

Research Article

A Graphical Alternating Conditional Expectation to Predict Hydrate Phase Equilibrium Conditions for Sweet and Sour Natural Gases

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Natural gas hydrate has been widely of concern due to its great potential in application to address problems including gas storage, transmission, separation techniques, and also as energy resource. Accurate prediction of hydrate formation phase equilibrium conditions is essential for the optimized design during natural gas production, processing, and transportation. In this study, a novel graphical alternating conditional expectation (ACE) algorithm was proposed to predict hydrate formation phase equilibrium conditions for sweet and sour natural gases. The accuracy and performance of the presented ACE model were evaluated using 1055 data points (688, 249, and 118 data points for sweet natural gas, CO₂-CH₄, and H₂S-CO₂-CH₄ systems, respectively) collected from literature. Meanwhile, a comparative study was conducted between the ACE model and commonly used correlations, including thirteen models for sweet natural gases, three models for CO₂-CH₄ binary system, and seven thermodynamic models for H₂S-CO₂-CH₄ ternary system. The obtained results indicated that the proposed ACE model produces the best results in prediction of hydrate phase equilibrium temperature for sweet natural gases and pressure for CO₂-CH₄ system with average absolute relative deviation (AARD) of 0.134% and 2.75%, respectively. The proposed quick and explicit ACE model also provides a better performance in prediction of hydrate phase equilibrium pressure for H₂S-CO₂-CH₄ ternary systems with AARD=5.20% compared with seven thermodynamic methods considered in this work, except for CPA/Electrolyte/Chen-Guo combined model (AARD=4.45%).

1. Introduction

Gas hydrates are regarded as the representatives of a class of compounds widely known as clathrates or inclusion compounds, which occur in appearance of a crystalline solid like water ice or dry ice. Generally, hydrates concomitantly consist of some guest molecules trapped in a cage structure built by host molecules. The most leading host molecule is water and the most common guest molecules include light hydrocarbons (CH₄), hydrogen sulfide (H₂S), carbon dioxide (CO₂), hydrogen (H₂), and nitrogen (N₂). Accurate calculation of natural gas hydrate formation phase equilibrium conditions not only is essential for an optimized design scheme of natural gas production, processing, and transportation (flow assurance), but also is of great significance for preventing [1, 2]

subsea/land oil and gas transport pipeline blockage, promoting the development of gas transmission and separation techniques [3–5].

For the natural gas hydrate formation phase equilibrium conditions, the primary problem is how to rapidly and precisely predict the hydrate phase equilibrium pressure or temperature as gas hydrates form. Up to now, various approaches have been presented to determine hydrate phase equilibrium pressure or temperature. These approaches can be mainly divided into five types: laboratory tests [6, 7], graphical methods [8, 9], empirical correlations [10–18], thermodynamic models [19–26], and artificial intelligence algorithms [27–30]. It is well known that the experimental determination of the hydrate formation phase equilibrium conditions is expensive and time-consuming, which limit the application of this

method. The empirical correlations and thermodynamic models were widely used for predicting the hydrate formation phase equilibrium conditions. The commonly applied empirical correlations to predict hydrate formation conditions are listed in the Appendix. These empirical correlations have two significant advantages: (1) simplicity and (2) high accuracy within the range of its application. However, as for thermodynamic models, in the early 1959, Van der Waals and Platteuw (vdW-P) [19] firstly provided a basic thermodynamic model to calculate hydrate phase equilibrium conditions, which could be seen as the beginning of intensive enthusiasm for following researches on hydrate formation thermodynamic models. Afterwards, the emerging thermodynamic models (e.g., Parrish-Prausnitz [20], Ng-Robinson [21], John et al. [22], and Eslamimanesh et al. [23]) for calculating hydrate phase equilibrium conditions were mainly derived from the various amendments to the classical vdW-P model. Currently, the most accepted method is based on the vdW-P model integrated with an equation of state to estimate hydrate phase equilibrium conditions [24–26, 31, 32].

Recently, with the increase of global energy demand and the decrease of conventional gas, more attentions have been paid to explore and exploit new sour natural gas fields. Natural gas containing H_2S and/or CO_2 is defined as sour gas, and also H_2S or/and CO_2 hydrates are more easily formed under lower pressure and higher temperature conditions in the presence of water. Therefore, it is more critical to calculate the hydrate phase equilibrium conditions of sour natural gas mixtures to avoid the subsea or land oil/gas pipeline hydrate plugging problems. Thus, several methods (K-factor [33], Baillie-Wichert [34], and Mann et al. [35]) and some software (CSMHYD, HYSIS, EQUI-PHASE Hydrate, and PROSIM) were applied to determine hydrate phase equilibrium conditions of sour natural gas. In early 1941, Wilcox et al. [33] proposed a semiempirical formula based on the K-factor to forecast the hydrate phase equilibrium temperature. PROSIM has poorer performance and larger errors compared with those from the other software-based thermodynamic models when it computes the hydrate phase equilibrium temperature for sour gas streams. Similarly, the Baillie-Wichert method should be also cautiously applied for gas mixtures with only CO_2 but without H_2S . In addition, the CO_2 mole concentration should be limited to no more than 5%. Note that when the temperature is below $55^\circ F(12.8^\circ C)$, all methods mentioned above fails to obtain error range of $\pm 3^\circ F(1.7^\circ C)$ in the process of hydrate phase equilibrium temperature prediction. In 1996, a classical hydrate thermodynamic model was presented by Chen and Guo [36, 37] on the basis of the two-step hydrate formation mechanism, which supposed that water activity coefficient was set as a unity. However, CO_2 and/or H_2S dissolution and reactions with water indicated that the water activity coefficient cannot be assumed to be unity. Afterward, according to Chen–Guo model, Sun and Chen [38] eliminated the assumption that the activity coefficient was unity and obtained the satisfied calculation results. In 2013, a novel thermodynamic model [39] was proposed to determine the pure and mixed sour gas hydrate formation pressures. The model took into account the impact of hydrogen bonding association in fluid phases

with great potential in application for accurately predicting hydrate phase equilibrium pressures of sour gases.

Recently, ZareNezhad and Aminian utilized an adaptive neurofuzzy inference system (ANFIS) [40] to predict the sour gas hydrate equilibrium dissociation pressure. It was interpreted from predicted results that the ANFIS model outperforms the existing thermodynamic models when H_2S mole fraction is higher than 10%. Similarly, an improved artificial neural network (ANN) was also provided by Soroush et al. [41] to predict the hydrate formation temperature over a wide range of gas mixtures. Different from those empirical correlations and thermodynamic models, such neural networks can only result in a “black box” instead of an explicit formula. In 2016, a least square support vector machine (LSSVM) model [42] was provided to predict natural gas hydrate formation temperature. The results revealed the superiority of LSSVM model in the form of high prediction accuracy.

However, there is still few reports of an empirical correlation to predict hydrate phase equilibrium conditions especially for sour natural gases. The purpose of this study is to develop a novel correlation of hydrate phase equilibrium conditions for sweet and sour natural gases using a graphical alternating conditional expectation (ACE) algorithm. The ACE algorithm and data acquisition are introduced in Section 2. The model of gas hydrate formation condition is developed in Section 3. Results and discussions are indicated in Section 4. Finally, in Section 5, the relevant conclusions are presented.

2. Methodology

2.1. ACE Algorithm. The ACE algorithm is a multivariate nonparametric regression method originally proposed by Breiman and Friedman [43] in 1985 and later perfected by Xue et al. [44] in 1997. The most fundamental idea behind ACE is to estimate the optimal transformations for multiple regressions, which matches the correlation between a random dependent (output) variable and multiple independent (input) variables. In this section, a detailed explanation about ACE is given and the general expressing formula of the nonparametric ACE algorithm is given as follows:

$$\theta(Y) = \alpha + \sum_{i=1}^N \phi_i(X_i) + \varepsilon \quad (1)$$

where θ and ϕ_i are defined as a function of the dependent output variable Y and the independent input variables X_i ($i = 1, 2, \dots, N$), respectively. N , α , and ε represent the dimensions of variables, the regression coefficient, and an error term, respectively.

