

Evaluation Of Empirical Correlations For Natural Gas Hydrate Predictions

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Abstract

A great number of petroleum engineering calculations require knowledge of natural gas hydrate formation conditions. Ideally, natural gas hydrate formation conditions are determined experimentally in the laboratory, but these data are not always available. Correlations are consequently used to determine values for natural gas hydrate formation conditions. In this research, the correlations of natural gas hydrate formation conditions determined by the gas gravity method are programmed and assessed with its respect to its capabilities to match experimental data published in the literature under varying system conditions (i.e. temperature, pressure, and composition). Also, statistical error analysis is used to evaluate the performance and the accuracy of the correlations for estimating natural gas hydrate formation to guide designers and operators in selecting the best correlations for their particular applications.

Introduction

A natural gas hydrate is a solid crystalline-like structure composed of cavities, formed by water molecules, which are stabilized by the inclusion of natural gas molecules smaller than n-butane. Hydrates were discovered in 1810 by Sir Humphrey Davey, yet only in the last half century has their occurrence been of interest to the natural gas industry. In 1934, Hammerschmidt determined that hydrates were the cause of plugged natural gas pipelines, thereby leading to the regulation of gas water content, and to the development of improved methods of prevention of hydrate plugs, including the injection of methanol and other inhibitors into the gas stream. Recent processing practice, with emphasis on extreme conditions of temperature, pressure, and sour gas composition, has caused a renewed interest in determining hydrate formation conditions. Typical operating problems include the fouling of heat

exchangers and other vessels, erosion of expanders, in addition to plug gage of transmission lines with the solid hydrate (1).

The best method for determining conditions of hydrate formation is to experimentally measure the formation at the temperature, pressure and composition of interest. Because it is impossible to satisfy the infinite number of conditions for which measurements are needed, hydrate formation prediction methods are needed to interpolate between measurements. However, such experimental endeavors are both time consuming and expensive relative to industrial needs for a number of hydrate formation conditions. Therefore some means of interpolation between the experimental results are needed, and ideally one would be able to extrapolate beyond the condition of the data (2).

The petroleum industry spends millions US dollars to combat the formation of hydrates. So, the accuracy of estimating the natural gas hydrates is extremely important for optimizing the cost of piping systems and processing units. Understanding how, when, and where gas hydrate form provides the engineer the method to predict the occurrences of hydrates. Therefore, an accurate and simplified model for predicting the calculations of natural gas hydrate is desirable (3). In this paper various correlations widely used in petroleum industry will be presented. A computer program is written employing these correlations. A comparative study will be presented based on computation using developed program.

Literature Review

Hydrates are solid crystalline inclusion compounds (Clathrates), which contain two components, referred to as host and guest. Free water molecules form a metastable crystal lattice, which is stabilized by light gas molecules (C_1 through C_4 paraffins, carbon dioxide, and hydrogen sulfide) occupying the crystal cavities (4,5). As gas processors use more severe conditions of lower temperature, denser phases, and more acidic gases, more data and more accurate prediction schemes will be required to prevent processing problems with hydrates. Whenever very small amounts of water are in the gas, the potential exists for hydrate formation. In this sense hydrates will continue to be a processing problem (6,7,8).

The gas gravity method is very simple for predicting the gas hydrate conditions. The gas gravity method was conceived by Katz of the GPSA Data Book. Also, the gas gravity method has served the gas processing industry well, as an initial estimate for a long period of time. To avoid tedious calculations based on GPSA's hydrate formation curve, a regression analysis was used to fit the GPSA's (9) hydrate formation curve to predict the hydrate forming conditions of natural gas. Based on the GPSA data book, hydrate equations were developed for gases where specific gravity was known. The available correlations for a specific gravity method to calculate the hydrate formation conditions are Sloan, Berge, Motiee, and Hammerschmidt correlations.

1- Berge method (10)

The equations for predicting hydrate temperatures are:

For $0.555 \leq \gamma_g < 0.58$

$$T = -96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2 + (\gamma_g - 0.555) / 0.025 \\ \times [80.61 \times P + 1.16 \times 10^4 / (P + 596.16) \\ - (-96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2)] \quad \dots (1)$$

And for $0.58 \leq \gamma_g < 1.0$

$$T = \{80.61 \times P - 2.1 \times 10^4 - 1.22 \times 10^3 / (\gamma_g - 0.535) \\ - [1.23 \times 10^4 + 1.71 \times 10^3 / (\gamma_g - 0.509)]\} / [P \\ - (-260.42 - 15.18 / (\gamma_g - 0.535))] \quad \dots (2)$$

Equations (1) and (2) are temperature explicit, i.e. temperature is calculated directly for a given pressure and specific gravity of the gas. An estimate for the pressure where hydrate formation is possible can be related to gas specific gravity and temperature.

