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Research Article

NUMERICAL ANALYSIS OF FLASH CALCULATION USING SOAVE REDLICH- KWONG EQUATION OF STATE WITH MATLAB

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ABSTRACT

Flash calculation is an important process in the industry to study the phase equilibrium. The mathematical modeling of flash calculation is getting significant in industrial problem solving. In this research, Soave Redlich Kwong (SRK) equation is used to calculate the thermodynamic properties of the mixture in the critical region. From the literature, experimental data is selected to study the behavior of four different binary mixtures. Mathematical modeling was performed to study the behavior of pressure with a mole fraction of the liquid phase and vapor phase mixture at equilibrium. An initial guess of K-values is done by using Wilson equation. The equilibrium is established when the convergence is occurring on applied condition of fugacity coefficient. The behavior is compared with the experimental data present in literature which show that this isothermal flash calculation almost follows the same trend like as experimental data.

Keywords: Mathematical modeling, flash calculation, Soave Redlich-Kwong equation of state, methane, carbon dioxide, hydrogen.

1. INTRODUCTION

In chemical engineering application, such as azeotropic distillation, supercritical extraction, petroleum and reservoir engineering the calculation of chemical and phase equation have great importance [22]. EOS has an important role in chemical engineering design. To study the mixture phase behavior at typical temperature and pressure ranges the equation of state is widely use and can be applied to mixtures of variety components ranging from light gas to heavy liquid [4; 6; 8; 19]. The phase equilibrium of mixtures depends on the suitable choice of mixing rules and on selected attractive term for pure components [13]. At the start, these equations are used only for non-polar and to some degree polar compounds. For polar and non-polar mixtures, the phase equilibrium is calculated by the equation of state. These equations are used to develop complex phase behavior model of the non-ideal mixture [20]. The cubic EOS have the inherent limitation of saturated liquid d ensity prediction by parameters obtained from critical parameters and acentric factor [3; 14; 21].

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The temperature, pressure and chemical potentials of the two phases at equilibrium state must be equal in heat, mass transfer and boundary displacement. When the chemical potential of the two phases is equal the fugacity became equal also. Above mentioned three limitations must be satisfied in chemical equilibrium for every component of the mixture [5].

The first equation of state developed was Van der Waals which estimates the existence of vapor liquid together. Subsequently, Redlich-Kwong equation was developed to improve the accuracy of Vander Waal equation by introducing the term of temperature dependence. Soave improved the Redlich-Kwong by introducing the more temperature dependence term which is a function of acentric function and this additional modification lead more precise calculation of vapor pressure liquid density and equilibrium ratio [19]. At some specific temperature, the value of this function become zero and after that, by increasing the temperature it also starts to increase. This modification is suitable for nonpolar compounds but not for polar compounds. After that Soave again give two parameters modification for temperature dependence function. This new modification lead to solving the thermodynamic properties for both polar and non-polar compounds with the best correlation with the experimental data [2; 18]. SRK is preferred to other equation of states in chemical and petroleum industry due to its simplicity and easy to use [1]. Constant critical compressibility factor and saturated liquid density prediction are the two limitations of SRK [9]. At high pressure and at a critical point it predicts the accurate fugacity of liquid compounds. SRK is used to study the volume liquid equilibrium, volume liquid-liquid equilibrium and liquid-liquid equilibrium [7]. In volume liquid equilibrium of mixture, SRK gives a satisfactory prediction of fugacity of both subcritical and supercritical compound in the mixture. However, at high temperature, the SRK behavior is not so satisfactory for heavy and polar compounds [12]. SRK EOS require critical pressure, critical temperature and acentric factor for all component of the mixture for the calculation of mean field attraction ‘a’ and effective volume pressure ‘b’ [10].

For mixture with a finite number of components, there are many numerical techniques to do the isothermal flash calculation. This calculation is done for those systems in which feed is divided into two phases’ liquid and vapor at vapor liquid equilibrium as shown in Figure 1.

