A Numerical Comparison of Soave Redlich Kwong and Peng-Robinson Equations of State for Predicting Hydrocarbons' Thermodynamic Properties

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Abstract—**Mixture phase equilibrium and thermodynamic properties have a significant role in industry. Numerical analysis of flash calculation generates an appropriate solution for the problem. In this research, a comparison of Soave Redlich Kwong (SRK) and Peng-Robinson (PR) equations of state predicting the thermodynamic properties of a mixture of hydrocarbon and related compounds in a critical region at phase equilibrium is performed. By applying mathematical modeling of both equations of states, the behavior of binary gases mixtures is monitored. The numerical analysis of isothermal flash calculations is applied to study the pressure behavior with volume and mole fraction. The approach used in this research shows considerable convergence with experimental results available in the literature.**

Keywords-Peng-Robinson; Soave Redlich-Kwong; equation of state; mathematical modeling; flash calculation; methane; carbon dioxide; hydrogen

I.   INTRODUCTION

Thermodynamic properties play a vital role in chemical engineering applications for chemical process design and simulations [1]. The equation of states (EOS) is mostly applied for an appropriate, valid and robust solution for the prediction of phase behavior at vapor-liquid equilibrium for all kind of mixtures containing light gases or heavy liquids [2-6]. EOS is unable to predict liquid density more accurately under a vast range of temperature, acentric factor and on critical points. However, the prediction can be made precisely by the attribution of temperature dependence factor and effective volume pressure parameter in the EOS [7-9]. The SRK and PR EOSs are mostly used in chemical industries for the prediction of vapor-liquid equilibrium and thermodynamic properties for both polar and nonpolar compounds containing mixtures [10, 11]. However, the PR EOS prediction of saturated liquid density, constant critical compressibility factor and vapor-liquid equilibrium for hydrogen and nitrogen is more precise compared to SRK [12-15]. The equations are involved in the study of vapor liquid, liquid-liquid and vapor-liquid-liquid equilibrium [16]. For the liquid compounds the prediction of fugacity, and on subcritical and supercritical the fugacity prediction by SRK is reliable, but when the temperature

becomes high in case of polar and heavy compounds, it cannot give accurate predictions [17, 18]. In PR and SRK calculation the critical compressibility factor and the Pitzer acentric factor is kept constant for all mixture compounds [6, 19-22]. This acentric factor is involved in the estimation of the mean field parameter and the effective volume for both SRK and PR EOSs. However, the relationship of an acentric factor with the mean field parameter and the effective volume is different for both equations [23]. Hydrogen/propane, methane/n-butane, carbon dioxide/propane and methane/n-decane mixtures are under study in this research. Because in chemical industries, gas solubility and phase equilibrium of hydrogen, methane and carbon dioxide containing mixtures have vital role [24]. At isothermal flash, the calculation is done at vapor-liquid equilibrium for separation of liquid and vapor phases as shown in Figure 1.
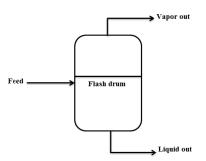
Fig. 1.   Isothermal flash process

The purpose of this study is to compare the innovative numerical approach used for SRK and PR EOS with experimental data obtained from the literature. In this numerical approach for both cubic equations of states the compressibility factor, pressure and temperature as algorithm's input and mole fraction of every mixture component in both liquid and vapor phases is obtained as result under the applied condition of ratio between liquid and vapor fugacity which generate more precise K-value than in the start of the algorithm. The relationship of pressure and volume under isothermal conditions for both SRK and PR EOSs model is compared, and pressure mole fraction relationship of both

models is compared with experimental data for all given mixtures. The comparison shows that in a mixture containing organic compounds the PR model is more precise in both phases. However, when the mixture contains both organic and inorganic compounds, the SRK model is more precise in the liquid phase compared to PR model.

II. MATHEMATICAL MODELING

The isothermal flash calculation is carried out for the phase equilibrium by iterating pressure to get the liquid and vapor fraction of the mixture. For satisfying the applied condition, iterating pressure applies the loop whereas the temperature and pressure are independent variables for this system. For K-values, where

$$k_i = \frac{y_i}{x_i} \tag{1}$$

In literature, empirical correlations are available for K values. In this case, the empirical correlation used is Wilson equation for K-value which is further used for the calculation of phase fraction. If the K-value approaches equilibrium, the convergence occurs for the solution.

$$k_i = \frac{\exp[5.37(1+\omega_i)(1-\frac{1}{T_{ri}})]}{p_{Ri}} \tag{2}$$

For the calculation of liquid and vapor mole fraction, the Richford Rice procedure is followed. On (5) for liquid mole fraction, the Newton-Raphson method is used, and the method uses the condition given in (7).

$$x_i = \frac{z_i}{L+(1-L)k_i} \tag{3}$$

$$y_i = k_i x_i \tag{4}$$

$$F(L) = \sum_{i=0}^{n_c} \frac{(1-k_i)z_i}{L+(1-L)k_i} \tag{5}$$

$$L^{new} = L^{old} - \frac{F(L^{old})}{\left(\frac{dF}{dL}\right)_{L^{old}}} \tag{6}$$

$$\left(\frac{L^{new}}{L^{old}}-1\right) < 10^{-5} \tag{7}$$

$$L = \frac{z_i - y_i}{x_i - y_i} \tag{8}$$

Equation of state parameters is calculated from given equations:

$$(aa)_m = \sum_{i=1}^{n_c}\sum_{j=1}^{n_c} x_i x_j (aa)_{ij} \tag{9}$$

$$(aa)_{ij} = (1-k_{ij})\sqrt{(aa)_i (aa)_j} \tag{10}$$

$$b_m = \sum_{i=1}^{n_c} x_i b_i \tag{11}$$

For the suitable VLE behavior of the given mixture, we can solve the SRK and PR EOS to get molar volumes of both phases [25]. Because of the difference in phase's composition, the two solutions are essential for roots of both cubic EOS. The iterative approach is applied to (12) for cubic roots of SRK EOS and to (13) for cubic roots of PR EOS.

$$p = \frac{RT}{V_m - b_m} - \frac{(aa)_m}{V_m(V_m + b_m)} \tag{12}$$

$$p = \frac{RT}{V_m - b_m} - \frac{(aa)_m}{V_m(V_m + 2b_m) - b_m^2} \tag{13}$$

Compressibility factor is calculated by using (14):

$$Z_L = \frac{pV_{mL}}{RT} \tag{14}$$

The fugacity and pressure relation give a dimensionless number which is the fugacity coefficient. The liquid phase fugacity for all components is calculated from (15) and for vapor phase a change is made in (15) by replacing x_i with y_i and L subscript with V.

$$\hat{f}_{iL} = p\exp\left(n\left(\frac{V_{mL}}{V_{mL}-b_{mL}}\right) + \frac{b_i}{V_{mL}-b_{mL}} + \left(\frac{2\sum_{j=1}^{n_c} x_j(aa)_{ij}}{RTb_{mL}}\right)\ln\left(\frac{V_{mL}}{V_{mL}+b_{mL}}\right) + \frac{b_i(aa)_{mL}}{RTb_{mL}^2}\left[\ln\left(\frac{V_{mL}+b_{mL}}{V_{mL}}\right) - \frac{b_{mL}}{V_{mL}+b_{mL}}\right] - \ln\left(\frac{z_L}{x_i}\right) \right) \tag{15}$$

To satisfy the equilibrium, (16) is used to converge the solution at certain liquid and vapor composition [26]. If the equilibrium is not satisfied, (21) is used for new K-value and again iterate the process until the satisfaction of equilibrium.

