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Empirical Model for Predicting Gas Hydrate Formation in Gas Pipelines

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Abstract: Natural gas production and processing covers from gas reservoir to processing facility. The former is the upstream of natural gas and it involves subsurface activities of the natural gas production. The latter is the downstream of natural gas and it involves surface processing of the natural gas. Natural gas hydrate formation occurs at the subsurface, but much concern is on the downstream of natural gas processing. In fact, the processing of the natural gas is to reduce the concentration of unwanted component in the gas stream, to avoid flow assurance issues when transporting the gas through pipelines. Hydrate formations affect gas flow rate and increase operating cost. Predicting hydrate formation condition, will enable gas pipeline operators to operate the facility to avoid hydrate formation. In this study, an empirical model was developed to predict hydrate formation temperature in gas pipeline. The independent variable for the model were pressure, gas specific gravity and methane composition (which existing models does not consider) and the target variable is temperature. Different functions (logarithmic, polynomial, exponential etc) were tested for the model and the best fit for the model were logarithmic and polynomial functions. This agreed with existing models which has either only logarithmic or polynomial functions. The results obtained from the developed nonlinear empirical model shows that the R-squared was 0.94 and the errors (residuals) between the observed and predicted temperature were scattered around zero. The model compares well with existing models, especially with model that contains logarithmic and polynomial function. The nonlinear empirical model has the capability to predict very low temperature of hydrate formation. It can be used as a first check in predicting gas hydrate formation temperature in pipeline, given the pressure, gas specific gravity and composition of the gas.

Keywords: Gas Hydrate, Empirical, Pipeline, Formation, Reservoir

1. Introduction

The effect of water vapor during natural gas transportation and measurement is a major issue in the gas industry. Water liquefies, freezes, and accumulates within the system, causing gas pipeline transmission to be disrupted. The solid crystals that develop resemble snow, and the passage of gas causes it to compress and gather at the lower points of the pipeline; these snow-like crystals are known to cause blockage in gas pipelines [9].

Gas hydrate is a form of crystalline solid in appearance, and it is composed of nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulphide (H_2S) and hydrocarbon gases: alkane gas and some heavy hydrocarbon composition. The formation occurs at a certain low temperature and high pressure. To put it simply, gas hydrate includes two parts: host molecule and guest molecule. Among them, the water molecule is the host molecule, and the light hydrocarbon or non-light hydrocarbon molecule is the guest molecule [12]. The network structure of gas hydrate is formed by water molecules under the action of hydrogen bonds, and there are some lattice holes in the hydrate, and light hydrocarbon or non-light hydrocarbon molecules exist in these holes. Under the action of intermolecular force, water molecules combine with light hydrocarbon or non-light hydrocarbon molecules to form hydrate in the end. Therefore, it is obvious that the structure and stability of gas hydrate will be affected by

factors such as the type and size of guest molecules and external conditions, and there are certain differences [12].

Guest molecules are contained in cages of a host lattice in gas hydrates, which are clathrate formations. They are crystalline forms of water in which the presence of gas molecules inside the crystal matrix (cage) at temperatures much above the freezing point of water aids in solid stability. It is made up of gas molecules (mostly methane) surrounded by a cavity of water molecules [16]. Gas hydrates normally develop when 90% of the cage is occupied which gives the gas a solid volume ratio of roughly 160% [2].

Gas hydrate cages are made up of hydrogen-bonded water molecules and typically contain a single gas molecule. Because hydrogen molecules are entrapped (caged) inside the crystal lattice of water molecules, the structure of hydrates is known as clathrates [16], Hydrates are formed when water and gas combine at low temperature and high pressure in pipes delivering natural gas. Because they are lighter than water, they frequently reside near the point of interface between oil and water. The crystals have a honeycombed structure with microscopic channels that allow gases to pass through, but additional accumulation completely blocks the flow in the pipe. Gas hydrates can also be found on subsea and ocean floors where conditions are favorable for formation; they trap enormous amounts of energy around subsea leaks and midline reserves [16]. Natural gas hydrates thrive in the sediments of the Polar Regions and the sediments that cover 90% of the ocean floor. Most natural gas hydrates contain more than 99% methane, with minor levels of CO_2 and H_2S present.

Gas hydrates can limit flowrate and potentially cause pipeline failures in addition to clogging pipelines. It is therefore important to be able to predict and prevent the formation of hydrates in natural gas pipelines.

One approach to predicting gas hydrate formation is the development of empirical models. These models use empirical data and statistical analysis to identify patterns and relationships between various factors that may influence hydrate formation, such as temperature, pressure, gas composition, and flow rate. These models can then be used to make predictions about the likelihood of hydrate formation under different conditions.

There are a number of different approaches that have been used to develop empirical models for predicting gas hydrate formation in natural gas pipelines. These approaches include the use of thermodynamic models, statistical models, and machine learning algorithms. Each approach has its own strengths and limitations, and the choice of approach will depend on the specific goals and needs of the study.

To develop an empirical model for predicting gas hydrate formation in natural gas pipelines, researchers will typically start by collecting data on the conditions under which hydrates have formed in the past. This data may include information on temperature, pressure, gas composition, and flow rate, as well as any other relevant factors. The data is then analyzed using statistical techniques to identify patterns and relationships that may be relevant to predicting hydrate formation. Once the data has been analyzed and the relevant patterns and relationships have been identified, the next step is to develop a model that can use this information to make predictions about the likelihood of hydrate formation under different conditions. This may involve developing a mathematical equation or using machine learning algorithms to develop a predictive model.

Overall, the development of an empirical model for predicting gas hydrate formation in natural gas pipelines is a complex process that requires a thorough understanding of the factors that influence hydrate formation, as well as advanced statistical and computational techniques.

2. Natural Gas Pipeline Condition and Hydrate Formation

Natural gas value chain starts from the gas reservoir to the surface facility. At the surface facility, the produced natural gas is processed or treated to remove unwanted component that may interfere with the transportation of the processed gas through gas pipeline. Natural gas pipelines are installed to transport gas from the source (processing facility) to the point of sale (consumers). Between the source and the point of sale, the transported gas passes through different terrains of both high and low temperature. At high temperature terrains, the natural gas is safe to transport to the point of sale without encountering flow assurance issues. However, at low temperature terrain, the component of the gas (including water vapour) tends to condense and fallout from the body of the gas, causing liquid accumulation in that section of the pipeline. Once this happens, hydrate formation is imminent.

Lili et al [19] stated that "due to the uneven distribution of resources, natural gas is mainly transported through long-distance pipelines and distributed to urban users through city gate stations and with the existence of throttling effect, the pressure regulation on the city gate station will produce a certain temperature drop.

Sun et al [37] and Li et al [18] stated that if the water dew point of gas is high, the water is likely to condensate during the pressure regulation, leading to the formation of hydrates and triggering a series of safety accidents to both stations and urban users.

Mohammad and Ayoub [24] stated that natural gas and water are combined, and in equilibrium in gas reservoirs, wells and pipelines and are transferred to the pipelines. The water in the natural gas, reduces the thermal value of natural gas, rising pressure or lowering the temperature during natural gas transfer leads to water condensation, and consequently this water in the liquid phase dramatically reduces the efficiency of the gas transmission pipelines. Finally, the excessive temperature-fall causes the formation of gas hydrate. When the water approaches its freezing point, a network of water molecules may form with holes in it.

The formation of gas hydrates is considered as an undesirable phenomenon in oil and gas pipelines and according to Hammerschmidt [9]; stated that the clogging of the natural gas transmission pipes was due to the formation of

gas hydrate crystals. Therefore, due to the importance of the continuation of natural gas flow in the gas pipelines, many researchers carried out various experiments on the hydrodynamic conditions of hydrate formation and methods of preventing its formation. The formation of gas hydrate through the pipelines considered mostly along with petroleum products. Natural gas transportation in pipelines dissipate heat energy, thereby cooling the gas and reducing its temperature. The attendant effect is liquid accumulation along the pipeline and increase in compressor cost once gas hydrate is formed.

Pipeline design and installation is a complex activity as it requires detailed pipeline profile. This profile shows the topology of the environment in which the gas pipeline is to be installed. Infact, it is the topology of the environment that makes the installation of the gas pipeline very complex. The topology makes some section of the pipeline to rise (vertical elevation) and horizontal bends with fittings on each joint. These conditions of the gas pipeline, assisted with changes in gas properties and gas flow conditions of temperature, pressure and compositions of the gas components, contribute to potentials and imminent conditions under which gas hydrate forms. Therefore, identifying and predicting gas hydrate formation should consider all these parameters.

3. Hydrate Formation Prediction

Shi et al. [35] stated that the formation of hydrates usually needs to meet three conditions:

1. The water condition that indicates enough liquid water in the system;
2. Reaching the temperature and pressure conditions for hydrate formation;
3. The gas flow is unstable, and there are hydrate seeds. The first condition is mainly based on the phase equilibrium theory.

Shi et al [35] and Mesbah et al [23] independently observed that the Soave–Redlich–Kwong (SRK) or Peng–Robinson (PR) equation of state (EOS) can be used to calculate and analyse the water content and water condensation in the natural gas transportation process, which are candidates for hydrate formation. Furthermore, in order to facilitate the calculation efficiency, many researchers have anticipated the correlation equations of hydrate formation temperature, pressure, and relative density through the thermodynamic model, but the calculation accuracy is limited [25, 31, 39].

Balakin et al. [3] utilized the Population Balance Method (CFD-PBM) modelling to investigate the density and deposition of gas hydrates inside industrial tubes in addition to computational fluid dynamics and modeling. The resulting model was capable of predicting the agglomeration and deposition of hydrate particles in turbulent oil-dominated flows. Omidi et al. [30] worked on vertical pipelines from which they modeled and simulated thermal decomposition of the hydrates around the vertical pipelines produced gas from sub-ocean sediments layers, and carried out analysis of the volume of the gas and hydrate analyzed and determine the pressure related to the related volume of the gas and hydrate. They understudied the effect of the gas flow in the vertical pipelines while porosity of the sediment layers and volume of the hydrate investigated. However, they found out that increasing the gas velocity in the pipelines will enhance the decomposition of the hydrate formed in the pipeline.

Naseer and Brandsatter [28] modelled the production of hydrate inside a pipeline-transported gas by using computational fluid dynamics (CFD)-Software. They found out that, some parts of the pipeline with a positive gradient considered the best place for accumulating water and forming gas hydrate. Hydrate formed in pipeline usually induced shear stress on the walls of the pipeline and according to Lorenzo et al. [20] developed a model that addresses sloughing and presented the sloughing model to determine the effective shear strength of the hydrate deposits considered a key property to predict hydrate detachment and accumulation in gas-dominated pipelines.

Musakaev et al. [26] focus their work on gas hydrate formation and dissociation gas reservoir and developed a mathematical model for decomposition of gas hydrate under a negative initial reservoir temperature (in degree Celsius). This model took into account the methane hydrate decomposition in a porous medium with both the frontal surface and extended zone of phase transitions. Saeedi-Dehghani et al. [33] research focus on gas hydrate inhibitors like methanol, Ethanol, and Mono Ethylene glycol and investigated the thermodynamic modelling of the gas hydrate production in the presence of these gas hydrate chemical inhibitors. Their model could predict the equilibrium temperature of the methane hydrate production. Inkong et al. [11] carried out research different from Saeedi-Dehghani et al. [33] by studying the effects of mixed MES (Methyl Ester Sulfonate) and SDS (Sodium Dodecyl Sulphate) hydrate promoters on formation and dissociation of gas hydrate kinetics. Their work aimed at facilitating the rate of hydrate formation towards improving its storage capacity for transportation. They revealed all concentrations of mixed surfactants enhanced the methane formation rate compared to pure water. Nevertheless, this did not significantly affect the rate of methane recovery. In another study, three phase (liquid-vapour-hydrate) equilibrium for some gas mixture containing methane with various compositions investigated by Lee et al. [16]. Results of their work illustrated that existing of large cavity occupying molecules (e.g., ethylene) increased non-linearly of the equilibrium curves. Various correlations have been presented in the literature for predicting the hydrate formation conditions. These correlations can be classified into three major methods. Graphical or chart methods; thermodynamic methods and empirical methods and these are the most used method in developing models for predicting the formation of natural gas hydrate in gas pipelines.

3.1. Graphical Method

The first method in predicting hydrate formation is the k-value method. According to Carson and Katz [4] the k-value utilizes the vapor–solid equilibrium constants for predicting hydrate-forming conditions. The method is based on the

concept that hydrates are solid solutions and that the hydrate forming conditions are predicted from empirically estimated vapor–solid equilibrium constants. The constant is estimated using Equation 1.

$$K_i = \frac{y_i}{x_i} \tag{1}$$

Or Equation 2.

$$y_i = K_i x_i \tag{2}$$

Where;

y_i is the mole fraction of the ith hydrocarbon component in the gas phase considered on a i water-free basis.

x_i is the mole fraction of the same component in the solid phase on a water-free i basis.

K_i is the equilibrium constant for the ith component in the liquid-vapour equilibrium phase.

However, the hydrate formation conditions should satisfy the following condition based on Equation 3:

$$\sum(y_i) = \sum(K_i x_i) = 1 \tag{3}$$

The presence of non-hydrocarbon gases (CO_2, N_2 and H_2S) may cause imprecise results.

Mann et al [22] presented new K-charts that cover a wide range of pressures and temperatures. These charts can be an alternate to the tentative charts constructed by Carson and Katz [14] which are not a function of composition of the natural gas. The new charts are based on the statistical thermodynamic calculations.

Another plot was developed by Katz [14] which was based on the gas–gravity plot. The plot was a relation of the gas hydrate formation pressure and temperature with gas gravity defined as the apparent molecular weight of a gas mixture divided by that of air, Equation 4.

$$\gamma_g = \frac{M_{ave}}{28.97} \tag{4}$$

This method is a simple graphical technique that may be useful for an initial estimate of hydrate formation conditions. The hydrate formation chart was generated from a limited amount of experimental data and a more substantial number of calculations based on the K-value method Equation 1 and Equation 2. Sloan [36] carried out a statistical analysis of the Katz chart and found out that this method is not accurate. For the same gas gravity, different mixtures may lead to about 50% error in the predicted pressure. Ahmed and Ali [2] stated that, over the last 50 years, enormous experimental data on hydrate formation conditions have been collected and hence a more accurate gas gravity chart can be developed. One purpose of this study is to develop such chart as will be explained later.

3.2. Thermodynamic Method

Statistical thermodynamics has been used to developed statistical model for predicting gas hydrate formation based on the composition and interaction of the components in the natural gas system. In addition, the statistical thermodynamic approach also accounts for the interactions between water molecules forming the crystal lattice and gas molecules. Many researchers (Parrish and Prausnitz [32], Nagata and Kobayashi [27], John et al. [13], Dharmawardhana et al [6] has also modified the model to enhance the prediction of gas hydrate formation conditions. Waals and Platteeuw [40] observed that temperature and pressure conditions are mainly studied by the thermodynamic model and at present, the thermodynamic models of hydrate formation can be divided into two main categories: the first is the van der Waals–Platteeuw [40] model based on the isotherm adsorption theory; and the second is the Chen–Guo model (Chen and G based on the mechanism of hydrate formation. Englezos [7] stated that the accuracy of predicting the gas hydrate formation pressures or temperature in systems containing carbon dioxide and aqueous electrolyte solutions is limited in application. For pure component systems excluding i-butane, an average error of 29% in pressure prediction can be expected. Lee and Chen [17] reported that for multicomponent systems, 25% average error in predicting gas hydrate formation pressure may be expected.