2- Motiee Method (11)

A regression method was used to determine six coefficients that would correlate temperature, pressure and specific gravity. The equations are as follows:

$$\text{Log}(P) = a_1 + a_2 T + a_3 T^2 + a_4 \gamma_g + a_5 \gamma_g^2 + a_6 T \gamma_g \quad \dots (3)$$

$$T = b_1 + b_2 \text{Log}(P) + b_3 (\text{Log}(P))^2 + b_4 \gamma_g + b_5 \gamma_g^2 + b_6 \gamma_g \text{Log}(P) \quad \dots (4)$$

3- Sloan method (12)

A regression method was used to determine fifteen coefficients that would correlate temperature, pressure and specific gravity. The correlation was fit in the temperature range of 34 to 60 °F , the pressure range of 65 to 1500 psi, and the gas gravity range from 0.552 to 0.9. The equations are as follows:

$$T = 1/[c1 + c2 (\ln p) + c3 (\ln \gamma) + c4 (\ln p)^2 + c5 (\ln p) (\ln \gamma) + c6 (\ln \gamma)^2 + c7 (\ln p)^3 + c8 (\ln \gamma) (\ln p)^2 + c9 (\ln \gamma)^2 (\ln p) + c10 (\ln \gamma)^3 + c11 (\ln p)^4 + c12 (\ln \gamma) (\ln p)^3 + c13 (\ln \gamma)^2 (\ln p)^2 + c14 (\ln \gamma)^3 (\ln p) + c15 (\ln \gamma)^4] \dots\dots\dots(5)$$

4- Hammerschmidt method (13)

Hammerschmidt gives the following relationship for initial hydrate forming temperature below:

$$T = 8.9 P^{0.285} \dots\dots\dots (3)$$

By transforming equation 3 to pressure explicit form, the equation for initial pressure calculation becomes:

$$P = (T/8.9)^{3.509} \dots\dots\dots(4)$$

Computer Program

Knowledge of hydrate formation is essential when designing gas and condensate units. A computer program to calculate the hydrate formation conditions by various correlations widely used in petroleum industry for a specific gravity method was developed. The included correlations are Sloan, Berge, Motiee, and Hammerschmidt. The program needs the required data for each correlation to calculate the hydrate formation conditions as input. The program will either predict temperature (s) for given input pressure (s) or vice versa. The program also requires pressure or temperature as input data along with the specific gravity of the gas. Also, the program reads the experimental data to compare the experimental data with the

output results of different correlations calculated by the program. The error analysis was used to check the performance, as well as, the accuracy, of the gas hydrate correlations by the experimental data. The accuracy of correlations relative to the experimental values is determined by various statistical means.

Error Analysis

The statistical error analyses were used to check the performance, as well as the accuracy, of the hydrate formation correlations.

Statistical Error Analysis. The accuracy of correlations relative to the experimental values is determined by various statistical means. The criteria used in this study were average percent relative error, average absolute percent relative error, minimum/maximum absolute percent relative error, and standard deviation.

Average Percent Relative Error. This is an indication of the relative deviation in percent from the experimental values and is given by

$$E_r = (1/n_d) \sum_{i=1}^{n_d} E_i$$

$$E_i = [(x_{est} - x_{exp}) / x_{exp}]_i \times 100, \quad i=1,2,\dots,n_d$$

The lower the value, the more equally distributed are the errors between positive and negative values.

Average Absolute Percent Relative Error. This is defined as

$$E_a = (1/n_d) \sum_{i=1}^{n_d} |E_i|$$

and indicates the relative absolute deviation in percent from the experimental values. A lower value implies a better correlation.

Minimum/Maximum Absolute Percent Relative Error. After the absolute percent relative error for each data point is calculated, $|E_i|, i=1,2,\dots,n_d$, both the minimum and maximum values are scanned to know the range of error for each correlation:

$$E_{\min} = \min_{i=1}^{n_d} | E_i |$$

and

$$E_{\max} = \max_{i=1}^{n_d} | E_i |$$

The accuracy of a correlation can be examined by maximum absolute percent relative error. The lower the value of maximum absolute percent relative error, the higher the accuracy of the correlation is.

