Model Development of a Suitable Equation of State for Multicomponent Multiphase Systems: Application to Crude Oil Phase Stability Requirements

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Received 30 April 2018, Revised 20 May 2018, Revised 23 May 2018, Accepted 24 May 2018

Abstract

Stability testing to determine whether or not a phase is stable is a necessary preliminary step for equilibrium calculations as well as a useful object of decision for design and management of reservoir operations. A suitable, and robust Equation of State (EOS) model has been developed to achieve this for a reservoir fluid system over a wide range of pressure conditions. This was done by incorporating the variable parameter ‘a’ approach (VPAA), which treats the attractive parameter as a variable regressed by two straight lines, into the Helmholtz stability criterion. The EOS model was tested on three oil wells with high, medium and low parameter ‘b’ values to predict phase stability status of the fluids over a wide range of pressure conditions. For Well-1, the vapor phase was unstable while the liquid phase was stable at 47.4 atm. For Well-2, the vapor phase was stable at 209 atm while the liquid phase was unstable. For Well-3 however, the vapor phase was stable at 45.7 atm, while two liquid phases were identified. The lighter one was unstable at the temperature of interest, while the heavier one was stable at 115.9 atm.

Keywords: Equation of state; phase stability; reservoir fluids; model; EOS parameter.

1. Introduction

Although a reservoir fluid may be composed of many thousands of compounds, the phase behavior fundamentals can be explained with some degree of accuracy by examining the behavior of pure species. The complexity of the defining model however increases as the number of species increases. Since reservoir fluids are made up of basically hydrocarbons, they, to some appreciable degree, follow similar patterns of phase behavior.

Studies of various hypotheses have led to recent deductions by Danesh [1], that the composition of a reservoir fluid depends on the depositional environment of the formation, its geological maturity and the migration path from the source to the trap rocks. Fluids advancing into a trapping reservoir are usually of different compositions. Reservoir fluids are generally considered, as stated by England and Mackenzie [2], to have attained equilibrium by maturity due to molecular diffusion and mixing over geological times. The compounds constituting a crude in an oil well are classified into groups for easy handling and analysis. This classification and subsequent characterization have proved helpful over the years. Despite this classification into groups of similar materials, based mainly on molecular structure and size, between 15 and 25 groups are often identified and are in regular use in laboratory studies of crude oils.

Equations of state (EOS) are required for the prediction of phase behavior of mixtures of hydrocarbons. The cubic EOS over the years was developed from the ideal gas law and has been applied to non-ideal cases with the inclusion of the attractive force and repulsive force parameters, ‘a’ and ‘b’, respectively. These equations have been successfully applied to pure liquids and gases even at high pressures as shown by Smith et al [3].

There are inherent deficiencies in the use of equation of state models, particularly for multicomponent, multiphase mixtures, such as reservoir fluids. Recent investigations have focused on removing these deficiencies. Therefore, the work reported herein presents, in this quest, a novel model that determines the stability status of a multicomponent, multiphase system, (reservoir fluids) over a wide pressure range. This model thus indicates at what pressure a phase split will occur at a specified temperature.

2. The Search for Reliable EOS Models

Peng-Robinson EOS, developed by Peng and Robinson [4] has gained wide application in the petroleum industry and its modifications by Patel and Teja [5], Ihaveri and Youngren [6], as well as Erdogmus and Adewumi [7] have led to improvements in the prediction of thermodynamic properties of reservoir fluids. In phase equilibrium calculations, it has become widely accepted, as enunciated by Baker et al [8], Michelsen [9], [10], Firoozabadi [11], as well as Firoozabadi and Pan [12], that phase stability analysis is a necessary preliminary step. Phase stability analysis is currently carried out using a stability testing approach which determines by point tests whether or not a system phase is stable at a specified temperature and pressure condition by minimizing the Tangent Plane Distance (TPD) function as shown by Michelsen [10], Baker et al. [8] and Nghiem et al. [13]. Improvements on the dimensionless TPD method of stability testing have been done by researchers who have extended the work to binary and ternary mixtures. The works of Firoozabadi and Pan [12] as well as Hendricks and van Bergen [14] among others extended stability testing to multicomponent mixtures like reservoir fluids by working in the reduced