3.3. Empirical Model Method

Abdulaga et al [1] stated that the "development of mathematical model for hydrate formation process during the transportation or movement of natural gas in pipelines requires a joint study of algebraic dependencies that take into account changes of thermodynamic state of the natural gas. These algebraic dependences are functions of the change in the humidity of natural gas depending on pressure and temperature, the change in the equilibrium of hydrate formation depending on pressure and temperature, the dependence of the transition point of hydrate formation temperature on the amount of methanol and the equation of state of real gas". Many researchers have carried out extensive studies on the transportation or movement of natural gas mixtures in fixed and variable cross-section area of pipelines under the following simplification conditions assumption: Based on some assumptions, linear and nonlinear model has been developed.

Hammerschmidt [9] developed the first and simplest correlation for the prediction of hydrate formation conditions. This simple correlation was temperature as a function of pressure Equation 5.

$$T = 8.9P^{0.285} \tag{5}$$

Where;

T is the gas hydrate formation temperature and P is the pressure.

Holder et al. [10] developed an empirical correlation for estimating the gas hydrate formation pressure of natural gas, which was a function of temperature only in Equation 6.

$$P = \exp\left(a + \frac{b}{T}\right) \tag{6}$$

Where;

a and b are empirical coefficients that depend on the

temperature range for each gas.

Makogon [21] developed a correlation which was based on the gas gravity of natural gas for selected pure gases.

$$\ln(P) = 2.3026\beta + 0.1144(T + kT^2)$$

Where;

$$\beta = 2.681 - 3.811\,\gamma + 1.679\,\gamma^2$$

$$K = -0.006 + 0.011\,\gamma + 0.011\,\gamma^2 \quad (7)$$

Towler and Mokhatab [39] developed an appropriate correlation which represent Katz gravity chart for predict hydrate formation temperature as a function of pressure and specific gravity,

$$T = 13.47\ln(b) + 34.57\ln(\gamma_g) - 1.675[\ln(b) \times \ln(\gamma_g)] - 50.32 \quad (8)$$

Where;

T is the gas hydrate formation temperature in ^{o}F.

P is the gas hydrate formation pressure in psia.

γ_g is the gas specific gravity.

Mottiee [25] developed correlation for predicting gas hydrate formation temperature as function of pressure and specific gravity, and used a regression method to determine coefficients that would correlate the temperature, pressure and specific gravity.

$$T = b_1 + b_2 log(P) + b_3\big(log(P)\big)^2 + b_4\gamma_g + b_5\gamma_g^2 + b_6\gamma_g log(P) \quad (9)$$

Where;

b_i $(i = 1, 2, 3, 4, 5, 6)$ are the correlation coefficient of the regression equation. Table 1 present the values of the correlation coefficients.

Table 1. *Constant values for the Coefficient in Motiee Empirical Model.*

Constant	values
b1	-238.24469
b2	78.99667
b3	-5.352544
b4	349.473877
b5	-150.854675
b6	-27.604065

Naseer and Brandsatter [28] developed an empirical model for predicting gas hydrate formation temperature as a function of pressure only,

$$T = 270.86 + 8.5274\ln(P) \quad (10)$$

Where;

P is the gas hydrate formation pressure of the natural gas.

In order to estimate the saturation temperature according to the partial pressure of the vapor in the natural gas hydrate formation system. Naseer and Brandsatter [28] developed the following equation,

$$T_{sat} = 16.335\ln(P) + 167.08 \quad (11)$$

Kobayashi et al [15] developed a correlation, to predict hydrate formation temperature. This correlation was based on Katz [4] gas gravity curves. Table 2 present the values of the correlation coefficients.

Table 2. *Constant values for the Coefficient in Kobayashi et al Empirical Model.*

Constant	Values	Constant	Values
A1	$2.771\text{x}10^{-3}$	A9	$-2.3729\text{x}10^{-4}$
A2	$-2.7822\text{x}10^{-3}$	A10	$-2.6841\text{x}10^{-5}$
A3	$-5.6493\text{x}10^{-4}$	A11	$4.661\text{x}10^{3}$
A4	$-1.2986\text{x}10^{-3}$	A12	$5.5542\text{x}10^{-4}$
A5	$1.40712\text{x}10^{-3}$	A13	$-1.47278\text{x}10^{-5}$
A6	$1.7857\text{x}10^{-4}$	A14	$1.3938\text{x}10^{-5}$
A7	$1.1303\text{x}10^{-3}$	A15	$1.4885\text{x}10^{-6}$
A8	$5.9728\text{x}10^{-4}$		

The above empirical models discussed for predicting hydrate formation conditions, shows that for some of the models, the input parameter is only one (pressure) and other, the inputs parameters are only two (pressure and gas specific gravity). However, there is a need for developing a new model and reliable model for predicting gas hydrate formation conditions with minimum of three input parameters that will include the compositions of the natural gas component. This model should address the followings: (1) require the least amount of input information (2) give high accuracy (3) be robust and less sensitive to noisy input data (4) can be continuously retain to a new input and output data. This study seeks to develop such model through nonlinear empirical model development using MATLAB nonlinear simulation toolbox and carry out statistical analysis to determine statistical parameters that measures the performance of the developed model.

4. Methods and Procedure

The method adopted in this study is divided into steps, as shown in the flow chart of Figure 1.

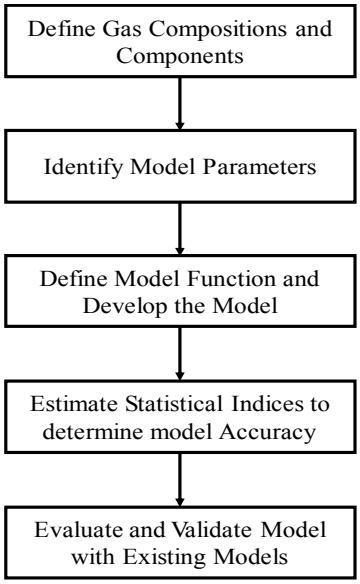

Figure 1. *Flow Chart of the Methods Adopted.*

4.1. Natural Gas Composition and Components

The composition and component of natural gas affects the systems hydrate formation, which depends on temperature, pressure and specific gravity of the natural gas. The materials that are utilized in this study are natural composition, Aspen HYSYS, MATLAB software and Statistical Analysis software to present and analysis the developed empirical model.

The Aspen HYSYS software was used to estimate the natural properties, such as pressure, temperature, specific gravity, average molecular weight of the gas. These parameters are estimated from the natural gas composition and component. The MATLAB software was used to develop the empirical model. The empirical model was nonlinear in nature and are complex to solve. Therefore, the nonlinear curve fitting tools box in the MATLAB software was deployed to develop and solve the empirical model. Statistical analysis software such as STATISTICA, was used to carryout statistical analysis to determine the performance of the model through error measurement and generate plots of the various parameters that is associated with the empirical model performance.

4.2. Nonlinear Empirical Model and Model Parameters

Nonlinear models are complex in expression, containing different functions. Most common functions in nonlinear models are natural logarithm, logarithm to base 10, exponential functions, trigonometric functions, and combination of polynomial functions. The performance of the nonlinear empirical model is dependent on the function that appear in the empirical model and the model constants. The prediction and estimation of parameters using nonlinear models are reliable, since it contains mathematical functions that describe the data. The hydrate formation empirical model in this study was nonlinear, this is to ensure that the performs well in predicting and estimation the formation condition of hydrate in natural gas, for any given temperature, pressure, specific gravity and composition of the methane component.

Hydrate formation models exist and populate published literature and books; however, these models focus on temperature and pressure, others included specific gravity in the model. In this work, a nonlinear empirical model was developed, and the model parameters include temperature, pressure natural gas specific gravity and composition of the methane component in the natural gas. The composition of the natural gas affects the hydrate formation condition of the gas. Therefore, the difference between this empirical model and all other others is the inclusion of composition of the natural gas. The composition of the natural changes as the process flow conditions (temperature and pressure) changes, thus causing a change in the hydrate formation condition.

