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A statistical method for assessment of the existing correlations of hydrate forming conditions

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Abstract

Hydrate formation in the oil and gas industries has been a serious problem for a long time. It may cause many difficulties for instance in gas pipelines blockages. In order to determine the hydrate forming condition, gas gravity method has been used. Several correlations have been proposed based on gas gravity method. Checking the accuracy of the applied correlations is important. In this paper, the leverage approach is used for this purpose. Leverage approach is a statistical method for detection outliers which identifies the applicability domain (AD) of hydrate data predicting correlations and the quality of the existing data. Moreover, the Williams plot is sketched, which is a graphical depiction for determination of the doubtful points. The obtained results showed the existing correlations are all statistically correct and valid to predict hydrate formation temperature, just one data point is out of the applicability domains, and none of the experimental data can be chosen as outliers.

Key words

hydrate formation conditions; gas gravity method; leverage approach; outlier detection

1. Introduction

Natural gas hydrates are crystalline solids, ice-like substances, which are composed of water and gas molecules (methane, ethane, propane, nitrogen, carbon dioxide, and hydrogen sulfide, etc.) held in a cage like ice structure (clathrate). The guest molecule is typically a gas or liquid which is trapped in water cages (host) that are composed of hydrogen-bonded water molecules [1−5]. Hydrates were discovered by Davy in 1810 [6]. The significance of hydrates was striking, when Hammerschmidt [7] determined the blockage reason of gas transportation pipelines could be gas hydrates while the gas being at or below its water dew point in petroleum industry in the early 1930s [1,2]. Furthermore, it was an introduction to more researches to predict the hydrate formation conditions of natural gases. The first problem faced predicting the conditions of pressure and temperature at which hydrates will form. There are several methods to predict the hydrate formation conditions in natural gas systems. These methods are divided into experimental methods and thermodynamic models. Most of the studies were carried out by studying the condition of hydrate formation (temperature and pressure).

The Katz gravity chart [8] is the simplest experimental method which can be used to predict the hydrate forming conditions. Although this method is a good method to predict the approximate pressure and temperature for hydrate formation, it can be a time-consuming and almost erroneous method [5]. Therefore, some correlations for gas gravity method have been proposed to calculate the hydrate formation conditions [9].

Some of the available correlations for predicting Hydrate formation conditions are Hammerschmidt (1934) [7], Berg (1986) [10], Kobayashi et al. (1987) [11], Motiee (1991) [12], Bahadori et al. (2009) [5] and Ghiasi (2012) [13]. By reviewing the error analysis of correlations in literatures of Bahadori et al. [5] and Ghiasi [13], Ghiasi correlation is more accurate and reliable than Bahadori et al. correlation. Also the Hammerschmidt [7] and Berg [10] correlations are discovered as the highest relative error correlations, respectively.

Identifying a group data which may differ from data presented in each model is essential.

In this study, a statistical method has been used to inspect whether there is any doubtful data, check the validity and applicability of the domain of all above mentioned correlations

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for predictinghydrate conditions and the quality of the existing experimental data. This purpose is carried out on the basis of Leverage approach [14–19]. In general, it would be of interest to suggest a statistically correct method for the detection of doubtful data and their quality along with the verification and domain of applicability of an existing correlation to anticipate the hydrate formation conditions.

2. Methodology

2.1. Leverage approach

The applicability domain (AD) is defined as the modeled response which makes the predictions with a known reliability. The aim of the applicability domain is to provide predicted values with a certain level of confidence. An accepted methodology for determining the applicability domain is the Leverage approach. In the present study, the leverage approach was employed to check the validity and the domain of applicability [15−18].

The Leverage approach [16,18,19] is useful to determine the influence of each observed value on each predicted value [20]. The relationship between the observed value and the predicted value is difficult to obtain. To overcome this problem, a symmetric matrix ($n \times n$), called "Hat matrix", was employed [21,22]. Equation (1) indicates that each predicted value ($\hat{y}_i$) is a linear function of the observed value y_i (1):

$$\hat{y}_i = H y_i \tag{1}$$

where, H is Hat matrix, which maps y_i into $\hat{y}_i$, given by the following equation:

$$H = X(X^T X)^{-1} X^T \tag{2}$$

X is an $m \times n$ matrix, in which *m* is the data and *n* corresponds to the parameters of the model. The superscript *T* refers to the transpose of the matrix [21,22].

The Leverage approach is one of the significant and reliable statistical methods to identify the outlier detections. Outliers are known as the points not explained well by the fitted model. Identifying these outliers is important because they can significantly influence the model [18,22]. The leverage method consists of graphical identification which is suitable for the detection of the influential points and outliers. This plot was known as the Williams plot which is a scatter plot of standardized residuals (defined as the difference between the predicted values and the corresponding data) versus the Leverages or Hat indices of each observation, as obtained from Equation (2). A warning leverage value (H*) is usually defined as Equation (3).

$$H^* = \frac{3p}{n} \tag{3}$$

where, *p* is the number of the model input parameters plus one, and *n* is the number of training points [16,22]. Williams plot is not only a simple and rapid way to identify AD detection, but also a suitable way to detect the outliers [16]. Observations with leverage values smaller than H* (vertical line in Williams plot) and standardized residuals between -3 and 3 are considered as influence observations on the model. "Good High Leverage" points are located within the range of $H^* \leq H$ and $-3 \leq R \leq 3$, which are not in the applicability domain (AD) of the model. The points are outlier or "Bad High Leverage" with standardized residuals greater than 3 or smaller than -3, whether H is greater or smaller than H^* [14,17,22].

2.2. Experimental method

The gas gravity method was developed by Katz (1945) [8]. The Katz gravity chart can be used to predict the approximate pressure and temperature for hydrate formation in natural gas systems. The virtue of this method is its simplicity. The curve is only a single chart, which is a plot of pressure and temperature where the specific gravity of the gas, as the third parameter, is known. This curve estimates the hydrate formation condition for gases having the same molecular weights. The experimental hydrate formation temperature data chosen from Katz gravity chart [8] have been used in this work.

2.3. Correlations

Some available correlations for gas gravity method [8] for predicting the hydrate formation conditions of natural gases are Hammerschmidt [7], Berge [10], Kobayashi et al. [11], Motiee [12], Bahadori et al. [5] and Ghiasi [13]. The results of the mentioned correlations, obtained from the similar temperature, pressure and gas gravity, were compared with each other under Leverage approach.

2.3.1. Hammerschmidt correlation

Hammerschmidt model (1934) [7] is one of the simplest correlations which can be used to obtain the approximate formation conditions of natural gas hydrates. The following relationship between pressure and temperature was determined as Equation (4) given below:

$$T = 8.9 P^{0.285} \tag{4}$$

where, T is the temperature (in ^{o}F) and P is the pressure (in lb/in^2). Best predictions are made in systems with low pressure and temperature, and with specific gravities less than 0.555.

2.3.2. Berge correlation [10]

There are two temperature Equations (5) and (6), for a given pressure and specific gravity of the gas. Temperature could be calculated directly for a given pressure and specific gas gravity.

For the gas specific gravity, γ_g, falling within the range of 0.555 and 0.579: