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Simulation of Thermodynamic Properties of Natural Gas Mixture Feedstock of Mellitah Gas Plant

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Abstract

Processing and transportation of natural gas (NG) depend on its characteristics, which are functional of the composition. The contribution of this work is to investigate the use of different equations of states (EoSs) for accurate prediction of thermodynamic and physical properties of onshore NG of Milletah. Among of these properties, z-factor, density, and viscosity of NG were studied for a wide range of pressures and temperatures. Modelling of the PVT properties-based on MATLAB logarithms for various mathematical correlations based on tested EoSs were established. The obtained results were compared with the famous Standing-Katz (S-K) chart. The common used four EoSs in the gas engineering calculations have been chosen and thoroughly examined for pseudo-reduced pressure and pseudo-reduced temperatures in ranges of 1–14 and 1-3, respectively. The results suggested that the Redlich Kwong cubic equation of state provides a bitter fit to S-K chart than the other EoSs. The prediction of molar volume is significantly dependent on the pressure in range of pseudo reduced pressure of 1-6, which means that the studied NG composition follows a compressible gas behavior in this pressure range. While the viscosity increased from $0.2*10^{-4}$ to $2*10^{-4}$ cP with increase in reduced pressure from 1 to 13. The relationship between viscosity and pressure is non-linear at low temperature, while it becomes a linear for high temperature.

Keywords: Milletah Oil & Gas–Libyan Branch; equations of state; simulation; matlab; compressibility factor; density; and viscosity.

1. Introduction

Now, NG is the main source of energy in the world [1,2]. In most cases, NG often contains some amounts of heavier hydrocarbon and non-hydrocarbon components that contribute to its thermodynamics properties [3]. Among these properties are compressibility factor, density, and viscosity. These properties are important for natural gas engineering calculations, such as petroleum reservoir, gas metering, gas compression, design of pipelines and surface facilities [4-7]. In particular, compressibility factor is the primary thermodynamic property that has been suggested to contribute significantly to NG behavior. It is essential to find precise and reliable estimation of natural gas properties for best usage. Most of NG behave as real gases, which have smaller volume than that of ideal gases, and hence real gases are said to be compressible.

Compressibility factor (i.e. gas deviation factor) is defined as the ratio of the real gas volume to the ideal volume, which is a measure of the gas deviation from perfect behavior. The deviation factor z, approaches unity as the pressure decreases and temperature increases, which indicated that the gas act as an ideal gas under these circumstances. The most common methods to obtain z-factor values are experimental measurements, equations of state (EoSs) methods and empirical correlations. Analytical methods are more attractive than experimental measurements because exper-

iments are expensive, and time consuming [6,8]. EoSs are an analytical expression connecting pressure, volume, and temperature to study gas behavior. Models-based EOSs become a simple method to determine z-factor values. Although most petroleum engineering use Peng-Robinson (PR) EOS or Soave-Redliche-Kwong (SRK) EOS, Equation such as Van der Waals (vdW) and Redliche-Kwong (RK) are also used [3,10]. The findings all highlight the fact that there is no agreement on the most suitable EoS for best prediction of thermodynamics properties of different types of gas mixtures [11].

Libya is a major oil and gas producer in Africa. Production of Libyan NG has been significantly increased after Milletah Oil & Gas (MOG) Libyan Branch was established in 2008. MOG is the main resource of natural gas (NG) for local use and also considered as the main supplier of Libyan NG to Europe [12].

The objective of this work is to investigate the use of different models-based on equation of state (EOSs) for prediction of thermodynamic properties of NG of Milletah and to examine their strengths and weaknesses. Since Katz chart has become an industry standard for predicting the volumetric behavior of natural gases, results were compared with S-K chart to test the strengths and weaknesses of all used EoSs.

2. Theory

Cubic equations are the simplest mathematical models that capable of representing the PVT behavior of both liquids and vapors with a wide range of temperatures and pressures. Four forms of EoSs (namely van der Waals (vdW), Redlich and Kwong (RK), Soave-Redlich-Kwong (SRK), and Peng-Robinson (PR) have been proposed to examine their ability to predict z-factor of Milletah natural gas mixture.