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space. Improvements in robustness, efficiency and accuracy of solution methods have been the focus of recent works. All stability testing methods however simply tell, at a specified T and P condition (or T and v or some other convenient pair of thermodynamic properties) whether or not a system is stable. It is thus challenging to have to carry out very many point stability tests over a wide range of temperature and pressure conditions by varying one property at a time. The work of Michelsen [15] showed that it is therefore needful to develop more efficient stability analysis methods which will be able to ‘search’ over a wide range of pressures and determine the conditions at which a system will become stable or unstable by splitting into two or more phases. Furthermore, it is not enough just to know whether or not a system is stable but models that can tell how stable a system is will be of great benefit in developing new and more efficient methods for stability analysis. This is the focus of this work; here we present a novel simple model which shows the stability status of a system over a wide pressure range and hence indicates at what pressure a phase split will occur (if it will occur) at the specified temperature. This was achieved by a very major modification of the attractive parameter in the Peng-Robinson cubic EOS.

In the works of Babalola and Susu [16], as well as Knudsen et al. [17], the Peng-Robinson Equation of State (which is cubic) was used to develop a model for predicting the stability limit of a pure system. This was found appropriate for representative paraffinic, naphthenic and aromatic compounds. The EOS having been developed for a pure substance has been modified to improve its generality and hence can be applied to binary, ternary, and even multi component mixtures [12], [13], [18]. For an EOS to be applied to a mixture, the parameters ‘a’ and ‘b’ (which are characteristic of pure substances) are calculated for mixtures using mixing rules. A lot of work by researchers including Mathias et al. [19] and Lin et al. [20] has yielded success in this regard for binary, ternary and also multicomponent mixtures.

There are inherent deficiencies in the use of equations of state particularly for multicomponent mixtures. Recent investigations have focused on removing these deficiencies. EOS models may predict highly erroneous results particularly for near critical conditions, even for well-characterized fluids. Real reservoir fluids contain thousands of components for which the principles of the mixing rules are highly limited. Danesh [1] has shown that some experimental errors, contained in the analyses of reservoir fluids and the fact that carbon groups are often not well defined result in poor EOS models. Compositional analyses are often not very reliable because they are based on equilibrated phases rather than the more accurate high-pressure fluid analysis. The thousands of compounds contained in the reservoir fluids are described by a limited number of pure substances and carbon groups. Generalized correlations often with significantly diverging results are used to estimate the critical properties of the carbon groups required for EOS-based calculations. All these factors further deteriorate prediction by EOS for real reservoir fluids [1]. Kaul and Thrasher [21] showed that the current approach in the industry is to calibrate or tune the EOS against experimental data generated at pertinent conditions for specific field studies. These tuned models serve for prediction beyond the conditions for which data are available. Perderson et al. [22] discussed some methods of tuning equations of state each of which requires a specific set of large amounts of data and could be quite involving and expensive. A much simpler alternative to tuning termed the ‘variable parameter a approach’ (VPAA) has been proposed by Babalola and Susu [18]; in this approach, the parameter ‘a’ of the Peng-Robinson Equation of State (PR-EOS) is taken no longer as a constant but as a variable.

In this work, the VPAA is employed in developing an EOS model that more accurately predicts the detailed phase behavior of multi component multiphase systems. The model is then applied to reservoir fluids from three Nigerian oil wells to graphically determine the stability status of the fluids over a wide range of pressures at the reservoir temperature.

3. Methodology

The necessity for tuning an Equation of state model is to make it perform accurately in predicting properties for which data measurements cannot be done and unless a model is tuned with the specific set of data for a particular fluid system, the errors are usually of great magnitudes [22]. It is desirous to develop EOS models that will not require tuning; such models will save much cost if they are relatively simple [1], Perderson et al [22], have frayed into this quest of a solution method without tuning, by using many experimental compositional analyses, which also could be expensive, to describe the composition of the fluid under consideration.