Standard Deviation (SD). Standard deviation is a measure of dispersion and is expressed as

$$SD = [1/(n_d - 1)] \sum_{i=1}^{n_d} E_i^2$$

where $(n_d - 1)$ are the degrees of freedom in multiple regressions. A lower value of standard deviation means a smaller degree of scatter.

Results and Discussion

The most common type of hydrate data taken is the formation temperatures and pressures. This type of data is most important to natural gas applications. We have compiled most available experimental data (14) of this type and compared it with predictions from Sloan, Berge, Motiee, and Hammerschmidt correlations. The experimental hydrate formation conditions data were compared with that calculated by the correlations included in the programs, Tables 1 - 7 show these comparisons.

Table 1 indicates that the hydrate formation conditions estimated by both Sloan and Berge correlations were the nearest to that of the experimental data. Also, they show the bad performance of Hammerschmidt correlation.

Table 2 indicates that the hydrate formation conditions estimated by Sloan correlation was the nearest one to that of the experimental data and Hammerschmidt correlation stood second in accuracy and Motiee correlation stood third in accuracy until temperature ≤ 60 °F and pressure < 2000 psi. However after 60 °F and at higher

pressure, the Motiee correlation is found to be best among other correlation. Berge correlation is found to be erroneous at pressure less than 300 psi.

Tables 3 to 7 indicate that the hydrate formation conditions estimated by Motiee correlation shows good agreement with the experimental data and Sloan and Hammerschmidt correlations give more errors at temperatures greater than 60 °F and at pressures greater than 2000 psi. Also, Tables 3 to 7 show Berge correlation gives more errors and bad performance at pressure less than 300 psi. and temperatures less than 50 °F.

Table 1 - Comparison Of Hydrate Formation Conditions Of 0.555 Gas Gravity

Pressure, psi	Experimental	Temperature, °F				Error, E			
		SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT	SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT
458	35	35.4	35.4	40.8	51.0	1.1	1.1	16.5	45.8
600	40	40.2	40.1	44.8	55.1	0.4	0.2	12.1	37.8
800	45	45.2	45.0	49.0	59.8	0.5	-0.1	8.9	32.9

	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
Er	0.70	0.40	12.50	38.81
Ea	0.70	0.40	12.50	38.81
Emin	0.40	0.10	8.90	32.90
E _{max}	1.10	1.10	16.50	45.80
SD	0.37	0.62	3.84	6.49

Table 2- Comparison Of Hydrate Formation Conditions Of 0.6 Gas Gravity

Pressure, psi	Experimental	Temperature, °F				Error, E			
		SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT	SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT
250	40	39.3	30.7	36.1	42.9	-1.7	-23.2	-9.8	7.3
480	50	49.4	51.5	46.1	51.7	-1.1	3.0	-7.9	3.4
980	60	59.4	65.3	56.0	63.4	-1.0	8.9	-6.7	5.6
2625	70	65.1	74.7	68.0	83.9	-7.1	6.7	-2.8	19.9

	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
Er	-2.30	4.65	-4.35	7.23
Ea	2.30	4.65	4.35	7.23
Emin	1.00	3.00	2.80	3.40
E _{max}	7.10	23.20	9.80	19.90
SD	3.46	2.97	2.65	8.94

Table 3- Comparison Of Hydrate Formation Conditions Of 0.65 Gas Gravity

Pressure, psi	Experimental	Temperature, °F				Error, E			
		SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT	SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT
110	30	34.5	4.4	27.5	34.0	14.9	-85.2	-8.3	13.3
390	50	53.5	52.2	47.4	48.7	7.1	4.3	-5.1	-2.5
2050	70	66.3	74.6	68.7	78.2	-5.3	6.5	-1.9	11.7

	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
Er	5.56	-24.79	-5.11	7.48
Ea	5.56	24.79	5.11	7.48
Emin	5.30	4.30	1.90	2.50
Emax	14.90	85.20	8.30	13.30
SD	10.17	52.35	3.20	8.71

Table 4 - Comparison Of Hydrate Formation Conditions Of 0.7 Gas Gravity

Pressure, psi	Experimental	Temperature, °F				Error, E			
		SLOAN	BERG	MOTIEE	HAMMERSCHMIDT	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
120	35	39.5	14.4	33.4	34.8	12.8	-58.7	-4.6	-0.5
340	50	54.8	51.7	49.2	46.9	9.6	3.3	-1.5	-6.3
690	60	63.4	65.3	58.7	57.3	5.6	8.9	-2.1	-4.4
3400	75	56.2	77.3	76.5	90.3	-25.1	3.1	1.9	20.4

