Article

Evaluation of Prediction Models for the Physical Properties in Fire-Flooding Exhaust Reinjection Process

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Abstract: The reinjection of the fire-flooding exhaust is a novel disposal process for handling the exhaust produced by the in-situ combustion technology. For reasonable process design and safe operation, it is of great significance to select an optimum property calculation method for the fire-flooding exhaust. However, due to the compositional particularity and the wide range of operating parameters during reinjection, the state equations in predicting the exhaust properties over the wide range of operating parameters have not been studied clearly yet. Hence, this paper investigates the applicability of several commonly-used equations of state, including the Soave–Redlich–Kwong equation, Peng–Robinson equation, Lee–Kesler–Plocker equation, Benedict–Webb–Rubin–Starling equation, and GERG-2008 equations. Employing Aspen Plus software, the gas densities, compressibility factors, volumetric coefficients, and dew points for five exhaust compositions are calculated. In comparison with the experimental data comprehensively, the result indicates that the Soave–Redlich–Kwong equation shows the highest precision over a wide range of temperature and pressure. The mean absolute percentage error for the above four parameters is 3.84%, 5.17%, 5.53%, and 4.33%, respectively. This study provides a reference for the accurate calculation of the physical properties of fire-flooding exhausts when designing and managing a reinjection system of fire-flooding exhaust.

Keywords: fire-flooding exhaust; reinjection process; equations of state; physical properties; MAPE

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1. Introduction

Heavy oil is abundant but difficult to exploit. To improve the production of heavy oil reservoirs, some enhanced oil recovery (EOR) methods [1,2] have been adopted, such as steam flooding [3], high-pressure nitrogen flooding [4], CO₂ flooding [5], fire flooding [6], microbial technology [7], and so on. Among them, taking the technical advantages of efficient oil displacement, low unit thermal cost, and wide applicability, the fire flooding technology is one of the most effective and promising ways to improve the thermal recovery of heavy-oil resources [8]. By combusting the air underground, the heat and mixed gas generated push the heavy oil from the gas injection well to the production well to realize short-distance displacement of heavy oil [9].

However, the combustion of heavy oil produces a large amount of exhaust gas, named fire-flooding exhaust, which contains both valuable and harmful components, such as methane, ethane, carbon dioxide, hydrogen sulfide, nitrogen, hydrogen, oxygen, etc. [10,11]. Table 1 compares the composition of fire-flooding exhausts with other greenhouse gasses referenced from published literature [12–18], including acid gas and flue gas. It can be seen that the composition of fire-flooding exhaust is considerably different from the other gases listed. Compared with the acid gas, the content of CO₂ and H₂S in the fire-flooding exhaust is lower. However, the latter contains much N₂ and other trace components. Compared

with flue gas, being equivalent in the content of N_2 and CO_2 , the fire-flooding exhaust has light hydrocarbons, H_2O , and trace amount of O_2 , H_2S , H_2 , and CO . It is conceivable that, with increasingly strict controls on environmental protection globally, how to efficiently and safely handle the exhaust gas which is produced by the fire flooding will become a key factor in restricting its worldwide application.

Table 1. Comparison of the components of acid gas, flue gas, and fire-flooding exhaust (unit: mol %).

Gas	CO_2	N_2	O_2	H_2	H_2O	H_2S	C_1	C_2	Others	Notes
Acid gas No.1	86					10				Acheson (Canada) [12]
Acid gas No.2	65					35				Lisbon (America) [12]
Acid gas No.3	100									Salah (Algeria) [12]
Flue gas No.1	15.6	84.4								Combustion gas in a thermal power plant [13]
Flue gas No.2	14.2	80.8	5							Reference [13]
Flue gas No.3	18.41	75.28	4.71		1.6					Reference [14]
Flue gas No.4	10	80	5			5				Reference [15]
Flue gas No.5	5–9	49–57	8–12		saturation					Reference [16]
Fire-flooding exhaust No.1	15.27	64.85	1.14				17.61			Liaohe Oilfield, China [17]
Fire-flooding exhaust No.2	13.29	73.6	0.35				11.87	0.36	C_3+ : 0.53	
Fire-flooding exhaust No.3	13.56	76.76	0.97	0.49	2.58	0.1	4.38	0.38	C_3+ : 1.01, CO : 0.15	Xinjiang Oilfield, China [18]

Some technologies—including burning [19], desulfurization [20], pressure swing adsorption [21], CO_2 separation [22], etc.—have been applied to effectively treat the harmful components in the fire-flooding exhaust. Unfortunately, the valuable hydrocarbon resource in it is wasted meanwhile. To improve the situation, like the acid gas injection procedure [23], a novel treatment strategy called the ‘fire-flooding exhaust reinjection process’ was proposed in an oilfield in northwest China [18]. In the proposed procedure, the fire-flooding exhaust will be dehydrated, compressed, and injected back into another proper oil reservoir, achieving zero emissions of harmful gases. Meanwhile, by adopting the principle of flue gas flooding [24], the novel process will make full use of the fire-flooding resource to enhance the oil recovery of the selected oil layers. Hence, it can be regarded as a promising method to realize multiple goals simultaneously, including waste handling, carbon capture and utilization, heavy oil enhancement, etc.

In the process, the exhaust needs to undergo dehydration, compression, pipeline transportation, cooling, and reinjection. Accordingly, the pressure will gradually increase to be higher than 20 MPa from the wellhead condition, with the temperature fluctuating over 160 K meanwhile, as shown in Figure 1 [18]. Together with the unique composition of fire-flooding exhausts, getting the physical properties accurately during the whole operation is a major problem to be solved for reinjection engineering.

Figure 1. Temperature and pressure change during the proposed reinjection process of the fire-flooding exhaust.

Simulation is the most economical and intuitive research method for oil and gas processing and transporting systems [25]. For the reinjection project of the fire-flooding exhaust, it can realize the prediction of the gas physical properties under different operating conditions, thus contributes to the precise design and safe operation. There is a number of chemical simulation software nowadays—such as Aspen HYSYS, Aspen Plus, Pro II, UniSim Design, etc.—which includes a variety of physical property calculation methods to achieve the above simulation goals. The first and most important step in numerical simulation is to select a precise physical property calculation method, which should provide a good approximation of the properties over the wide process ranges of pressure, temperature and composition [26]. Whether the prediction equation is suitable or will not directly affect the reliability of the calculation results [27].

