Phase Behavior Comparison for Pure Components using Equation of State (EOS)

by

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Dissertation submitted in partial fulfillment of the requirements for the Bachelor of Engineering (Hons) Petroleum Engineering

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NURULHUDA BT. ABDUL HAMID

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Department
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Approved by,

____

(DR. KHALIK M. SABIL)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(NURULHUDA BINTI ABDUL HAMID)

ABSTRACT

Vapor-liquid equilibrium (VLE) is important in determining the conditions under which the volume of vapor and liquid can exist in different pressures and temperatures. Equations of State (EOS) are the equations that relate these variables, pressures, temperatures and volumes (PVT). According to the requirements of engineering applications, cubic EOS are preferable to predict VLE properties. (Li & J.Yan, 2009) Such EOS that been used in this paper Peng-Robinson (PR), since this equation is among the popular in petroleum and chemical industry. A new EOS is also use as a comparison with PR, which is Nasrifar-Moshfeghian (NM EOS). Several other EOS were also introduced for comparison purposes. The calculated data will be compared with experimental data, collected from several experimental works done by previous studies. Comparisons will be made through these data and the compatibility of either EOS is estimated.

CHAPTER 1

1.1 Introduction

Hydrocarbon systems found in petroleum reservoirs are known to display multiphase behavior over wide ranges of pressures and temperatures. The chemistry of hydrocarbon reservoir fluids is very complex. Methane, often a predominant component of natural gases and petroleum reservoir fluids, is a gas, nC_5 and hydrocarbons as heavy as nC_{15} may be in the liquid state. (Firoozabadi, 1999) Consequently, the most important phases that occur in petroleum reservoirs are liquid phase and gas phase. (Ahmed T. , 2007) These phases are relating to each other in pressures, temperatures and volume (PVT). An approach that clearly portrays this PVT relationship is phase behavior study. The subject of phase behavior, however, focuses only on the state of equilibrium, where no changes will occur with time if the system is left at prevailing constant pressure and temperature. (Dinesh, 1998) The conditions under which gases and liquids phases exist are a matter of considerable practical importance. Phase diagram is one type of diagram that aid in determination of these conditions. Figure 1 shows the typical phase diagram of a pure substance.

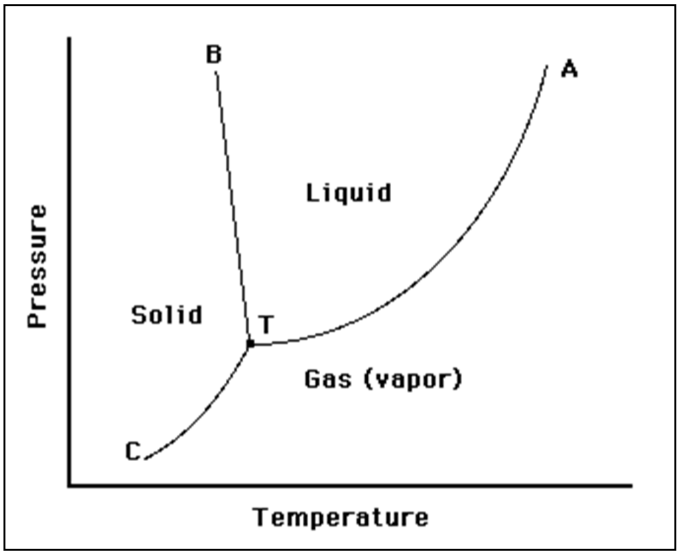
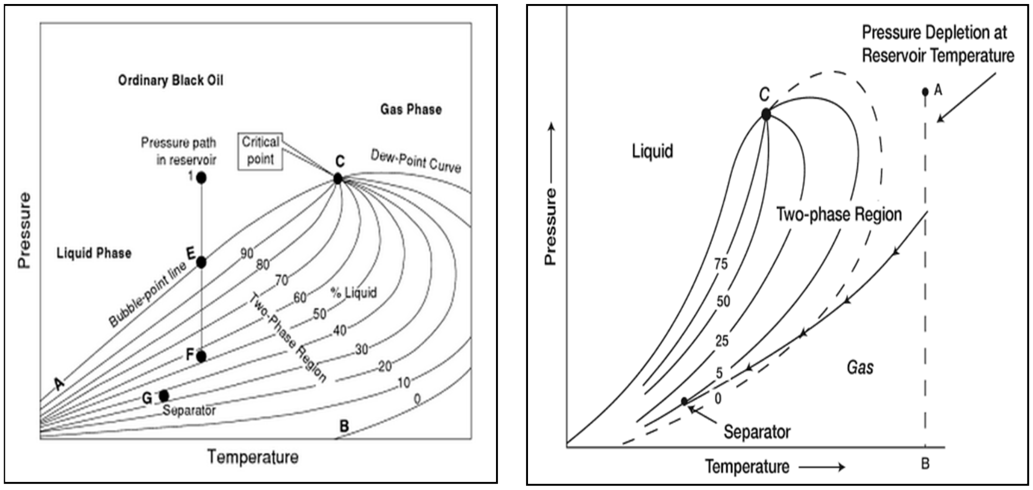


Figure 1 Phase Diagram of Pure Substance (McCain, 1990)

From Figure 1, line AT is the line where both gas (vapor) and liquid coexist. This line is commonly known as the vapor pressure curve as it shows the pressure exerted by the vapor coexisting with its liquid at any temperature. Point A is the critical point, representing critical temperature and critical pressure of that substance. Critical temperature for a pure substance can be defined as the temperature above which the gas cannot be liquefied regardless of the pressure applied. Similarly, critical pressure is the pressure above which liquid and gas cannot coexist regardless of the temperature. If a system with more than one component is under consideration, these definitions of critical properties are invalid.



(a) (b)

Figure 2 Typical Phase Diagram For (A) Ordinary Black Oil (B) Wet Gas (McCain, 1990)

An equation of state (EOS) is an analytical expression relating the pressure, P, to the temperature, T and the volume, V. A proper description of this PVT relationship for real hydrocarbon fluids is essential in determining the volumetric and phase behavior of petroleum reservoir fluids and predicting the performance of surface separation facilities. The main advantage of using an EOS is that the same equation can be used to model the behavior of all phases, thereby assuring consistency when performing phase equilibria calculations. (Ahmed T. , 2007)

The equations of state are divided into two main groups, which are cubic and non-cubic. An equation of state (EOS) is desired to represent the volumetric behavior of pure substance in the entire range of volume, both in the liquid and gaseous state. (Firoozabadi, 1999)

1.2 Project Background

The first and simplest EOS is the ideal gas equation or ideal gas law, which is:

$$PV = nRT$$

Equation 1 Ideal Gas Law

Van der Waals has improved the ideal gas equation by included the parameters that representing the attractive, a, and repulsive, b, intermolecular forces.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Equation 2 Van der Waals EOS

