrates the inflexibility of two-parameter EOS for matching both the vapor pressure and volume. The inclusion of a third parameter relaxes the above limitation. The third parameter is generally determined by employing volumetric data.

2.2.1 Esmaeilzadeh-Roshanfekr (ER) EOS

Both of PR and SRK equations assume a fixed value of the critical compressibility factor for all substances and, as a result, the predicted values for saturated liquid density differ considerably from their experimental values. On the other hand, some equations of state proposed by Schmit and Wenzel (Schmit G. & Wenzel H., 1980) and Patel and Teja (Patel N.C., Teja A.S., 1982) introduced a third parameter to their equations. This suggestion led to the introduction of a substance dependent critical compressibility which allowed them to reproduce more accurate the experimental saturate liquid density at a particular temperature. Their work showed that the optimum value of substance critical compressibility was not equal to the experimental critical compressibility of the fluid of interest. Using the generalized Van der Walls theory, Esmaeilzadeh and Roshanfekr used a mathematically simple cubic EOS to model attractive interactions between molecules. The proposed equation of state in their work is as follows (Esmaeilzadeh & Roshanfekr, 2006)

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+c)+c(v-c)} \tag{12}$$

Where "a" is a function of temperature and "b" and "c" are constants. In this EOS $a(T)$ and b are derived as:

$$a(T_c) = \Omega_a \frac{(RT_c)^2}{P_c}.\alpha(T_r) \tag{13}$$

$$b = \Omega_b \frac{(RT_c)}{P_c} \tag{14}$$

$$c = \Omega_c \frac{(RT_c)}{P_c} \tag{15}$$

This EOS predicts saturated liquid density more accurately than the PT and PR EOS. The results for the calculation of vapor pressure of pure components for light hydrocarbons show that Eq. (12) has the lowest deviation and for heavy hydrocarbons the PT EOS yields the lowest deviation (for Tr < 0.75). The prediction of thermodynamic properties of light and intermediate hydrocarbons by Eq. (12) is superior to other EOS studied in this work. Moreover, It is found that Esmaeilzadeh-Roshanfekr EOS is most accurate for predicting gas-condensate properties, while the original SRK and PR equations remain reliable for oil samples. (Bonyadi et al., 2007)

2.2.2 Schmidt-Wenzel EOS (SW)

Liquid density prediction at T_r=0.7 by SRK and PR for pure substances is associated with noticeable deviation from reliable values. Note that SRK is more reliable for substances with small acentric factors, whereas PR gives reliable data for compounds with acentric factors around (1/3). Based on the above observation, Schmidt and Wenzel incorporated the acentric factor as the third parameter in the attractive term as,

$$P = \frac{RT}{v-b} - \frac{a_c\alpha}{v^2 + (1+3\omega)bv - 3\omega b^2} \tag{16}$$

Substituting acentric factor values of zero and $1/3$ in the Schmidt-Wenzel EOS (SW) will reduce it to SRK and PR respectively, where these equations predict the liquid density reliably. SW can, therefore, be considered a general form of SRK and PR (Danesh, 1998). The authors used the boundary conditions at the critical point, Eq.(4.9) to determine a_c, and b, as

$$a_c = \Omega_{ac} \frac{R^2 {T_c}^2}{P_c} \tag{17}$$

$$b = \Omega_b \frac{RT_c}{P_c} \tag{18}$$

Where

$$\Omega_{ac} = [1 - \eta(1-q)]^3 \tag{19}$$

$$\Omega_b = \eta q \tag{20}$$

In above equations η is the critical compressibility factor, and is related to the correlating parameter q, by

$$\eta = {}^{1}/_{[3(1+q\omega)]} \tag{21}$$

and q, defined as b/v_c, is the smallest positive root of the following equation,

$$(6\omega + 1)\, q^3 + 3q^2 + 3q - 1 = 0 \tag{22}$$

with an approximate value of,

$$q = 0.25989 - 0.0217\, \omega + 0.00375\omega^2 \tag{23}$$

Schmidt and Wenzel selected the same form of a as proposed by Soave, but correlated, m, with the acentric factor and reduced temperature by matching vapor pressure data of pure compounds as is discussed in details in Schmidt et al, 1980. The inclusion of ω in EOS as the third parameter by Schmidt and Wenzel resulted in a variable calculated critical compressibility, according to the value of acentric factor. The predicted values are, however, about 15% higher than the true values. This was known to the authors, but was accepted as the price for an overall optimum accuracy in predicted volumes (Danesh, 1998).