The work of Babalola and Susu [18], in addressing this issue, showed mathematically that when the variable parameter ‘a’ curve is regressed by using two straight lines for a reservoir fluid sample from an oil well—one straight line for pressures below bubble point pressure and another for pressures above it, the need for tuning would be automatically eliminated. They inferred that the regression by the straight lines intrinsically ‘tunes’ the EOS model for more accurate performance. This approach, termed the Variable Parameter ‘a’ Approach (VPAA), was proposed in their work as a means to overcome the challenges encountered when using mixing rules in dealing with heavy reservoir systems. We therefore here incorporate the VPAA into a modified Peng-Robinson EOS and apply the Helmholtz free energy criterion for intrinsic stability to develop a new EOS model for which no tuning is required.

3.1 Model Development

The Helmholtz energy stability criterion is given as:

\[ A_{vp} = \left( \frac{\partial P}{\partial v} \right)_{T,N} = 0 \] (1)

The Peng-Robinson EOS is given as

\[ P = \frac{RT}{v-b} - \frac{a_c a}{v(v+b)+b(v-b)} \]

(2)

where

\[ a_c = 0.457235 R^2 T_c^2 / P_c \]
\[ b = 0.077796 RT_c / P_c \]
\[ a = [1 + m (1 - T_c^{0.5})]^2 \]
\[ m = 0.37464 + 1.5422 \omega - 0.26992 \omega^2 \]

for lighter components and

\[ m = 0.3796 + 1.485 \omega - 0.1644 \omega^2 + 0.01667 \omega^3 \]

for heavier components.
We employ the VPAA in which parameter ‘a’ being a straight line is given by

\[ a_c = a_1 P + a_2 \]  \tag{3}  

Hence \( a_c \) is a function of \( P \). Therefore, the PR-EOS is modified thus

\[ P = \frac{RT}{v-b} - \frac{(a_1 P + a_2) a}{v(v+b)+b(v-b)} \]  \tag{4}  

Let

\[ [v(v + b) + b(v - b)] = Q \]  \tag{5}  

Thus:

\[ P = \frac{RT}{v-b} - \frac{a_1 P a}{Q} - \frac{a_2 a}{Q} \]  \tag{6}  

Eq. (6) can be re-arranged to yield

\[ P = \frac{RTQ}{(v-b)(Q+a_1 a)} - \frac{a_2 a}{(Q+a_1 a)} \]  \tag{7}  

Eq. (7) is the modified EOS for application to multi-component mixtures.

Applying the Helmholtz free energy criterion for intrinsic stability, we will differentiate the modified EOS [Eq. (7)] with respect to \( V \) (volume) and at constant \( T \) (Temperature) and \( N \) (Number of components). Thus for one mole,

\[ \frac{\partial P}{\partial V} = \frac{(v-b)(Q+a_1 a)[RT(2v-2b)]-RTQ[(Q+a_1 a)+(v-b)(2v+2b)]}{(v-b)^2(Q+a_1 a)^2} - \frac{-a_2 a(2v+2b)}{(Q+a_1 a)^2} = 0 \]  \tag{8}  

So that

\[ \frac{RT(v-b)(Q+a_1 a)(2v+2b)-RTQ(Q+a_1 a)+RTQ(v-b)(2v+2b)}{(v-b)^2(Q+a_1 a)^2} + \frac{a_2 a(2v+2b)}{(Q+a_1 a)^2} = 0 \]  \tag{9}  

Let

\[ (v-b)(Q + a_1 a)(2v + 2b) - Q(Q + a_1 a) + Q(v-b)(2v + 2b) = Y \]  \tag{10}  

So that

\[ \frac{RTY}{(v-b)^2(Q+a_1 a)^2} + \frac{a_2 a(2v+2b)}{(Q+a_1 a)^2} = 0 \]  \tag{11}  

The expression for \( T \) therefore becomes

\[ T = \frac{-a_2 a(2v-2b)(v-b)^2}{BY} \]  \tag{12}  

Substituting Eq. (12) into Eq. (7) we have

\[ P = \frac{RTQ}{(v-b)(Q+a_1 a)} \]  \tag{13}  

Substituting for \( Q \) from Eq. (5) and \( Y \) from Eq. (10) and simplifying, we obtain

\[ 3Pv^6 + 10Pbv^5 + (4Pa_1 a - 5Pb^2 - 5a_2 a)v^4 + (4Pa_1 ab - 28Pb^3 + 8a_2 ab)v^3 + (5Pb^4 - 16Pa_1 ab^2 + Pa_1 a^2 - 14a_2 ab^2 + a_1 a_2 a^2)v^2 + (10Pb^5 - 4Pa_1 ab^3 - 2Pa_1 a^2 b - 8a_2 ab^3 - 2a_1 a_2 a^2 b)v + \left( \frac{Pa_1 ab^4 - Pa_1 a^2 b^2 - 3Pb^6}{Q+a_1 a} \right) = 0 \]  \tag{14}  

