Modeling the Effect of CO_2 on Thermodynamic Behavior of CO_2/Libyan Natural Gas Mixture

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ABSTRACT

A great challenge has been done for utilization of natural gas (NG) for potential applications at various operating conditions. Accurate thermo-physical properties of NG play an important role in design and processing of NG systems. Among of these properties, compressibility factor, density, and viscosity of gas mixtures provide the feasibility of a given process. Carbon dioxide (CO_2) is present in large quantities that produced from NG reservoirs. Understanding the effect of CO_2 on thermodynamic properties of Libyan NG is important for developing the next generation of modern applications. The major thermodynamic properties considered in the present study were compressibility factor, density, and viscosity. The objective of this work is to investigate the effect of CO_2 content on properties of Libyan NG using theoretical calculations. MATLAB logarithms were developed to predict the thermo-physical properties of Libyan NG with different CO_2 concentrations. The effect of CO_2 on thermodynamic behavior of NG mixture under different conditions of pressure and temperature was studied using the Redlich Kwong equation of state (RK-EoS). CO_2 concentration has a great impact on the CO_2/NG mixture properties. The results revealed that the compressibility factor of CO_2/NG mixture is inversely proportional with the CO_2 concentration; however, as CO_2 content increases the gas mixture density increases.

Keywords: Libyan natural gas; Carbon dioxide; Thermodynamic Properties; z-factor; Gas density; Viscosity of gas mixture.

1. Introduction

Since many decades, the world depends strongly on the natural gas (NG) as a major source for energy supply. The main challenge for using this energy for wide different applications is how to utilize and process the NG from its reservoir to the place where the energy needed. The key role in designing and processing of NG system is to identify its accurate thermo-physical properties. The most important gas mixture properties in the design calculations are compressibility factor, viscosity and density of the gas mixture [1-4].

In particular, compressibility factor is a measure of the gas deviation from perfect behavior and is defined as the ratio of the real gas volume to the ideal volume [1,2]. In simple way, the density is equal to number of molecules multiply molecular weight over the occupied volume. The viscosity is the fluid (Liquid or Gas) property of resistance to flow and may be thought of as a measure of fluid friction [2].

Viscosity and density are essential physical quantities to describe the statics and dynamics behaviors of gas mixtures. These properties only can describe more than half of the fluid properties [2]. Gathering density and viscosity data on a NG gives manufacturers the ability to predict how it behaves in the real world. Availability of these properties provide analog for good concertation of NG transportation systems and contribute for excellent design processes with high production [4].

In the most cases, NG often contains some amounts of heavier hydrocarbons and non-hydrocarbons (impurities), which have a significant contribution to change the thermodynamic behavior of the NG [3]. In case of enhanced oil recovery (EOR) process, carbon dioxide (CO_2) is widely used as injected gas to the gas-oil reservoirs for increasing the reservoir pressure. The injected CO_2 will mix with the NG/oil; therefore, the thermodynamic properties of these products are directly affected due to the change of CO_2 concentration in the products. Hence, effect of CO_2 on densities and viscosities of gas mixtures is considered very important [5].

Generally, the thermodynamic properties are obtained experimentally and theoretically. Equations of state (EoSs) and empirical correlations are considered the common methods to predict thermodynamic behaviors of NG when unavailable experimental data. In addition, analytical methods are more attractive than experimental work because experiments are expensive, time consuming, and sometimes are not applicable [6,7]. Previously, we reported a study for fitting the equations of state for predicting the thermodynamic properties of Libyan NG mixture [1]. The results revealed that the Redlich Kwong cubic equation of state (RK-EoS) provides a bitter fit to Standing and Kataz chart (K-Z). Therefore, in this study, Redlich Kwong (RK) was used as the model for predicting the NG properties. The objective of the present work is to investigate the effect of CO_2 composition on the viscosity and density of the Libyan NG mixture at different range of temperatures and pressures.