2.2.3 Patel-teja (PT) EOS

Patel N.C., Teja A.S. (1982) modified the attractive term by including a more flexible third parameter. (Patel et al., 1982) The authors found that the use of true critical compressibility factor will result in the overall loss of accuracy in predicted density, a conclusion also reached by Schmidt and Wenzel. For more details the reader is recommended to referred to Patel N.C., Teja A.S.(1982).

3. Heavy oil characterization

Heavy-oil fluids contain large concentrations of high-molecular weight components, including a large content of the plus fractions, such as C7+. For crude oils and reservoir fluids, the basic laboratory data are usually presented in the form of the composition of hydrocarbons up to hexanes and the heptane-plus fraction (C7+), with its molecular weight and specific gravity calculations (Danesh 1998; Ahmed 2007). The constituents of a hydrocarbon system are classified in two categories: the well-defined components and the undefined petroleum fractions, which are those heavy compounds lumped together and identified as the plus-fraction [i.e., C7+ (Ahmed 2007)]. Several samples of heavy oil indicate that the plus fraction C10+ contains a molar fraction close to 70% and that the fraction C80+ is also representative with values close to 2% (Pedersen et al. 2004). The importance of characterizing the plus fraction arises when the modeled fluid has high molecular weight and high density (heavy oil). Characterization of plus fraction usually consists of three parts: (1) splitting the fraction into a certain number of component groups called SCNs; (2) estimation of the physicochemical properties of the SCN; and (3) lumping of the generated SCNs (Pedersen et al. 2006).

3.1 Splitting method

Several methods have been developed to estimate the mole distribution of the compounds in the plus fraction (Katz et al. 1978; Pedersen et al. 1982; Ahmed et al. 1985; Whitson 1983). Heptanes plus (C7+) fractions are expressed by a distribution model and the fractions heavier than C6 have been lumped into pseudo-components with approximately equal weight fraction of each pseudo-component (i.e. molar averaging). Often, the exact chemical composition of a HC fraction is not known, therefore, pseudoization defines these HC fractions and allows the determination of EOS parameters Splitting and lumping are the two

main types of the pseudoization. A common feature among these methods is that components with the same number of carbon atoms are lumped in groups called SCNs with a single predefined value for properties like Pc, Tc, ω, Tb, M, and density ρ. Whitson (1983) proposed a method using the TPG distribution in order to estimate the mol fraction as a function of the molecular weight. The molecular weights used are the generalized values presented for each SCN (Katz and Firoozabadi 1978). Generalized correlations have been developed to generate critical properties for the SCN including those by Twu (1984), Ahmed (1985), Kesler-Lee (1976), Riazi-Daubert (1987), and Edmister (1958). Riazi-Daubert, and Edmister correlations are used.

Whitson (1983) used TPG distribution to estimate the mole fraction of the SCNs within the Cn+ fraction. TPG is defined (Whitson 1983) as a function of the molecular weight (M) by the following equation:

$$P(M) = \frac{(M-\eta)^{\alpha-1}\exp\left(-\frac{M-\eta}{\beta}\right)}{\beta^{\alpha}\Gamma(\alpha)} \tag{24}$$

where η is the minimum molecular weight present in the C_{n+} fraction, α is used to fit the shape of the distribution, and Γ is the gamma function. Whitson recommended Γ = 92, the molecular weight of toluene, as a good estimation of η, if C7+ is the plus fraction; for other plus fractions, following is used as approximation:

$$\eta = 14n - 6 \tag{25}$$

and

$$\beta = \frac{M_{cn+} - \eta}{\alpha} \tag{26}$$

where M_{Cn+} is the molecular weight of the Cn+ fraction. The mole fraction of an SCN is then generated by calculation of the cumulative frequency of occurrence between the limits M_{i-1} and M_i multiplied by the mole fraction of the Cn+ fraction.

$$Z_i = Z_{C_{n+}} + \int_{M_{i-1}}^{M_i} p(x)dx \tag{27}$$

where i is the SCN and M_i is the molecular weight of the SCN usually defined as the molecular weight of the normal component.