Some well-known equations of state (EoS)—such as the Peng–Robinson (PR) equation, the Soave–Redlich–Kwong (SRK) equation, the Lee–Kesler–Plocker (LKP) equation, the Benedict–Webb–Rubin–Starling (BWRS) equation, etc.—have been used or modified to study the natural gas treatment, acid gas treatment, reinjection, and other energy fields. Zhou et al. [28] combined PR and Patel–Teja equation to predict the densities and viscosities of the acid gas during an acid gas reinjection process. Wang et al. [29] developed the Peng–Robinson-cubic-plus-association (PR-CPA) EoS with a pseudo-chemical reaction approach to calculate the solubility of acid gases in aqueous alkanolamines solutions. Based on the SRK equation, Hussain [15] established a HYSYS model to perform a feasibility analysis of recovering carbon dioxide from flue gas. The SRK equation was also used to calculate the saturation pressure of the crude oil and its mixtures with pure and impure CO₂ by Pereira et al. [30]. Modekurti et al. [24] conducted a dynamic modeling of a multistage CO₂ compression system, in which the LKP method was used in the property prediction for the compression section. Adom et al. [31] applied the BWRS model to predict the compressibility factor, enthalpy, and heat leakage at various pressures for determining the factors which affect the BOG in typical LNG tanks of different capacities. Combining the PR and the eNRTL activity coefficient equation, Wan et al. [32] conducted an acid gas-chemical solvent model to simulate the desulfurization and decarbonization process of a natural gas treatment plant.

Research results reveal that the accuracy of calculation methods for physical property forecasting closely relates to the composition and operation condition studied. A comparative study of different prediction models is helpful to master their applicability in different scenarios, which benefits in model selection. W. Yan et al. [33] made a comparative study of non-cubic models (PC-SAFT and BWRS) and cubic models (SRK and PR) in several important aspects related to PVT modeling of reservoir fluids. The result shows that the non-cubic models are clearly advantageous in density calculation of pure components and some HP and HT fluids. Compared with the NIST results, M. Bertini et al. [34] evaluated 10 property methods for pure and mixture of CO₂ for power cycles, including the cubic-type, virial-type, Helmholtz-type, and SAFT-type. G.D. Marcoherardino et al. [35] conducted an analysis of the performance of five EoSs on CO₂+C₆F₆, revealing that although all equations converge at low temperature, the big difference and non-convergence occurs at higher temperatures. The region close to the critical point is the most difficult to be modeled. Varzandeh [36] compared the GERG-2008 with other cubic and non-cubic EoS in calculation of the phase equilibrium and physical properties of natural gas related systems. A similar study was carried out by Yuan et al. [27]. After conducting a comprehensive comparison and analysis among the SRK, PR, and GERG-2008 equations, the GERG-2008 equation was recommended as the basis for the property calculation in the natural gas liquefaction processes. Many similar studies exist that are not enumerated here.

However, according to the papers published, there is little literature studying the application of the above EoSs in predicting the physical properties of the fire-flooding exhaust. Considering the compositional singularity of the fire-flooding exhaust and the wide range of operating parameters accompanied with the reinjection procedure, the accuracy of property calculation methods is unclear yet. Since every model has its applicable boundary, the purpose of this research is to investigate the application of some commonly-used EoSs in predicting the physical properties of the fire-flooding exhaust within a wide range of pressure and temperature. The EoSs evaluated in this work include the PR, the SRK, the LKP, the BWRS, and the GERG-2008 equations. Using a HPHT physical property analyzer and the Aspen Plus software, the physical properties were detected and predicted, including the gas densities, compressibility factors, volumetric coefficients, and dew point temperatures for five exhaust compositions which were collected from a real oilfield. A comprehensive comparison and analysis between the experimental data and the calculated value for the five equations was then conducted. This work is helpful to select a precise property calculation method when simulating and designing a reinjection system which is used to reduce the emission of the harmful gas produced by the fire flooding process. It can be applied in the simulation of other waste treatment processes, too.

2. Equations of State to Be Evaluated

2.1. Soave–Redlich–Kwong EoS

Redlich and Kwong [37] proposed a modified cubic EoS with two parameters, which obtained satisfactory results at the pressure above the critical temperature. A modification of this equation was developed by Soave [38], thus the SRK equation was obtained. It was the first EoS to be associated with the acentric factor and could be applied to all non-polar substances [39], particularly for multicomponent mixtures. The equation is given below:

$$\begin{aligned}
 p &= \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \\
 a(T) &= \alpha(T)0.42747R^2T_c^2/p_c \\
 b &= 0.08664RT_c/p_c \\
 \alpha(T) &= \left[1 + m\left(1 - (T/T_c)^{0.5}\right)\right]^2 \\
 m &= 0.480 + 1.5741\omega - 0.1715\omega^2
 \end{aligned} \tag{1}$$

Where p , R , T , and v is the pressure, gas constant, temperature, and molar volume respectively, a and b are parameters of the EoS, only related to physical properties, T_c is the critical temperature, and ω is the acentric factor.

For mixtures, mixing rules are expressed as

$$\begin{aligned} a &= \sum_i \sum_j x_i y_j (a_i a_j)^{0.5} (1 - k_{ij}) \\ b &= \sum_i y_i b_i \\ T_{cm} &= \sum_i x_i T_{ci} \\ p_{cm} &= \sum_i x_i p_{ci} \end{aligned} \quad (2)$$

where x_i and x_j is the molar fractions of components i and j , T_{cm} and p_{cm} is the critical temperature and critical pressure of the mixture, respectively, a_i and b_i are the pure component parameters obtained from Equation (1), and k_{ij} is the binary interaction parameter of the SRK equation.