This gives us a 6th-order polynomial;

\[ Av^6 + Bv^5 + Cv^4 + Dv^3 + Ev^2 + Fv + g = 0 \]  \tag{15}  

where

\[ A = 3P \]
\[ B = 10Pb \]
\[ C = (4Pa_1 a - 5Pb^2 - 5a_2 a) \]
\[ D = (4Pa_1 ab - 28Pb^3 + 8a_2 ab) \]
\[ E = (5Pb^4 - 16Pa_1 ab^2 + Pa_1 a^2 - 14a_2 ab^2 + a_1 a_2 a^2) \]
\[ F = (10Pb^5 - 4Pa_1 ab^3 - 2Pa_1 a^2 b - 8a_2 ab^3 - 2a_1 a_2 a^2 b) \]
\[ G = 4Pa_1 ab^4 - Pa_1 a^2 b^2 - 3Pb^6 - a_1 a_2 a^2 b^2 + 5a_2 ab^4 \]

Eq. (15) was solved for its six roots using MATLAB software application at various pressures to give the stability limit curve. These were plotted for each well on a Pressure-volume plot.

The T-isotherm was obtained by rearranging the modified EOS for multi component mixtures [Eq. (7)]. Thus:

\[ P = \frac{RTv^2 + 2RTbv - RTb^2 - a_2 av + a_2 ab}{v^3 + bv^2 - 3b^2 v + b^3 a_v - a_1 ab} \]  \tag{16}  

Cross-multiplying and collecting like terms, we have another polynomial;

\[ Jv^3 + Kv^2 + Lv + M = 0 \]  \tag{17}  

where

\[ J = P \]
\[ K = Pb - RT \]
\[ L = a_1 aP - 3Pb^2 - 2RTb + a_2 a \]
\[ M = Pb^3 - a_1 aPb + RTb^2 - a_2 ab \]

Eq. (17) was solved using the MATLAB software application to obtain three roots at various pressures and the result was used to plot the T-isotherm for each of the three wells considered on a Pressure-volume plot.
The limit of stability for the crude in each well was determined. This was accomplished by locating the point of intersection of the stability curve and the T-isotherm when displayed on the same graph at the temperature of the reservoir. If such a limit exists, then the intersection of these two plots indicates the limit of stability. Below the pressure at this point of intersection of the two curves, the substance is unstable. If the two curves do not meet within the temperature range of interest, then there is no limit of stability for that mixture and the mixture is said to be unstable within the pressure range considered.

The authors believe that the error propagated by the assumption that parameter ‘a’ is a constant for a multi component mixture, is responsible for the deficiencies of equations of state such that tuning and sometime elaborate adjustments are then required. From previous works by Babalola and Susu [18], plots for the three wells have been shown to exhibit significant variations of parameter ‘a’ with pressure. Each of these plots was regressed to obtain a best fit. According to Jenson and Jeffreys [24], the ‘best fit’ in graphical methods is a matter of opinion and not necessarily the curve passing through the average points. In deciding the best fit for the plotted points, the least squares method was not used because they observed that the sensitivity of parameter ‘a’ to pressure was not constant. The sensitivity reduced with pressure decrease, and the best fit line was further enhanced by using two straight lines (instead of just one) to model the variation of parameter ‘a’ with pressure. The data for the three wells used in this work was obtained from the conventional PVT data of three oil wells in Nigeria. The pressure and volume values were obtained from the PVT data while the parameter ‘a’ values were calculated using Eq. (2). The best-fit straight lines for the three wells considered in this work are given below: (for Well-1, the two straight lines have the same gradient)

For Well-1,
\[ a(10^{-6}) = 0.99982P - 47.2175 \] (For all P)

For Well-2,
\[ a(10^{-6}) = 0.09854P + 16.167 \] (For \( P > P_b \))
\[ a(10^{-6}) = -0.0299P + 0.500 \] (For \( P < P_b \))