3.2 Correlations used to estimate physicochemical properties of the SCN

In a hydrocarbon mixture, the critical properties (critical pressure "Pc", critical temperature "Tc" and accentric factor "ω") must be given for each component. These properties are well known for pure compounds (like methane, ethane, etc.), but nearly all naturally occurring gas and crude oil fluids contain some heavy fractions that are not well defined. There arises the need of adequately characterizing these undefined plus fractions in terms of their critical properties (Gastón, 2007).

Several correlations have been developed to estimate the physical properties of petroleum fractions and are in principal function of the specific gravity, the boiling point temperature and the molecular weight Riazi-Daubert (1987), Twu (1984), Ahmed (1985), Kesler-Lee (1976), and Edmister (1958); in this study, the Riazi-Daubert (1986) has been used.

3.2.1 Riazi-Daubert correlation

Riazi-Daubert's correlation is utilized to obtain physical properties of the plus fraction using the laboratory reported MW and SG as heavy fraction parameters. This study uses Riazi and Daubert, since it is the one mostly used in the industry; for calculating the accentric factor, Riazi-Daubert uses the Edmister's correlation (Riazi, M. R., Daubert, T. E. (1987)). The proposed relationship is:

$$\Theta = a\mathrm{MW}^{b}\mathrm{SG}^{c} \exp\left[d\mathrm{MW} + e\mathrm{SG} + f\,(\mathrm{MW}\,.\,\mathrm{SG})\right] \tag{28}$$

Where:

Θ = some physic property.

a-f = coefficients for each physic property (Table 1).

The Edmister's correlation for the accentric factor is P_c and T_c dependent is given by (Edmister, W.C., 1958):

$$\omega = \frac{3}{7}\,\frac{\log({}^{P_c}/_{14.7})}{{}^{T_c}/_{T_b} - 1} - 1 \tag{29}$$

$\boldsymbol{\Theta}$	$\boldsymbol{T_c}$	$\boldsymbol{P_c}$	$\boldsymbol{T_b}$
$\boldsymbol{a}$	544.4	45203	6.77857
$\boldsymbol{b}$	0.2998	-0.8063	0.401673
$\boldsymbol{c}$	1.0555	1.6015	-1.58262
$\boldsymbol{d}$	-0.00013478	-0.0018078	0.00377409
$\boldsymbol{e}$	-0.61641	-0.3084	2.984036
$\boldsymbol{f}$	0.0	0.0	-0.00425288

Table 1. Riazi and Daubert's coefficients

3.3 Lumping methods and mixing rules

The generation of an appropriate mole distribution that represents the plus fraction usually requires splitting the plus fraction into large number of components (SCN) with their respective mole fractions and physical properties. The use of a large number of components in a reservoir simulation is time consuming. Lumping is defined as the reduction of the number of components used in EOS calculations for reservoir fluids. After lumping many components into a minimum number of hypothetical components, it is necessary to determine the characterization parameters (critical temperature, critical pressure, and acentric factor) for each lumped hypothetical component for use in the equations of state using some mixing rules. Phase equilibrium calculations are very sensitive to the values of the characterization parameters in the equations of state. Conventional mixing rules, which are inconsistent with the equation of state itself, are usually applied to calculate the characterization parameters of the lumped pseudocomponents. The inadequacy of this characterization method often results in inaccurate predictions of phase equilibria. Another problem is that the binary interaction parameters between the lumped hypothetical components, which are often needed in the phase behavior calculations, are difficult to obtain. The common practice is to set the binary interaction parameters equal to zero for all hydrocarbon-hydrocarbon interactions, while nonzero values may be used for interactions

with non-hydrocarbons (Chorng H. Twu and John E. Coon, 1996). Pedersen et al. (2006) states that lumping consists of

- Deciding what carbon number fractions are to be lumped into same pseudocomponent.
- Deciding the mixing rules that will average T_c, P_c, ω of the individual carbon number fractions to one T_c, P_c, ω to represent the lumped pseudocomponents.