4.3. Empirical Model Development

Hydrate formation location in natural gas value chain is mainly pipeline gas, where environmental conditions affects the flow conditions of the gas in the pipeline. Hydrate formation is due to low temperature and/or high pressure in the pipeline. The low temperature conditions trigger hydrate formation once the flow temperature is below the hydrate formation temperature. In other words, once the hydrate formation pressure is higher than the flow pressure, hydrate formation is trigger. Therefore, the location of natural gas in the gas processing value chain considered in this study was pipeline gas and the composition of the gas was those related to processed gas. Four different compositions of natural gas were used in this study to estimate the flow condition of hydrate formation. The nature of the natural gas considered in this study are sweet, sour, wet and dry gas. The sour natural gas contains carbon dioxide (CO_2), hydrogen sulphide (H_2S) and Nitrogen (N_2). The range of the carbon dioxide and hydrogen sulphide composition are $0.01 \leq CO_2 \leq 0.08\ and\ 0.02 \leq H_2S \leq 0.06$. The wet natural gas contains high composition of heavier components and water vapour (H_2O). The composition of methane was varied from 1.0 to 0.4 mole fraction and at each composition of the methane, the temperature, pressure and specific gravity of the natural gas were estimated. To enhance the performance of the model, 83 data points were generated from the natural gas compositions and components. The components of the natural gas include carbon dioxide (CO_2), hydrogen sulphide (H_2S) and Nitrogen (N_2), water vapour (H_2O), methane, ethane, propane, iso-butane, normal-butane, iso-pentane, normal-pentane, hexane and heptane plus. The hydrate formation conditions (temperature, pressure), and specific gravity were estimated for the 83 data points. The depended variables are the temperature and the independent variables are pressure, specific gravity of the gas and the composition of methane in the natural gas. Therefore, the functional representation of the model is temperature as a function of pressure, specific gravity and mole fraction of methane in the composition.

$$T = f(P, \gamma_g, y_m) \tag{12}$$

The dependencies of the temperature on the independent variables were examined to determine the degree and functional relationship between the variables. The functional relationship is either inverse; indicating that as one parameter increase, the other will decrease, or, direct; indicating that as one parameter increase, the other will increase. This dependency examination is important to decide the functions that make up the model and to enhance the performance of the model with reliable results. Figure 2 shows the plot of temperature against pressure to examine the degree and functional relationship between them. The Figure 2 shows that the temperature and pressure of the natural gas have an inverse functional relationship, as the scatter plotted points scatters in decrease order towards the right. This agrees with the formation condition of gas hydrate: low temperature and high pressure. This behavior tends to be logarithmic in nature, thus a logarithmic function may enhance the performance of the model.

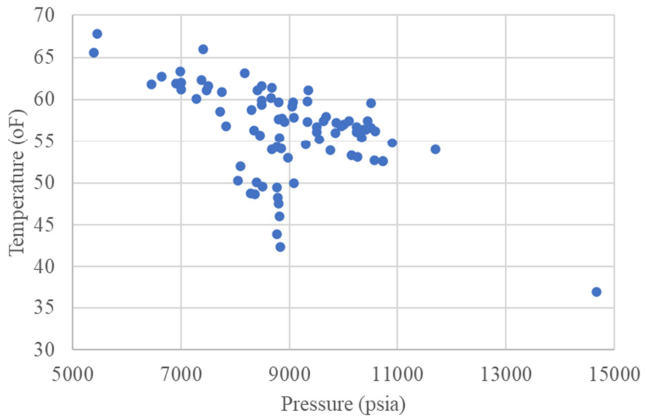

Figure 2. *Scatter Plot of Temperature and Pressure Relationship.*

Figure 3. present the degree and functional relationship of temperature and natural gas specific gravity and composition of methane in a scatter plot. The natural gas composition of methane exhibits the same functional relationship as the temperature and pressure relationship (inverse). The increase of natural gas composition of methane component decreases the tendency for the gas to form hydrate. This is possible since natural gas with low to very low composition of heavier component have little chances of hydrate formation. In a similar manner, as in the case of temperature and pressure, a logarithmic function will be involved.

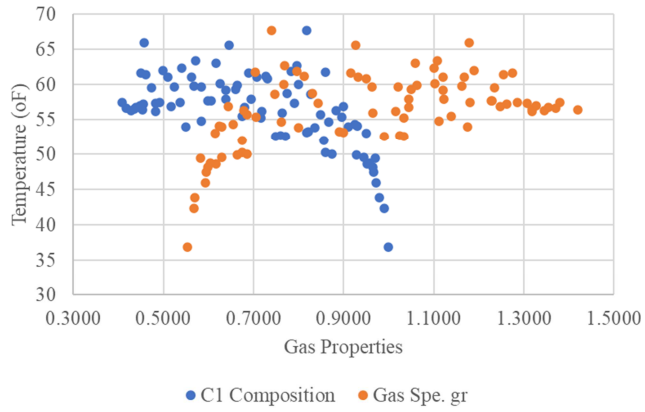

Figure 3. *Scatter Plots of Temperature and Gravity and Composition Relationship.*

The Figure 3. also present the degree and functional relationship between the temperature and natural gas specific gravity in a scatter plot. The scatter plot shows that there exists almost, a direct relationship between the temperature and specific gravity of the natural gas. However, below 0.7 mole fraction of methane, the relationship is direct as increase in one will increase the other. But above 0.7 gas gravity, the temperature almost remains constant as the natural gas specific gravity increase. Above 0.7 gravity, the natural gas composition increases in the heavier components and decreases in the methane component, indicating wet natural gas. Therefore, a polynomial function will fit well in the nonlinear empirical model.

Based on the degree and functional relationship of the variables, Equation 12 can be rewritten as:

$$T = f(Log, polynomila, others) \quad (13)$$

The nonlinear empirical model was developed in four different model functions: the first function contains only logarithm, the second contains only polynomials, the third contains logarithm and polynomial and the fourth contains logarithm; polynomial and other functions. The four different nonlinear model were solved to determine the model coefficients and performance. The nonlinear model with the best performance were selected and analysis was carried out.

4.4. Statistical Indicators of the Nonlinear Empirical Model

The statistical software was used to estimate statistical parameters that measures the performance of the model. The statistical parameters used in the study are R-squared, mean square error, and normal probability plot of expected value. The R-squared is defined in Equation 14 as:

$$R^2 = \frac{\Sigma(y-y_i)^2}{\Sigma(y-\bar{y})^2} \quad (14)$$

Where;

y_i is the observed value of the dependent variable of each composition of methane in the natural gas.

$\bar{y}$ is the mean of the dependent variable and y is the predicted value.

The value of R-squared (R^2) measures the closeness of the observed values to the predicted values from the nonlinear model. Therefore, R-squared close to one (1), indicates that the observed and predicted values are very close with very little error and thus the model will predict very well the dependent variable (hydrate formation temperature) given the independent variables (pressure, specific gravity and composition of methane). R-squared close to zero (0) indicates the errors between the observed and the predicted are very large and thus the model will perform very poorly.

The mean square error, Equation 15; was another parameter that was used to test the performance of the model. The mean square error measures the square of the difference of the observed and predicted values. A very low mean square error indicates that the nonlinear model will perform very well and a high or too high mean square error, indicate that the nonlinear empirical model will perform very poorly.

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(y - y_i)^2 \quad (15)$$

The statistical parameters were estimated for each of the four different nonlinear model function to determine which of the model will predict accurately the condition of hydrate formation temperature. The first model with only logarithmic function performs poorly as the R-squared was very low; below 0.50 and the mean square error was very high above 3.02. the prediction from this nonlinear model did not match well with the observed data. The second model with only polynomial did not perform poorly, but the statistical parameters were not good enough to accept the model for hydrate formation prediction. This is because, the condition of the pipeline flow conditions may change, and if the nonlinear model is deployed to predict hydrate formation, the

predicted result may not be reliable, therefore the third nonlinear model function was developed. This model contains logarithmic and polynomial functions, though, the performance was not poor, but it has the same behavior with the nonlinear model containing only polynomial.