$$\left(\frac{\widehat{f_{iV}}}{\widehat{f_{iL}}}-1\right) < 10^{-5} \tag{16}$$

$$\widehat{\phi_{iV}} = \frac{\widehat{f_{iV}}}{y_i\, p} \tag{17}$$

$$\widehat{\phi_{iL}} = \frac{\widehat{f_{iL}}}{x_i\, p} \tag{18}$$

$$\frac{\widehat{\phi_{iL}}}{\widehat{\phi_{iV}}} = \frac{\widehat{f_{iL}}\, y_i}{\widehat{f_{iV}}\, x_i} \tag{19}$$

$$\frac{\widehat{\phi_{iL}}}{\widehat{\phi_{iV}}} = \frac{y_i}{x_i} \tag{20}$$

$$k_i^{new} = \frac{\widehat{f_{iL}}}{\widehat{f_{iV}}} k_i^{old} \tag{21}$$

The overview of the iterative method is explained in the flow chart shown in Figure 2. The operating parameters for EOS modeling are given in Table I.

TABLE I.   OPERATING PARAMETERS

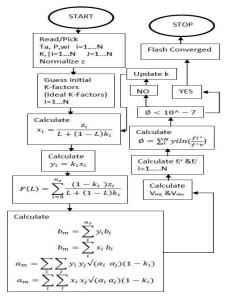| Parameters	Hydrogen Propane		Methane n-butane	
	Hydrogen	**Propane**	**Methane**	**n-butane**
T_c (K)	33.2	370	190.82	425.32
P_c (atm)	12.8	41.8	45.8	37.42
ω	0.205	0.153	0.012	0.199
T (K)	310.93		310.93	
P (atm)	13 - 433		3.536 - 136	
	Carbon dioxide propane		**Methane n-decane**	
	Carbon dioxide	**Propane**	**Methane**	**n-decane**
T_c (K)	304.2	370	190.82	617.8
P_c (atm)	73	41.8	45.8	21.1
ω	0.268	0.153	0.012	0.49
T (K)	277.56		477.594	
P (atm)	5.4 - 37.9		3.536 - 136	

Fig. 2.   Flow chart of the flash calculation

III.   RESULTS AND DISCUSSION

Numerical analysis approach is applied for both SRK and PR EOS on four sets of binary mixtures: hydrogen/propane, methane/n-butane, carbon dioxide/propane and methane/n-decane with a tolerance level of 10^{-7}. Under isothermal conditions for hydrogen, methane, and carbon dioxide the behavior of pressure with volume is observed. Figures 3-5 show the decrease in pressure by the increasing volume for SRK and PR EOS when the temperature is less than the critical compared to when the temperature is close to critical. After some interval, the point from where there is no remarkable change in pressure is reached. In the case of mixture of hydrogen/propane, wide deviation has been reported. This is caused by the presence of hydrogen in the system. In order to overcome this deviation the binary interaction parameter is used. In vapor phase, the phase behavior shows no difference between SRK and PR EOS model results with experimental data [27] but in the liquid phase, the phase behavior results of SRK model show less deviation compared to the results of PR model.
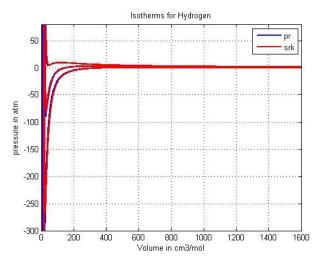

Fig. 3.   Isotherms for Hydrogen
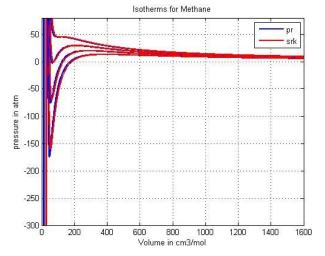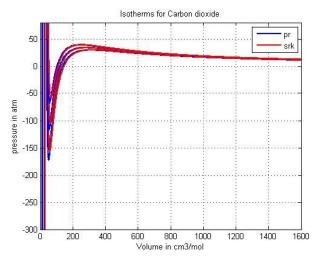

Fig. 4.   Isotherms for Methane

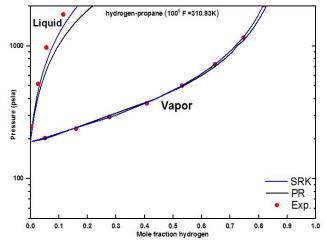Fig. 5.   Isotherms of Carbon dioxide

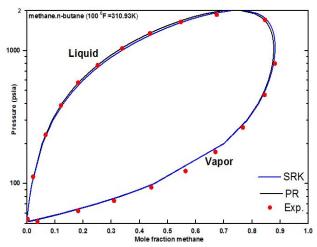Fig. 6.   Mole fraction of hydrogen at various pressures