For Well-3,
\[ a(10^{-6}) = -0.02522P + 15.889 \] (For \( P > P_b \))
\[ a(10^{-6}) = 0.0157P + 8.778 \] (For \( P < P_b \))

Other parameters of Eq. (7), which were obtained from data and open literature are:

- \( T \) = well temperature. This is from the PVT data
- \( P_b \) = bubble point pressure. This is also from the PVT data.
- \( b \) = Equation of state parameter. This is the molar volume of the crude at infinite pressure and is calculated using the expression given in Eq. (2)
- \( a_c \) = Equation of state parameter which is now a variable as given in Eq. (3)
- \( \alpha \) = Equation of state parameter. This is calculated using the expression given in Eq. (2).
- \( R \) = gas constant = 82.06 cm³.atm/mol.K

The other EOS parameters given above are presented for the three wells treated in this work in Table 1.

**4. Results And Discussion**

The robustness of the new EOS model is demonstrated by the simulation of the stability of the fluid phases present in three oil wells. The uniqueness of each well is pictured clearly by the model in the graphs generated.

**WELL-1**

Eq. (15) was solved for well-1 and six roots were obtained. Only two of these roots were positive. Spieggl [25] has shown that every root which had a real and an imaginary part (complex root) had its conjugate as a root too. Only the real part of a complex root was considered meaningful in this result. The imaginary part only indicates at what quadrant of the imaginary axes (plane) the root occurred. All negative roots have no physical meaning since we are interested in volume, which cannot be negative. The two roots obtained at various pressure intervals yielded the stability curve of the vapor and liquid phases as shown in Figure 1.

![Figure 1. Stability Limit Curves for Well-1.](image-url)

By solving Eq. (17) for its three roots, only two positive roots were obtained within the pressure range of interest. This gave the T-isotherm for the vapor and liquid phases which were displayed on the same graph as the stability curves as shown in Figure 2. The points of intersection of the stability curve and the isotherm gives the stability limit for each phase. The vapor phase stability curve and isotherm did not intersect showing that the vapor phase was unstable while the liquid phase stability limit is read off from the intersection of its stability curve and isotherm as 47.4 atm.
Theoretically, the stability limit curve (spinodal curve) intersects the T-isotherm at the point of stability of the system. This was demonstrated mathematically for pure and binary systems by Model and Reid [26] and validated using the experimental works of Skipov and Ermakov [27]. These works were very closely matched by the work of Babalola and Susu [16]. The EOS model developed in this work is an extension of this Helmholtz energy stability criterion approach to multicomponent multiphase systems. There are strong theoretical indications that accurate stability analyses can be more easily achieved by models based on Helmholtz energy criterion than those based on Gibbs energy stability criterion [26]. Nichita [28] explained that the difficulty in phase split determination consists in the fact that the Gibbs energy-based TPD objective function is highly non-linear and non-convex and hence does not guarantee that the global minimum will be found. As far as the authors are aware, this is the first extension of Helmholtz energy stability criterion to multicomponent multiphase systems.

As expected from theory, this model is relatively simple and has several other advantages. It not only determines qualitatively whether or not a system is stable at specified temperature and pressure conditions, but also shows quantitatively how far from stability the said system is. The extent of stability and metastability of fluid systems are outside the scope of this paper and will be addressed in subsequent works.

**WELL-2**

For WELL-2, the solutions of Eqs. (15) and (17) yielded two positive roots in each case; the larger value for the vapor phase and the smaller for the liquid phase. The resulting plots are as shown in Figure 3. For the vapor phase, volume decreased slightly initially with increasing pressure, then went through a sudden rise around the bubble point pressure (P_b) and began to slightly decrease again after undergoing a maximum at 230 atm. For the liquid, the volume increased slightly initially with pressure rise, went through a little drop at a pressure of about 210 atm, and began to rise gently again. Very small intervals of pressure rise were simulated around this region for closer monitoring.

In Figure 4, the T-isotherm for the vapor phase intersects the vapor stability limit curve at 218 atm. The T-isotherm for the liquid phase comes very close but does not intersect the stability limit curve. Such near-stability scenarios call for quite involving investigations that are currently on-going. However, it is hoped that helpful findings that will enhance phase behavior control tools in reservoir operations and management will emerge therefrom. Challenges arising mainly from the inaccuracies of EOS models, especially at near critical conditions [29], will be reduced with such models as this which do not require tuning. Danesh [1] emphasized that an EOS that could predict phase behavior data reasonably well without requiring any tuning would be the best option.