The fourth nonlinear model function contains all functions (logarithmic, polynomial and others). The nonlinear model was tested for different degrees of the polynomial. The polynomial of degree one (1) fails to predict accurately the hydration formation conditions, as the R-squared and mean square error were too low and too high. The second-degree polynomial was also tested, which did not perform poorly, but may fail accurate prediction when flow conditions change. The third-degree polynomial was imposed on the nonlinear empirical model and was found to be satisfactory as its R-square and mean square error were very high and very low. The developed nonlinear model from these function shows a better performance with third degree polynomial, than all the other model function. Therefore, this model was accepted and statistical analysis were carried out on it. The R-squared estimated was above 0.9 and the mean squared error was very low, about 0.0204.

4.5. Validation of the Nonlinear Empirical Model

The existing empirical models for predicting hydrate formation conditions, either depends on (1) one flow condition (temperature or pressure) or (2) two flow conditions (pressure and gas specific gravity or temperature and gas specific gravity). For case one, if the dependent variable is temperature, then the flow condition becomes the pressure. The reverse can also be the case, where the flow condition is temperature, and the dependent variable becomes pressure. Some of the existing models have complex expression and are tedious to evaluate, while others have simple expression and are simple to evaluate. However, the models are compared side-by-side to evaluate their performance prediction of hydrate formation conditions.

In this study, to further determine the accuracy of the nonlinear empirical model developed in this work, the model prediction was validated with other hydrate formation prediction models. The empirical models for the validation were selected based on the functional dependent variables in the model. The functional dependent variable in the developed nonlinear empirical model are pressure, gas specific gravity and methane composition in the natural gas. Therefore, for the selected models, the functional variables are pressure and specific gravity. The models selected for the validation are: Towler and Mokhatab [39]; Hammerschmidt [9]; Naseer and Brandsatter [28]; and Motiee [25]. The Towler and Mokhatab [39] empirical model, Equation (16), contains three functional variables (temperature, pressure and gas specific gravity). The Hammerschmidt [9] empirical model is a very simple correlation, and it contains only two variables (temperature and pressure), Equation (17). The Naseer and Brandsatter [28] empirical model, Equation (18), is also a simple correlation with only two functional variables (temperature and pressure). The Motiee [25] correlation, Equation (19), has three functional variables (temperature, pressure and specific gravity. Table 3 is a summary of all the empirical models used in the validation.

$$T = 13.47\ln(P) + 34.27\ln(\gamma_g) - 1.675(\ln(P)\ln(\gamma_g)) - 20.35 \quad (16)$$

$$T = 8.9P^{0.285} \quad (17)$$

$$T = 270.86 + 8.5274\ln(P) \quad (18)$$

$$T = b_1 + b_2 log(P) + b_3(log(P))^2 + b_4\gamma_g + b_5\gamma_g^2 + b_6\gamma_g log(P) \quad (19)$$

Table 3. *Summary of Nonlinear Empirical model for validation.*

S/N	Empirical Model	Dependent Variable	Independent Variables
1	Naseer and Brandsatter (2011)	Temperature (K)	Pressure (MPa)
2	Towler and Mokhatab (2005)	Temperature (°F)	Pressure (psia) and Specific gravity
3	Motiee (1991)	Temperature (°F)	Pressure (psia) and Specific gravity
4	Hammerschmidt (1934)	Temperature (°F)	Pressure (psia)
5	This Work (2023)	Temperature (°F)	Pressure (psia), Specific gravity and composition of methane

The popular measure and method of validation was the average deviation (AD) and percentage average absolute deviation (AAD) method and it is given in Equation (20) and Equation (21).

$$AD = \left(\frac{1}{n_p}\right)\sum\left(\frac{T_{pred}-T_{obs}}{T_{obs}}\right) \quad (20)$$

$$AAD = 100\left(\frac{1}{n_p}\right)\sum\left|\frac{T_{pred}-T_{obs}}{T_{obs}}\right| \quad (21)$$

Where;

T_{pred} is the temperature of the hydrate formation condition predicted by the model.

T_{obs} is the observed temperature.

n_p is the number of data points.

The difference between these two equations is the inclusion of the absolute value in Equation (20). A small average deviation (AD) and a relatively large percentage average absolute deviation (AAD) indicates that the errors tend to cancel out (where some are positive and some are negative) and less bias in the prediction. If both the average deviation (AD) and percentage average absolute deviation (AAD) are large indicating that there is a bias in the prediction – a tendency to either over predict (if the AD is negative) or under predict (if the AD is positive) the experimental data.

5. Results

The results and all the analysis including performance and validation associated with the results obtained in this study are presented below.

5.1. The Nonlinear Empirical Model

The functionality of the model based on the degree and functional relationship of the variables, is rewritten as:

$$T = f(Log, polynomila, others)$$

Equation (13) shows that a nonlinear empirical model exists, and the functions involved in the model are logarithmic, polynomial and other functions. The model was developed and tested on 95% confidence level, indicating that 5% error is allowed. The developed nonlinear empirical model is presented in Equation (22).

$$T = a\ln\left(y_{C1}P\gamma_g^b\right) + cP\gamma_g^3 + dP\left(\frac{y_{C1}}{\gamma_g}\right)^e + f \qquad (22)$$

Where;

T is the gas hydrate formation temperature (^oF)

y_{C1} is the composition of methane in the natural gas composition (mole fraction)

P is the hydrate formation pressure (psia)

γ_g is the natural gas specific gravity (dimensionless)

The values of the coefficients a, b, c, d, e and f in the nonlinear empirical model are given in Table 4.

Table 4. *Values of Coefficients in the Nonlinear Empirical Model.*

Coefficient	Estimate
a	-12.2864
b	-0.6085
c	-0.0005
d	-0.0001
e	4.1187
f	169.8531

The statistical parameters of the coefficients in nonlinear model were evaluated to determine the performance of the model. Table 5 present the standard error, t-value, p-value and lower and upper confidence limit for each of the coefficients. The standard errors for the coefficients are minimal and within acceptable limit for a better performance of the model. The p-values also shows similar characteristics as that of the standard error. The lower and upper confidence limit falls withing the 95% confidence interval test, which also indicates a better performance of the model.

The statistical test analysis for the nonlinear empirical model shows that the logarithmic, polynomial functions are best for the predicting hydrate formation temperature for natural gas in gas pipelines. It also in agreement of existing nonlinear empirical models for predicting hydrate formation temperature. These models include the Towler and Mokhatab [39] model, which contains logarithmic function only; Hammerschmidt [9] model, which contains polynomial function only; Naseer and Brandsatter [28] model which contains logarithmic function only; and Motiee [25] model, which contains both logarithmic function and polynomial function.

Table 5. *Statistical parameters for the Nonlinear Empirical model.*

	Est	St - error	t-value - df = 77	p-value	Lo con lm	Up. Con lm.
aa	-12.2864	1.26361	-9.72323	0.000000	-14.8026	-9.7702
kk	-0.6085	0.47447	-1.28257	0.203491	-1.5533	0.3362
bb	-0.0005	0.00011	-4.40938	0.000033	-0.0007	-0.0003
ee	-0.0001	0.00016	-0.49854	0.619523	-0.0004	0.0002
ii	4.1187	2.91197	1.41440	0.161274	-1.6798	9.9172
dd	169.8531	10.86422	15.63418	0.000000	148.2197	191.4865

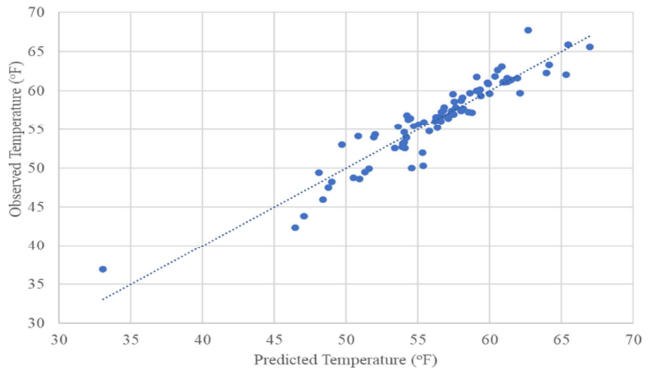

Figure 4. *Measurement Plot for Observed and Predicted Hydrate formation Temperature.*

The nonlinear empirical model was tested to predict the hydrate formation temperature of natural gas and the results compared with the observed data for the natural gas. Figure 4. is cross plot of the observed data points and the predicted date points. The cross-plot measures the closeness of the observed data points and the predicted data points. The closeness is the error between the observed and the predicted points, which was used to determine the correlation coefficient of the cross-plot. The correlation is the R-square and it determines the degree of closeness and between the observed data point and the predicted data points. The R-squared determine was 0.94, which is close to 1, indicating a better gas hydrate formation temperature prediction of the nonlinear empirical model.