The early generic cubic equation of state (Equation 2.1) yields three different complex roots for molar volume, which can be solved by trial and error. Although the molar volume is very important for most NG applications, the selecting of initial guess value is difficult due to its wide range. Therefore, the modern forms of equations of state have been modified by replacing the molar volume parameter with its relationship with z-factor as given in Equation 2.2. The simplest of these equations is that can be solved for z-factor because of its small range (mostly from 0 to 1). The general form of modified EoS is given by Equation 2.3.

$$V = \frac{RT}{P} + b - \frac{a(T)}{P}\frac{V-b}{(V+\epsilon b)(V+\sigma b)} \tag{2.1}$$

$$V = \frac{ZRT}{P} \tag{2.2}$$

$$Z = 1 + \beta - q\beta\frac{Z-\beta}{(Z+\epsilon\beta)(Z+\sigma\beta)} \tag{2.3}$$

$$\beta = \frac{\Omega P_r}{T_r} \tag{2.4}$$

$$q = \frac{\Psi\alpha(T_r)}{\Omega T_r} \tag{2.5}$$

Where P_r and T_r are reduced pressure and temperature of pure components, respectively. The expression $\alpha(T_r)$ is a function in T_r and ω. The numerical assignments for parameters ϵ, σ, Ω, ω and Ψ are depending on the type of EoS as shown in Table 2.1.

Other gas properties such as density and viscosity are defined by the following relations.

$$\rho_g = \frac{pM_g}{ZRT} \tag{2.6}$$

$$\mu_g = 1 * 10^{-4} k_v EXP[x_v \left(\frac{\rho_g}{62.4}\right)^{\gamma_g}] \tag{2.7}$$

$$k_v = \frac{(9.4 + 0.02M_g)T^{1.5}}{(209 + 19M_g + T)} \tag{2.8}$$

$$x_v = 3.5 + \frac{986}{T} + 0.01M_g \tag{2.9}$$

Where, ρ_g is the density of the gas mixture in g/cm^3 , μ_g is the viscosity in cp, M_g is the molecular weight of gas mixture, R is the universal gas constant, γ_g is the specific gravity for gas, and x_v is the parameter used to calculate γ_g.

3. Methodology

In this study, the data for estimation of compressibility factor was obtained from renowned laboratories of MOG company as seen in Table 3.1. Using Equation 2.3, a MATLAB program was established for computing compressibility factor for reduced pressure and reduced temperatures

Table 2.1: Parameter Assignments for generic EoS

E.O.S.	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	Z_c
VdW	1	0	0	1/8	27/64	3/8
RK	$T_r^{\frac{-1}{2}}$	1	0	0.08664	0.42748	1/3
SRK	$\alpha_{SRK}\ (T_r;\omega)$	1	0	0.08664	0.42748	1/3
PR	$\alpha_{SRK}\ (T_r;\omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07779	0.45724	0.30740

$$\alpha_{SRK}\ (T_r;\omega) = [1+(0.480+1.574\omega-0.176\omega^2)(1-T_r^{\frac{1}{2}})]^2$$

$$\alpha_{SRK}\ (T_r;\omega) = [1+(0.37464+1.54226\omega-0.26992\omega^2)(1-T_r^{\frac{1}{2}})]^2$$

in ranges of 1–14 and 1-3, respectively. Firstly, based on the NG composition, critical pressure (P_C) and critical temperature (T_C) for gas mixture were calculated using Equations 3.1 and 3.2, respectively. Then, The reduced pressure (P_r) and reduced temperature (T_r) are calculated as defined in Equations 3.3 and 3.4, respectively.

Table 3.1: Composition of MOG gas mixture used in this study

Component	Formula	Mole Fraction
Hydrogen Sulphide	H_2S	0.0127
Carbon Dioxide	CO_2	0.1565
Nitrogen	N_2	0.0459
Methane	C_1	0.7006
Ethane	C_2	0.0440
Propane	C_3	0.0176
i-Butane	i-C_4	0.004
n-Butane	n-C_4	0.0067
i-Pentane	i-C_5	0.0030
n-Pentane	n-C_5	0.0030
n-Hexane	n-C_6	0.0029
n-Heptane	n-C_7	0.0180
n-Octane	n-C_8	0.0008
n-Nonane	n-C_{9+}	0.0002
Water	H_2O	0.02

From Table 2.1, the appropriate numerical assignments of ϵ, σ, Ω, ω and Ψ were entered as input parameters. Next, parameters β and q were estimated using Equations 2.4 and 2.5, respectively. The four predicted z-values that obtained from EOSs, namely vdW, RK, SRK, and PR, were compared with the S-K Chart. Finally, the best value of the z-factor was used to obtain the molar volume, density, and viscosity.