Through converting the original linear function problem of an N -dimensional variable $X = (X_1, X_2, \dots, X_N)$ into the problem of N independent one-dimensional functions, $(\phi_i, i = 1, 2, \dots, N)$, the constructed ACE model achieves optimal transformations in logarithmic or actual space. Thus, the eventual aim of ACE model is to minimize the error variance (ε^2) of the transformed dependent output variable on the sum of transformed independent input variables. The ε^2 is defined as follows:

$$\varepsilon^2(\theta, \phi_1, \phi_2, \dots, \phi_N) = E \left\{ \left[\theta(Y) - \sum_{i=1}^N \phi_i(X_i) \right]^2 \right\} \quad (2)$$

Particularly with the constrain,

$$\begin{aligned} E[\phi_1(X_1)] &= E[\phi_2(X_2)] = \dots = E[\phi_N(X_N)] = 0, \\ E[\theta^2(Y)] &= 1 \end{aligned} \quad (3)$$

Then a series of single functions is employed to minimize the error variance (ε^2) with respect to $\phi_1(X_1)$, $\phi_2(X_2)$, ..., $\phi_N(X_N)$ and $\theta(Y)$, which was obtained from the following equations:

$$\phi_i(X_i) = E \left[\theta(Y) - \sum_{j \neq i}^N \phi_j(X_j) \mid X_i \right] \quad (4)$$

$$\theta(Y) = \frac{E \left[\sum_{i=1}^N \phi_i(X_i) \mid Y \right]}{\|E \left[\sum_{i=1}^N \phi_i(X_i) \mid Y \right]\|} \quad (5)$$

With respect to equations mentioned above, the alternating conditional expectation algorithm developed by (4) and (5) involved two stage operation processes, including (i) estimation of conditional expectations and (ii) iterative minimization of error variance (ε^2). Though iterative process of minimizing the error variance (ε^2), the real-valued measurable zero-mean functions $\phi_i(X_i)$, $i = 1, 2, \dots, N$, and $\theta(Y)$ are translated into optimal transformations $\phi_i^*(X_i)$, $i = 1, 2, \dots, N$, and $\theta^*(Y)$. In the transformed space, the relationship of the dependent output $\theta^*(Y)$ and independent input $\phi_i^*(X_i)$ is expressed as follows:

$$\theta^*(Y) = \sum_{i=1}^N \phi_i^*(X_i) + \varepsilon^* \quad (6)$$

where ε^* denotes the error that is not obtained by the application of the ACE transformations and is defined to obey a normal distribution with zero mean. It should be noted that ρ^* was calculated as a correlation coefficient between the transformed dependent output variable and the sum of transformed independent variables (with the constrains: $E[\theta^2(Y)] = 1$, $E[\phi_1(X_1)] = 1$) as follows:

$$\rho^* = \max_{\theta(Y), \phi_1(X_1), \dots, \phi_N(X_N)} \left\{ E \left[\theta(Y) \sum_{i=1}^N \phi_i(X_i) \right] \right\} \quad (7)$$

In the process of ACE transformation, the minimum regression error, ε^* , is replaced by calculating maximum multiple correlation coefficient, ρ^* as (8).

$$\varepsilon^* = 1 - \rho^{*2} \quad (8)$$

Assuming that the transformation function $\theta(Y)$ is strictly monotonic and reversible, the dependent output variable for any data point is finally given as follows:

$$Y = \theta^{*-1} \sum_{i=1}^N \phi_i^*(X_i) \quad (9)$$

In consequence, the following criteria may indicate most of the advantages of the newly proposed ACE algorithm over

the conventional multivariate parametric regression methods and artificial intelligence algorithms (e.g., ANN and SVM):

- (1) No requirement for a prior assumption of a function form and the optimal transformations are merely relying on the data set.
- (2) Normalization and stabilization of error variance distribution.
- (3) Applicable for the dual cases of bivariate and multivariate regression.
- (4) Different from ANN and SVM, such transformations can result in an explicit formula instead of "black box".
- (5) It can effectively avoid probability for convergence to the local optimum, and it leads to fewer adjustable parameters.
- (6) A graphical interface program has been efficiently developed to compute ACE simulation results (GRACE) [44].
- (7) Acceptable generalization performance.

2.2. Data Acquisition. Adequate data on sweet and sour natural gases hydrate phase equilibrium conditions are crucial for developing an empirical correlation since the comprehensiveness, diversity, and validity of the collected database have a dominating influence on the accuracy and reliability of the correlation. Meanwhile, due to the toxicity of H_2S and the corrosion of H_2S/CO_2 to the device, the experimental data on the hydrate phase equilibrium conditions of sour gases with H_2S/CO_2 content are scarce in the open literature, which has been also identified as an important and challenging task. In this work, 1055 experimental data sets of hydrate formation conditions for sweet (688 datasets) and sour (367 datasets) natural gases were collected from published literature [7, 8, 18, 45–48]. The ranges of all the experimental gas hydrate formation conditions considered in this work are given in Table 1. Note that we do not employ the water content as a variable although the water content plays an important role in the hydrate phase equilibrium temperature and pressure. This is because there is no connection between the deviation in the predicted hydrate phase equilibrium conditions and the water content.

3. Model Development of Gas Hydrate Formation Condition

The superiority of ACE algorithm to other conventional multiple regressions is that it can flexibly employ actual and logarithmic space of the variables (e.g., $\ln(CH_4)$, $\ln(P)$, $\ln(T)$... etc.) to reveal the intrinsic regularity in input and output variables when the functional form between them is implicit. Moreover, it is necessary to determine the independent and dependent variables which should be considered as a high priority. So, the trial-and-error approach could be applied in comparing and verifying all possible combinations of the output and input variables in either logarithmic or actual space. To evaluate the performance of ACE model,

TABLE I: The ranges of all the experimental gas hydrate formation conditions.

Constituent	Minimum	Maximum	Average	Standard deviation
C ₁ (mole percent)	0	100	71.38	26.01
C ₂ (mole percent)	0	25	10.56	7.49
C ₃ (mole percent)	0	13.3	5.63	4.83
C ₄ (mole percent)	0	8.5	2.86	2.83
C ₅₊ (mole percent)	0	6.04	2.00	2.02
H ₂ S (mole percent)	0	26.62	10.91	6.38
CO ₂ (mole percent)	0	100	37.02	32.46
γ _g (Gas gravity)	0.54	1.03	0.74	0.15
P (kPa)	367.65	289900	21647.01	63.96
T (K)	272.66	299.7	284.27	22.73