2.2. Peng–Robinson EoS

The SRK equation is not accurate in predicting liquid density. For hydrocarbon components (except for the methane), the predicted liquid density is generally smaller than the experimental data. To further improve the prediction accuracy of physical parameters and phase equilibrium, Peng and Robinson [40] developed a two-constant EoS based on the Soave's model. It showed great advantages in predicting liquid phase density. The equation is given below as

$$\begin{aligned} p &= \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \\ a(T) &= 0.45724\alpha(T)R^2T_c^2/p_c \\ b(T) &= 0.07780RT_c/p_c \\ \alpha(T) &= \left[1 + k\left(1 - (T/T_c)^{0.5}\right)\right]^2 \\ k &= 0.37464 + 1.5422\omega - 0.26992\omega^2 \end{aligned} \quad (3)$$

where the notation declarations and mixing rules are consistent with the SRK equation.

2.3. Lee–Kesler–Plocker EoS

The LKP equation is a modified LK equation proposed by Plocker, Knapp, and Prausnitz [41]. It retained the prototype of the LK equation but modified the mixing rule. The LKP equation is applicable to the liquid phase, especially with good accuracy in the calculation of the physical properties of hydrocarbons. It was deemed to be the best method for forecasting the gas thermophysical properties [42]. The equation is expressed as

$$\begin{aligned} Z &= Z^{(0)} + \frac{\omega}{\omega^{(r)}} \left(Z^{(r)} - Z^{(0)} \right) \\ Z = \frac{p_r v_r}{T_r} &= 1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^3} + \frac{c_4}{T_r^3 v_r^2} \left(\beta + \frac{\gamma}{v_r} \right) \exp\left(-\frac{\gamma}{v_r}\right) \\ B &= b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \\ C &= c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \\ D &= d_1 + \frac{d_2}{T_r} \end{aligned} \quad (4)$$

where Z is the compression factor, 0 and r represents the simple and reference fluid parameters, respectively, and $b_1 \sim b_4$, $c_1 \sim c_4$, d_1 , d_2 , β , and γ are model constants.

For mixtures, mixing rules are expressed as

$$\begin{aligned}
 T_{cm}v_{cm}^{0.25} &= \sum_i \sum_j x_i x_j v_{cij}^{0.25} T_{cij} \\
 v_{cm} &= \sum_i \sum_j x_i x_j v_{cij} \\
 \omega_m &= \sum_i x_i \omega_i \\
 T_{cij} &= (T_{ci} T_{cj})^{0.5} k_{ij} \\
 v_{cij} &= \frac{1}{8} \left(v_{ci}^{1/3} + v_{cj}^{1/3} \right)^3
 \end{aligned} \tag{5}$$

where k_{ij} represents the binary interaction parameter of the LKP equation.

2.4. Benedict–Webb–Rubin–Starling EoS

To expand the application range and improve the accuracy at high pressure and low temperature, Benedict–Webb–Rubin conducted an 8-parameters method which was applied in a gas–liquid system in 1940, called BWR equation [43]. Compared with the SRK and PR method, the equation performed high accuracy in predicting the thermophysical properties of light hydrocarbons and their mixtures. However, it had poor adaptability to the mixtures with more non-hydrocarbon gases, heavier hydrocarbon components, and lower temperatures ($T_r < 0.6$). Combining the thermodynamic data of C₁~C₈ alkanes, Staring and Powers [44], Starling and Han [45], updated the BWR model to an 11-constant equation, namely the BWRS equation, which showed high prediction accuracy for the physical properties of hydrocarbon, CO₂, H₂S, and N₂. The BWRS equation is given as

$$\begin{aligned}
 p = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \rho^2 + \left(bRT - a - \frac{d}{T} \right) \rho^3 \\
 + \alpha \left(a + \frac{d}{T} \right) \rho^6 + \frac{c\rho^3}{T^2} (1 + \gamma \rho^2) \exp(-\gamma \rho^2)
 \end{aligned} \tag{6}$$

where $A_0, B_0, C_0, D_0, E_0, \gamma, a, b, c, d$, and α are the parameters of BWRS equation of which form are shown in reference [44].

2.5. GERG-2008 EoS

As an international standard named ISO20765-2 [46], the GERG-2008 equation is the extension of the GERG-2004 model [47]. This equation covers 21 natural gas components, including CH₄, N₂, CO₂, C₂H₆, C₃H₈, C₄H₁₀, I-C₄H₁₀, C₅H₁₂, I-C₅H₁₂, C₆H₁₄, C₇H₁₆, C₈H₁₈, C₉H₂₀, C₁₀H₂₂, H₂, O₂, CO, H₂O, H₂S, He, and Ar. Being explicit in the Helmholtz free energy as a function of density, temperature, and composition, the GERG-2008 equation was constructed by fitting a large number of experimental data to obtain the regression coefficients. Furthermore, it has been improving and upgrading with more experimental data nowadays [48]. Hence, it showed excellent predictive performance in the gas phase, liquid phase, supercritical region, and vapor–liquid equilibrium states for mixtures of the components mentioned above, and was regarded as the most comprehensive calculation method in predicting natural gas thermophysical properties. However, for the fire-flooding exhaust, the precision has not been assessed and needs to be studied. The equation is expressed as

$$a(\rho, T, \bar{x}) = a^o(\rho, T, \bar{x}) + a^r(\rho, T, \bar{x}) \tag{7}$$

Using the dimensionless form of Helmholtz free energy $\alpha = a/(RT)$, the following equation is deduced (note that α^o does not depend on δ and τ of the mixture but ρ and T)

$$\begin{aligned}
 \alpha(\delta, \tau, \bar{x}) &= \alpha^o(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x}) \\
 \delta &= \rho/\rho_r, \tau = T/T_r
 \end{aligned} \tag{8}$$

The dimensionless form of the Helmholtz free energy for the ideal-gas mixture α^0 is given by

$$\alpha^0(\rho, T, \bar{x}) = \sum_{i=1}^N x_i [\alpha_{oi}^0(\rho, T) + \ln x_i] \quad (9)$$

The residual part of the Helmholtz free energy is expressed as

$$\alpha^r(\delta, \tau, \bar{x}) = \sum_{i=1}^N x_i \alpha_{oi}^r(\delta, \tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta, \tau) \quad (10)$$

For mixtures, the mixture density and mixture temperature are given below as

$$\begin{aligned} \frac{1}{\rho_r(\bar{x})} &= \sum_{i=1}^N x_i^2 \frac{1}{\rho_{ci}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{v,ij} \gamma_{v,ij} \cdot \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \cdot \frac{1}{8} \left(\frac{1}{\rho_{ci}^{1/3}} + \frac{1}{\rho_{cj}^{1/3}} \right)^3 \\ T_r(\bar{x}) &= \sum_{i=1}^N x_i^2 T_{ci} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \cdot \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{ci} \cdot T_{cj})^{0.5} \end{aligned} \quad (11)$$

The detailed expressions involved in the above equations can be seen in reference [47].