**WELL-3**

The solution to Equation (15) yielded six roots for WELL-3 three of which were positive at each pressure value. Two of these roots corresponded to the liquid phase while one was for the vapor phase. These resulted in three stability limit curves for the fluid system in WELL-3 indicating one vapor phase and two liquid phases as shown in Figure 5. From Figure 6, the conditions at which these split phases are stable can easily be read off.
This is quite intriguing and is a major hallmark advantage of this model. As far as the authors are aware, no model yet predicts the conditions for phase split by a simple ‘search’ over a wide range of pressures. For the vapor phase, the volume decreased with increase in pressure and went through a sudden rise at the bubble point pressure and then began to decrease again at a slower gradient with further increase in pressure. For the lighter liquid phase, the stability limit curve showed a steady decrease in volume with increase in pressure, a slight but sudden rise around the bubble point pressure and then further decrease with increase in pressure at an even slower gradient. For the heavier liquid phase, the volume remained almost constant with increase in pressure, rose very slightly at the bubble point pressure and decreased very slowly with further increase in pressure. It is evident that the volume rise around the bubble point pressure is somewhat in direct proportion to the molar volume of the phase concerned.

Two T-isotherms were obtained, one for the vapor phase and the other for the two liquid phases. The vapor phase T-isotherm intersects the vapor phase stability limit curve at a pressure of 45.7 atm. This is shown in Figure 6 but is further enlarged and extended for clearer observation in Figure 7.

The T-isotherm for the liquid phases does not intersect the stability limit curve for the lighter liquid but intersects that of the heavier liquid at a pressure of 115.9 atm. as enlarged for clarity in Figure 8. This implies that the lighter liquid was unstable at the well temperature and over the pressure range considered while the heavier liquid was found to be stable at 115.9 atm. The summary of these results are shown in Table 2.

<table>
<thead>
<tr>
<th>WELL</th>
<th>STABILITY LIMIT (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor</td>
<td>Liquid 1</td>
</tr>
<tr>
<td>1</td>
<td>Unstable</td>
</tr>
<tr>
<td>2</td>
<td>209</td>
</tr>
<tr>
<td>3</td>
<td>45.7</td>
</tr>
</tbody>
</table>

Some of these cases of instability may actually include cases of metastability for which some thermodynamic properties may be readily manipulated to bring about stability under the reservoir conditions. Models that will distinguish between these two states for multicomponent systems are yet to be developed, but the basic theoretical principles have been delineated by researchers [30].
5. Conclusions

The following conclusions are derivable from this work:
1. The Equation of state model developed in this work is an improvement on the advances made so far in the quest for a reliable EOS model as evidenced in various works cited here. It takes account of virtually all the factors that contribute to the phase behavior of crude oils while minimizing the unwanted influence of error propagation due to large data usage in model development and applications.
2. This EOS model gives not only the detailed phase behavior of any crude but also clearly indicates the number of phases present and their paths of intrinsic stability.
3. Of great practical significance is the capacity of the model to show the splitting of the liquid phase in Well-3. This is likely to be connected with the particularly low molecular weight (overall) of the crude from this well which also resulted in its low value of parameter ‘b’ as shown in Table 4.
4. With this model, an oil well phase scenario, over a wide pressure range, can be seen at a glance for well-informed decisions on design, operations and management of the well during production.

6. Nomenclature

\[ A_{NV} = \text{Helmholtz free energy} \]
\[ \alpha_a = \text{Equation of state attractive force parameter} \]
\[ b = \text{Equation of state repulsive force parameter (co-volume)} \]
\[ \omega = \text{acentric factor} \]
\[ T = \text{Temperature} \]
\[ P = \text{Pressure} \]
\[ v = \text{molar volume} \]
\[ R = \text{Universal gas constant} \]
\[ P_b = \text{Bubble point pressure} \]
\[ TPD = \text{Tangent Plane Distance} \]
\[ EOS = \text{Equation of State} \]

References