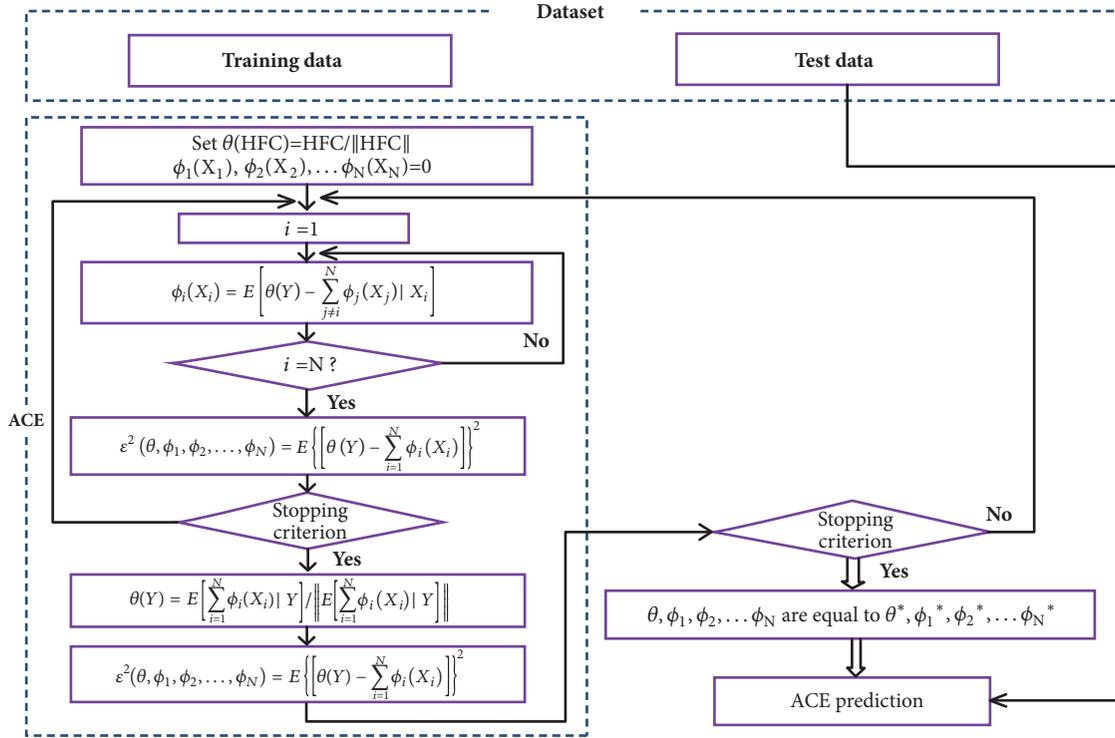


FIGURE 1: The flowchart of the newly proposed ACE model.

its accuracy was compared with some well-known empirical correlations or thermodynamic models that are commonly adopted to determine the hydrate phase equilibrium conditions. The flowchart of the proposed ACE model is briefly described in Figure 1.

3.1. Sweet Natural Gases. For sweet natural gases hydrate formation condition, temperature is set as dependent output variable. Among the 688 data points, 563 points were selected to establish the ACE model and the remaining 125 points were used to validate the model. Meanwhile, all possible combinations of the output and input variables in either logarithmic or actual space were tested. After a series of tests, the best relationship is acquired as follows:

$$T = f(P, \ln(P), \gamma_g) \quad (10)$$

Figure 2 shows the corresponding optimal transformations of P , $\ln(P)$, and γ_g for sweet natural gases determined by ACE algorithm. The optimal transformation of T versus the sum of the optimal transformation of P , $\ln(P)$ and γ_g is illustrated in Figure 3. Consequently, a series of simple polynomials were used to match every optimal transform of T as shown in Figure 2(d), the prediction model of sweet natural gases hydrate formation temperature is yielded from the inverse of the optimal transformation of sweet natural gases hydrate formation temperature:

$$T = 286.12178562 + 7.19497216S - 1.28612859S^2 - 0.11078924S^3 + 0.10637874S^4 \quad (11)$$

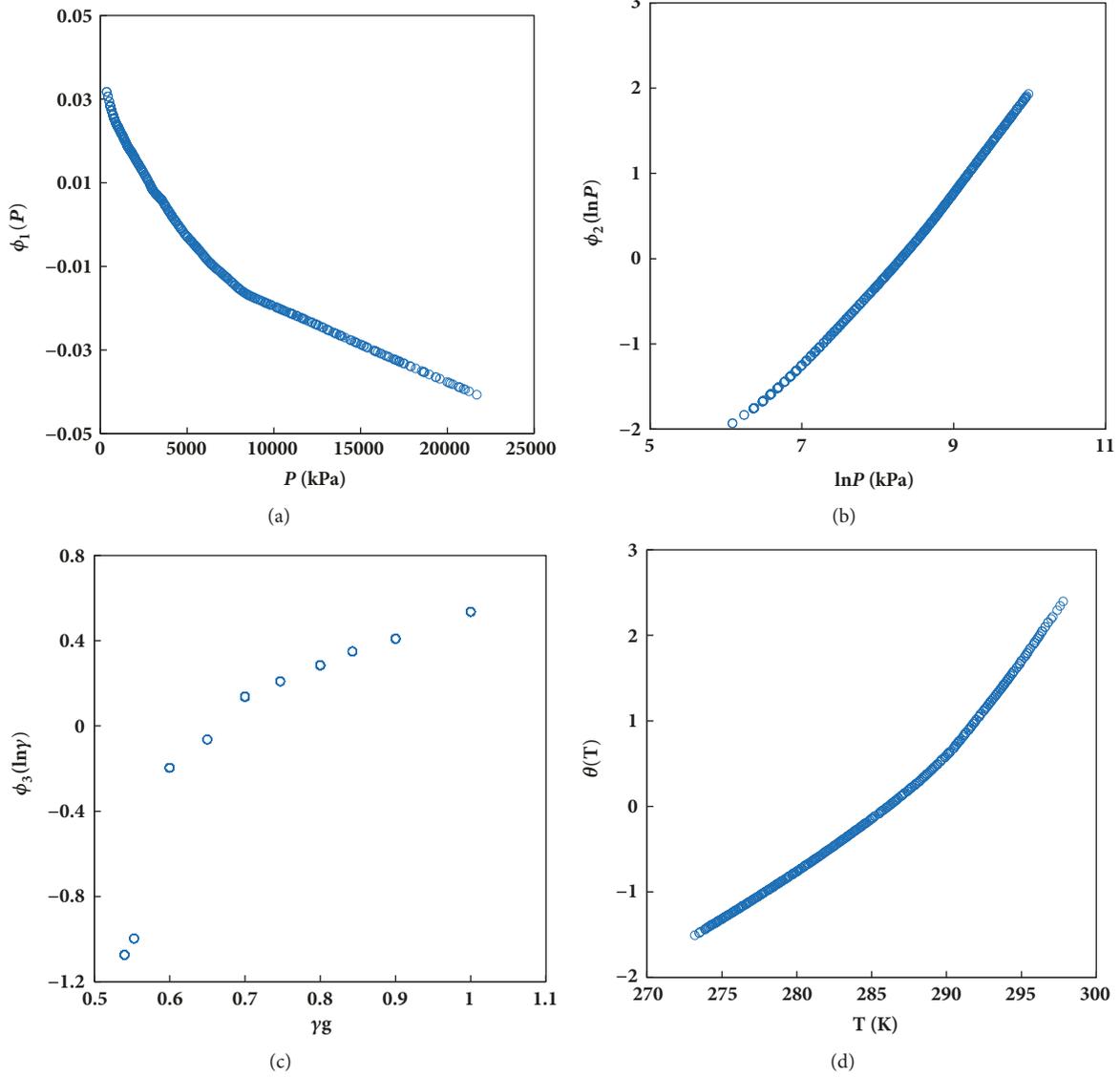


FIGURE 2: Optimal transformation of variables as determined by ACE for (a) pressure, (b) pressure in the logarithmic space, (c) gas gravity, and (d) temperature.

Here

$$S = \sum_{i=1}^3 \phi_i(X_i) = \sum_{i=1}^3 \sum_{j=0}^5 a_{ij} x_i^j \quad (12)$$

where the model coefficients a_{ij} are listed in Table 2.

3.2. Sour Natural Gases

3.2.1. CO₂-CH₄ Binary System. CO₂ hydrate has attracted increasing researchers' attention due to its great application potentials in many fields including CO₂ capture and sequestration from flue gases, steam reforming processes, hydrogen (H₂) storage, water desalination, etc. These promising applications are held back for the problems related to the CO₂ hydrate formation condition. In this section, hydrate

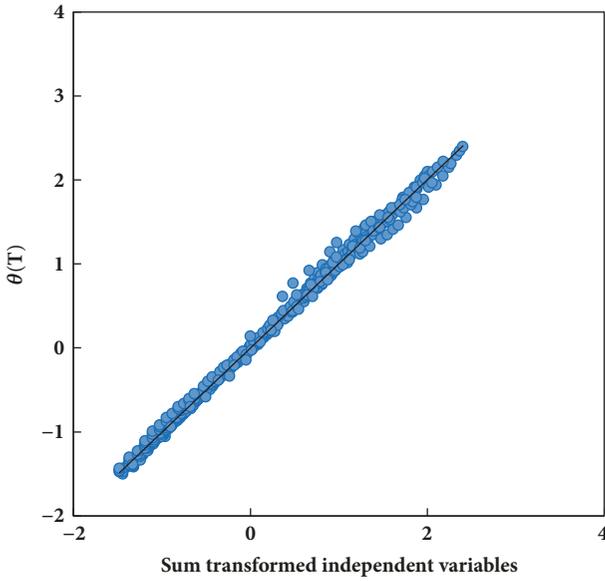
TABLE 2: Fitted coefficients of each independent variable for sweet natural gases.