The above property calculation methods have been embedded in the Aspen Plus software which can be used as a platform to analyze the accuracy of each EoS. In Aspen Plus, the above property methods are named as SRK, PENG-ROB, LK-PLOCK, BWRS, and GERG2008. In this paper, for the SRK equation, the PR equation, the LKP equation, and the BWRS equation, the binary interaction parameters of Knapp et al. [49] were used. The precision of the five models mentioned is analyzed by comparing the calculation results with the experimental data.

3. Accuracy Analysis of the Calculation Models for the Physical Properties in the Fire-Flooding Exhaust Reinjection Process

In order to find out the most precise physical equation among the five EoSs for the fire-flooding exhaust reinjection process, a comparison between the experimental data and the calculated value under the same temperature and pressure for different physical properties is needed. In this study, the properties of five representative fire-flooding exhausts collected from an oilfield in the northwest China were detected. The gas compositions are shown in Table 2.

Table 2. Compositions of five fire-flooding exhaust samples.

Sample Name	Composition (mol%)									Analysis Method
	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ +	N ₂	CO ₂	O ₂	H ₂	H ₂ S	
Sample 1	1.9	0.14	0.07	0.08	78.13	17.59	2.07	-	0.02	PVT property analysis
Sample 2	3.08	0.22	0.11	0.074	80.4	15.2	0.25	0.53	0.088	
Sample 3	4.49	0.29	0.13	0.16	77.76	13.93	3.27	-	0.062	
Sample 4	5.61	0.36	0.16	0.2	79.22	13.98	1.15	-	0.088	
Sample 5	0.97	0.095	0.04	0.034	81.89	16.97	3.5	-	0.011	

The experimental data, including the densities, the compressibility factors, the volumetric coefficients and the dew point temperatures for the mentioned components above, is obtained through a high pressure (HP) and high temperature (HT) physical property analyzer of which parameters are shown in Table 3. This equipment is particularly used to detect the physical properties and phase states of formation fluids. Combining the field operating parameters and the experimental condition, the tested pressure of 4–25 MPa was set, while the tested temperature contained 303.15 K, 333.15 K, 363.15 K, and 393.15 K. After the experimental testing, a total of 1351 valid experimental data was obtained, which was used for the model evaluation and analysis.

Table 3. Equipment parameters used in this study.

Technical Indicators	Value
Working pressure	0–100 MPa
Working temperature	From ambient temperature to 473.15 K
Pump capacity	500 mL
Pump precision	0.0001 mL

Some indicators are necessary for evaluating the performance of the prediction models. The common used includes the correlation coefficient (CC), the mean squared error (MSE), the mean absolute error (MAE), the mean absolute percentage error (MAPE), the root mean square error (RMSE), the normalized root mean squared error (NRMSE), and the mean absolute range normalized error (MARNE) [50]. These indicators are defined as

$$CC = \frac{\text{cov}(x^{\text{cal}}, x^{\text{exp}})}{\sqrt{D(x^{\text{cal}})D(x^{\text{exp}})}} \quad (12)$$

$$MSE = \frac{1}{N} \sum_{i=1}^N (x_i^{\text{exp}} - x_i^{\text{cal}})^2 \quad (13)$$

$$MAE = \frac{1}{N} \sum_{i=1}^N |x_i^{\text{exp}} - x_i^{\text{cal}}| \quad (14)$$

$$MAPE = \frac{1}{N} \sum_{i=1}^N \left| \frac{x_i^{\text{cal}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right| \times 100\% \quad (15)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i^{\text{cal}} - x_i^{\text{exp}})^2} \quad (16)$$

$$NRMSE = \frac{1}{\bar{x}^{\text{exp}}} \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i^{\text{cal}} - x_i^{\text{exp}})^2} \quad (17)$$

$$MARNE = \frac{1}{N} \sum_{i=1}^N \frac{|x_i^{\text{cal}} - x_i^{\text{exp}}|}{\max(x_i^{\text{cal}})} \times 100\% \quad (18)$$

where x^{cal} is the calculated value, x^{exp} is the experimental value, N is the dataset size.

For different goals and data sets, the significance of every indicator—such as MAE, MSE, and RMSE—is not the same [51]. According to the similar literature published [30,52], in our work, the MAPE is employed as the main criterion to evaluate the accuracy of different prediction methods.

In the following paragraphs, Section 3.1 Sections 3.2–3.4 are the detailed comparison results between the calculated and the experimental data. Tables 4, 6, and 8 lists the comparison of gas densities, compressibility factors and volumetric coefficients for Sample 1 as an example, respectively. The comparison of dew point temperature for the five samples is illustrated from Figures 2–6. Tables 5, 7, 9, and 10 shows the prediction accuracy for each model in predicting the four properties, respectively. An overall summary was conducted in the Results.

Figure 2. Experimental and calculation results of dew points for Sample 1.

Figure 3. Experimental and calculation results of dew points for Sample 2.

Figure 4. Experimental and calculation results of dew points for Sample 3.

Figure 5. Experimental and calculation results of dew points for Sample 4.

Figure 6. Experimental and calculation results of dew points for Sample 5.