$$P_C = \sum_{i=1}^{n} P_{ci} y_i \tag{3.1}$$

$$T_C = \sum_{i=1}^{n} T_{ci} y_i \tag{3.2}$$

$$P_r = P/P_c \tag{3.3}$$

$$T_r = T/T_c \tag{3.4}$$

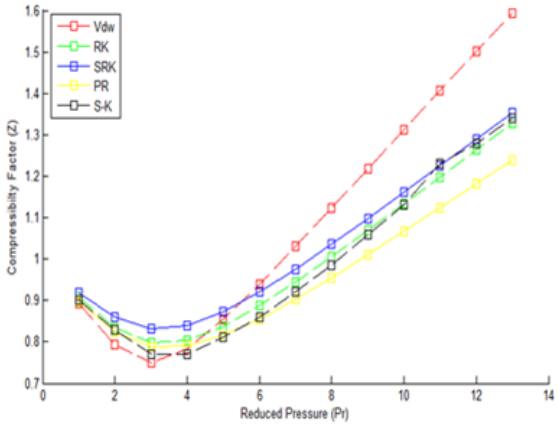
Where P_{ci} and $T_{ci}$are the critical pressure and critical temperature of pure component i, respectively; and yi is the mole fraction of component i. P_r and T_r are reduced pressure and reduced temperature, respectively, and P_C and T_C are critical pressure and critical temperature of the gas, respectively.

4. Result and Discussion

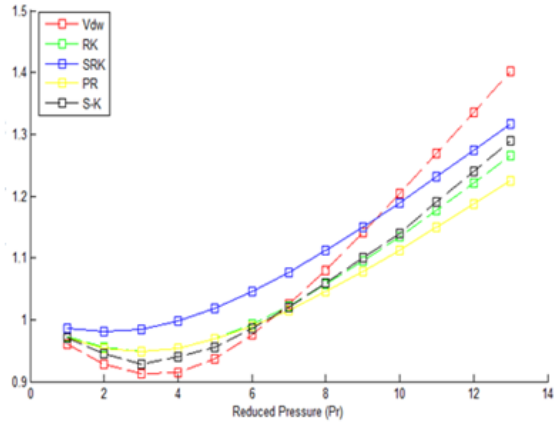
4.1. Compressibility Factor

Figure 4.1 shows the relationship between reduced pressure P_r and compressibility factor for used EoSs using three different reduced temperatures (T_r= 1.5, 2, and 3). As clearly shown in all Figures, the change z factor with reduced pressure has the same trend in all EoSs. At low temperature, as seen in Figure 4.1a, the values of z-factor are decreased with P_r to a certain values, and then the values of z-factor gradually increased to reach a high value. For example, Figure 4.1, for T_r is 1.5, in all EoSs applied, z factor starts to decrease from about 0.9 at P_r of 1 to less than 8 at P_r of 3, then start to increase gradually up to 1.6 at P_r of 13. However, at high temperature

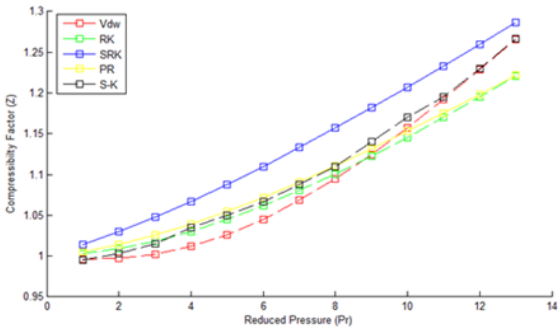
(T_r=3), the results indicated a slightly different behaviour as shown in Figure 4.1c where the z-factor increases for all P_r values. These results are in agreement with literature [3].



(a)



(b)



(c)

Figure 4.1: The relationship between reduced pressure P_r and compressibility factor for used EoSs at (a) T_r = 1.5, (b) $_{T_r}$ = 2, (c) $_{T_r}$ = 3