Variables	P	$\ln(P)$	γ
Equation order	5	3	5
a_0	0.0328	-1.6722	-344.7917
a_1	-9.2945E-06	-0.9369	2157.1707
a_2	3.8474E-10	0.1715	-5381.1832
a_3	1.7341E-14	-0.0041	6685.0702
a_4	-1.9660E-18	0	-4132.0454
a_5	4.2860E-23	0	1016.1832
R^2	0.99960	0.99995	0.99503

formation condition data for CH₄-CO₂ binary system was sorted and collected from different literature [45, 46]. For

TABLE 3: Fitted coefficients of each independent variable for CO₂-CH₄ systems.

Variables	CO ₂	CH ₄	T
b ₀	3.02180508E-01	-1.40918983E-01	2.28446201E+05
b ₁	-5.27602603E-03	-4.0110216E-03	-3.37125293E+03
b ₂	9.84237658E-05	4.82131738E-04	1.86483689E+01
b ₃	3.19929491E-06	-2.09059521E-05	-4.58298269E-02
b ₄	-3.53114022E-08	4.11983407E-07	4.22234349E-05
b ₅	1.30009467E-10	-3.49154166E-09	0
b ₆	0	1.07521804E-11	0
R ²	0.99996	0.99996	0.99993

FIGURE 3: Optimal transformation of T versus the sum of the optimal transformation of P , $\ln(P)$ and γ_g .

CO₂-CH₄ system, hydrate phase equilibrium pressure is set as an output variable. Similarly, working with CO₂-CH₄ streams, 189 out of the 249 data points were chosen to construct the ACE model and the remaining 60 points were employed to validate the model. The best relationship is given as follows:

$$P = f(T, \gamma(\text{CO}_2), \gamma(\text{CH}_4)) \quad (13)$$

Figure 4 shows the corresponding optimal transformations of P , $\gamma(\text{CO}_2)$, $\gamma(\text{CH}_4)$ for CH₄-CO₂ binary system. Figure 5 illustrates the optimal transformation of P versus the sum of the optimal transformation of T , $\gamma(\text{CO}_2)$, and $\gamma(\text{CH}_4)$.

According to the same principles above, the prediction model of CO₂-CH₄ system hydrate formation pressure can be obtained from the inversion of the optimal transformation of CO₂-CH₄ hydrate formation pressure:

$$\begin{aligned}
 P = & 3532.28347937 + 1916.45044862M \\
 & + 156.20490991M^2 - 57.40863195M^3 \quad (14) \\
 & + 6.63719421M^4
 \end{aligned}$$

$$M = \sum_{i=1}^3 \phi_i(X_i) = \sum_{i=1}^3 \sum_{j=0}^6 b_{ij} x_i^j \quad (15)$$

where the model coefficients b_{ij} are listed in Table 3.

3.2.2. H₂S-CO₂-CH₄ Ternary System. In recent years, due to the decrease of conventional natural gas, sour natural gases have been becoming subsequent candidates for economical and clean energy supply. Kashagan field, Shah field, Limestone field [41], and Puguang gas field from China are typical sour gas reservoirs with high H₂S content. The precise knowledge of hydrate phase equilibrium conditions for sour natural gas with high H₂S content is an essential prerequisite for any sour gas processing and pipeline engineering activity. To the best of our knowledge, there are few reports of an empirical correlation for predicting sour natural gases hydrate equilibrium conditions. Thus, the ACE algorithm was proposed for predicting the sour gas hydrate phase equilibrium conditions. For H₂S-CO₂-CH₄ ternary system, hydrate formation pressure is set as an output variable. In view of the data for H₂S-CO₂-CH₄ ternary system, the 118 data points were used for training data sets and 59 points were used for validating the feasibility and effectiveness of the model. The best expression form is shown as follows:

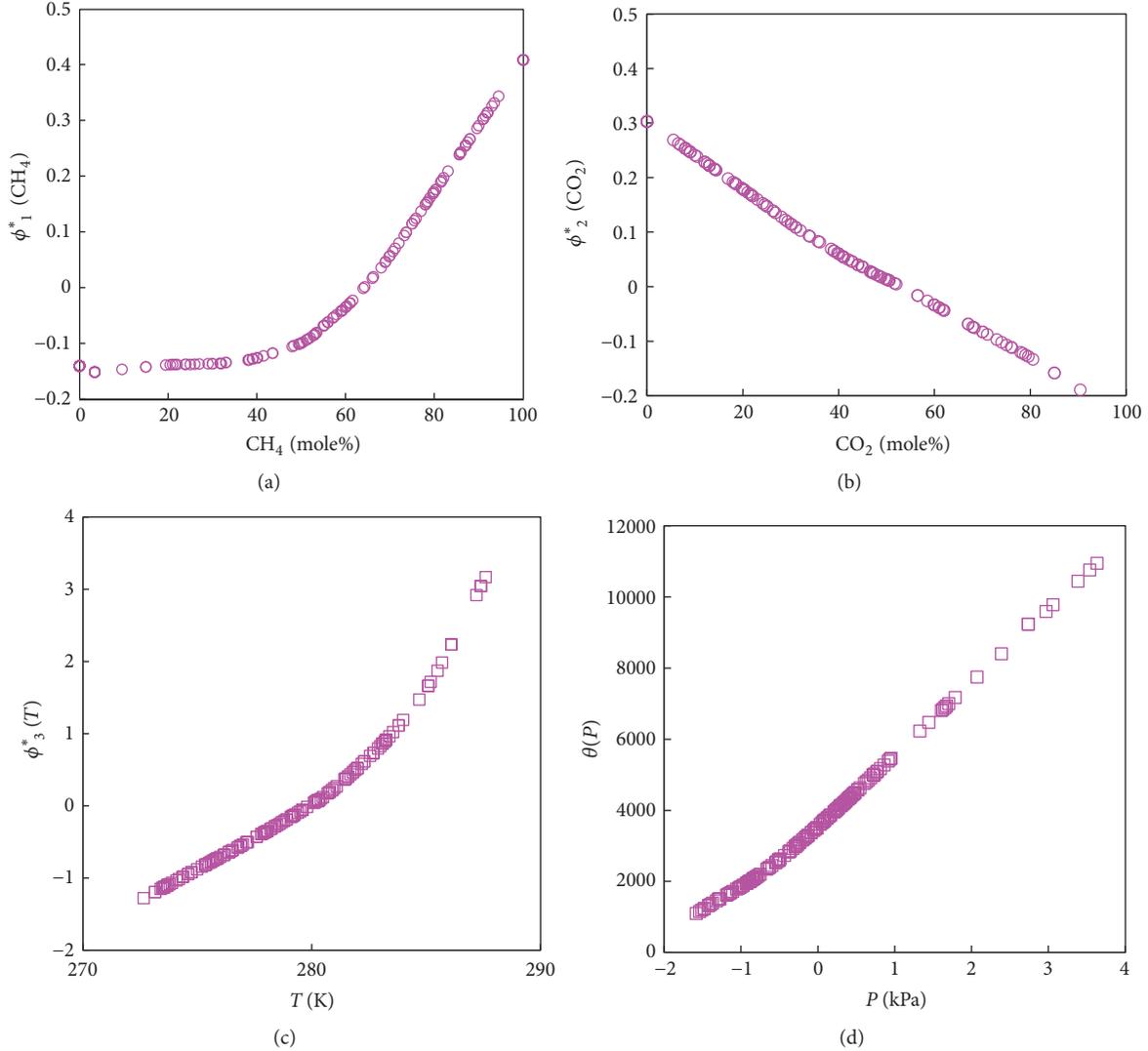
$$P = f(T, \gamma(\text{H}_2\text{S}), \gamma(\text{CO}_2), \gamma(\text{Ln}(\text{CH}_4))) \quad (16)$$