2. Theory

Cubic equations of state (EoSs] are the simplest models that predicting the PVT behavior of fluids (liquid and gases) with a broad range of temperatures and pressures. Many forms of equations of state have been used to predict NG compressibility factor (z-factor) and consequently the other gas properties such as viscosity and density [1].

The general form of the cubic equation of states is given in Eq.1. The solution of this equation provides three different complex roots for molar volume. However, the disadvantage of this form is that it can be solved only by trial and error method. However, it was difficulty of guessing the initial value of molar volume for the trial and error method.

Therefore, the modern form of the equations of state have was obtained by replacing the molar volume parameter with z-factor according to the relationship that is given in Eq.2. Eq. 3 shows the final version of the general form of the modern EoSs. Table 1 illustrates the parameters that presented in Eq.3 belong to the most widely used EoSs [1].

$$V = \frac{RT}{P} + b - \frac{\alpha(T)}{P}\frac{V-b}{(V+\epsilon b)(V+\sigma b)} \tag{1}$$

$$V = \frac{ZRT}{P} \tag{2}$$

$$Z = 1 + \beta - q\beta\frac{Z-\beta}{(Z+\epsilon\beta)(Z+\sigma\beta)} \tag{3}$$

$$\beta = \Omega\frac{P_r}{T_r} \tag{4}$$

$$q = \frac{\Psi\alpha(T_r)}{\Omega T_r} \tag{5}$$

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 1.

Table 1: Parameters 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	$T_r^{-1/2}$	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

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

$$\alpha_{PR}(T_r;\omega)=\left[1+(0.37464+1.54226\omega-0.26992\omega^2)(1-T_r^{1/2})\right]^2$$

The gas density (ρ_g) and viscosity (μ_g) of gas mixtures are defined as given in the following relations.

$$\rho_g = \frac{pM_g}{ZRT} \tag{6}$$

$$\mu_g = 1 * 10^{-4} k_v EXP\left[x_v\left(\frac{\rho_g}{62.4}\right)^{\gamma_g}\right] \tag{7}$$

$$k_v = \frac{(9.4 + 0.02M_g)T^{1.5}}{209 + 19M_g + T} \quad (8)$$

$$x_v = 3.5 + \frac{986}{T} + 0.01M_g \quad (9)$$

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, $\gamma_g$is the specific gravity for gas, and x_v is the parameter used to calculate γ_g.

3. Methadolog

In this work, the thermodynamic properties of compressibility factor, viscosity and density of Libyan NG were theoriically predicted. Table 2 list the used the data of Libyan NG, which was obtained from Milletah Oil and Gas (MOG) Company. Matlab logarithm of Redlich Kwong equation (RK-EoS)was launched for predicting the z-factor, viscosity, and density of NG mixtures with different CO_2 compositions at various values of reduced temperatures and reduced pressures.

Table 2 The composition of gas mixture.

Component	Formula	Composition %
Hydrogen Sulphide	H_2S	01.27
Carbon Dioxide	CO_2	15.65*
Nitrogen	N_2	04.59
Methane	C_1	70.06
Ethane	C_2	04.40
Propane	C_3	01.76
i-Butane	i-C_4	00.40
n-Butane	n-C_4	00.67
i-Pentane	i-C_5	00.30
n-Pentane	n-C_5	00.30
n-Hexane	n-C_6	00.29
n-Heptane	n-C_7	01.80
n-Octane	n-C_8	00.08
n-Nonane	n-C_{9+}	00.02
Water	H_2O	02.00

*In this study, the CO_2 composition was changed, but the composition ratios of the other gases mentained constants.