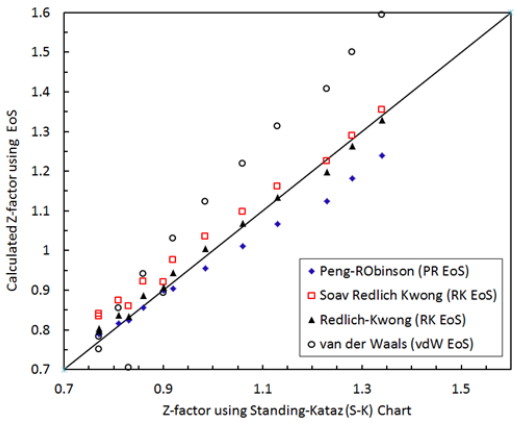


Figure 4.2: Comparison between the z-factor using EoSs and S-K Chart

Since S-K presented a generalized z-factor chart, the z-values that obtained from S-K was represented in Figures 4.1 and 4.2. To make sure the better selection of EoS for best description of gas behavior, z-factor results of the various EoSs for different reduced temperature were compared with the values that obtained from S-K Chart. As seen in Figure4.2, the results indicated that vdW EoS is not suitable to describe the behavior of MOG gas. The other three EoSs provide a slightly deviation with z-factor from (S-K) data. Among of these three EoSs, RK EoS has successfully captured the physical trend of changing the gas compressibility factor versus P_r at a fixed T_r. Therefore, the RK EoS is chosen for further thermodynamic calculations of present gas mixture. Other researchers reported that PR and SRK EoSs showed good description for behavior of other natural gas mixtures [11]. This difference is due to the composition of the gas mixture. The phase change of gas mixture is a function of applied pressure, while PR and SRK EoSs have very good prediction of gas and liquid thermodynamic properties [11].

4.2. Molar Volume

Figure 4.3 shows the change of molar volume calculated by RK EoS with reduced pressure at different values of reduced temperature (T_r = 1.5, 2, and 3). Reference values of molar volume are used to determine the best fit based on S-K chart. The comparison of predicted and referenced molar volumes using the RK EoS and S-K Chart, respectively shows a very good fit for all values

of T_r. Therefore, the RK EoS consistently under predicts the molar volume over the entire reduced pressure ranges of interest. As seen from Figure 4.2, the volume of NG mixture shrinks to more than 50% of its starting value (at P_r=1) regardless of temperature for reduced pressure less than 6, which follow a gas compressible behavior. However, the molar gas volume is slightly changed with reduced pressure in the range of 6 – 13 and then, incompressible gas behavior is observed.

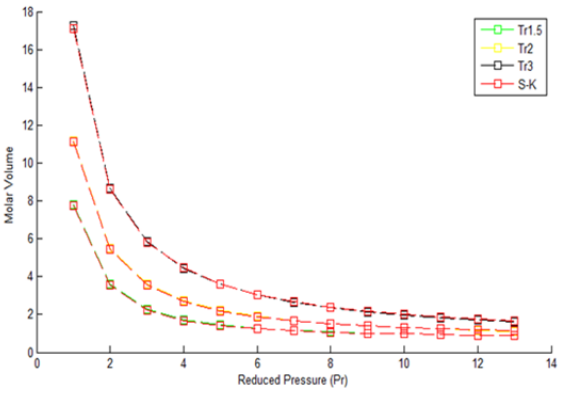


Figure 4.3: Comparison of the molar volume of MOG gas mixture obtained in this study with reference S-K Chart

4.3. Density of Gas Mixture

In this section, the density that obtained by R–K EoS were compared with density values calculated from S-K Chart. The density at a given temperature and pressure is determined using Equation 2.6 by applying the z-factor values that obtained by RK EoS and S-K chart. As seen in Figure 4.4, results indicated that the density data of gas mixture increases notably with increasing reduced pressure for a fixed reduced temperature. At low temperature (T_r = 1.5), results showed that the effect of pressure on the density is nonlinear, while the density tends to be a linear with an increase in temperature (T_r = 2 and 3). These observations are in agreement with literature [13].

Figure 4.4 also shows a comparison of the density of MOG gas mixture obtained in this study with calculated density using the S-K Chart. It is apparent that the RK EoS provides an excellent fit of density data with the S-K Chart at T_r= 2 and 3 for P_r up to 10. Then, with increasing reduced pressure, the RK EoS densities slightly diverge from the calculated density using the S-K Chart. At T_r =1.5 for 3 $<P_r<$ 9, The RK EoS

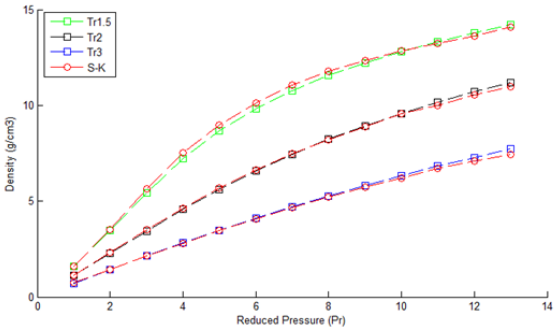


Figure 4.4: Comparison plot of density-based on z-factor form the RK EoS and S-K Chart at different reduced temperatures

exhibit a low deviation of the MOG gas mixture density data. It can be conclude that the density values obtained by RK EoS were fit to S-K reference density data for all ranges of P_r and T_r, which provides an evidence for the predictive capability of the RK EoS with MOG gas mixture. The results indicated that the density predictions are more reliable when the fit is made to the S-K data collected at the higher temperatures.