The difference between the observed data points and the predicted data points is the error (residuals) of each data point. The errors were plotted against observed data points and predicted data points in Figure 5. and Figure 6. Both plots are scattered plots and it determine how scattered are the errors (Residual) around the observed temperature and predicted temperature. More of the observed temperature values are scattered within + 2 to - 2 of the residual data points, which is also an indication of the better performance of the nonlinear model. The scattered plot of the residual and

the predicted temperature shows similarly characteristics as that of the residuals and the observed temperature.

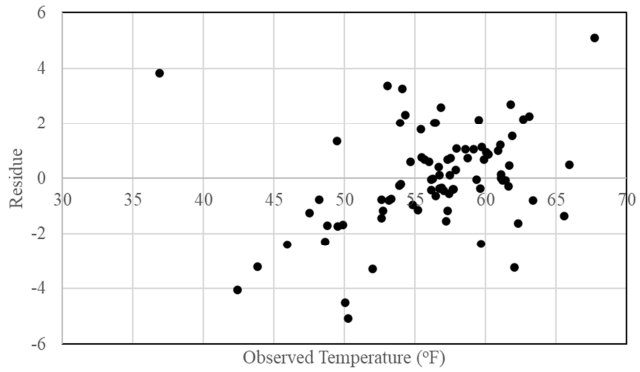

Figure 5. *Scatter Plot of Residual Against Observed Hydrate Formation Temperature.*

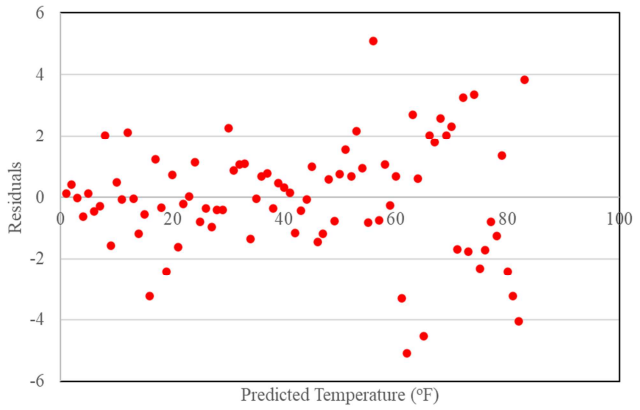

Figure 6. *Scatter Plot of Residual against Predicted Hydrate Formation Temperature.*

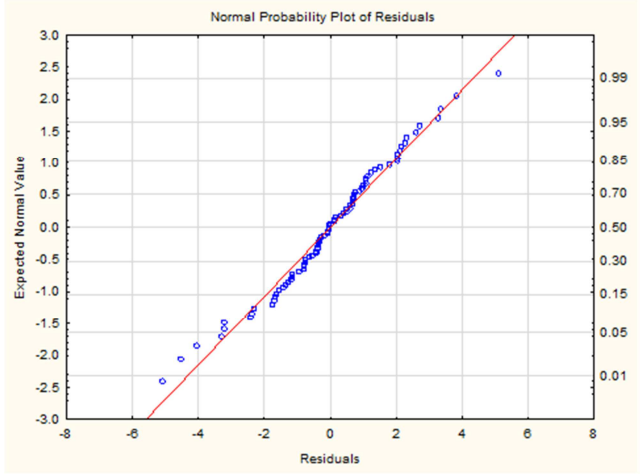

Figure 7. *Normal Probability Plot for Residuals with Expected Normal Value.*

To further analysis the error (residual) data points, the residual data points were fitted with normal probability distribution function (PDF) and the expected normal values were obtained and their probability. Figure 7. is a normal probability plot of residuals, and it shows that majority of the expected normal value and the probability are scattered within the +2 to -2 residual data points, with probability as high as 0.95 (95%).

5.2. Validation of the Empirical Model

The performance of the model has been tested based on the estimation of the statistical parameters that determine prediction capability of the nonlinear empirical model. thereafter, the model was validated with existing model of the same type but with different mathematical function and number of independent variables. The selected models for the validation are: Towler and Mokhatab [39]; Hammerschmidt [9]; Naseer and Brandsatter [28]; and Motiee [25].

The Towler and Mokhatab [39] was validated with the nonlinear empirical model developed in this study, Figure 8. The Towler and Mokhatab [39] model developed in this study predicted temperature as low as 48°F (8.90C) and as high as 120°F (48.9°C), for gas specific range of 0.598 to 1.397 and methane composition of 0.459 to 0.964 mole fraction, indicating that hydrate formation is possible within these temperature range. However, the developed model can predict gas hydrate formation temperature to 69°F (20.56°C).

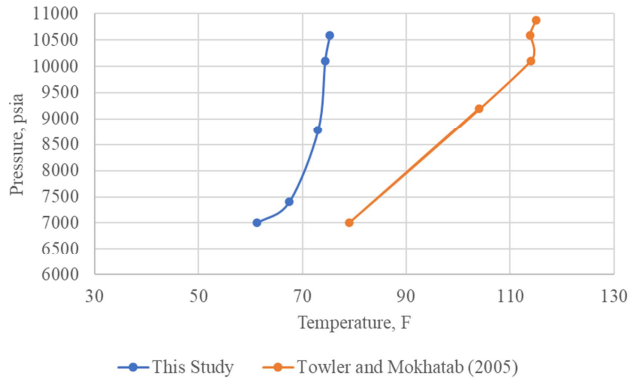

Figure 8. *Predicted and Observed Temperature for Towler-Mokhatab and this Work Models.*

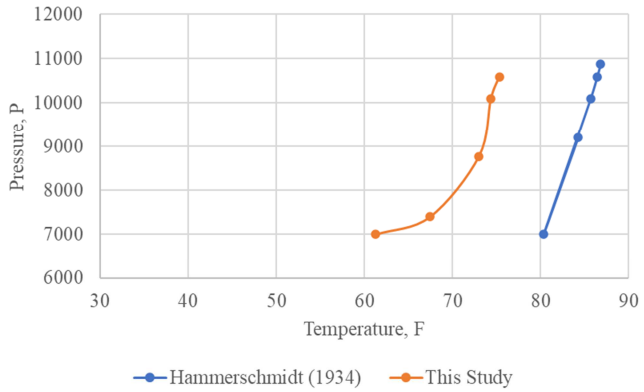

Figure 9. *Predicted and Observed Temperature for Hammerschmidt and this Work Model.*

The Hammerschmidt [9] model was also validated with the nonlinear empirical model developed in this study, Figure 9. Both nonlinear empirical models can predict temperature as low as 48°F (8.90C) and as high as 89°F (31.67°C) for gas specific range of 0.598 to 1.397 and methane composition of

0.459 to 0.964 mole fraction. However, within the gas specific gravity range, the Hammerschmidt [9] model temperature prediction is within 80°F (26.67°C) to 88°F (31.11°C), whereas the developed model in this study can predict gas hydrate formation temperature as low as 48°F (8.9°C) and as high 69°F (20.56°C).

The empirical model validation continues with Naseer and Brandsatter [28]. The nonlinear empirical model developed in this study was validated with the nonlinear empirical model of Naseer and Brandsatter [28], Figure 10. Both nonlinear empirical models can predict temperature as low as 48°F (8.90C) and as high as 89°F (31.67°C) for gas specific range of 0.598 to 1.397 and methane composition of 0.459 to 0.964 mole fraction. However, Naseer and Brandsatter [28] model prediction is within 88°F (31.1°C) and 96°F (35.56°C), whereas the developed nonlinear empirical model can predict gas hydrate temperature as low as 48°F (8.9°C) within the gas specific gravity and methane composition in the natura gas.