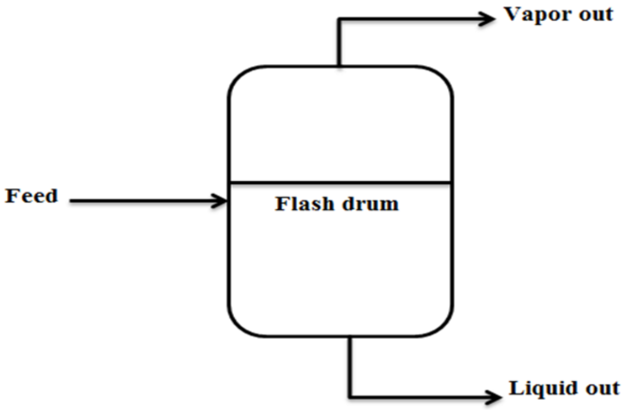

Figure 1. Isothermal flash process

The process to do the flash calculations the SRK equation of state is used to find out the volumes of liquid and vapor phases. In literature, the vapor and liquid mole fraction are used as input. In this model, the value of compressibility factor is used as input to the algorithm. The algorithm used this value to calculate the vapor and liquid mole fraction. In the flash calculation, the challenging task is to solve t he differential of SRK equation by changing the pressure to find out the volume of both liquid and vapor phases. To overcome this issue, the innovative mathematical approach is used in MATLAB by applying the Newton-Raphson method. This is basic aim of this research. The volume of both phases' leads to finding out the compressibility factor. Compressibility factor is used to find out mole fractions of both phases. After that fugacity, the calculation is down. The convergence of both phases fugacity leads to solving the most accurate K-values.

In this research, experimental data of different mixtures are taken from literature and by applying numerical technique the behavior between pressure and mole fraction of liquid and vapor phase mixture equilibrium is noted. This behavior is compared with the experimental date it shows that the results from numerical technique are following the same trend as the experimental behavior of mixtures.

2. MATHEMATICAL MODELING

For phase equilibrium, the isothermal flash calculation is done around vapor fraction by iterating pressure. The temperature and pressure are two independent variables. Loop is applied for iterating pressure to satisfy the applied condition.
Guess initial K values, where

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

There are some empirical correlations to calculate the phase fraction by K-value. Wilson equation is used to find the K-value. If the K-value is near to the equilibrium the solution will converge.

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

Richford Rice procedure is used to calculate the liquid mole fraction (x_i) and vapor mole fraction (y_i) of the mixture. On equation (5) the Newton-Raphson method is applied to solve the value of liquid mole fraction by applying the condition of equation (7)

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

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

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

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

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

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

Calculate the equation of state parameters

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

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

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

For the molar volume of both liquid and vapor phase, solve the SRK EOS which gives the appropriate vapor liquid equilibrium behavior of mixture [16]. As the composition of both phases is different, so for the roots of cubic EOS, two different solutions are required. The iterative method is used to solve the cubic roots of the EOS.

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

Calculate the compressibility factor

$$Z_L = \frac{pV_{mL}}{RT} \tag{13}$$

Calculate the fugacity in both phases for each component. For vapor phase fugacity replace the x_i with y_i and subscript L with V. The purpose of fugacity calculation is to find out the deviation of gases from ideal behavior. The fugacity is the effective pressure of real gases calculated at a constant temperature. The fugacity coefficient which is dimensionless quantity is the relation between the fugacity and the ideal gas pressure.