3.1. Accuracy Analysis of the Prediction Models for the Gas Density

The density is the most important and fundamental property for process design. Using the Aspen Plus software, the densities of the collected fire-flooding exhausts were calculated by employing the five prediction models under the same conditions as the experiments. The total number of the experimental data for the five samples is 378. Table 4 shows the experimental and the calculation results of Sample 1 as an example. By comparing with the experimental data, Table 5 lists the prediction accuracies for each model. The comparison result shows that, the SRK equation performs the minimum overall MAPE in calculating gas density, followed by the BWRS equation. Although the PR equation shows the highest prediction accuracy for Sample 4 and 5, its overall prediction accuracy is the lowest among the five equations. In comparison, the calculation accuracy of the SRK equation is maintained at a relatively high level for the five sample compositions as a whole. Therefore, it can be considered that the SRK equation is the suitable model for predicting the density of fire-flooding exhausts during the reinjection process.

Table 4. Experimental data and calculated results of the gas density for Sample 1.

Experimental Data			Calculated Results				
<i>T</i> (K)	<i>p</i> (MPa)	ρ (kg/m ³)	SRK	PR	LKP	BWRS	GERG-2008
			ρ (kg/m ³)				
303.15	24.040	280.818	287.1567	303.4508	296.5895	285.2223	295.9078
	22.020	260.102	265.6166	280.0517	274.2284	264.7271	273.7772
	20.000	238.235	245.3392	258.0877	253.0746	245.2787	252.7865
	18.047	217.519	222.6385	233.5732	229.3109	223.3094	229.1533
	16.027	194.501	199.0326	208.1689	204.5558	200.2309	204.488
	14.007	171.483	175.4618	182.899	179.8466	176.9487	179.8341
	11.919	147.315	151.2386	157.043	154.5195	152.7901	154.5381
	9.899	121.995	125.6173	129.8411	127.8607	127.0213	127.8929
	8.013	97.826	101.4431	104.3418	102.8719	102.5618	102.9049
	5.993	72.506	75.33706	77.02617	76.09284	76.06897	76.11882
	3.973	48.338	50.19588	50.98595	50.5133	50.56582	50.52896
333.15	24.040	242.839	252.8345	265.6839	259.5303	251.8671	259.5332
	22.020	224.425	234.3723	245.7615	240.4981	234.2006	240.5679
	20.067	207.161	215.8794	225.8603	221.3727	216.3539	221.4786
	18.047	188.747	196.0967	204.6345	200.8674	197.0882	200.9854
	16.027	169.182	175.68	182.8025	179.6819	177.015	179.7921
	14.007	149.616	154.6753	160.4283	157.8923	156.1701	157.9821
	11.987	127.749	133.1463	137.5982	135.5974	134.6212	135.6611
	9.966	105.882	111.1749	114.4223	112.9163	112.4723	112.9546
	7.946	85.166	88.85869	91.03211	89.98197	89.86304	90.00016
	5.993	63.299	67.06426	68.3602	67.70458	67.73198	67.7106
	3.906	40.281	43.65127	44.22782	43.92035	43.9755	43.92078
363.15	24.040	218.670	227.4674	237.9229	232.4172	227.0283	232.7277
	22.088	202.558	211.2601	220.5309	215.8245	211.4446	216.1178
	20.067	186.445	193.9769	202.0344	198.0834	194.6852	198.3424
	17.980	169.182	175.5751	182.4016	179.1564	176.6794	179.3675
	16.027	153.069	157.8771	163.5837	160.933	159.2082	161.0933
	14.007	134.655	139.1037	143.6979	141.5992	140.5207	141.7069
	11.987	115.090	119.8922	123.4378	121.8317	121.2511	121.8923
	9.966	95.524	100.2885	102.87	101.7001	101.4656	101.7242
	7.946	74.808	80.34766	82.07417	81.28466	81.25334	81.28522
	5.993	56.394	60.81249	61.84254	61.36381	61.41528	61.35442
	4.512	41.432	45.86356	46.46801	46.1824	46.24224	46.17241
393.15	24.040	197.954	207.4401	216.1139	211.2069	207.3155	211.6463
	22.088	182.992	192.5665	200.2326	196.0667	192.9535	196.4434
	20.067	168.031	176.7583	183.399	179.9353	177.5635	180.2405
	18.047	153.069	160.5257	166.1658	163.3382	161.627	163.5694
	16.027	136.957	143.878	148.5513	146.294	145.148	146.4537
	14.007	120.844	126.8295	130.5811	128.8292	128.1415	128.9249
	11.987	104.731	109.4004	112.2884	110.9786	110.6362	111.0221
	10.034	87.468	92.2155	94.33903	93.3977	93.28213	93.40498
	8.013	70.205	74.1197	75.54289	74.92288	74.94003	74.90869
	5.993	51.790	55.7396	56.57545	56.21509	56.2795	56.19466
	4.714	40.281	43.97169	44.50469	44.27556	44.33777	44.25744

Table 5. MAPEs of experimental and calculated results in the gas density prediction.

MAPE	SRK	PR	LKP	BWRS	GERG-2008	Number of Experimental Data Sets
Sample 1	4.62%	8.13%	6.50%	5.32%	6.54%	76
Sample 2	2.92%	6.21%	4.62%	3.46%	4.66%	77
Sample 3	3.91%	7.33%	5.61%	4.46%	5.68%	75
Sample 4	4.95%	2.14%	3.50%	4.59%	3.45%	76
Sample 5	2.82%	0.80%	1.28%	2.39%	1.23%	74
Overall MAPE	3.84%	4.92%	4.30%	4.04%	4.31%	-

3.2. Accuracy Analysis of the Prediction Models for the Compressibility Factor

Defined as the ratio of the actual gas volume to the ideal value, the compressibility factor, also called Z-factor, is a dimensionless parameter representing the degree to which a real gas deviates from an ideal gas. It depends on the working condition and fluid composition. Considering that the PVT relationship can be calculated when the compressibility factor is given, it is significant for prediction other gas properties.

Using the Aspen Plus software, the compressibility factors of the collected fire-flooding exhausts were predicted by employing the five prediction models under the reinjection condition. The total number of the experimental data for the five samples is 377. Table 6 shows the experimental and the calculation results of the compressibility factors for Sample 1 as an example. By comparing with experimental data, Table 7 lists the prediction accuracies for each model. The comparison result shows that, in the prediction of compressibility factor, the SRK equation performs the minimum overall MAPE, followed by the BWRS equation, while that of the LKP, GERG-2008, and PR equation stands the highest. Although the PR equation shows the highest prediction accuracy for Sample 5, that of SRK equation is maintained at a relatively high level for the five sample compositions as a whole in comparison. Therefore, it can be considered that the SRK equation is the suitable model for predicting the compressibility factor of fire-flooding exhausts during the reinjection process.