Whitson's method is described for estimating the number of MCN groups needed for adequate plus-fraction description, as well as which SCN groups belong to the MCN group. The proposed distribution model is similar to a folded log-normal distribution. The number of MCN groups, N_g , is given by

$$N_g = \text{Int} [1 + 3.3 \log_{10} (N - n)] \quad (30)$$

For black-oil systems, this number probably can be reduced by one (Whitson 1983).
The molecular weights separating each MCN group are taken as

$$M_l = M_n \{\text{Exp} [(1 / N_g . \ln (M_N / M_n)]\}^l \quad (31)$$

where M_N is the molecular weight of the last SCN group (which may actually be a plus fraction), and 1= I, 2 ... N_g. Molecular weights of SCN groups falling within the boundaries of these values are included in the MCN group, I.
Recently, Rudriguez et al. developed a method based on a modification of Whitson's approach. The approach is based on the fact that single carbon number groups (SCN), may represent hundreds of different compounds with the same number of carbon atoms. These compounds can be classified in different types: paraffins, naphtenes and aromatics. Uncertainty of the types and distribution of compounds present in each single carbon number indicates that the average value of molecular weight of a single carbon number is different from one sample to another. The modification of Whitson's method includes a simple procedure to determine the value of the fitting parameter (α); and a new definition of the limits used to calculate the frequency of occurrence for each single carbon number. The developed method is based on that the molecular weight is not uniquely related to carbon numbers due to the hidden exponential increase of number of isomers/components with increasing the carbon numbers. In the method, TPG distribution from Whitson's approach is used to characterize the plus fraction and generate molecular weight / carbon number function. It is, also used to find the best trend fit to the experimental data by solving for parameter. The limiting molecular weight, for each carbon number, is determined to fit the mole fraction that is corresponding to the carbon number. Linear extrapolation of the limiting molecular weight as a function of the carbon number is used here to extend the characterization to the missing data of the higher carbon number (Rodriguez et al., 2010). The reader is recommended to refer to Rodriguez et al. 2010, for further discussion of the proposed method.

3.4 Mixing rules

Mixing rule for calculating critical properties (including acentric factor and specific gravity) of MCN groups is discussed here. Molar and volumetric properties of MCN groups are always calculated using the mixing rules

$$M_l = \sum_i^l {}^{z_i}/_{z_l} M_i \quad (32)$$

$$\gamma_l = \frac{1}{\left[\sum_i^l \frac{\left(f_{wi}/f_{wl}\right)}{\gamma_i}\right]} \tag{33}$$

pseudocritical volume should be calculated using weight fractions

$$V_{pcl=} \sum_i^l \left(f_{wi}/f_{wl}\right).V_{ci} \tag{34}$$

where z_l and f_{wl} are the sums of z_i and f_{wi} found in MCN group l. MCN acentric factors are usually calculated using Kay's mixing rule.

In the next section, a case study is presented in order to implement correct characterization procedures using the described method in previous sections. The sample is a black oil sample collected from an Omani reservoir with specified plus fraction analyzed in the laboratory.

4. Case study: Fahud oil sample characterization

A typical reservoir oil sample collected from an Omani reservoir (Fahud) has been taken into consideration for VLE analysis and characterization scheme.

4.1 Sample selection

A set of PVT reports from different fields in north and central of Oman have been reviewed to choose a sample for our case study having an API of 37.76. The selected sample is a bottom hole sample (BHS) at the depth of 2550 m and the recorded reservoir temperature of 95 ^{0}C.

4.2 Laboratory measurement

The sample is analyzed to indentify the components through the Liquid Gas Chromatograph, AGILENT Technologies, model 7890A. The column name is DB-1 with length of 60 (m) with a diameter of 0.250 (mm) and film thickness of 0.25 (um) column temperature is -60 t0 3250C. The compositional analysis defined the mole composition of several SCN until it reaches to C7. The critical properties of these elements were obtained from Reid et al. (1986). Lastly the pseudo-component (which represents the heptanes plus-fraction of the fluid, in this case C7+) is characterized using the later described Riazi-Daubert correlation (Riazi, M. R., Daubert, T. E. (1987)). Table 2 shows the results of the compositional analysis of this crude oil sample.

4.3 Methodology

The compositional simulator utilized is reservoir simulation Eclipse (Property of Schlumberger) *PVTi* module. It uses the PR-EOS with the modifications on the volume shift, the quadratic mixing rule and Lorenz-Bray-Clark viscosity correlation. For estimation of the undefined element properties, Riazi-Daubert correlation is used (Riazi, M. R., Daubert, T. E. (1987)). This software has been used to find the phase envelop of the reservoir sample and estimation of different characteristics of the oil sample.