In the initial step, the critical temperature (T_c) and critical pressure (P_c) for gas mixture were calculated using Eqs.10 and 11, respectively. Then, the reduced temperature (T_r) and reduced pressure (P_r) were evaluated using Eqs. 12 and 13, respectively.

$$T_C = \sum_{i=1}^{n} T_{ci} y_i \quad (10)$$

$$P_C = \sum_{i=1}^{n} P_{ci} y_i \quad (11)$$

$$T_r = \frac{T}{T_c} \quad (12)$$

$$P_r = \frac{P}{P_c} \quad (13)$$

Where P_{ci} and T_{ci} are the critical pressure and critical temperature of pure component i, respectively; y_i is the mole fraction of component i. T_r and P_r are reduced temperature and reduced pressure, respectively. T_c and P_c are critical temperature and critical pressure of the gas mixture, respectively.

The second step, the compressibility factor (Z) was estimated using RK-EoS as given in Eq. 3. RK-EoS was found the best EoSs for prediction the compressibility factor of the Libyan gas mixture [1]. Finally, the density and viscosity of the gas mixture were predicted using Eqs. 6, and 7 respectively.

Since the main objective of this study is to investigate the effect of CO_2 composition in the NG properties, the composition of CO_2 in the gas mixture was varied from 10 % to 50%. Besides, the densities and viscosities of these gas mixtures were evaluated at different temperatures and pressures.

4. Results and Discussion

4.1 Compressibility Factor

The compressibility factor as a function of reduced pressure and reduced temperature has been computed using Redlich Kwong equation of state (RK-EoS). The predicted results using RK-EoS were compared with the z-factor that previously obtained from Standing-Katz (S-K) chart and the results are shown in Figure 1.

The properties were evaluated at different reduced pressure ranging from 1 to 13, and at reduced temperatures of 1.5, 2, and 3. The S-K chart was used as a reference chart to examine the reliability of using RK-EoS in predicting the compressibility factor. As clearly seen from Figure 1, the behaviour of the compressibility factor that obtained using RK-EoS is in a good agreement with that obtained by S-K chart. As previously reported by Salem and his co-workers [1], among of the equations of state, RK-EoS showed the best fit to S-K chart to describe the Libyan NG behavior. Therefore, the RK-EoS was selected in this study for predicting the further thermodynamic properties of the gas mixture.

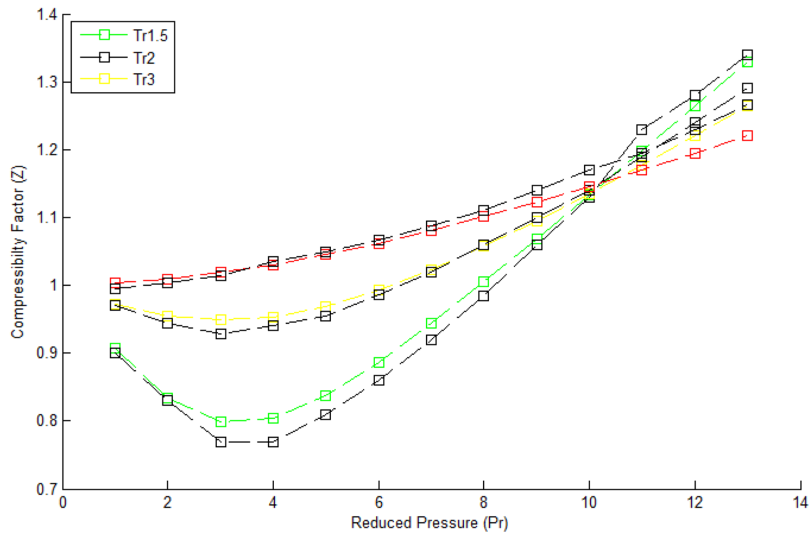


Figure 1 Effect of reduced temperature on the compressibility factor at various pressures: RK-EoS in coloured lines and S-K in Black lined [1].