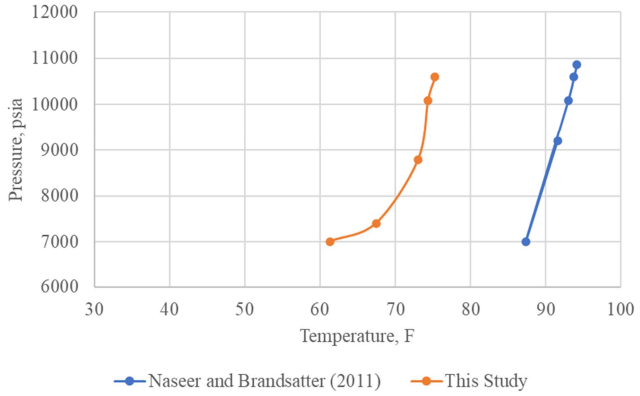

Figure 10. *Predicted and Observed Temperature for Naseer-Brandsatter and this Work Models.*

Finally, the Motiee [25] nonlinear empirical model was validated with the nonlinear empirical model developed in this work, Figure 11. The prediction temperature range for the Motiee [25] model was wider than that of Towler and Mokhatab [39]; Hammerschmidt [9] and Naseer and Brandsatter [28], with very low gas hydrate formation temperature of 34.81°F (1.56°C) and high gas hydrate formation temperature of 84.5°F (29.17°C). However, the gas hydrate formation temperature prediction range of the nonlinear model developed in this study is within the predicted hydrate formation temperature of Motiee [25], indicating that the developed model behaviour is similar to that of Motiee [25]. This is because, the developed model and Motiee [25] model have some similarity: both models as nonlinear; both models have logarithmic function; and both models have polynomial function.

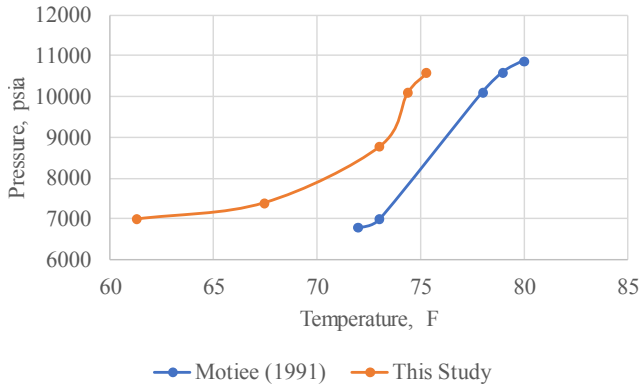

Figure 11. *Predicted and Observed Temperature for Motiee and this Work Models.*

The validation of the developed empirical model with existing models continues with estimation of the percentage absolute average deviation statistical parameter (%AAD). Table 6. present the numerical values of the percentage absolute average deviation statistical parameter for each model. The %AAD of the developed model was 25.74% and that of Motiee [25] which it compares very well has %AAD of 29.79%. Hammerschmidt [9] has the lowest %AAD of 10.6%, but its prediction temperature range 80°F (26.67°C) to 88°F (31.11°C), for the given gas specific gravity and methane composition is very small. The reason for the small temperature range is functional relationship of the model, which was only polynomial in nature. Naseer and Brandsatter [28] has the next lower %AAD of 17.29% and its prediction temperature range was 88°F (31.1°C) and 96°F (35.56°C), indicating the functionality of the model, which was only logarithmic function. Towler and Mokahtab [39] which follows next with %AAD of 23.22% has only logarithmic function in its model. The developed model and Motiee [25] model have both logarithmic function and polynomial function, hence their prediction capability.

Table 6*. Percentage Absolute Average Deviation for the Different Models.*

	Naseer & Brandsatter, 2011	Towler & Mokhatab, 2005	Motiee 1991	Hammerschmidt 1934	This Study
	0.331817	0.0185339	0.1722738	0.2252028	0.2816335
	0.2290153	0.4933317	0.468987	0.1330489	0.2618601
	0.2003984	0.470998	0.5506015	0.1058906	0.259685
	0.0763204	0.02755	0.0406554	0.010168	0.2453544
	0.0269471	0.1507007	0.2571741	0.055717	0.2384045
% AAD	17.289963	23.222285	29.793836	10.600546	25.738749

6. Discussion

The formation of the natural gas hydrates in gaseous regions in gas pipeline, affects fluid velocities. This attributed to the reduced cross-sectional area (due to the hydrate formation) imposed upon the flowing fluid. In other words, the gas hydrate formed at the inlet of the geometry, at

the bottom of the pipe and in some parts of the gas pipelines contribute to gas velocity loss. Predicting the onset of hydrate in gas pipelines is a solution that will avoid gas velocity loss due to hydrate formation. Several models exist to predicts the hydrate formation condition of temperature and pressure in the gas pipelines. These models are nonlinear in nature. However, in this study, a nonlinear empirical model containing logarithmic function and polynomial function was developed. The model prediction of gas hydrate formation temperature was well in agreement with existing models that contains logarithmic and polynomial function. For example, the Motiee [25] nonlinear empirical function. Although, the Motiee [25] empirical model, did not consider the composition of the component of the gas, which was considered in the developed model, the prediction of this model and the developed model in this study covers wide range of gas hydrate formation temperature for wide range of gas specific gravity. In addition, the model was able to predict very low gas hydrate temperature, which other model could not, as their hydrate formation temperature prediction covers a small range of temperature. These models contain either only logarithmic function or polynomial function.

7. Conclusions

One of the most important problems in the gas pipeline transportation to be considered during operations is natural gas hydrate formation, which causes excess pressure drop along the gas pipeline. Overtime, it ultimately leads to the pipeline plugging. Natural gas hydrate formation is predominant in downstream operation sector of the oil and gas industry, causing a lot of production problems. Hence, the need to know and understand how to predict the hydrate formation conditions of temperature and pressure.

Natural gas transportation in gas pipeline operations can be safe if the temperature of the gas pipeline terrain through which the gas is transported is high, above the hydrate formation condition of temperature. On the other hand, it can be damaging, if the terrain temperature is very low, below the hydrate formation temperature. Therefore, predicting the condition of the onset of gas hydrate formation is important to avoid flow assurance issues. This was the focus of this study, which seeks to develop an empirical nonlinear model to predict the temperature at which natural gas hydrate will form when transported through gas pipelines. The composition and component of the natural gas include both sweet and sour gas. This is to increase the scope of the applicability of the model in predicting gas hydrate formation temperature. In addition, the three input parameters (pressure, gas specific gravity and methane composition) were used instead of the one parameter (pressure) or two parameters (pressure and gas specific gravity) used by existing models to predict the hydrate formation temperature. After series of simulation and modelling with different mathematical functions, a nonlinear model containing logarithmic function and polynomial function was developed, which fits very well with R-square above 0.9. the need for the nonlinear model was to enhance the capability of the model in predicting natural gas hydrate formation temperature. The mean square error (MSE) and the R-square factors indicate that the model performs very well in predicting gas hydrate formation conditions. To test the reliability of the developed model, it was validated with four different existing models. The calculated percentage absolute average deviation shows that it was less than other models with one or two inputs.

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References

[1] Abdulaga G. Ijabika S. Javida D. (2022), Building a Mathematical Model to Prevent Hydrate Formation in Gas Pipelines. Physics and Engineering. DOI: 10.21303/2461-4262.2022.002541.

[2] Amir H. Mohammadi, Dominique Richon (2010). "Gas Hydrate phase Equation in the presence of Ethylene Glycol or Methanol Aqueous solution, Industrial and Engineering Chemistry Research, Vol 49, No. 18, pp. 8865-8869.

[3] Ahmed A. E., & Ali M. E., (1998), A New Correlation for Predicting Hydrate Formation Conditions For Various Gas Mixtures and Inhibitors, College of Engineering and Petroleum, University of Kuwait, Kuwait.