Table 6. Experimental data and calculated results of the compressibility factors for Sample 1.

Experimental Data			Calculated Results				
T (K)	p (MPa)	Z-Factor	SRK	PR	LKP	BWRS	GERG-2008
303.15	23.937	1.068	1.023277	0.9685329	0.9907489	1.029885	0.9929652
	21.924	1.058	1.009767	0.9578203	0.9780867	1.013005	0.9796722
	19.911	1.046	0.9978164	0.948761	0.9674312	0.997747	0.9684879
	17.897	1.037	0.9876324	0.9416031	0.9590299	0.9844297	0.9596604
	15.884	1.028	0.9794267	0.9366147	0.9531164	0.9734118	0.9534156
	13.982	1.022	0.9736777	0.9341457	0.9499896	0.9654592	0.9500521
	11.857	1.016	0.969746	0.9342527	0.9494519	0.9597842	0.9493242
	9.843	1.016	0.9685981	0.9374025	0.9518559	0.9578699	0.95161
	8.054	1.017	0.9697594	0.9428633	0.9563227	0.9591882	0.9560161
	6.040	1.023	0.9735473	0.9521314	0.9638359	0.9641602	0.9635069
333.15	4.027	1.026	0.9799269	0.964771	0.9737839	0.972774	0.9734824
	23.826	1.119	1.053305	1.002581	1.02615	1.057001	1.026104
	21.812	1.107	1.040927	0.992916	1.014469	1.04136	1.01415
	19.911	1.092	1.030247	0.984908	1.004752	1.027752	1.00426
	17.897	1.080	1.020125	0.977761	0.995994	1.01479	0.995405
	15.996	1.070	1.011791	0.972414	0.989282	1.004124	0.988676
	13.982	1.061	1.00438	0.968403	0.983941	0.994745	0.983383
	12.081	1.056	0.998814	0.966326	0.980644	0.987919	0.980178
	9.843	1.053	0.994167	0.966208	0.979005	0.982693	0.978681
	8.054	1.050	0.991999	0.968062	0.979455	0.980868	0.97925
	6.040	1.052	0.991263	0.972347	0.981814	0.981448	0.981725
	4.027	1.052	0.992357	0.97906	0.986085	0.984868	0.986072

Table 6. Cont.

Experimental Data			Calculated Results				
			SRK	PR	LKP	BWRS	GERG-2008
T (K)	p (MPa)	Z-Factor	Z-Factor				
363.15	23.826	1.146	1.074154	1.027168	1.051283	1.075896	1.049874
	21.924	1.133	1.062964	1.018457	1.040509	1.061792	1.039098
	20.022	1.118	1.052476	1.010554	1.03067	1.048585	1.029326
	18.009	1.106	1.042205	1.003162	1.021358	1.035726	1.020153
	15.996	1.094	1.032867	0.99688	1.013273	1.024199	1.012268
	13.982	1.086	1.02454	0.991822	1.006502	1.01419	1.00574
	11.969	1.080	1.017298	0.988108	1.00112	1.00589	1.000624
	9.955	1.074	1.011214	0.985859	0.99719	0.999483	0.996956
	7.942	1.070	1.006353	0.985193	0.994758	0.995138	0.994752
	5.928	1.064	1.002771	0.986223	0.993851	0.992989	0.994007
	4.251	1.062	1.000795	0.988451	0.994265	0.992942	0.994485
393.15	24.049	1.176	1.089354	1.045624	1.069927	1.090022	1.067705
	21.924	1.160	1.077203	1.036135	1.057981	1.074814	1.055969
	20.022	1.145	1.066871	1.028292	1.048042	1.061976	1.046273
	18.009	1.133	1.056536	1.020722	1.038355	1.049295	1.036894
	15.996	1.124	1.046874	1.013983	1.029599	1.037687	1.028482
	13.982	1.113	1.037938	1.008155	1.021842	1.027295	1.021088
	11.969	1.104	1.029779	1.003322	1.015149	1.018271	1.014754
	9.955	1.097	1.022451	0.999575	1.00958	1.010764	1.009513
	7.942	1.091	1.016004	0.997002	1.005188	1.004915	1.005386
	6.040	1.085	1.010766	0.995733	1.00216	1.001027	1.002521
	4.810	1.080	1.007835	0.995547	1.000793	0.9994	1.001202

Table 7. MAPEs of experimental and calculated results in the compressibility factor prediction.

MAPE	SRK	PR	LKP	BWRS	GERG-2008	Number of Experimental Data Sets
Sample 1	5.72%	8.78%	7.39%	6.34%	7.42%	76
Sample 2	9.48%	12.35%	11.00%	9.94%	11.03%	76
Sample 3	3.78%	6.86%	5.34%	4.32%	5.41%	75
Sample 4	1.92%	4.94%	3.44%	2.45%	3.49%	76
Sample 5	4.93%	1.51%	3.11%	4.27%	3.06%	74
Overall MAPE	5.17%	6.89%	6.06%	5.46%	6.08%	-

3.3. Accuracy Analysis of the Prediction Models for the Volumetric Coefficient

The volumetric coefficient refers to the gas volume under the specified condition for the unit volume of gas at the standard condition. It is a function of the gas compressibility factor. Using the Aspen Plus software and the computational relation, the volumetric coefficients of the fire-flooding exhaust samples were calculated by employing the above five prediction models under the detection conditions. The total number of the experimental data for the five samples is 379. Table 8 shows the experimental and the calculation results of Sample 1 as an example. By comparing with the experimental data, Table 9 lists the prediction accuracies for each model. The comparison results show that the model precision is greatly affected by the gas composition. Among the evaluated methods, the SRK equation performs the highest accuracy, followed by the BWRS equation, while the PR, LKP, and GERG-2008 equations bring out bigger errors. Therefore, it can be considered that the SRK equation is suitable for predicting the volumetric coefficient of fire-flooding exhausts during the reinjection process.