4.2 Effect of CO_2 Concentration on the Viscosity of Gas Mixture

Viscosity of NG mixture is very important quantity for knowing how the production and transportation processes are designed. Pressure and temperature have great influence on the viscosity behavior of NG mixture. Viscosity of the gas mixture is evaluated using Eq.7 by applying the z-factor that obtained from RK-EoS. The composition of CO_2 in the gas mixture has been varied from 10% to 50% and for each case the viscosity was calculated. Figure 2 shows the viscosity of the NG mixtures with different CO_2 compositions at different reduced temperatures.

As seen in Figure 2, the results indicated that the viscosity of gas mixture increase with an increase in the amount of CO_2. This finding is very important to take in account because the design of the production and transportation process strongly depends on determination of accurate value of viscosity. In addition, the results demonstrate that the viscosity of gas mixture is proportional with the reduced pressure. For example, at Tr = 1.25, the viscosity of the gas mixture was increased from 1 to 2.5 cp with an increase in the reduced pressure from 4 to 8. This seems to be quite logic because the viscosity dependent with the density, which is increased with the system pressure. Furthermore, it is clearly that all cases predicted that the viscosity have nonlinear relationship with the reduced pressure at the low values; however, it became nearly linear at high values of reduced pressure. Therefore, there is no effect of the reduced pressure at high reduced pressure values. On the other hand, the viscosity has inverse relationship with reduced temperature. Figure 3, displays the viscosity of gas as a function in the reduced temperatures at CO_2 composition of 0.1565. The results indicated that the viscosity has linearly proportional relationship at low reduced temperatures; however, it increases nonlinearly at high reduced temperature.

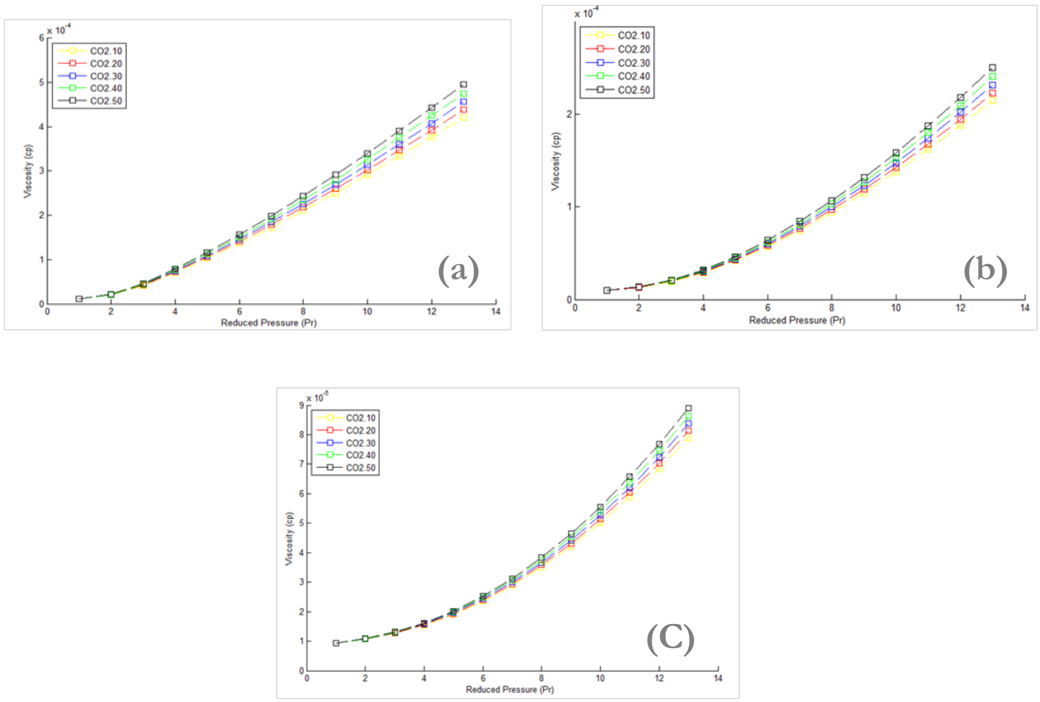


Figure 2 the effect of CO_2 on the viscosity of natural gas mixture at different reduced temperatures; **(a)** at T_r = 1.25, **(b)** at T_r = 1.5, and **(c)** at T_r = 2.