$$\hat{f}_{iL} = pexp\left(\ln\left(\frac{V_{mL}}{V_{mL} - b_{mL}}\right) + \frac{b_i}{V_{mL} - b_{mL}} + \left(\frac{2\sum_{j=1}^{n_c} x_j (aa)_{ij}}{RTb_{mL}}\right) ln\left(\frac{V_{mL}}{V_{mL} + b_{mL}}\right) + \frac{b_i (aa)_{mL}}{RTb_{mL}^2}\left[ln\left(\frac{V_{mL} + b_{mL}}{V_{mL}}\right) - \frac{b_{mL}}{V_{mL} + b_{mL}}\right] - ln\left(\frac{Z_L}{x_i}\right)\right) \tag{14}$$

If the condition of vapor fugacity and liquid fugacity is given in equation (15) satisfied the equilibrium [17] the solution will converge at recent vapor and liquid composition for pure fluid at VLE else uses the equation (20) to update the new K-value and again repeat the process till equilibrium achieved.

$$\left(\frac{\widehat{f_{iV}}}{\widehat{f_{iL}}} - 1\right) < 10^{-5} \tag{15}$$

$$\widehat{\emptyset_{iV}} = \frac{\widehat{f_{iV}}}{y_i\, p} \tag{16}$$

$$\widehat{\emptyset_{iL}} = \frac{\widehat{f_{iL}}}{x_i\, p} \tag{17}$$

$$\frac{\widehat{\emptyset_{iL}}}{\widehat{\emptyset_{iV}}} = \frac{\widehat{f_{iL}}}{\widehat{f_{iV}}}\frac{y_i}{x_i} \tag{18}$$

$$\frac{\widehat{\emptyset_{iL}}}{\widehat{\emptyset_{iV}}} = \frac{y_i}{x_i} \tag{19}$$

$$k_i^{new} = \frac{\widehat{f_{iL}}}{\widehat{f_{iV}}} k_i^{old} \tag{20}$$

The flow chart shown in Figure 2 has been used in the process to obtain results through mathematical modeling.It highlights the iterative procedure which is carried out to obtain accurate results.