Figure 6 shows the corresponding optimal transformations of $\text{Ln}(\text{CH}_4)$, $\gamma(\text{H}_2\text{S})$, $\gamma(\text{CO}_2)$, T for H₂S-CH₄-CO₂ ternary system. Figure 7 illustrates the optimal transformation of P versus the sum of the optimal transformation of T , $\gamma(\text{H}_2\text{S})$, $\gamma(\text{CO}_2)$, and $\gamma(\text{Ln}(\text{CH}_4))$. It can be observed from Figure 6(d) that the prediction model of hydrate formation pressure for H₂S-CO₂-CH₄ ternary system can be obtained using the inverse of the optimal transformation of H₂S-CO₂-CH₄ system hydrate formation pressure by means of the relationship between P and the optimal transformation of P :

$$\begin{aligned}
 P = & 3071.53247668 + 2397.78194746N \\
 & + 664.55818302N^2 - 225.73062145N^3 \\
 & + 4.00015796N^4 + 182.03009278N^5 \\
 & + 57.41346032N^6 \quad (17)
 \end{aligned}$$

TABLE 4: Fitted coefficients of each independent variable for H₂S-CO₂-CH₄ systems.

Variables	H ₂ S	CO ₂	ln(CH ₄)	T
Equation order	2	2	2	2
c ₀	4.91981951	3.99716313	40.13531836	95.41442257
c ₁	-4.52315342E-01	-3.92997270E-01	8.83934459	-0.84492771
c ₂	1.15488583E-04	9.20810840E-04	-4.13616715	0.00178585
R ²	0.99991	0.99965	0.99950	0.99995

FIGURE 4: Optimal transformation of variables as determined by ACE for (a) CH₄, (b) CO₂, (c) temperature, and (d) pressure.

$$N = \sum_{i=1}^3 \phi_i(X_i) = \sum_{i=1}^3 \sum_{j=0}^2 c_{ij} x_i^j \quad (18)$$

where the model coefficients c_{ij} are listed in Table 4.

4. Results and Discussions

To evaluate the performance of the presented ACE model and other commonly used models considered in this work, statistical analyses such as average absolute relative deviation

(AARD), root mean square error (RMSE), standard deviation (SD), and coefficient of determination (R^2) were performed between the experimental and predicted values as follows.

$$AARD = \frac{100}{N} \sum_{i=1}^N \left| \frac{X_i^{\text{exp}} - X_i^{\text{pre}}}{X_i^{\text{exp}}} \right| \quad (19)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (X_i^{\text{exp}} - X_i^{\text{pre}})^2} \quad (20)$$

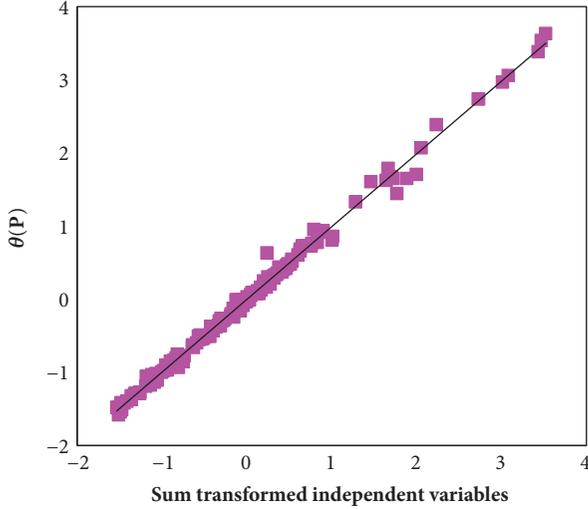


FIGURE 5: Optimal transformation of P versus the sum of the optimal transformation of P , $y(\text{CO}_2)$, $y(\text{CH}_4)$ for CO_2 - CH_4 system.

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{X_i^{\text{exp}} - X_i^{\text{pre}}}{X_i^{\text{exp}}} \right)^2} \quad (21)$$

$$R^2 = 1 - \frac{\sum_{i=1}^N (X_i^{\text{exp}} - X_i^{\text{pre}})^2}{\sum_{i=1}^N (X_i^{\text{exp}} - X_i^{\text{ave}})^2} \quad (22)$$

where N represents the number of experimental data points, X_i^{exp} and X_i^{pre} stand for the experimental and predicted value corresponding to experiment i , respectively, and X_i^{ave} is the average of all the experimental values.

4.1. Sweet Natural Gases. The scatter diagram (cross-plot) of a comparison between the experimental results and calculated temperature using ACE model is presented in Figure 8. It is clearly shown in Figure 8 that a tight cloud of data points about 45° line for testing data sets illustrates an excellent fitting between experimental data and calculated values by the proposed ACE model.

Moreover, the predicted hydrate formation temperature of sweet natural gases for testing data sets from the proposed ACE model was compared to 13 commonly used correlations listed in Figure 9.

It can be concluded from Figure 9 that the proposed ACE model produces the lowest global AARD (0.134%). In the descending order of exactness Ghayyem et al., Ghiasi, Amin et al. (2016), Amin et al. (2015, first), Amin et al. (2015, second), Bahadori and Vuthaluru, Zahedi et al., Towler and Mokhatab, Kobayashi et al., Motiee, Berge, Hammerschmidt, and Makogon correlation come in sequence order, respectively. And the corresponding mean AARDs are 0.164%, 0.371%, 0.399%, 0.492%, 0.504%, 0.757%, 0.848%, 1.114%, 1.456%, 1.645%, 1.735%, 2.076%, and 3.093%, respectively.

4.2. Sour Natural Gases

4.2.1. CO_2 - CH_4 System. The cross-plot (Figure 10) compares experimental pressure with calculated data using ACE model

TABLE 5: Comparison of ACE model with Adisasmito et al's equation to predict hydrate formation pressure for CO_2 - CH_4 binary system.

Train set	AADR	SD	RMSE	R^2
ACE model	2.20	0.033	134.00	0.9954
Adisasmito et al.	2.45	0.038	140.00	0.9952
ACE model	3.43	0.065	483.87	0.9724
Adisasmito et al.	4.53	0.063	411.40	0.9711
ACE model	2.75	0.043	251.53	0.9873
Adisasmito et al.	2.95	0.045	235.93	0.9862

for CO_2 - CH_4 system. The excellent agreement between ACE model prediction and the experimental values validate our ACE model for the CO_2 - CH_4 system.

Moreover, a comparison between predictions proposed by Adisasmito et al. [18] and the ACE model is conducted for the same training and testing data sets. The results are listed in Table 5.

In Table 5, the predictions of the proposed ACE model, of which AARD for total data is 2.75% including AARD=3.43% for testing data, are slightly better than those of Adisasmito's model, of which AARD is 2.95% including AARD=4.53% for testing data.

In addition, a comparison between the proposed ACE model and two commonly software-based thermodynamic models, including CSMGem [49] and HWHYD [50], was also made for 9 data points collected in the open literature [48]. The predicted phase equilibrium pressures and AARDs are listed in Table 6. As can be seen in Table 6, the AARD of the predicted phase equilibrium pressure by ACE, CSMGem, and HWHYD models are 3.50%, 5.06%, and 9.67%, respectively, indicating that the presented ACE model owns a better accuracy than the two commonly thermodynamic models considered in present work in prediction of hydrate dissociation conditions for CO_2 - CH_4 binary system.