The above Equation 2 in terms of volume or compressibility factor takes a cubic form as follow:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \frac{ab}{P}$$

$$Z^3 - (1 + B)Z^2 + AZ + AB = 0$$

Equation 3 Cubic Van der Waals EOS

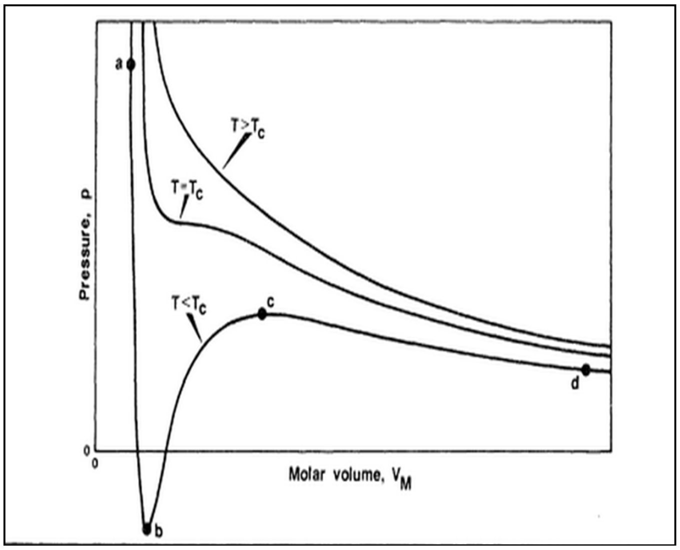


Figure 3 Isotherms PV Diagrams for Two Constans EOS (McCain, 1990)

Point ‘b’is called Van der Waals loop, exists when temperature,T, is below than critical temperature, T_c. Values at point ‘b’are used to determine the molar volumes of the equilibrium gas and liquid, which later will be replaced by a ‘tie-line’that connects these two volumes. The connection drawn based on the equality of chemical potential for both phases.

Van der Waals type EOS are often referred to as cubic EOS. (Dinesh, 1998) After the appearance of van der Waals type of EOS, there many authors have proposed variations in the semi-empirical relationship. One of the most successful modifications was that made by Redlich and Kwong (1949). One of the more recent modifications of RK equations is that proposed by Soave (1972). The Soave-Redlich-Kwong(SRK) equation has rapidly gained acceptance by the hydrocarbon processing industry because of the relative simplicity and its capability for generating reasonably accurate equilibrium ratios in VLE calculations. However, there still are some shortcomings, which the SRK equation and the original RK equation have in common.

The most evident is the failure to generate satisfactory density values for the liquid even though the calculated vapor densities are generally acceptable. (Peng & B.Robinson, 1976) The performance between Peng-Robinson EOS and SRK EOS is very similar, except that PR EOS estimates slightly better behavior at the critical point. This make PR EOS somewhat better suited to gas or condensate systems. (Adewumi, 2008)

$$P = \frac{RT}{V-b} - \frac{a(T)}{v^2 + u_1 bV + u_2 b^2}$$

Equation 4 General Two-Parameters EOS Equation

where the first term on the right-hand side of **Equation 4** is the repulsive term and ther second term is the attractive term. Different EOS using different parameters of u_1 and u_2 .

Table 1 Values for Parameter EOS Equation (Moshfeghian & Nasrifar, 2001)

EOS	**Parameters**
Van der Waals	$u_1 = u_2 = 0$
Soave-Redlich-Kwong (SRK)	$u_1 = 1$, $u_2 = 0$
Peng-Robinson	$u_1 = 2$, $u_2 = -1$

Peng and Robinson has introduced a new equation that offers the same simplicity as the SRK equation and although both equations predict vapor densities and entalphy values with reasonable accuracy, more accurate liquid density values can be obtained with the new equation. In regions where engineering calculations are frequently required, the new equation gives better agreement between predictions and experimental PVT data. (Peng & B.Robinson, 1976)

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}$$

Equation 5 Peng-Robinson EOS

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$$

Equation 6 Cubic Peng-Robinson EOS

Peng and Robinson conserved the temperature dependency of the attractive term and the acentric factor introduced by Soave. However, they presented different fitting parameters to describe this dependency and further manipulated the denominator of the pressure correction (attractive) term. The gas and liquid phases become identical at the critical point. The coefficients “a” and “b” are made functions of the critical properties by imposing the criticality conditions.

$$a_c = 0.45724\frac{R^2T_c^2}{P_c} \qquad b = 0.07780\frac{RT_c}{P_c} \qquad a(T) = a_c\alpha$$

$$\alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r})\right]^2$$

Equation 7 Coefficients for PR EOS

At temperatures other than critical temperature, the equations become:

$$a(T) = a(T_c) \cdot \alpha(T_r, \omega) \qquad b(T) = b(T_c)$$

Equation 8 Coefficients for PR EOS (cont.)

EOS are basically developed for pure components, but applied to multi-component systems by employing some mixing rules to determine the parameters for mixtures. The mixing rules are considered to describe the prevailing forces between molecules of different substances forming the mixture.

1.3 Problem Statement

The vapor-liquid equilibrium (VLE) hydrocarbon is of great importance especially to the design and operations at the surface. Since these processes cover a large range of operating conditions, from normal atmosphere to supercritical state, and involve multi-components, the experimental data alone cannot satisfy the requirements of the engineering applications. There are thousands of cubic and non-cubic EOS. Several studies by previous investigators have concluded generally about EOS that the reliabilities of these equations vary for different properties, components and conditions.

Cubic EOS with more than two constants may not improve the prediction of complex reservoir fluids. In fact, most of the cubic equations have the same accuracy for phase behavior prediction of complex hydrocarbon systems; the simpler equations often do better. (Firoozabadi, 1999) Therefore, Peng-Robinson EOS is selected due to the simplicity and reliability than many other equations. Plus, a new EOS namely Nasrifar-Moshfeghian also is taking into account for comparison purposes.

1.4 Objectives

An equation of state (EOS) with the least number of input parameters is the most desirable since it will reduce the difficulties. PR EOS is a common equation used in the present petroleum and chemical industry. This EOS has proven to applicable in the industry. However, PR EOS might slightly less accurate than other available EOS in predicting certain behavior and properties of natural gas mixtures and components. In this paper, several properties of pure components commonly found in natural gas will be compared. The predicted or calculated results in simulator will be compared to experimental data found in book to measure the accuracy of the EOS.

1.4.1 Scope of Study

This paper will focus in the study of EOS. One of the factors determines the phase behavior is the composition of the hydrocarbon fluid. Since EOS has been proven by many studies that is effective in predicting phase behavior, all the properties for phase behavior will be calculated using EOS and this calculated values will be compared with experimental data from previous studies to measure the accuracy and effectiveness of EOS in predicting phase behavior.