4.4. Viscosity of Gas Mixture

Viscosity of NG mixture is one of the most important properties for NG transportation and processing. Among the physical properties, pressure and temperature have large influence on the viscosity behavior of NG mixture. Therefore, effects of applied pressure and temperature on viscosity of studied gas mixture were also investigated. Even though a number of viscosity models have been proposed in literature, in this study, the viscosity of gas mixture is determined using Equation 2.7 by applying the z-factor values that obtained by RK EoS and compared with S-K chart. Figure 4.5 illustrates the change of viscosity data of the gas mixture with reduced pressure at T_r values of 1.5, 2 and 3. As shown that the viscosity increase with pressure for all temperature values and that is appear clearly at low temperature (T_r = 1.5). This behavior is attributed to the free volume of gas mixture. As the applied pressure increases, a reduction in the free volume leads to an increase in the viscosity. The results indicated that viscosity of this gas mixture is decreased with increase temperature. These observations are in good agreement with reported results [14, 15]. It is important to note that as temperature increase,

the effect of pressure on viscosity of gas mixture decrease and become insignificant at high temperature (T_r= 3).

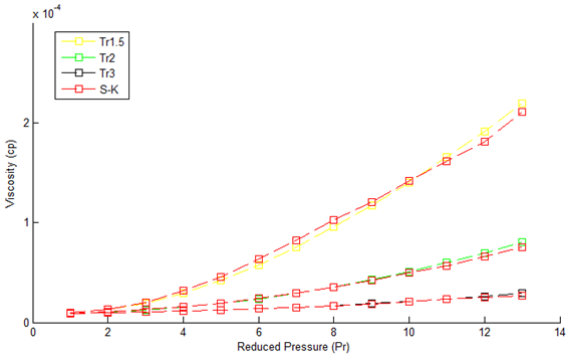


Figure 4.5: Viscosity versus pressure behavior of MOG gas mixture

As also seen in Figure 4.5, it is apparent that RK EoS gives an excellent viscosity prediction for the gas mixture at $T_r \geq 2$. However, the viscosity prediction at T_r= 1.5 deviate from reference S-K values. In the region of reduced pressures from 1-12, RK EoS gives superior predictions for high temperatures. However, at temperature as low as $T_r = 1.5$, viscosity predictions are good fit only at reduced pressures lower than 5. The results indicated that the viscosity values of gas mixture that obtained using RK EoS represents a very small deviations as compared to viscosities from S-K chart.

The particular parameters that are needed in Equation 2.7 were obtained from Equations 2.6, 2.8, and 2.9. A set of density values, which were obtained based on RK EoS method, and S-K chart were used in Equation 2.7. As seen in Figures 4.4 and 4.5, the excellent prediction of viscosity values is dependent on density values. Therefore, accurate density values are important for prediction of gas mixture viscosities.

5. Conclusion

Prediction of the thermodynamic properties for NG mixture of MOG was investigated using four existing equations of states (EOSs) in literature. The NG mixture data were correlated to the EOSs that provide a means for interpolating the compressibility factor over a range of reduced temperatures from 1.5 to 3 and reduced pressures up to 14. The results showed that RK EOS is the best cubic EOS that provides accurate predictions of z-factor, density and viscosity of the studied NG mixture, while the other existing EOSs perform higher deviation compared with the results from S-K chart. Although at low temperature the predictions of density and viscosity were deviate from the S-K chart values by certain percentage, the RK EOS give good predictions of thermodynamic properties at P_r up to ∼13over reduced temperature range of $T_r = 2$ to $T_r = 3$. However, it out-prediction the properties at P_r >12, indicating that the actual predictive of the MOG gas mixture is significantly weaker due to the volume fraction phenomena. In summary, the present study reports that RK EOS is the better equation for predations of thermodynamic properties for NG mixture at MOG conditions. In order to confirm this investigation, it will be necessary to fit the EOSs to experimental densities and viscosities data in the range of studied temperatures and pressures.

6. Acknowledgment

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