4.2.2. H_2S - CO_2 - CH_4 System. In Figure 11, the cross-plot compares experimental pressure with calculated data by ACE model for H_2S - CO_2 - CH_4 system. The overall AARD, RMSE, SD, and R^2 are 7.20%, 453.29, 0.10, and 0.97, respectively. The predicted results show a good agreement with the experimental values. Careful examination of Figure 11 reveals that ACE model can perfectly reproduce the results at lower hydrate formation pressure. Meanwhile, at higher hydrate formation pressure, the discrepancy between the experimental values and predicted values by ACE model is somewhat larger for H_2S - CO_2 - CH_4 ternary systems.

In order to evaluate the accuracy of ACE model, the prediction results are also compared with values calculated using other thermodynamic models from ZareNezhad and Ziaee [41] for 59 experimental data on sour nature gas mixtures taken from the literature [47]. The comparison results were presented in Table 7.

It can be observed in Table 7 that the predictions by the proposed ACE model are in good consistency with the experimental data with mean AARD=5.20% and better than the seven thermodynamic methods,

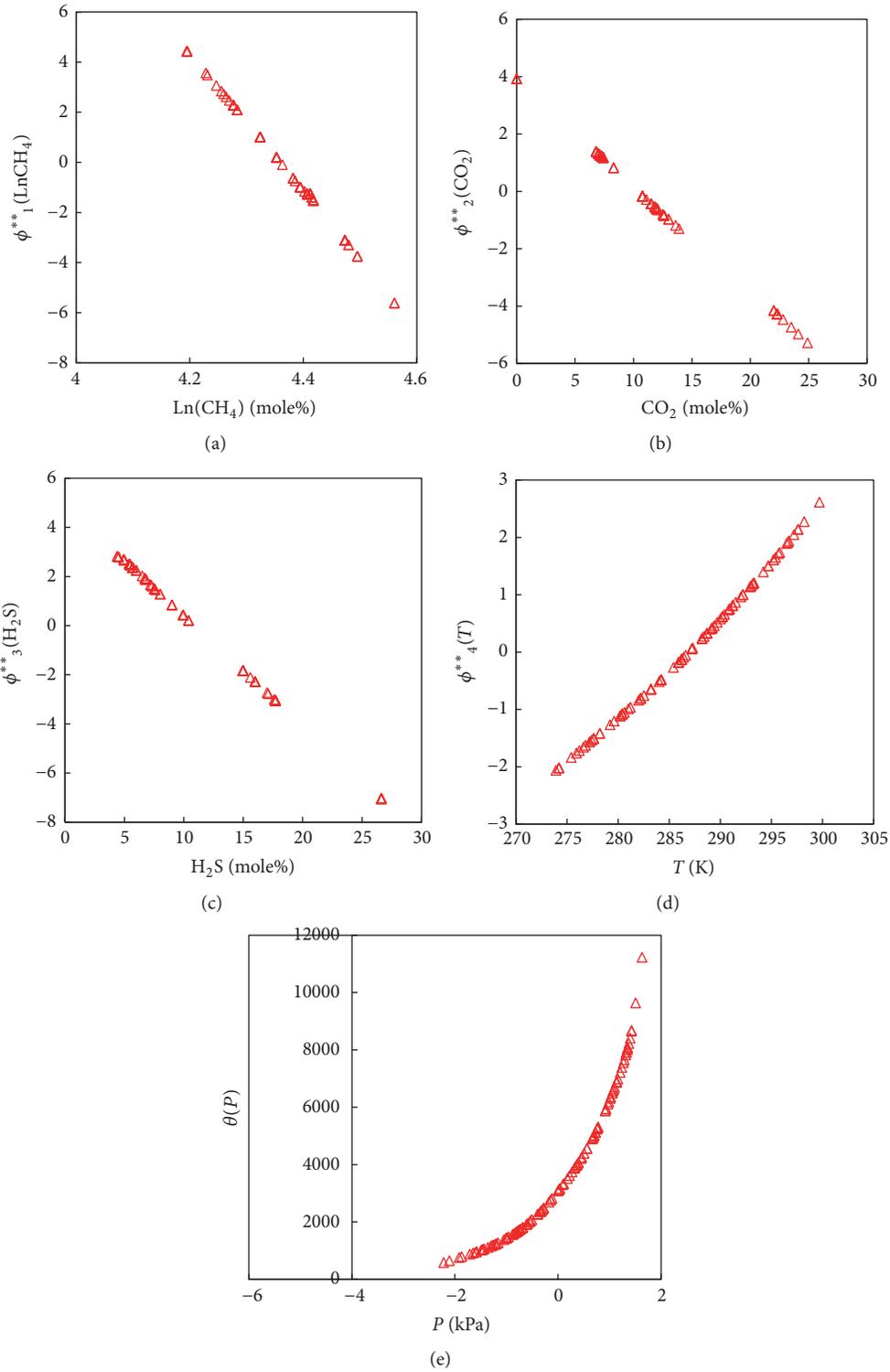


FIGURE 6: Optimal transformation of variables as determined by ACE for (a) $\text{ln}(\text{CH}_4)$, (b) CO_2 mole percent fraction, (c) H_2S mole percent fraction, (d) temperature, and (e) pressure.

except for CPA/Electrolyte/Chen–Guo combined model (AARD=4.45%).

In addition, compared to the thermodynamic models, the ACE model has one enormous advantage: it provides quick

and explicit calculations of the hydrate phase equilibrium pressure for $\text{H}_2\text{S}-\text{CO}_2-\text{CH}_4$ ternary system over a wide range of phase equilibrium temperature and H_2S content, which avoids complex calculations by the thermodynamic models.

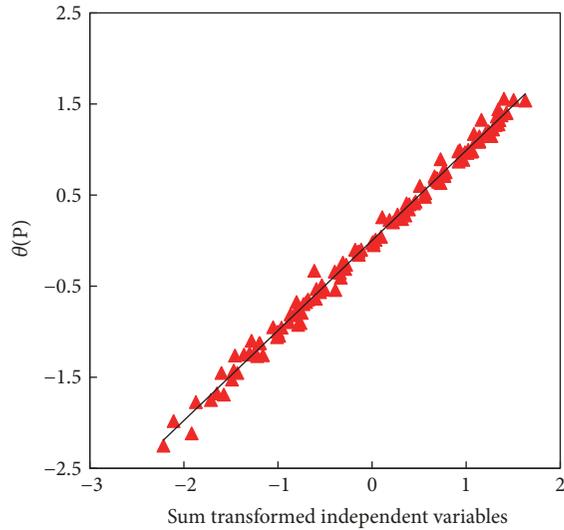


FIGURE 7: Optimal transformation of P versus the sum of the optimal transformation of independent variables for $H_2S-CO_2-CH_4$ system.

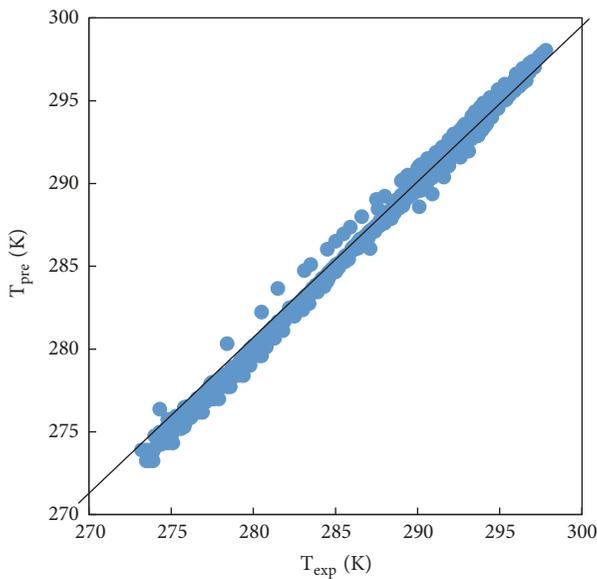


FIGURE 8: Comparison of experimental data with ACE testing outputs.

Careful examination of Table 7 shows that the ACE model gives the best results with overall AARD=4.09% for H_2S content range from 9.93% to 26.62%, which covers the mostly of natural gas fields with high H_2S content. Note that the result of (17) is less accurate in prediction of CO_2-CH_4 hydrate formation pressure by setting the H_2S content as zero, indicating that (17) cannot be reduced to (14). The reason may be that the (17) was proposed on the basis of experimental data containing H_2S component, while H_2S content has an important influence on the results of hydrate phase equilibrium conditions for $H_2S-CO_2-CH_4$ ternary system.

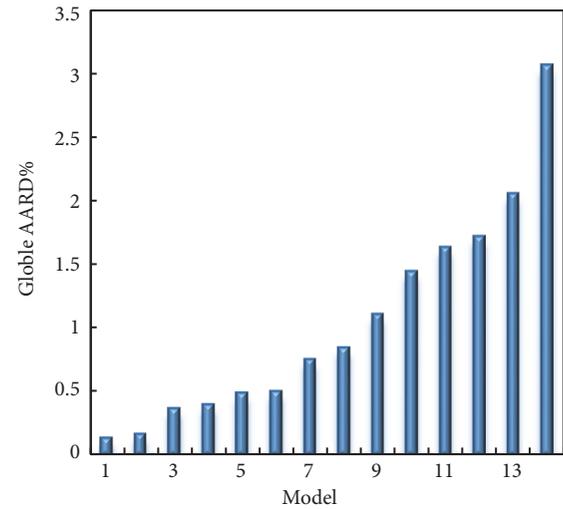


FIGURE 9: Global AARD of different correlations: (1) this work; (2) Ghayyem et al.; (3) Ghiasi; (4) Amin et al. (2016); (5) Amin et al. (2015, first); (6) Amin et al. (2015, second); (7) Bahadori and Vuthaluru; (8) Zahedi et al.; (9) Towler and Mokhtab; (10) Kobayashi et al.; (11) Motiee; (12) Berge; (13) Hammerschmidt; and (14) Makogon correlation.

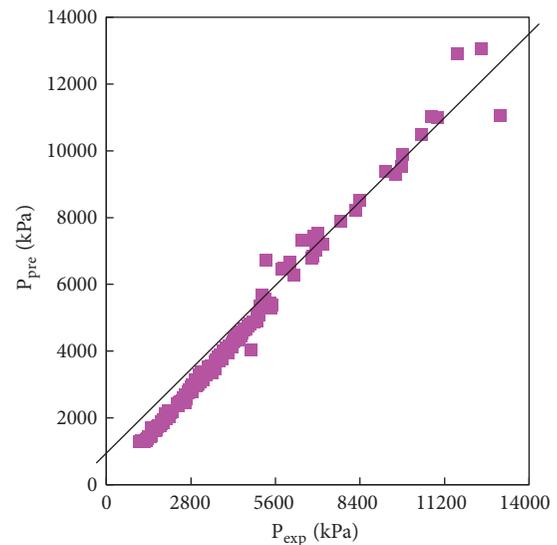


FIGURE 10: Comparison of the experimental P with ACE test data for CO_2-CH_4 system.

5. Conclusions

In this work, the ACE model was proposed to predict hydrate formation phase equilibrium conditions for both sweet and sour nature gases. Among the 1055 experimental data from literature, three data groups (688, 249, and 118 data points) were used to train, test, and evaluate the performances of the ACE model for sweet and sour natural gases. The presented ACE model gives the best matching result among 13 commonly used correlations with mean AARD of 0.134% for sweet natural gases. The ACE model produces better results than Adisasmito et al., CSMGem

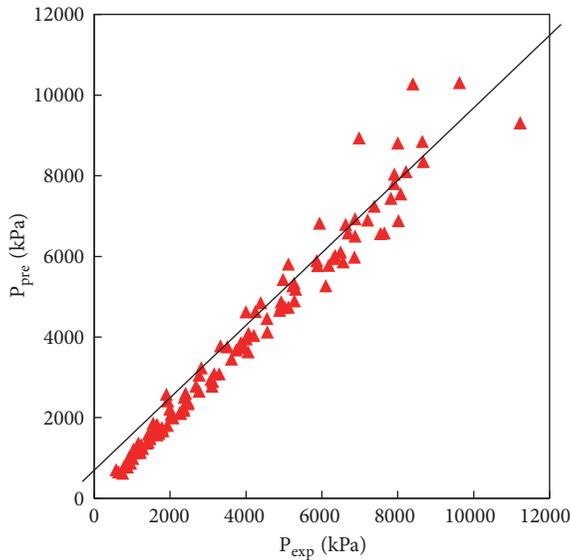
TABLE 6: Comparison between experimental (P_{exp}) and predicted (P_{pre}) hydrate formation pressures by using ACE model, CSMGem model [48], and HWHYD model [49] for CO_2 - CH_4 system.

P_{exp} (kPa)	ACE model(kPa)	ARD%	CSMGem model(kPa)	ARD%	HWHYD model(kPa)	ARD%
4030	3953	1.90	3980	1.24	4180	3.72
5480	5248	4.24	5670	3.47	5860	6.39
8270	8083	2.26	8710	5.32	8840	6.89
2720	2716	0.15	2780	2.21	2970	9.19
3610	3373	6.57	3680	1.94	3940	9.14
6090	6737	10.62	7340	20.53	7620	25.12
2720	2757	1.37	2730	0.37	2850	4.78
3210	3160	1.56	3260	1.56	3420	6.54
4700	4834	2.86	5120	8.94	5390	14.68
AARD		3.50		5.06		9.67

 TABLE 7: Comparison of AARD of the predicted hydrate formation pressures by different models for H_2S - CO_2 - CH_4 systems.

Gas mixture	AARRD%							
	ACE	M2	M3	M4	M5	M6	M7	M8
87.65% CH_4 +7.40% CO_2 +4.95% H_2S	5.98	4.13	4.39	8.24	9.27	—	—	7.31
82.45% CH_4 +10.77% CO_2 +6.78% H_2S	8.86	2.84	2.89	7.67	9.36	4.97	5.81	8.11
82.91% CH_4 +7.16% CO_2 + 9.93% H_2S	3.07	3.91	4.02	7.59	6.98	2.48	4.48	8.43
77.71% CH_4 +7.31% CO_2 +14.98% H_2S	2.05	2.77	4.31	10.0	11.0	5.55	6.81	10.0
75.48% CH_4 +6.81% CO_2 +17.71% H_2S	4.78	4.35	7.65	11.1	12.5	7.62	9.96	12.2
66.38% CH_4 +7.00% CO_2 +26.62% H_2S	6.44	8.67	14.6	16.6	19.0	15.3	17.6	17.6
Mean AARD%	5.2	4.45	6.31	10.2	11.35	7.18	8.93	10.6

(M2: CPA/Electrolyte/Chen–Guo model; M3: SRK/Electrolyte/Chen–Guo model; M4: SRK/Electrolyte/vdW-P model; M5: SRK/vdW-P model; M6: Patel-Teja/Electrolyte/Chen–Guo model; M7: Patel-Teja/Chen–Guo model; M8: CSMGem software)


 FIGURE 11: Comparison of the experimental P with calculated test data by ACE model for H_2S - CO_2 - CH_4 system.

and HWHYD models with AARD less than 3.5% for CO_2 - CH_4 binary system. The proposed ACE model has better performance in prediction of hydrate formation pressure for H_2S - CO_2 - CH_4 ternary systems with mean AARD=5.20%

with respect to seven thermodynamic methods considered in this work, except for CPA/Electrolyte/Chen–Guo combined model (AARD=4.45%). Moreover, the most advantage of the ACE model is that it provides quick and explicit calculations of the hydrate formation conditions.

Appendix

Here are the empirical correlations for hydrate formation condition representation.

Hammerschmidt (1934)

$$T = 8.9 * P^{0.285} \quad (A.1)$$

Makogon (1981)

$$\log(p) = \beta + 0.0479(t + kt^2) - 1 \quad (A.2)$$

where $k = 0.011\gamma^2 + 0.011\gamma - 0.006$, $\beta = 1.679\gamma^2 - 3.811\gamma + 2.681$.