CHAPTER 2

2.1 Literature Review

Firoozabadi (1988) discussed about the use of several cubic equations of state (EOS) in predicting vapor/liquid equilibria (VLE) such as PR and SRK, and volumetric behavior of reservoir-like and real reservoir fluids. He also examined on the differences between these equations. He concluded that these equations can reliably predict phase behavior of complex reservoir crude and gas-condensate systems away from the critical and retrograde regions.

Ahmed (1988) has reviewed eight equations of state (EOS's) and compared their ability to predict the volumetric and phase equilibria of gas-condensate systems. Included in his study are the Peng-Robinson (PR) and the Soave-Redlich-Kwong (SRK). He found that PR equation exhibits a superior predictive capability for volumetric properties of condensate systems accurately.

A.Turek et. al. reported that if a generalized equation of state (EOS) can match experimental data, then it can be used in a reservoir simulator to calculate the phase equilibria necessary for the prediction of fluid compositions, densities and viscosities during a displacement process. (A.Turek, S.Metcalfe, Yarborough, & Jr., 1983)

Li & J. Yan (2009) evaluated the reliabilities of five cubic EOS's including Peng-Robinson (PR), Patel-Teja (PT), Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK) and 3-parameter 1-temperature-dependent (3P1T) for predicting VLE of CO_2 and binary CO_2 –mixtures containing CH_4, H_2S, SO_2, Ar, N or O_2. These predictions were based on comparisons with the collected experimental data. Results show that for the VLE properties of binary CO_2-mixtures, PR, PT and SRK are generally superior to RK and 3P1T.

Below are some descriptions on SRK and PR EOS:

Table 2 Comparison of Literatures

EOS	**Descriptions**
Soace-Redlich-Kwong (SRK)	• Soave modified RK EOS by introducing a temperature-dependent function to modify the attraction parameter • One of the most popular EOS in hydrocarbon industry • Quite capable of predicting VLE for liquid mixtures, but, it is not very satisfactory for predictions of liquid compressibility
Peng-Robinson (PR)	• Capable of predicting the liquid density as well as vapor pressure in order to further improve VLE predictions • It is recommended for hydrocarbon processing such as gas processing, refinery and petrochemical processes.

(Li & J.Yan, 2009)

The Nasrifar-Moshfeghian (NM) EOS found to predict accurately the vapor pressure of pure compounds, especially near the critical point, and the bubble point pressure of binary mixtures. using NM EOS, the saturated liquid densities of pure compounds and typical binary mixture also beend correlated accurately. The prediction ability of NM EOS for predicting thermal properties is comparable to the PR EOS and SRK EOS. (Moshfeghian & Nasrifar, 2001)

Chatterjee et. al. mentioned that characterization of formulation components in pre-formulation and formulation studies will be made easier if a rapid method to evaluate the evaporation characteristics of an ingredient in the formulation is developed. Their study aims at providing a simple and rapid thermogravimetric method for estimating the vapor pressure characteristics using the Antoine equation as the analytical tool. (Chatterjee, Dolimore, & Alexander, 2001)

CHAPTER 3

3.1 Methodology

This paper will use PR EOS and the mixing rules as follow:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

Equation 4 Peng-Robinson EOS

Using Matlab, the PR EOS is coded and values of equilibrium properties can be calculated. Such code for PR EOS of a pure substance is attached as the **Appendix 1**.

The new Nasrifar-Moshfeghian (NM) EOS has been developed and published in 2001. Since then, there are several attempts of comparison between this new EOS and available EOS. The NM EOS is also a two-parameter or two-constants EOS. So, this can be a good criteria for comparing with PR EOS. Nasrifar-Moshfeghian (NM) EOS is also simulated for comparison. This new EOS predicted more accurate value for hydrocarbon properties since NM EOS considered to alter different EOS to suit better with different conditions.

$$P = \frac{RT}{V-b} - \frac{a_c\alpha(T_r)}{V^2-2bV-2b^2}$$

$$a_c = 0.497926\frac{R^2T_c^2}{p_c} b_c = 0.094451\frac{RT_c}{p_c}$$

Equation 9 Nasrifar-Moshfeghian EOS

Vapor pressure is one of the main point that make the phase diagram. Vapor pressure can be obtained mathematically by using Antoine equation (**Equation 10**) or using Lee-Kesler equation (**Equation 11)** which can directly produce the vapor pressure by inserting different value of temperature. Antoine equation considers only certain range of temperature and due to lack of accuracy; calculating vapor pressure is chose to be done by trial and error method.

$$\log_{10}(P) = A - \frac{B}{(T + C)}$$

Equation 10 Antoine Equation

P: Vapor pressure of the component, mmHg
T: Temperature, °C
A, B, C: Component specific constants

$$P_v = P_c \exp(A + \omega B)$$

Equation 11 Lee and Kesler Vapor Pressure Equation

$$A = 5.92714 - \frac{6.09648}{T_r} - 1.2886 \ln(T_r) + 0.16934(T_r)^6$$

$$B = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.4357(T_r)^6$$

Trial and error method is a method where random temperatures were assumed closely to the vapor pressure at that particular temperature, guiding by several references to obtained approximately correct vapor pressure of that substance. **Appendix 4** is the Matlab code for trial and error method combining Antoine equation and Peng-Robinson EOS.

Many EOS has been developed to correlate the PVT variables for real gases with experimental data. A correction factor is introduced to express more accurate PVT relationship. This factor called the gas compressibility factor, gas deviation factor or simply the Z-factor. The Z-value is measuring the deviated value of real gases from the ideal gas conditions. (Ahmed T. , 2007)