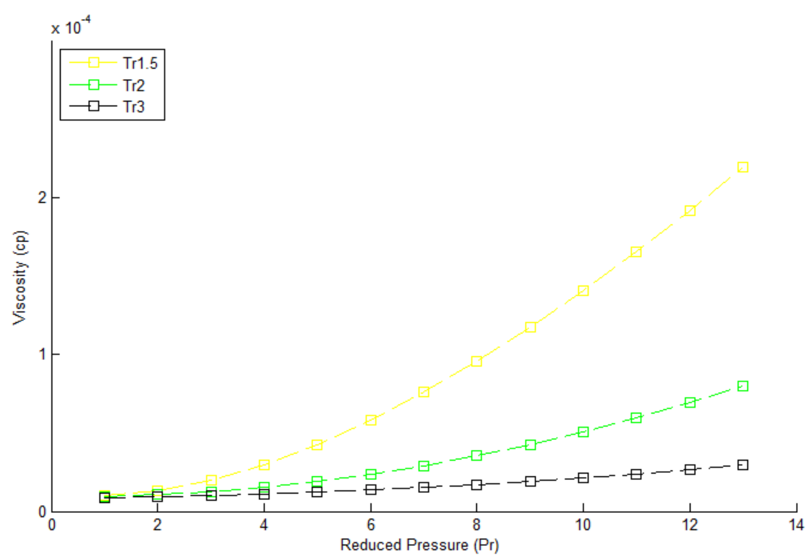


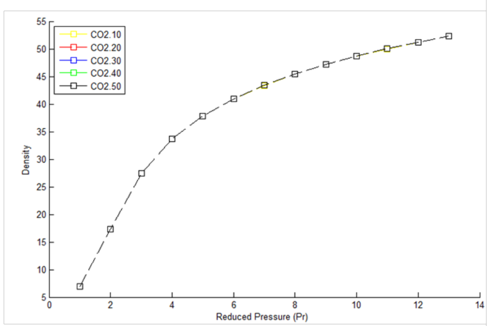
Figure 3 The viscosity of MOG gas mixture versus reduced pressure at different reduced temperatures.

4.3 Effect of CO_2 Composition on the Density of Gas Mixture

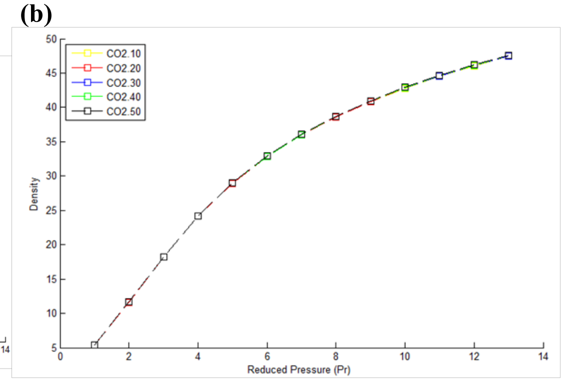
In this part, the density of the gas mixture has been evaluated using Eq.6 with z-factor values obtained from RK-EoS. Figure 4 shows the effect of CO_2 composition on the density of the gas mixture at different reduced pressures and reduced temperatures. As seen in Figure 4, the density of the gas mixture doesn't remarkably change with varying CO_2 concentration in gas mixture. In addition, the behaviour of the gas density seems to be identical at all values of CO_2 compositions. However, the numerical values of the densities indicate that there is a slight increase in the gas density with increase the concentration of CO_2.