Berge (1986)

$$T = -96.03 + 25.37 \ln(P) - 0.64 \ln(P)^2 + \frac{\gamma - 0.555}{0.025} * \left(80.61P + \frac{11600}{P + 599.16} - 96.03 \right) + 25.37 \ln(P) - 0.64 \ln(P)^2 \quad (A.3)$$

where $0.555 \leq \gamma \leq 0.58$.

$$T = \frac{-12300 + 80.61P - 21000 - (1220/(\gamma - 0.535)) - (1710/(\gamma - 0.509))}{P - 260.42 - (15.18/(\gamma - 0.535))} \tag{A.4}$$

where $0.58 \leq \gamma \leq 1$.

Kobayashi et al. (1987)

$$T = 1 \times \left[A_1 + A_2 \ln(\gamma_g) + A_3 \ln(P) + A_4 \ln(\gamma_g)^2 + A_5 \ln(\gamma_g) \ln(P) + A_6 \ln(P)^2 + A_7 \ln(\gamma_g)^3 + A_8 \ln(\gamma_g)^2 \ln(P) + A_9 \ln(\gamma_g) \ln(P)^2 + A_{10} \ln(P)^3 + A_{11} \ln(\gamma_g)^4 + A_{12} \ln(\gamma_g)^3 \ln(P) + A_{13} \ln(\gamma_g)^2 \ln(P)^2 + A_{14} \ln(\gamma_g) \ln(P)^3 + A_{15} \ln(P)^4 \right]^{-1} \tag{A.5}$$

Motiee (1991)

$$T = -283.24469 + 78.99667 \log(P) - 5.352544 \log(P)^2 + 349.473877\gamma - 150.854675\gamma^2 - 27.604065 \log(P\gamma) \tag{A.6}$$

Towler and Mokhatab (2005)

$$T = 13.47 \ln(P) + 34.27 \ln(\gamma) - 1.675 \ln(P) \ln(\gamma) - 20.35 \tag{A.7}$$

Bahadori and Vuthaluru (2009)

$$T = \exp\left(a + \frac{b}{P} + \frac{c}{P^2} + \frac{d}{P^3}\right) \tag{A.8}$$

where

$$\begin{aligned} a &= A_1 + B_1M + C_1M^2 + D_1M^3, \\ b &= A_2 + B_2M + C_2M^2 + D_2M^3 \\ c &= A_3 + B_3M + C_3M^2 + D_3M^3, \\ d &= A_4 + B_4M + C_4M^2 + D_4M^3 \end{aligned} \tag{A.9}$$

Zahedi et al. (2009)

$$T = 1 \times \left[A_0 + A_1 \ln(P) + A_2 \ln(P)^2 + A_3 \ln(P)^3 + A_4 \ln(\gamma_g) + A_5 \ln(\gamma_g)^2 + A_6 \ln(\gamma_g)^3 + A_7 \ln(\gamma_g) \ln(P) + A_8 \ln(P) \ln(\gamma_g)^2 + A_9 \ln(P)^2 \ln(\gamma_g) + A_{10} \ln(\gamma_g)^2 \ln(P)^2 \right]^{-1} \tag{A.10}$$

$$T = 1 \times \left[A_0 + A_1 \ln(P) + A_2 \ln(P)^2 + A_3 \ln(P)^3 + A_4 \ln(P)^4 + A_5 \ln(\gamma_g) + A_6 \ln(\gamma_g)^2 + A_7 \ln(\gamma_g)^3 + A_8 \ln(\gamma_g)^4 + A_9 \ln(\gamma_g) \ln(P) + A_{10} \ln(\gamma_g)^2 \ln(P) + A_{11} \ln(\gamma_g)^3 \ln(P) + A_{12} \ln(\gamma_g) \ln(P)^2 + A_{13} \ln(\gamma_g)^2 \ln(P)^2 + A_{14} \ln(\gamma_g)^3 \ln(P)^2 + A_{15} \ln(\gamma_g) \ln(P)^3 + A_{16} \ln(\gamma_g)^2 \ln(P)^3 + A_{17} \ln(\gamma_g)^3 \ln(P)^3 \right]^{-1} \tag{A.11}$$

Ghiasi (2012)

$$T = A_0 + A_1M + A_2M^2 + A_3 \ln(P) + A_4 \ln(P)^2 + A_5M \ln(P) \tag{A.12}$$

Hosseini-Nasab (2012)

$$\begin{aligned} \ln(P) &= c_0 + c_1 \ln(T) + c_2T^2P_v + c_3\frac{1}{T}P_v + c_4T^2 \\ &+ c_5T \ln(\gamma) + c_6 \ln(\gamma) \ln(T) P_v \\ &+ c_7 (\ln(\gamma))^2 \ln(T)^2 P_v^2 \\ &+ c_8 \ln(\gamma) \ln(T) P_v^2 \end{aligned} \tag{A.13}$$

where $\log(P_\omega^v) = a_\omega^v + b_\omega^v/T + c_\omega^v \log(T) + d_\omega^v T + d_\omega^v T^2$.
Riazi (2014)

$$T = A_1 e^{((P-A_2)/A_3)^2} + A_4 e^{((P-A_5)/A_6)^2} + A_7 e^{((P-A_8)/A_9)^2} + A_{10} e^{((P-A_{11})/A_{12})^2} + A_{13} e^{((P-A_{14})/A_{15})^2} \tag{A.14}$$

Gharryem et al. (2014)

$$T = A + \frac{B}{\gamma_g} + C \ln(P) + D \exp(\gamma_g^G) + E \ln(P)^2 + F \ln(P) \exp(\gamma_g^H) \tag{A.15}$$

Amin et al. (2015)

$$\ln(T) = a + b\left(\frac{1}{P}\right) + c\left(\frac{1}{P^2}\right) + d\left(\frac{1}{P^3}\right) \tag{A.16}$$

where

$$\begin{aligned} a &= A_1 + B_1\gamma_g + C_1\gamma_g^2 + D_1\gamma_g^3, \\ b &= A_2 + B_2\gamma_g + C_2\gamma_g^2 + D_2\gamma_g^3, \\ c &= A_3 + B_3\gamma_g + C_3\gamma_g^2 + D_3\gamma_g^3, \\ d &= A_4 + B_4\gamma_g + C_4\gamma_g^2 + D_4\gamma_g^3 \end{aligned} \quad (\text{A.17})$$

Amin et al. (2016)

$$\begin{aligned} T &= A_0 + A_1\gamma_g + A_2\gamma_g^2 + A_3 \ln(P) + A_4 \ln(P)^2 \\ &\quad + A_5\gamma_g \ln(P) \end{aligned} \quad (\text{A.18})$$

For $M \leq 20.276g$

$$\begin{aligned} T &= -128.7742 + 29.025M - 0.6429M^2 \\ &\quad + 24.6018 \ln(P) - 0.4857 \ln(P)^2 \\ &\quad - 0.4722M \ln(P) \end{aligned} \quad (\text{A.19})$$

For $M \leq 20.276g$

$$\begin{aligned} T &= 167.0905 + 0.8934M + 0.007M^2 \\ &\quad + 19.7239 \ln(P) - 0.6275 \ln(P)^2 \\ &\quad - 0.1245M \ln(P) \end{aligned} \quad (\text{A.20})$$

Adisasmito et al. (1991)

$$\ln(P) = A + BT^{-1} + Cy + DT^{-2} + EyT^{-1} + Fy^2 \quad (\text{A.21})$$

The coefficients of these correlations are indicated by A-H, a-d, and γ . The detailed values of model coefficients refer to [10–18].

Data Availability

The data used to support the findings of this study are included within the supplementary information file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Supplementary Materials folder is the supplementary information, unzip the folder, it contains the data files for all the figures (Figure 2–Figure 11) in the manuscript. The name of file in the folder corresponds to the figure title in the manuscript. (*Supplementary Materials*)

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