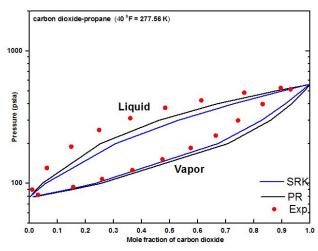Fig. 7.   Mole fraction of methane at various pressures

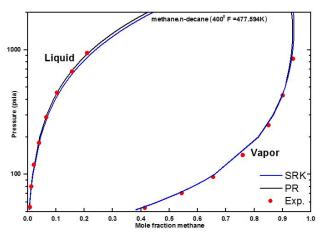Fig. 8.   Mole fraction of carbon dioxide at various pressures

Fig. 9.   Mole fraction of methane at various pressures

However, the graphical trend of SRK and PR model follow the same trend of experimental outcomes as shown in Figure 6. The presence of carbon dioxide in the mixture will generate a deviation in the prediction of phase behavior. Figure 8 shows that in the liquid phase the deviation of PR EOS from experimental results is less than that of SRK model, however in vapor phase the deviation of SRK is less compared to PR model but the trend of phase behavior for both SRK and PR EOS model follows the experimental phase behavior. In a binary mixture of methane/n-butane and methane/n-decane the phase behavior predicated by PR EOS model is more precise with experimental results compared to SRK model in liquid phase but in the vapor phase, both SRK and PR EOS are both accurate as shown in Figures 7, 9. This shows that in critical conditions the prediction of phase behavior can be done in a precise way for hydrocarbon mixtures. However, there is a wide difference in volatilities of methane and n-decane, but the mixing rules of the EOS have applied accurately.

IV.   CONCLUSIONS

In this study, numerical analysis is applied on SRK and PR EOS for pressure relation with mole fraction and volume for binary mixtures of hydrogen/propane, methane/n-butane, carbon dioxide/propane and methane/n-decane. The mole fraction relation with pressure for all binary mixtures is acquired at vapor-liquid equilibrium by making an iteration of pressure in the certain domain under critical conditions. The prediction of phase behavior by SRK and PR EOS models show that both models give an accurate prediction for the system of methane/n-butane and methane/n-decane with experimental results under critical conditions. However, in hydrogen/propane mixture the phase behavior in liquid phase predicted by SRK model show less deviation with experimental data compared to PR model. This is due to the presence of lighter gases such as hydrogen in the mixture and low mixture pressure. VLE is affected by the presence of carbon dioxide in carbon dioxide/propane mixture due to which deviation is reported up to a finite range of pressure. The PR model shows less deviation with experimental data in the liquid phase, but SRK model shows less deviation in the vapor phase. The trend of deviation for both SRK and PR with experimental data decreases with increase in pressure and at high pressures it

become almost insignificant. The isotherm from SRK and PR showed that the pressure initially decreases, after it starts increasing and finally reaches constant behavior. In a mixture containing only organic compounds the approach used for PR EOS is more precise with experimental data of pressure and mole fraction at both phases. However, when the mixture contains inorganic and organic compounds the approach used for SRK EOS results in more precise pressure and mole fraction relationship with experimental data in the liquid phase.

NOMENCLATURE

PR EOS = Peng-Robinson equation of state

f_L = fugacity of a component in a mixture (Pa)

K_i = K-values of nth component (dimensionless)

k = binary interaction parameter (dimensionless)

L = Liquid mole fraction (dimensionless)

P_c = critical pressure (atm)

P = pressure (Pa)

R = ideal gas constant

t = time (seconds)

T_c = critical temperature (Kelvin)

T = temperature (Kelvin)

V = vapor mole fraction

x = x-coordinate

x_i = mole fraction of ith component in liquid

y_i = mole fraction of an ith component in the vapor

ω = acentric factor

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