3.2 Research Methodology

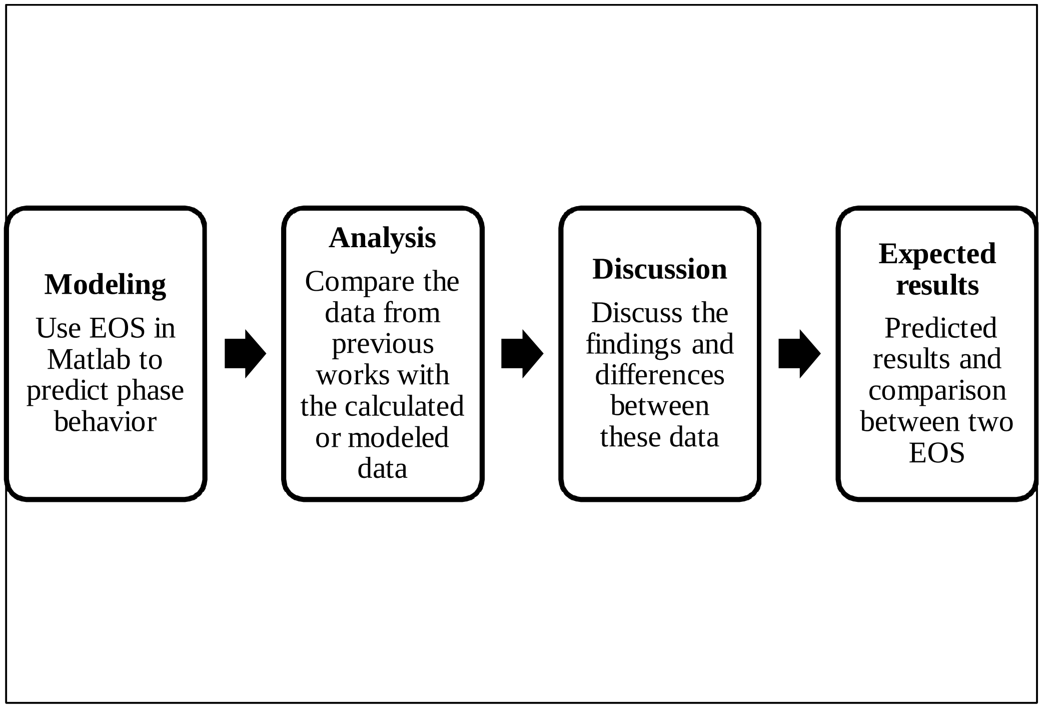


Table 3 Gantt Chart

Project Activities (FYP 1)	**Sept**	**Oct**		**Nov**		**Dec**		**Jan**
	2	**1**	**2**	**1**	**2**	**1**	**2**	**1**
Basic data gathering		🟫	🟫					
Familiarization with Matlab					🟥	🟥	🟥	🟥
Modeling simple EOS						🟩	🟩	
Gathering codes for EOS				🟦	🟦	🟦	🟦	🟦
Produce simple phase behavior and VLE curves in Matlab								🟨
Analysis								🟨

Project Activities (FYP 2)	**Jan**	**Feb**		**Mar**		**Apr**		**May**
	2	**1**	**2**	**1**	**2**	**1**	**2**	**1**
Vapor pressure codings	🟫	🟫	🟫					
Vapor pressure verifications			🟥	🟥	🟥			
Codings vapor pressure for different EOS				🟩	🟩	🟩	🟩	
Codings compressibility values for different EOS					🟦	🟦	🟦	
Analysis								🟨

CHAPTER 4

4.1 Results and Discussion

Using Matlab codes in **Appendix 1** and **Appendix 2**, these following **Figure 3** and **Figure 4** are the graphical results of Peng-Robinson and Nasrifar-Moshfeghian EOS respectively.

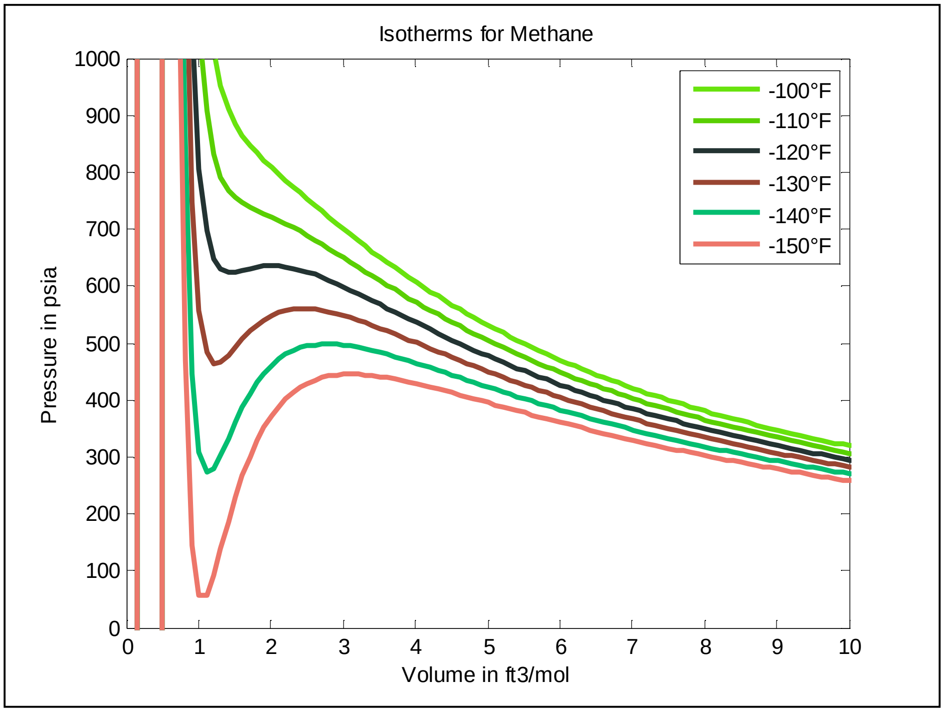


Figure 4 Isotherms for Pure Methane using PR EOS (Critical Temperature =-116.67°F , Critical Pressure = 666.4 psia)

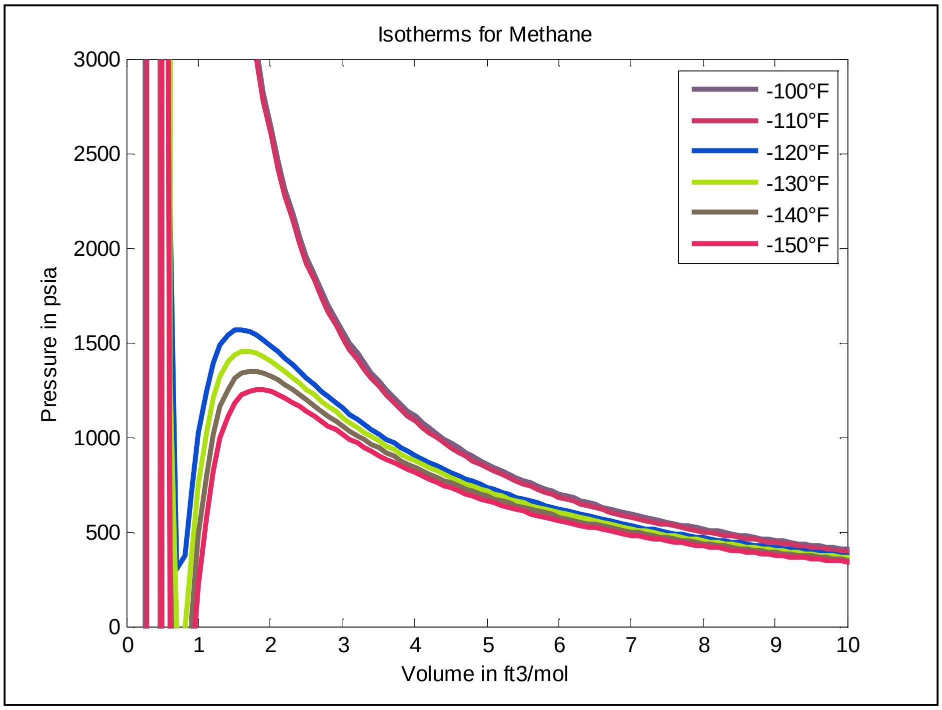


Figure 5 Isotherms for Pure Methane using NM EOS (Critical Temperature =-116.67°F , Critical Pressure = 666.4 psia)