Furthermore, Figure 4 shows that the gas density increases notably with increasing reduced pressure, especially at high reduced temperature. At low reduced temperature, the density was sharply increased at beginning and then, it became increased gradually to reach equilibrium. However, the density values increased linearly with reduced pressure. Figure 5 shows the effect of reduced temperature on the gas mixture at fixed CO_2 composition of 0.1565. The results showed that the density has an inverse relation with the reduced temperatures. For instant, the density values were read 5, 7, and 12 g/cm^3 for decreasing the reduced temperature as 1.25, 2.0, 3.0, respectively.

(a)



(b)



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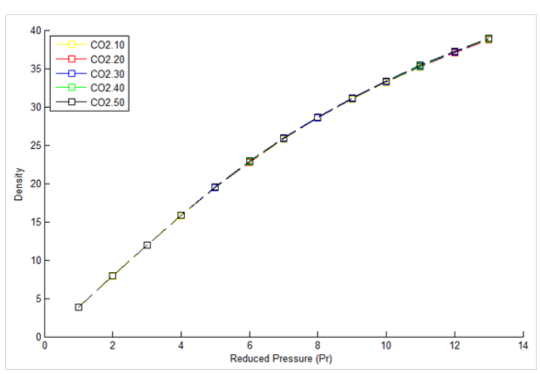

Figure 4 the effect of CO_2 Concentration on the density of natural gas mixture at different reduced temperatures; (a) at $T_r = 1.25$, (b) at $T_r = 1.5$, (c) at $T_r = 2$.

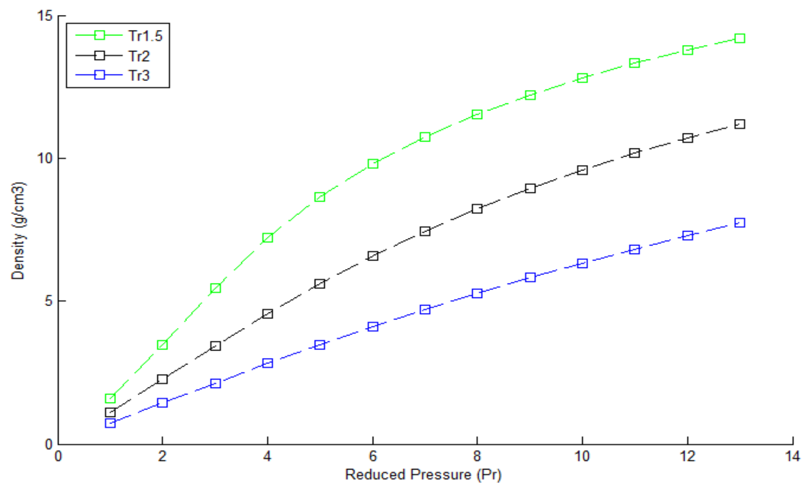

Figure 5 The density of MOG gas versus reduced pressure at different reduced temperatures.

5. Conclusions

Prediction of thermodynamic properties of Libyan NG under diverse conditions is very important in designing and processing of NG system. Among of these properties, density and viscosity have significant contribution to describe more than half of the other properties belong to gas mixtures. Redlich Kwong equation of state (RK-EoS) was used in this work to investigate the effect of CO_2 composition in the Libyan NG mixture of MOG on its viscosity and density. The data of NG mixture with different compositions of CO_2 was correlated to RK-EoS to obtain the compressibility factor of the gas over a range of reduced pressures from 1 to 14 and reduced temperatures from 1.5 to 3. Then, the z-factor obtained from RK-EoS was used to predict the viscosity and density of the mixture over mentioned conditions. The results showed that the increase of CO_2 content in the gas mixture leads to an increase in the viscosity. It also revealed that the density of the mixture is slightly increased with the increase in the CO_2 content. This finding is very useful to gas manufacturers for better design of gas piping and storage system. Moreover, this study demonstrated that the viscosity and density are increased with increase of the applied pressure. Nonetheless, the results showed that the density and viscosity are inversely proportional to the operating temperatures.

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