Table 8. Experimental data and calculated results of the volumetric coefficient for Sample 1.

Experimental Data			Calculated Results				
			SRK	PR	LKP	BWRS	GERG-2008
<i>T</i> (K)	<i>p</i> (MPa)	Volumetric Coefficient	Volumetric Coefficient				
303.15	24.142	0.004700	0.0044496	0.0042107	0.0043081	0.0044798	0.004318
	22.018	0.005036	0.0048105	0.0045625	0.0046594	0.0048266	0.0046671
	20.106	0.005456	0.0052081	0.0049508	0.0050489	0.0052093	0.0050546
	18.053	0.006043	0.0057391	0.0054704	0.0055721	0.0057218	0.0055759
	16.000	0.006715	0.0064198	0.006138	0.0062464	0.0063813	0.0062485
	14.018	0.007638	0.0072822	0.0069861	0.0071046	0.007221	0.0071051
	12.035	0.008897	0.0084485	0.0081363	0.0082691	0.0083627	0.0082681
	9.982	0.010743	0.0101717	0.0098408	0.0099932	0.0100593	0.0099907
	8.071	0.013345	0.0125957	0.0122457	0.0124207	0.0124583	0.0124167
	6.018	0.017878	0.0169603	0.0165884	0.0167919	0.0167972	0.0167862
	4.035	0.026942	0.0254551	0.0250607	0.0252952	0.025269	0.0252873
333.15	24.142	0.005288	0.005036	0.004792	0.004906	0.005056	0.004906
	22.089	0.005791	0.005438	0.005185	0.005299	0.005442	0.005297
	20.177	0.006211	0.005891	0.005629	0.005744	0.005879	0.005741
	18.124	0.006882	0.006491	0.00622	0.006337	0.006459	0.006333
	16.071	0.007722	0.007255	0.006972	0.007093	0.007201	0.007089
	14.089	0.008729	0.008216	0.00792	0.008048	0.008138	0.008043
	12.035	0.010156	0.00956	0.009249	0.009386	0.009455	0.009382
	9.982	0.012170	0.011476	0.01115	0.011299	0.011344	0.011295
	8.071	0.015108	0.01416	0.013818	0.013981	0.014001	0.013978
	6.089	0.020144	0.018756	0.018396	0.018576	0.01857	0.018574
	4.035	0.030384	0.02833	0.027949	0.02815	0.028116	0.02815
363.15	24.142	0.005959	0.005597	0.005351	0.005478	0.005609	0.005471
	22.089	0.006463	0.006049	0.005794	0.005921	0.006043	0.005913
	20.106	0.006966	0.006576	0.006314	0.00644	0.006553	0.006431
	18.053	0.007722	0.007251	0.006979	0.007106	0.007206	0.007097
	16.142	0.008561	0.00804	0.007759	0.007887	0.007974	0.007879
	14.018	0.009820	0.00918	0.008886	0.009018	0.009087	0.009011
	12.035	0.011331	0.010617	0.010311	0.010447	0.010498	0.010442
	10.053	0.013513	0.012635	0.012316	0.012458	0.012488	0.012455
	8.000	0.016871	0.015799	0.015465	0.015616	0.015622	0.015615
	6.018	0.022410	0.020929	0.020579	0.02074	0.020723	0.020743
	4.389	0.030636	0.028636	0.028272	0.028443	0.028406	0.028449
393.15	24.142	0.006715	0.006138	0.005891	0.006028	0.006142	0.006016
	22.089	0.007218	0.006636	0.006382	0.006517	0.006622	0.006505
	20.106	0.007806	0.007217	0.006955	0.007089	0.007184	0.007077
	18.124	0.008561	0.00793	0.00766	0.007793	0.007876	0.007782
	16.142	0.009484	0.008823	0.008544	0.008677	0.008747	0.008667
	14.089	0.010827	0.01002	0.009731	0.009864	0.009918	0.009857
	12.035	0.012506	0.011635	0.011335	0.011469	0.011505	0.011465
	10.053	0.014940	0.013831	0.01352	0.013656	0.013673	0.013655
	8.071	0.018549	0.017121	0.016796	0.016936	0.016933	0.016939
	6.089	0.024508	0.022572	0.022234	0.022379	0.022354	0.022387
	4.885	0.030636	0.028053	0.027707	0.027855	0.027816	0.027866

Table 9. MAPEs of experimental and calculated results in the volumetric coefficient prediction.

MAPE	SRK	PR	LKP	BWRS	GERG-2008	Number of Experimental Data Sets
Sample 1	6.22%	9.28%	7.89%	6.83%	7.92%	76
Sample 2	9.28%	12.12%	10.78%	9.74%	10.81%	77
Sample 3	4.08%	7.11%	5.61%	4.59%	5.67%	76
Sample 4	2.92%	5.97%	4.49%	3.41%	4.53%	76
Sample 5	5.16%	1.74%	3.34%	4.49%	3.29%	74
Overall MAPE	5.53%	7.24%	6.42%	5.81%	6.44%	-

3.4. Accuracy Analysis of the Prediction Models for Dew Point

Forecasting dew points involves the calculation of both gas and liquid properties, including the compressibility factor, fugacity, etc. The calculation accuracy reflects the ability of each EoS in predicting phase equilibrium parameters. Using the Aspen Plus software, the dew point lines of the fire-flooding exhaust samples were calculated by employing the above five models. The total number of the experimental data for the five samples is 217. Figures 2–6 show the experimental and predicted value of dew point temperatures under different pressures for the five samples, respectively. It can be seen that, except for the BWRS equation, the discontinuity of dew point lines occurs within some pressure range when the other four equations were adopted. According to the literature published, it stands for the non-convergence or non-solution at the specified conditions for solving the liquid-vapor equilibrium [35,53,54]. The case happens for both cubic and non-cubic equations, especially near the critical zone. Improvements can be done from the aspects of model description, mathematical algorithm, etc.