No.	Component	[mol %]
1	*N2*	1.67
2	*CO2*	0.24
3	*CH4*	41.2
4	*C2H6*	3.45
5	*C3H8*	1.65
6	*I-C4H10*	0.56
7	*N-C4H10*	1.75
8	*I-C5H12*	0.82
9	*N-C5H12*	1.56
10	*C6H14*	3.32
11	*C7+*	43.78

C7+ MW (gr/mol): 271
C7+ SG (gr/cm3): 0. 848

Table 2. compositional analysis of Fahud crude oil sample

4.4 Phase envelop of the Fahud oil sample

The oil sample analyzed in this study is initially composed of more than about 20 mole% heptanes and heavier compounds which is representative of Black oil type of reservoir fluid. Its phase envelope, therefore, is the widest of all types of reservoir fluids, with its critical temperature well above the reservoir temperature (T_c=828K compared to T_{res}=366K). Phase diagram of this sample is plotted using the Eclipse software as in fig. 1.

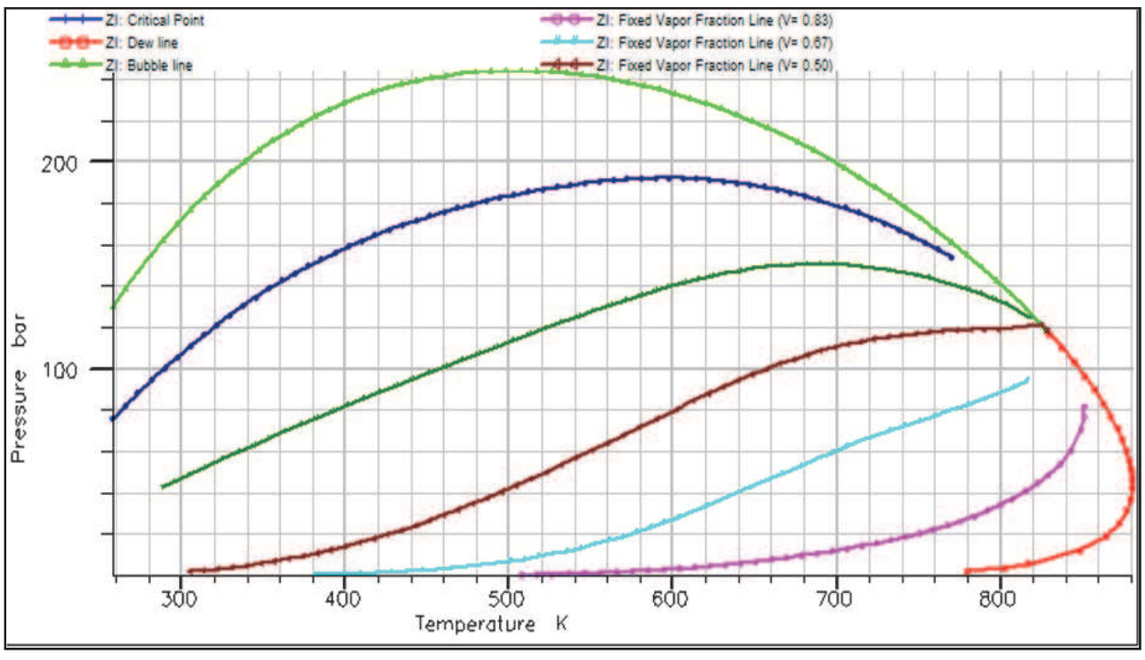


Fig. 1. Phase envelope of Fahud oil sample generated by Eclipse-*PVTi*.

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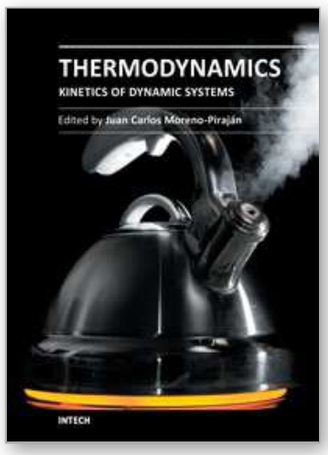
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