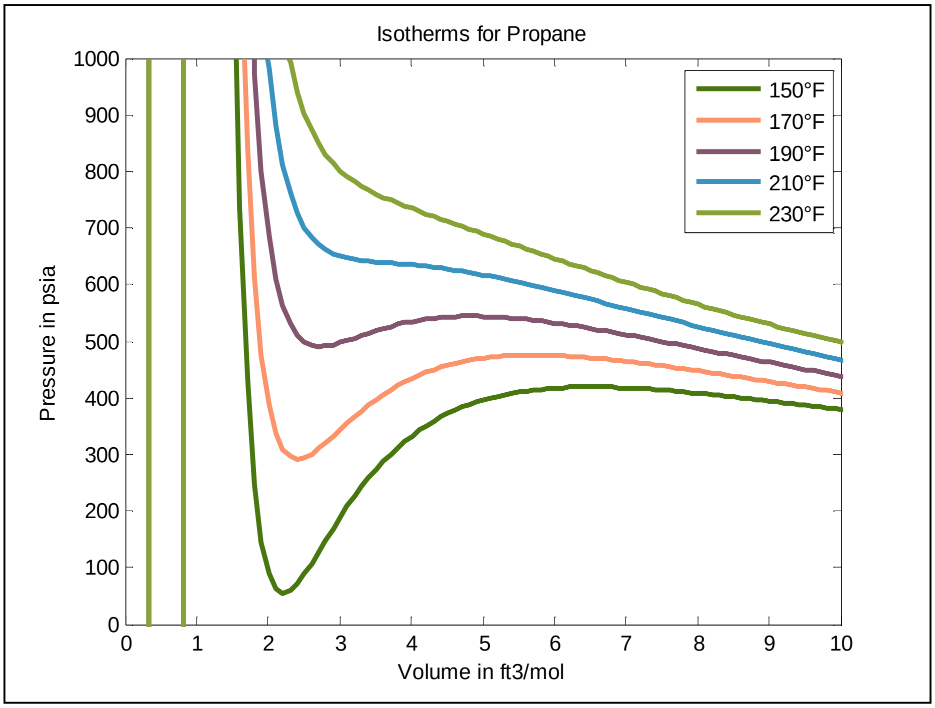


Figure 6 Isotherms for Pure Propane using PR EOS (Critical Temperature = 206.06 °F=, Critical Pressure = 616 psia)

Several trial and error estimates for vapor pressure using different temperature done and following are the results. **Appendix 3** and **Appendix 4** are the code for estimating vapor pressure.

Table 4 Trial and Error Estimation of Vapor Pressure using Peng-Robinson EOS for Different Temperature

Propane (Critical temperature: 206.06 °F Critical pressure: 616 psia)	
Temperature (°F)	**Vapor pressure**
10	46.474
20	55.7768
30	66.4301
40	78.5454
50	92.2443
100	188.9713
150	345.447
180	475.9442
190	526.5658
Isobutane (Critical temperature: 274.46 °F Critical pressure: 527.9 psia)	
10	14.4526
20	17.8572
30	21.8556
40	26.5145
50	31.9031
100	72.4096
150	143.0382
200	255.2066
n-butane (Critical temperature: 305.62 °F Critical pressure: 550.6 psia)	
10	9.2703
20	11.6202
30	14.417
40	17.7166
50	21.5781
100	51.5736

150	105.9849
200	194.9397
Isopentane (Critical temperature: 369.10 °F Critical pressure: 490.4 psia)	
10	2.9075
20	3.7618
30	4.8094
40	6.0805
50	7.608
100	20.4045
150	45.8298
200	90.3263
n-Pentane (Critical temperature: 385.8 °F Critical pressure: 488.6 psia)	
10	2.0084
20	2.6339
30	3.4108
40	4.3648
50	5.5244
100	15.5616
150	36.3025
200	73.6989

*Fahrenheit **(°F)** to Rankine **(°R) = (°F) + 460**

Tabulated results show that by increasing temperature, the vapor pressure is increasing too. The temperature is increased until it approaches the critical value, which the resulted vapor pressure is going to complex numbers. The complex numbers referred to points where only one phase is exists.

Using code in **Appendix 5** and values in **Table 5 (Appendix 6)**, vapor pressures estimated using Antoine equation and results plotted in following figures:

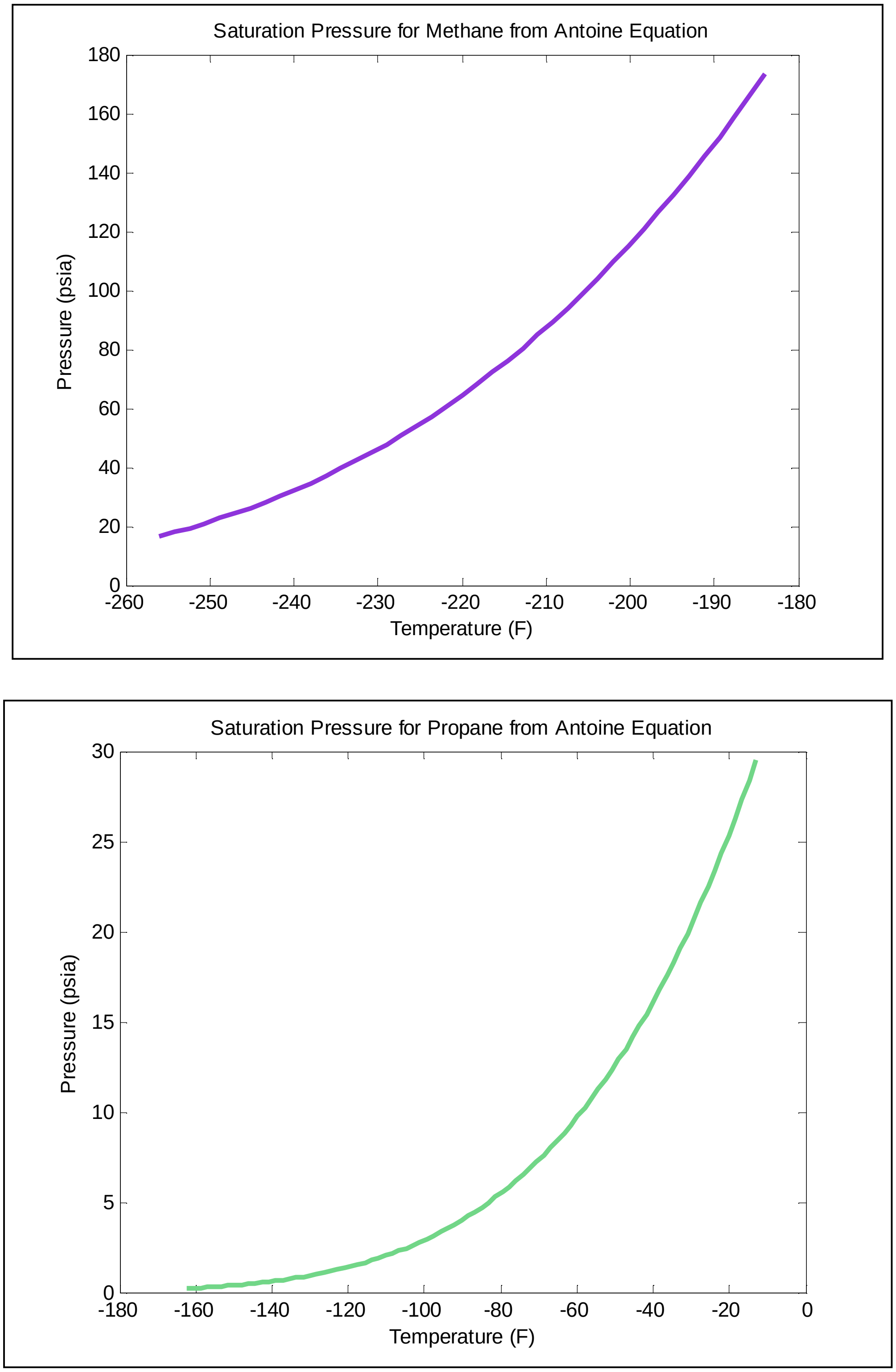


Figure 7 Saturation Pressure for using Antoine Equation

The plot using different range of temperature since Antoine constants only apply accurately in this range. Different components have different constants. Thus, would have different range. Comparing **Table 4** and **Figure 6**, we can say that the calculated vapor pressure from Peng-Robinson EOS is behave likely like what expected the vapor pressure to be, which is the vapor pressure will increase as temperature increase.

Vapor pressure also being calculate using Lee-Kesler for comparison with Peng-Robinson vapor pressure estimated.

Table 5 Vapor Pressure(psia) Values Calculated using Different Methods

Compound	Engineering data book (Experimental)	PR EOS_Matlab	AAD	Lee Kesler	AAD
Methane	5000				
Ethane	800			792.1506	
Propane	188.64	188.9712	0.001755725	189.3548	0.003789228
Isobutane	72.581	72.4095	0.002362877	72.9471	0.00504402
n-Butane	51.706	51.5736	0.002560631	51.9316	0.00436313
Isopentane	20.445	20.4045	0.001980924	20.3289	0.00567865
n-Pentane	15.574	15.5616	0.000796199	15.4859	0.005656864
n-Hexane	4.9597	5.0132	0.010786943	4.882	0.01566627
n-Heptane	1.689	1.6569	0.019005329	1.571	0.069863825

$$AAD\ (Average\ of\ Absolute\ Deviation) = \frac{|Calculated\ value - Experimental\ value|}{Experimental\ Value}$$

$$Total\ AAD = \frac{100}{Number\ of\ values\ calculated}\sum AAD$$

Equation 12 Average of Absolute Deviations

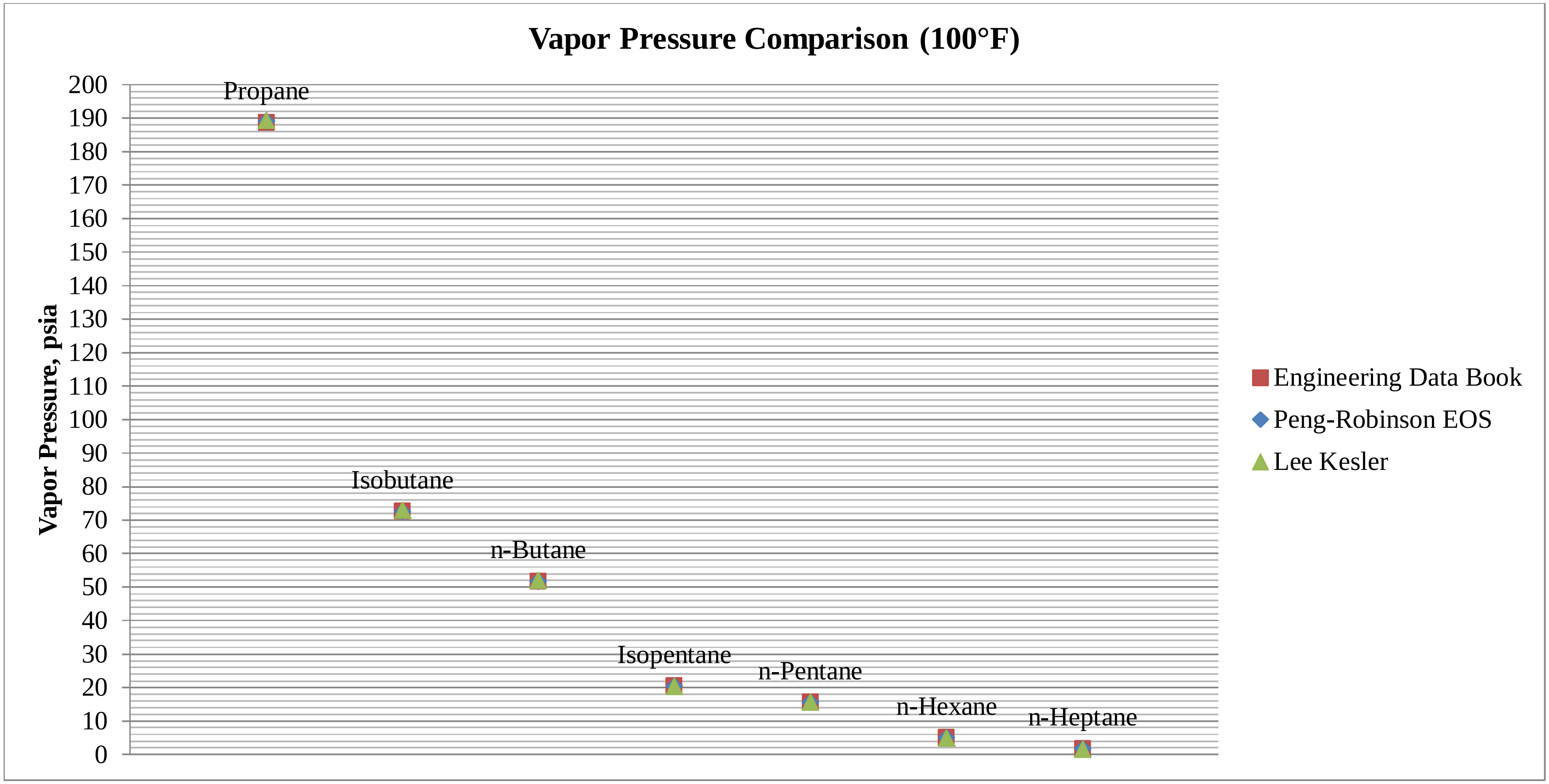


Figure 8 Vapor Pressure Comparison

Simulator cannot calculate vapor pressure for methane and ethane since both components expected to have very large vapor pressure at 100°F, which beyond the limitation of considered condition. Comparing the results in above figure, all the values are closely or stack onto each other proved that all the values obtained by all three methods approximately similar. Lee Kesler is more generalized form of vapor pressure equation compared to Antoine equation since Antoine equation is limited within certain range of temperatures for the equation to have valid results. At the end, both equation can be used to prove the function of Peng-Robinson in estimating vapor pressure of pure hydrocarbon components.