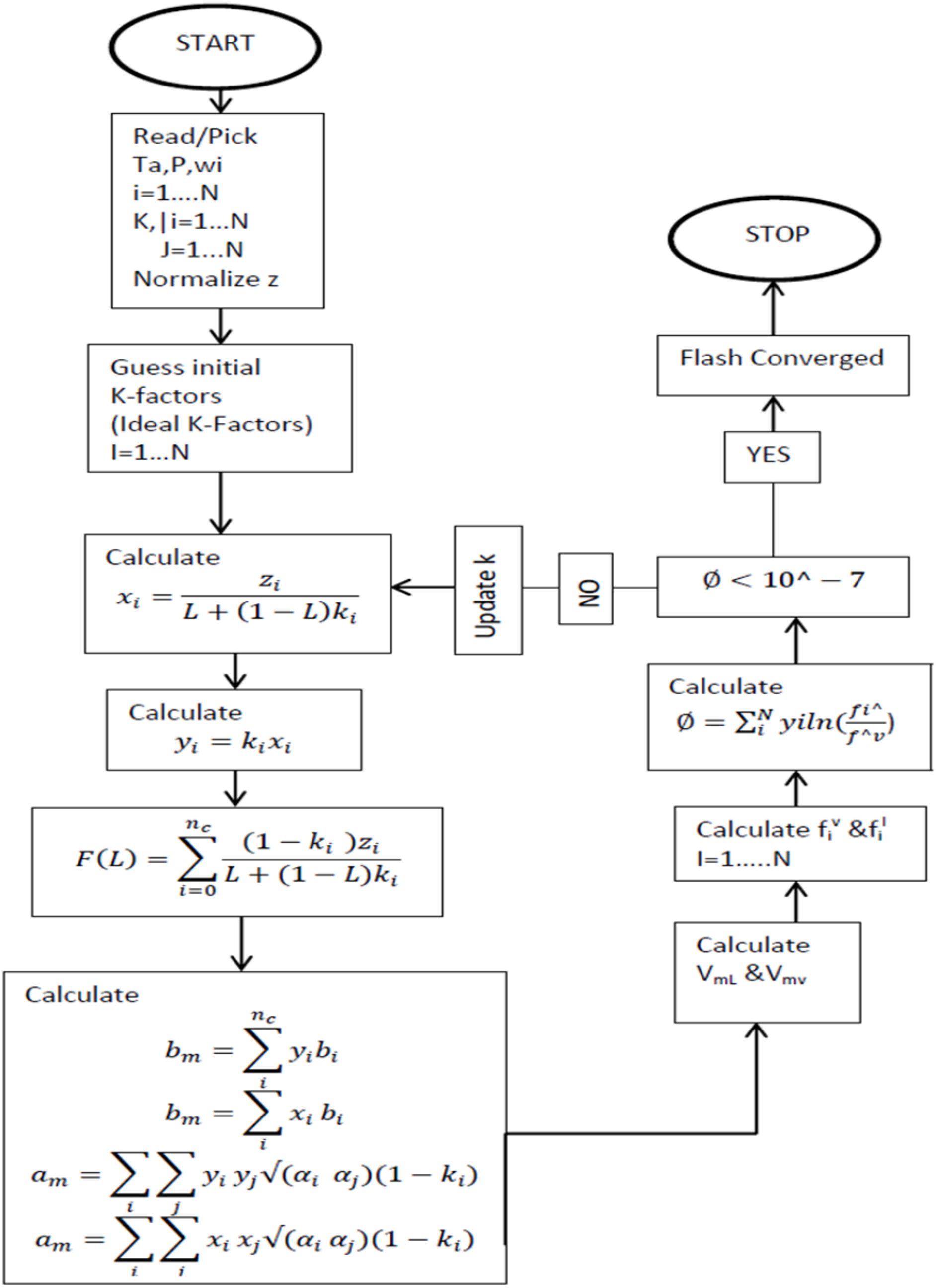

Figure 2. Flow chart of the flash calculation

The operating parameters of all the cases for flash calculation using SRK is given in Table 1.

Table 1. Operating parameters for flash calculation

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

3. RESULTS AND DISCUSSION

The mathematical model is applied on all mixtures hydrogen propane, methane n-butane, carbon dioxide propane and methane n-decane. The phase behavior, mixing rule ability and behavior of mathematical and experimental approach is noted of every case. The isotherms of pressure-volume relationship are obtained for the hydrogen, methane and carbon dioxide [11]. The temperature varying from 1.15 K to 34.15, 110.15 K to 190.15 K and 233.15 K to 263.15 K respectively as shown in figure 3-5. The isotherm shows that when the pressure become near to zero the behavior of gases starts becoming constant with respect to pressure.