Meanwhile, for every model, as the pressure increases, the deviation between the experimental and calculated value increases gradually. With the non-convergence points excluded, Table 10 lists the prediction accuracy of the calculation models. It can be found that, the LKP equation performs the highest accuracy with a MAPE of 3.71%, followed by SRK equation of which MAPE is 4.33%. Errors brought by other equations are beyond 5%. Although the prediction accuracy of the dew points through the LKP equation is slightly higher than the SRK equation, the latter has stronger computational convergence than the former over the whole pressure range. Hence, considering the prediction accuracy and computational convergence, the SRK equation is suitable for predicting the dew points of fire-flooding exhaust during the reinjection process.

Table 10. MAPEs of experimental and calculated results in the dew point prediction.

MAPE	SRK	PR	LKP	BWRS	GERG-2008	Number of Experimental Data Sets
Sample 1	2.81%	2.84%	1.70%	8.20%	3.78%	43
Sample 2	1.56%	2.44%	3.80%	6.85%	3.02%	43
Sample 3	7.31%	8.84%	3.17%	9.84%	7.59%	43
Sample 4	3.73%	4.51%	4.72%	8.68%	3.71%	44
Sample 5	6.22%	8.52%	5.15%	8.91%	9.65%	44
Overall MAPE	4.33%	5.43%	3.71%	8.50%	5.55%	-

4. Results

Comparing all the predicted data with the experimental data, the overall summary of the calculation accuracy for each EoS is shown in Table 11.

Table 11. Summary of the precisions of the five physical property calculation methods.

Overall MAPE	SRK	PR	LKP	BWRS	GERG-2008
Gas density	3.84%	4.92%	4.30%	4.04%	4.31%
Compressibility factor	5.17%	6.89%	6.06%	5.46%	6.08%
Volumetric coefficient	5.53%	7.24%	6.42%	5.81%	6.44%
Dew point	4.33%	5.43%	3.71%	8.50%	5.55%

It can be found that, for calculating the different physical properties, the precision of the evaluated equations is uneven. The SRK equation performs well in predicting the gas densities, but the calculation of compressibility factors and volume coefficients has a notable deviation, exceeding 5%. The PR equation shows good accuracy in terms of the gas density prediction, whereas the errors of the compressibility factors and volume coefficients computation happen to be around 7%. The LKP equation has the highest precision in forecasting the dew points, but it is not accurate enough in calculating the compressibility factors and volume coefficients with the *MAPE* of beyond 6%. The BWRS equation has good precision in forecasting the gas densities, but the biggest error of 8.50% is observed when it is used to conduct the dew point calculation. The GERG-2008 equation also achieves good performance in the gas density prediction. However, a big error of more than 6% exists for computing the compressibility factors and the volume coefficients. Hence, it is revealed that although the GERG-2008 equation is considered as the international standard model for the natural gas, it is not entirely suitable for the fire-flooding exhaust.

Above all, for the five samples of the fire-flooding exhaust tested, the SRK equation takes the minimum *MAPE* in predicting the properties mentioned. In terms of dew point prediction, although the accuracy of the LKP equation is slightly higher than that of SRK equation, the latter has stronger computational convergence than the former over the whole pressure range. Taking both the prediction accuracy and computational convergence into consideration, the SRK equation is recommended as the basic prediction method for the physical properties during the reinjection of the fire-flooding exhaust.

5. Conclusions

Accurate prediction of the physical properties with the change of working conditions is of significant importance for the design and simulation of the reinjection processes of fire-flooding exhaust. In this paper, five property calculation methods—including PR, SRK, LKP, BWRS, and GERG-2008 EoS—were evaluated in predicting the properties of the fire-flooding exhaust under the conditions of reinjection process. By employing the Aspen Plus software, four properties of five representative fire-flooding exhaust compositions which collected from an oilfield in northwest China were calculated, including the gas densities, compressibility factors, volumetric coefficients, and dew point temperatures. Through a comprehensive comparison and analysis with 1351 sets of experimental detecting data, it is revealed that the SRK equation shows the best prediction performance among the five studied equations, thus it can be recommended as the basis for the property prediction in the reinjection process of the fire-flooding exhaust.

The result in this paper is helpful to select a precise property calculation method for the fire-flooding exhaust under the wide range of temperature and temperature. Thus the reinjection system can be simulated and designed in higher accuracy, which will reduce the harmful gas emission made by the in-situ combustion in a novel and efficient way. Although the compositions were collected from China, it is believed that this work can also provide reference for the study of other similar gases globally. By applying the SRK equation, the high-accuracy prediction on the physical properties and phase transition can be conducted. This is the prerequisite to carry out theoretic and applied research for the related gas. Considering the components in this study contain hydrocarbons, nitrogen, carbon dioxide, hydrogen sulfide, etc., with the increasingly higher standards on the environmental protection, the results can be also applied in the waste treatment processes.

Since more detailed components of other countries or regions have not been found out from the published literature unfortunately, our work was based on the samples collected from Chinese oilfields. Although it is believed that the samples used in this study are representative, whether the result is suitable for other oilfields can be further evaluated by the researchers based on more local component data.

Meanwhile, the binary interaction parameters of Knapp et al. were used for the SRK equation, the PR equation, the LKP equation, and the BWRS equation. The prediction accuracy can be improved through the regression of binary parameters using more experimental data.

Finally, the experimental data in this paper were obtained without a water component. There may be trace amounts of water in the fire-flooding exhaust during the reinjection process. Considering the influence of water on gas physical properties, the prediction accuracy of cubic EoSs, virial EoSs, and GERG-2008 can be further studied based on the research results of this paper.

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Abbreviations

EoS	equation of state
PR	Peng–Robinson
SRK	Soave–Redlich–Kwong
LKP	Lee–Kesler–Plocker
BWRS	Benedict–Webb–Rubin–Starling
PR-CPA	Peng–Robinson cubic plus association
PC-SAFT	perturbed chain-statistical associating fluid theory
NRTL	non-random two liquid
NIST	National Institute of Standards and Technology
PVT	pressure, volume, and temperature
LNG	liquefied natural gas
BOG	boil-off gas
HPHT	high pressure and high temperature
CC	correlation coefficient
MSE	mean squared error
MAE	mean absolute error
MAPE	mean absolute percentage error
RMSE	root mean square error
NRMSE	normalized root mean squared error
MARNE	mean absolute range normalized error

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