[4] Balakin B. V., Lo S., Kosinski P., Hoffman A. C., (2016), Modelling Agglomeration and Deposition of Gas Hydrate in Industrial Pipelines with Combined CFD-PBM Technique, Chemical Engineering Science, 153, 45-57.

[5] Carson, D. B. Katz, D. L. (1942), Natural Gas Hydrates, Trans., AIME 146 150.

[6] Chen, G. J., & Guo, T. M. (1996). A new approach to gas hydrate modelling. Chemical Engineering Journal, 71 (2), 145-151.

[7] Dharmawardhana, P. B. Parrish, W. R. Sloan, E. D. (1980), Experimental thermodynamic parameters for the prediction of natural gas hydrate dissociation conditions, Ind. Eng. Chem. Fundamentals 19 (4), 410 – 414.

[8] Englezos, P. (1992), Computation of the incipient equilibrium carbon dioxide hydrate formation conditions in aqueous electrolyte solutions, Ind. Eng. Chem. Res. 31, 2232–2237.

[9] Frank J., Mark C. and Mark G. (2008), Hydrocarbon Exploration and production. Second Edition, Elsevier UK.

[10] Hammerschmidt, E. G. (1934). Formation of gas hydrates in natural gas transmission lines. Industrial & Engineering Chemistry, 26 (8), 851-855.

[11] Holder G. D., Zetts S. P., Pradhan N. (1988) Rev Chem Eng 5: 1–70.

[12] Inkong K., Rangsunvigit P., Kulprathipanja S., (2016), Effects of Mixed Surfactants on Methane Hydrate Formation and Dissociations, Chemical Engineering Transaction, 52, 151-156, DOI: 10.3303/CET1652026.

[13] Jianwei L. (2021), Research on Formation Prediction Model of Gas Hydrate, 3rd International Conference on Green Energy and Sustainable Development IOP Conf. Series: Earth and Environmental Science 651 (2021) 032088, doi: 10.1088/1755-1315/651/3/032088.

[14] John V T, Papadopoulos K D, Holder K D. A (1985), generalized model forpredicting equilibrium conditions for gas hydrates. AIChE Journal, 31 (2): 252-259.

[15] Katz, D. L. (1945). Prediction of conditions for hydrate formation in natural gases. Trans. AIME, 160 1945 140–144.

[16] Kobayashi, R., Song, K. Y., & Sloan, E. D. (1987). Phase behavior of water/hydrocarbon systems. Petroleum Engineering Handbook.

[17] Lee J. W., Kang S. P., (2013), Formation Behaviours of Mixed Gas Hydrate Including Olefin Compounds, Chemical Engineering Transaction, 32, 1921-1926, DOI: 10.3303/CET13332321.

[18] Lee, M. J. Chen, J. T. (1993), Fluid property prediction with the aid of neural networks, Ind. Eng. Chem. Res. 32, 995–997.

[19] Li, D. Q. Ai, M. Y. Wang Y. B. (2012), Hydrate Accident and Prevention in Sebei-Xining-Lanzhou Gas Pipeline," Oil and Gas Storage and Transportation, vol. 31, no. 4, pp. 267–269, 2012.

[20] Lili Z. Sirui Z. Yaxin M. Fangmei J. and Yue Z. (2021), Natural Gas Hydrate Prediction and Prevention Methods of City Gate Stations. Hindawi Mathematical Problems in Engineering Volume, https://doi.org/10.1155/2021/5977460.

[21] Lorenzo M. D., Aman Z. M., Kozielski K., Norris B. W. E., Johns M. L., May E. F., (2018), Modelling Hydrate Deposition and Sloughing in Gas-Dominant Pipelines, Journal of Chemical Thermodynamics, 117, 81-90.

[22] Makogon, Y. F. (1981), Hydrates of Natural Gas, PennWell, pp. 12–13.

[23] Mann, S. L. McClure, L. M. Poettmann, F. H. Sloan, E. D. (1989), Vapor–Solid Equilibrium Ratios for Structure I and II Natural Gas Hydrates, Proc. 68th Ann. Gas Proc. Assoc. Conv., San Antonio, TX, March 13–14, pp. 60–74.

[24] Mesbah, M. Habibnia, S. Ahmadi S. (2020), Developing a Robust Correlation for Prediction of Sweet and Sour Gas Hydrate Formation Temperature," Petroleum.

[25] Mohammad, R. T. and Ayoub R. K. (2018), Study of Different Models of Prediction of the Simple Gas Hydrates Formation Induction Time and Effect of Different Equations of State on them. Heat and Mass Transfer, Springer-Verlag GmbH Germany, part of Springer Nature. https://doi.org/10.1007/s00231-018-2508-y.

[26] Motiee, M. (1991). Hydrocarbon Process, Int Ed, 70 (7), 98.

[27] Musakaev N. G., Khasanov M. K., Borodin S. L., (2018), The Mathematical Model of Gas Hydrate Deposit Development in Permafrost, International Journal of Heat and Mass Transfer, 118, 455-461.

[28] Nagata, I. Kobayashi, R. (1966), Predictions of Dissociation Pressures of Mixed Gas Hydrates from Data for Hydrates of Pure Gases with Water, Ind. and Eng. Chem. Fundamentals 5 (6), 466 – 469.

[29] Nasser M., Brandstatter W., (2011), Hydrate Formation in Natural Gas Pipelines, Computational Methods in Multiphase Flow VI, WIT PRESS, 261-270.

[30] Heng-Joo, and Donald B. Robinson. (1976) The Measurement and Prediction of Hydrate Formation in Liquid Hydrocarbon-Water Systems. AIChE Vol. 15, 293-298.

[31] Omidi M., Shahsavand A., Share Mohammadi H., (2016), Modelling and Simulation of Hydrate Thermal Dissociation Around Gas Production Pipe from Sub-Oceanic Sediment, Journal of Natural Gas Science and Engineering, 32, 48-58.

[32] Ostergaard, K. K. Tohidi, B. and Danesh, A. (2000), A General Correlation for Predicting the Hydrate-Free Zone of Reservoir Fluids," SPE Production and Facilities, vol. 15, no. 4, pp. 228–233.

[33] Parrish W. R, and Prausnitz J. M. (1972) Ind Eng Chem Des Dev 11: 26–35.

[34] Saeedi Dehghani A. H., Badizad M., (2016), Thermodynamic Modelling of Gas Hydrate Formation in Presence of Thermodynamic Inhibitors with a New Association Equation of State, Fluid Phase Equilibria, 427, 328-339.

[35] Sajjad J. and Leila, V. (2018), Mathematical Modeling of the Gas Hydrate Formation in a 90^{o} Elbow Utilizing CFD Technique. Chemical Engineering Transactions, 70, 2167-2172 DOI: 10.3303/CET1870362.

[36] Shin, W. Park, S. Ro, H. Koh, D. Y. Seol, J. Lee, H (2012), Phase equilibrium measurements and the tuning behavior of new sII clathrate hydrates, J. Chem. Thermodynamics. 44; 20–25.

[37] Sloan, E. D. (1984), Phase Equilibrium of Natural Gas Hydrates, Proceedings of 63rd GPA Convention, 163–169.

[38] Sun, C. Y. Huang, Q. and Chen, G. J. (2006), Progress of Thermodynamics and Kinetics of Gas Hydrate Formation, Journal of Chemical Industry and Engineering (China), no. 5, pp. 1031–1039.

[39] Tarek A. (2006), Reservoir Engineering Handbook, Third Edition. Elsevier Gulf Publishing House Linacre House, Jordan Hill, Oxford OX2 8DP, UK.

[40] Towler B. F. and Mokhatab S. (2005), Quickly Estimate Hydrate Formation Conditions in Natural Gases. Journal of Hydrocarbon Processing. 84 (4): 61–62.

[41] Jwaals J. V. D. and Platteeuw, J. (1958), Clathrate solutions. Advances in chemical physics, 1-57.