Lastly, compressiblity values were compared using code in **Appendix 7**. The values estimated from Peng-Robinson approximately close to the values in book, which were obtained my experiments. Thus, Peng-Robinson can be used for estimation of Z-factor also.

Table 6 Compressibility Values

	Engineering Data Book	**Peng-Robinson EOS**	**AAD**
Methane	0.998	0.9975	0.000501
Ethane	0.9919	0.9907	0.00121
Propane	0.9825	0.9816	0.000916
Isobutane	0.9711	0.9715	0.000412
n-Butane	0.9667	0.9692	0.002586
Carbon dioxide	0.9943	0.9939	0.000402

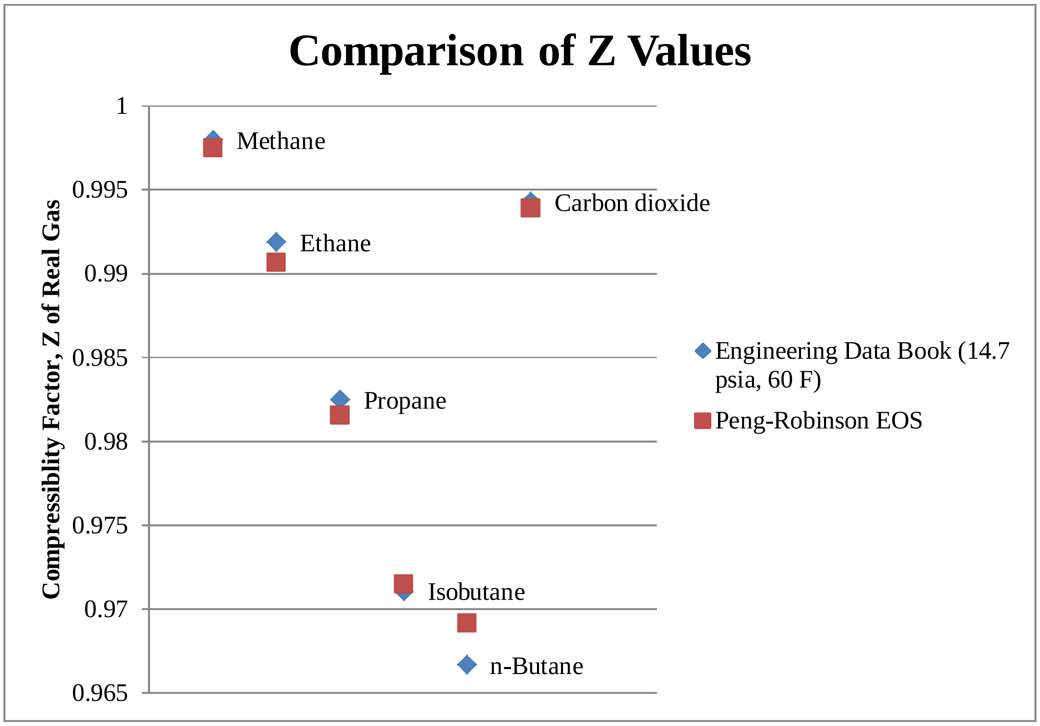


Figure 9 Comparison for Compressibility Values

4.2 Conclusion

EOS is an analytic expression relating pressure to volume and temperature. Cubic EOS aims to predict the thermodynamic properties of hydrocarbon. The most important properties of pure compounds are the vapour pressure and saturated liquid density. Once an EOS is developed, it is usually applied to calculate many properties. Thus, prediction through several properties is needed to examine the accuracy of the EOS. PR EOS is one of the best EOS that can be used for prediction of natural gas phase behavior according to previous studies. Therefore, PR EOS is chose to be used in this study. Expected results should be both calculated and experimental data match closely to each other. Evolution of EOS from the simplest ideal gas law proved that EOS need to be improved in order to ensure the accuracy of their usage in current industry. More changes have been discovered in hydrocarbon production after many years and these improvements in EOS help to make the previous EOS are applicable until today.

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APPENDICES

Appendix 1

```
% Methane’s critical temperature and pressure and acentric factor
Tc=343.33; % R
Pc=666.4; %psia
Omega=0.0104;
% universal gas constant
R = 10.732;
% b and m for the PR EOS
b =0.07780*R*Tc/Pc;
m =0.37464 + 1.54226*Omega - 0.26992*Omega^2;
j=1;
for i=100:10:150 % F
    v=0.01:0.1:3000; %molar volume
    T(i)=460-i;%temperature
    % reduced temperature
    Tre=T(i)/Tc;
    % a for the PR EOS
    a=0.45724*(R*Tc)^2/Pc*(1 + m*(1 - sqrt(Tre)))^2;
    % PR EOS
    P=R*T(i)./(v - b) - a./(v.*(v + b)+b*(v-b));

% plotting isotherms for T varying from 310°R to 360°R

h=plot(v,P);
set(h,'color',rand(1,3),'linewidth',2.5);
hold on
axis([0 10 0 1000])
xlabel('Volume in ft3/mol')
ylabel('Pressure in psia')
title('Isotherms for Methane')
end
```

Appendix 2

```
% Methane’s critical temperature and pressure and acentric factor
Tc=343.33; % R
Pc=666.4; %psia
w=0.0104;
% universal gas constant
R = 10.732;
% m for the NM EOS
m = 0.4857 + 1.6308*w - 0.2089*w^2;
j=1;
for i=100:10:150
    v=0.01:0.1:2500; %molar volume
    T(i)=460-i; %temperature
% reduced temperature
Tre=T(i)/Tc;
if Tre<=1
    alfa=(1 + m*(1 - sqrt(Tre)))^2;
else Tre>1
    b1=0.25*(12-11*m+m^2);
    b2=0.5*(-6+9*m-m^2);
    b3=0.25*(4-7*m+m^2);
    alfa=(b1/Tre)*(b2/Tre^2)*(b3/Tre^3);

end


% a for the NM EOS
a = 0.421875*(R*Tc)^2/Pc*alfa;
b = 0.079246*R*Tc/Pc;
c= (v + b/sqrt(3)).^2;

% NM EOS
P=R*T(i)./(v-b) - a./(v.*c);

% plotting isotherms for T varying from 310°R to 360°R

h=plot(v,P);
set(h,'color',rand(1,3),'linewidth',2.5);
hold on
axis([0 10 0 3000])
xlabel('Volume in ft3/mol')
ylabel('Pressure in psia')
title('Isotherms for Methane')
end
```

Appendix 3

```
% calculate the vapor pressure of a pure substance
% calculate the vapor pressure using peng robinson EOS

% first, calculate those coefficients which are not pressure
dependent

R=10.732; % psia cu ft / lb mole R
T=350+460; %R
Tc=385.8+460; % Tc CHANGE
Tr=T/Tc;
Pc=488.6; % psia CHANGE
b=0.0778*R*(Tc/Pc);
ac=0.45724*(((R^2)*(Tc^2))/Pc);
w=0.2514; %w CHANGE
alfa=(1+((0.37464+1.54226*w-0.26992*(w^2))*(1-sqrt(Tr))))^2;
aT=ac*alfa;



% try and error value of P
P=300; %must always be below critical pressure, if not, the results
are unreliable
for i=1:100
% calculate compressibility factor
A=(aT*P)/((R*T)^2);
B=(b*P)/(R*T);
Z=roots([1 -(1-B) (A-2*B-3*(B^2)) -(A*B-(B^2)-(B^3))]);
Zv=Z(1,1);
Zl=Z(3,1);
fg=exp(Zv - 1 - log(Zv-B) -
A/(2*B*sqrt(2))*log((Zv+(1+sqrt(2))*B)/(Zv+(1-sqrt(2))*B)));
fgG=fg*P;
fl=exp(Zl - 1 - log(Zl-B) -
A/(2*B*sqrt(2))*log((Zl+(1+sqrt(2))*B)/(Zl+(1-sqrt(2))*B)));
flL=fl*P;
error=fg-fl;
if abs(error)<(10^-6)
    P
    fgG=fg*P;
    flL=fl*P;
    break
else
    P=P*(fl/fg);
end
end
```

Appendix 4

```
R=10.732; % psia cu ft / lb mole R

T=35+460; %R
Tc=274.46+460; % Tc CHANGE
Tr=T/Tc;
Pc=527.9; % psia CHANGE
b=0.0778*R*(Tc/Pc);
ac=0.45724*(((R^2)*(Tc^2))/Pc);
w=0.1852; %w CHANGE
alfa=(1+((0.37464+1.54226*w-0.26992*(w^2))*(1-sqrt(Tr))))^2;
aT=ac*alfa;

% try and error value of P
AA=6.91048; %CHANGE
BB=946.35; %CHANGE
CC=246.68; %CHANGE
TC=(T-32-459.67)/1.8;
P=((AA-(BB/(CC+TC)))^10)*0.01934; %Antoine equation

for i=1:10
% calculate compressibility factor
A=(aT*P)/((R*T)^2);
B=(b*P)/(R*T);
Z=roots([1 -(1-B) (A-2*B-3*(B^2)) -(A*B-(B^2)-(B^3))]);
Zv=(Z(1,1));
Zl=Z(3,1);
fg=exp(Zv - 1 - log(Zv-B) -
A/(2*B*sqrt(2))*log((Zv+(1+sqrt(2))*B)/(Zv+(1-sqrt(2))*B)));
fgG=fg*P;
fl=exp(Zl - 1 - log(Zl-B) -
A/(2*B*sqrt(2))*log((Zl+(1+sqrt(2))*B)/(Zl+(1-sqrt(2))*B)));
flL=fl*P;
error=fg-fl;
if abs(error)<10^-6
    P
    fgG=fg*P;
    flL=fl*P;
    break
else
    P=P*(fl/fg);
end
end
```

Appendix 5

```
% for propane between -108 and -25 degrees C

A=6.80398;
B=803.81;
C=246.99;

% temperature range

T=-108:-25;

% antoine's equation

log10P=A-B./(T+C);

% computing P mmHg

Psat=10.^log10P;

% construct the desired plot

TF=T.*1.8+32;
Ppsia=Psat.*0.01933677928;
Ant=plot(TF,Ppsia);
set(Ant,'color',rand(1,3),'linewidth',2.5);
xlabel('Temperature (F)');
ylabel('Pressure (psia)');
title('Saturation Pressure for Propane from Antoine Equation');
```

Appendix 6

Table 7 Antoine Constants for Several Compounds

Formula	**Compound Name**	**A**	**B**	**C**	**T_{min}**	**T_{max}**
CO_2	Carbon dioxide	9.8106	1347.79	273	-119	-69
CH_4	Methane	6.69561	405.42	267.777	-181	-152
C_2H_6	Ethane	6.83452	663.7	256.47	-143	-75
C_3H_8	Propane	6.80398	803.81	246.99	-108	-25
C_4H_{10}	Butane	6.80896	935.86	238.73	-78	19
C_4H_{10}	Isobutane	6.91048	946.35	246.68	-87	7
C_5H_{12}	Pentane	6.87632	1075.78	233.205	-50	58
C_5H_{12}	Isopentane	6.83315	1040.73	235.445	-57	49
C_6H_{14}	Hexane	6.87024	1168.72	224.21	-25	92
C_7H_{16}	Heptane	6.89385	1264.37	216.636	-2	123
C_8H_{18}	Octane	6.9094	1349.82	209.385	19	152
C_9H_{20}	Nonane	6.9344	1429.46	201.82	39	179
$C_{10}H_{22}$	Decane	6.96375	1508.75	195.374	58	203

(C.L. Yaws, 1989)

Appendix 7

```
function [Z,fhi,density] = PengRobinson(T,P,Tc,Pc,w,MW,Liquido)

R=10.732; % gas constant [=] J/(mol K)
T=60+460;
P=14.7;
Tc=-116.67+460;
Pc=666.4;
w=0.0104;
MW=16.043;
Liquido=1;

% Reduced variables
Tr = T/Tc ;
Pr = P/Pc ;

% Parameters of the EOS for a pure component
m = 0.37464 + 1.54226*w - 0.26992*w^2;
alfa = (1 + m*(1 - sqrt(Tr)))^2;
a = 0.45724*(R*Tc)^2/Pc*alfa;
b = 0.0778*R*Tc/Pc;
A = a*P/(R*T)^2;
B = b*P/(R*T);

% Compressibility factor
Z = roots([1 -(1-B) (A-3*B^2-2*B) -(A*B-B^2-B^3)]);

ZR = [];
for i = 1:3
   if isreal(Z(i))
    ZR = [ZR Z(i)];
   end
end

if Liquido == 1
    Z = min(ZR);
else
    Z = max(ZR);
end

% Fugacity coefficient
fhi = exp(Z - 1 - log(Z-B) -
A/(2*B*sqrt(2))*log((Z+(1+sqrt(2))*B)/(Z+(1-sqrt(2))*B)));
if isreal(fhi)
    density=P*MW/(Z*R*T);
    result = [Z fhi density]
else
    'No real solution for "fhi" is available in this phase'
    result=['N/A' 'N/A' 'N/A'];
end
```

(Piero.R, 1998)