	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
Er	-2.46	3.83	-0.43	2.44
Ea	2.46	3.83	0.43	2.44
Emin	5.60	3.10	1.50	0.50
Emax	25.10	58.70	4.60	20.40
SD	18.99	3.28	2.19	14.92

Table 5 - Comparison Of Hydrate Formation Conditions
Of 0.8 Gas Gravity

Pressure, psi	Experimental	Temperature, °F				Error, E			
		SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT	SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT
72	30	33.6	-4.6	32.0	30.1	12.1	-115.4	6.8	0.4
280	50	54.4	49.7	52.0	44.3	8.7	-0.5	4.0	-11.3
1700	70	64.2	74.8	72.8	74.1	-8.2	6.9	4.0	5.9

	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
Er	4.19	-36.33	4.92	-1.67
Ea	4.19	36.33	4.92	1.67
Emin	8.20	0.50	4.00	0.40
Emax	12.10	115.40	6.80	11.30
SD	10.89	68.58	1.60	8.80

Table 6 - Comparison Of Hydrate Formation Conditions Of 0.9 Gas Gravity

Pressure, psi	Experimental	Temperature, °F				Error, E			
		SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT	SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT
110	40	41.3	19.0	42.3	34.0	3.2	-52.6	5.8	-15.1
230	50	51.9	46.0	52.1	41.9	3.9	-8.0	4.3	-16.1
2600	75	49.6	77.0	76.6	83.7	-33.9	2.7	2.1	11.6

	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
Er	-8.94	-19.30	4.07	-6.54
Ea	8.94	19.30	4.07	6.54
Emin	3.20	2.70	2.10	11.60
Emax	33.90	52.60	5.80	16.10
SD	21.60	29.31	1.86	15.70

Table 7- Comparison Of Hydrate Formation Conditions Of 1.0 Gas Gravity

Pressure, psi	Experimental	Temperature, °F				Error, E			
		SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT	SLOAN	BERG	MOTIEE	HAMMER-SCHMIDT
60	35	33.3	-8.6	34.8	28.6	-5.0	-124.5	-0.5	-18.3
195	50	47.0	42.1	50.0	40.0	-6.1	-15.8	0.0	-20.0
440	60	55.9	61.7	58.8	50.4	-6.9	2.8	-2.0	-15.9

	SLOAN	BERG	MOTIEE	HAMMERSCHMIDT
Er	-5.98	-45.83	-0.81	-18.09
Ea	5.98	45.83	0.81	18.09
Emin	5.00	2.80	0.00	15.90
Emax	6.90	124.50	2.00	20.00
SD	0.94	68.76	1.02	2.04

Conclusions

We quantitatively compare the experimental data with four widely used hydrate prediction correlations in petroleum industry namely Hammerschmidt, Berge, Motiee, and Sloan methods. A computer program was developed to calculate hydrate predictions based on the above correlations. The results of the hydrate prediction conditions estimated by the mentioned correlations were compared with the experimental data. From these comparative study it can be concluded that

- 1- Motiee correlation results close to the experimental when the specific gravity of the gas is greater or equal 0.65. But when the specific gravity of the gas is less than 0.65 and at temperature greater than 60 °F and at higher pressure greater than 2000 psi, the correlation of Motiee is found to be best among other correlations.
- 2- Berge correlation results better prediction when the specific gravity of gas is equal 0.555. It shows bad performance with increasing the specific gravity of gas and when temperature is less than to 50 °F and pressure is less than 200 psi.
- 3- Sloan correlation results better prediction when the specific gravity of the gas is equal 0.555 and it stood second in accuracy after Berge correlation. But, with increasing the specific gravity of the gas and increasing the pressure greater than 1500 psi more errors may predict.
- 4- Hammerschmidt correlation results bad prediction when the specific gravity of the gas is equal 0.555. But, with increasing the specific gravity of the gas greater than 0.8 and increasing the pressure, more errors may be predicted. Hammerschmidt correlations are the simplest one and may be used as an initial value for the prediction of the hydrate conditions. It gives good predictions with low pressures and temperatures.

Nomenclature

a, b and c	: coefficients obtained by regression.
E_r	: average Percent Relative Error
E_a	: average Absolute Percent Relative Error
E_i	: the relative deviation in percent of an estimated value from an experimental value
$E_{min.}$: Minimum Absolute Percent Relative Error
$E_{max.}$: Maximum Absolute Percent Relative Error
n_d	: no. of points
T	: temperature, ° F
P	: pressure, psia
SD	: standard deviation
x_{est}	: represent the estimated values
x_{exp}	: represent the experimental values
γ_g	: specific gravity (air=1.0)

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