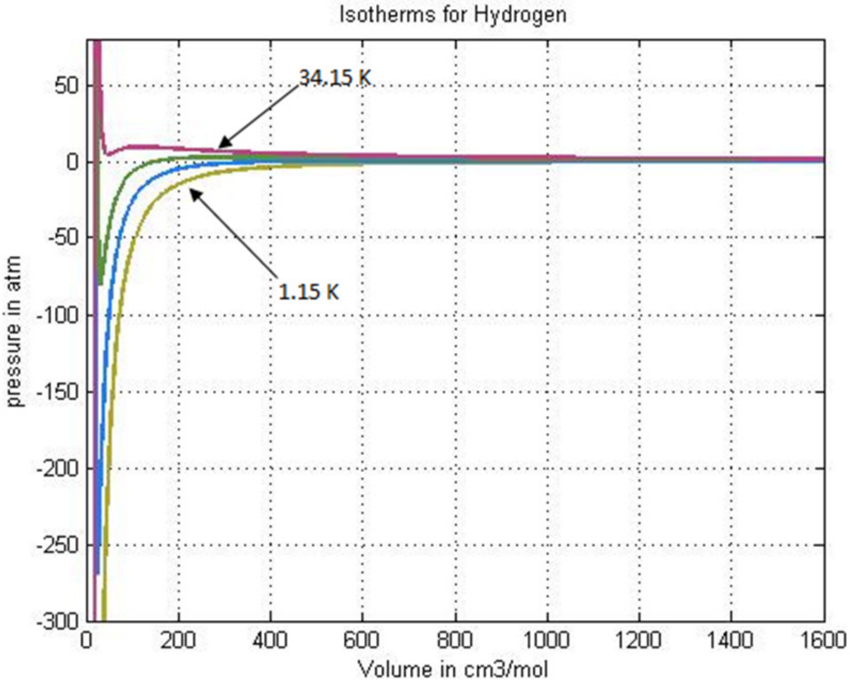

Figure 3. Isotherms for Hydrogen

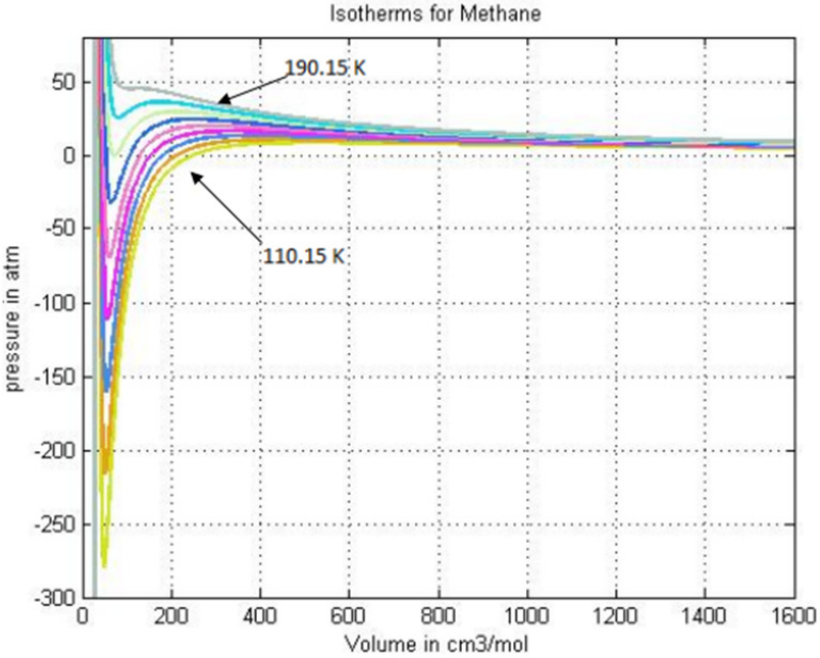

Figure 4. Isotherms of Methane

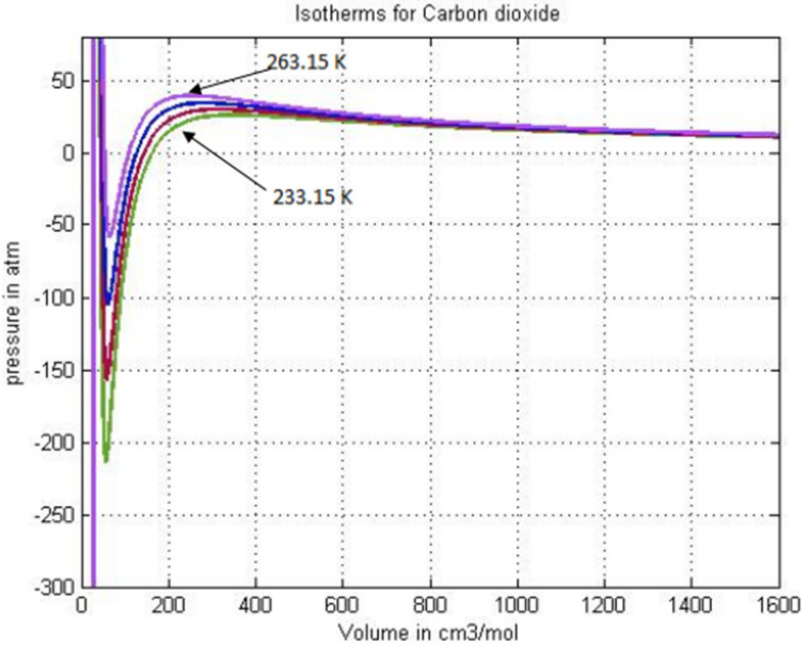

Figure 5. Isotherms of Carbon dioxide

Due to the presence of hydrogen in a mixture of hydrogen and propane the range of pressure become limited and huge deviation is noted in the mixture. For the more accurate behavior of hydrogen-containing mixture, the binary interaction parameter is used. By this convergence between phases become more accurate as shown in figure 6. In methane n-butane mixture the phase behavior for both phases coverage almost as the experimental behavior of mixture. This presents that the accurate prediction can be generated at the critical conditions of the mixture as shown in figure 7. In figure 8 The deviation is noted in a mixture containing polar compounds and mixture containing carbon dioxide. But for pure components, the vapor pressure is regenerated in more accurately. The mixture of methane and n-decane having a huge difference between volatilites. The mixing rules of EOS are accurately followed by the mixture. When the graphical trend of mixture taken from calculated and experimental results compared with each other show that graph from calculated results follows the experimental trend as shown in figure 9.

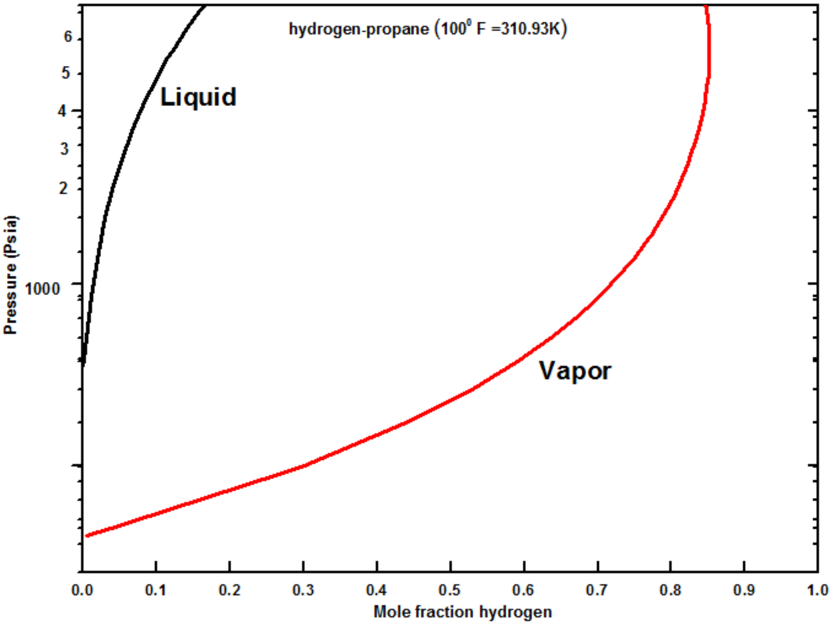

Figure 6. Mole fraction of hydrogen at various pressures

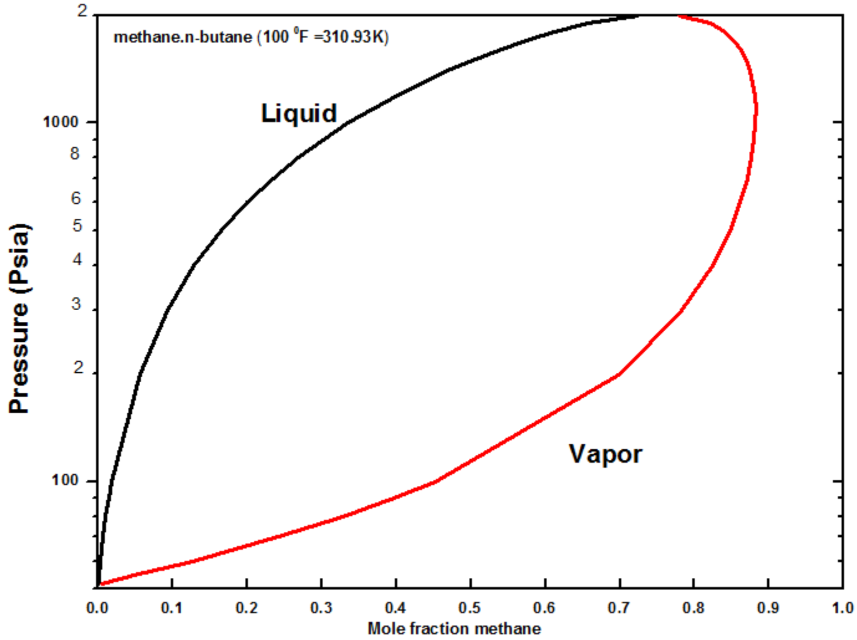

Figure 7. Mole fraction of methane at various pressures

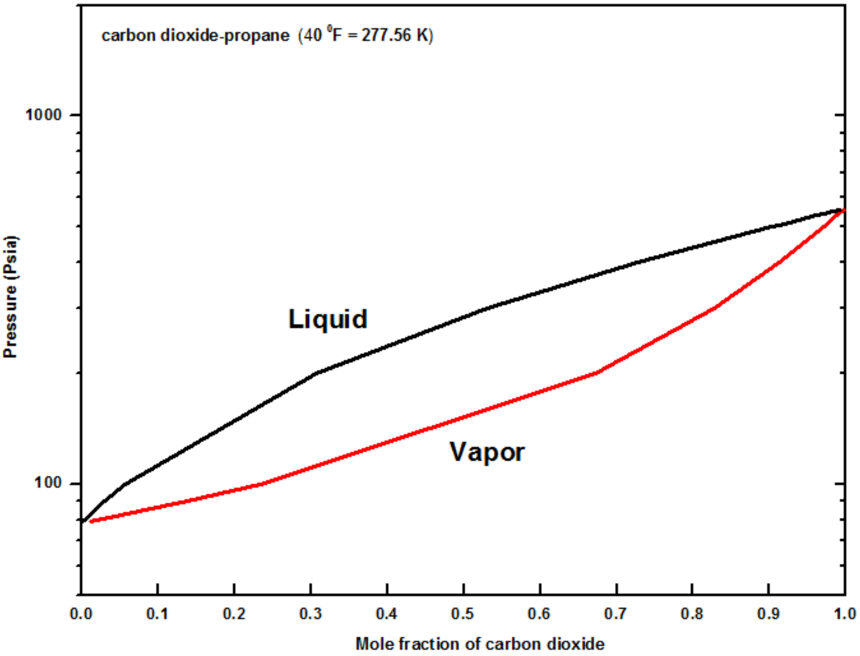

Figure 8. Mole fraction of carbon dioxide at various pressures

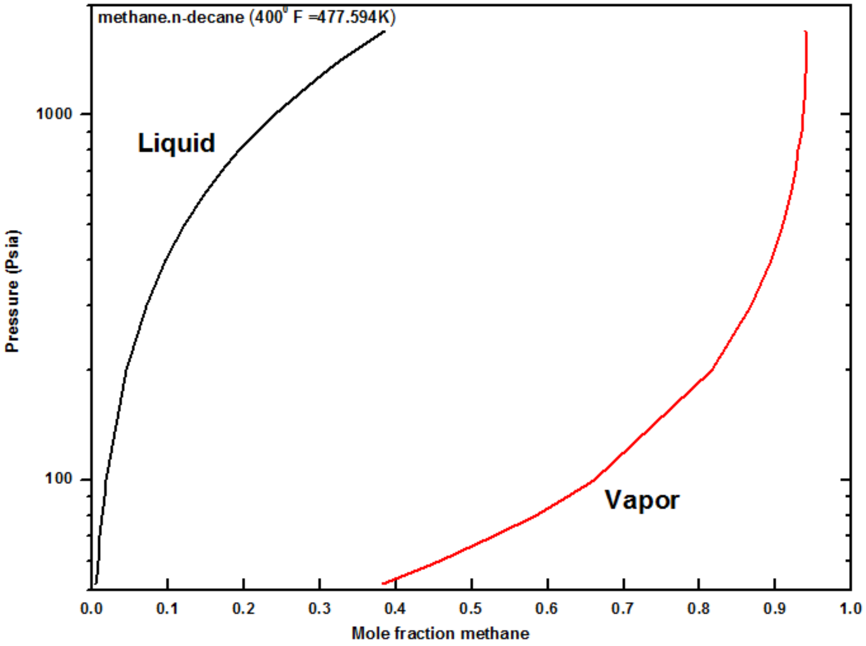

Figure 9. Mole fraction of methane at various pressures

Comparison based on the pressure of experimental [15]and model for all the cases are given in Table 2.

Table 2. Comparison of experimental and model pressure data

	Hydrogen propane			**Methane n-butane**		
Mole fraction	Exp.	Model value	Change (%)	Exp.	Model value	Change (%)
Liquid phase						
0.1	1505.7	1299.0	13.7	329.4	339.8	3.2
0.2	2844.7	2498.0	12.2	621.7	612.9	1.4
0.3	4312.8	3968.0	8.0	927.8	903.9	2.6
0.4	5772.2	5438.0	5.8	1254.7	1198.5	4.5
0.5				1554.0	1508.6	2.9
Vapor phase						
0.6	605.3	600.0	0.9	138.0	144.9	5.0
0.7	904.3	899.0	0.6	194.6	197.6	1.6
0.8	1809.8	1799.0	0.6	328.3	334.4	1.8
0.9						
1						
	Carbon dioxide Propane			**Methane n-decane**		
Liquid phase						
0.1	151.5	114.0	24.8	456.3	415.5	8.9
0.2	217.3	152.7	29.8	926.5	851.3	8.1
0.3	268.4	197.3	26.5			
0.4	318.9	232.4	27.1			
0.5	361.1	280.4	22.3			
Vapor phase						
0.6	195.7	177.6	9.2	82.9	80.9	2.4
0.7	261.9	214.3	18.2	116.0	113.8	1.9
0.8	367.9	277.3	24.6	184.7	180.1	2.5
0.9	500.4	379.8	24.1	430.7	420.1	2.5
1	557.2	526.8	5.5			

4. CONCLUSIONS

In this research for phase equilibrium the mathematical modeling is applied on SRK EOS on four set of applied for four set of mixtures to discuss the phase behavior. The results of mathematical modeling are following same behavior of experimental result which shows that modeling by using SRK EOS give a reliable solution to predict the phase behavior. Here the mole fraction of a component of both phases at VLE is estimated at different pressures which show the dependence of pressure on mole fraction at VLE. The comparison of modeling and experimental results show that our approach to the problem is accurate the deviation of model results of carbon dioxide propane mixture is found due to the presence of carbon dioxide in the mixture.

NOMENCLATURE

SRK= Soave Redlich Kwong
$\widehat{f_\iota}$ = 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, Pa m^3/K mole
t=time, seconds
T_c=critical temperature, Kelvin
T=temperature, Kelvin
V=vapor mole fraction
x=x-coordinate,
x_i=mole fraction of i^{th} component in liquid
y_i =mole fraction of an i^{th} component in the vapor
ω=acentric factor
$\emptyset_i$=fugacity coefficient for a component in a mixture. Dimensionless

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