

Investigation of CO₂ Hydrate Formation in the presence of Gasoline

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ABSTRACT

In this research, an experimental investigation was carried out in the existence of gasoline on the Carbon Dioxide hydrate. This was done to replicate or Understanding the development of gas hydrates in multi-phase transmission pipelines. The experiments are conducted in a Rocking cell Gas hydrate reactor, and thermodynamic equilibrium conditions are determined. The tests were performed with Deionized water, Carbon dioxide gas as a pure system and Gasoline, Deionized Water, and Carbon dioxide Gas as a multiphase system. The performance of the multiphase system displayed an inhibition effect when compared to that of a straightforward method. Then, a prediction model is proposed to determine the gas hydrate formation temperature (HFT) and gas hydrate formation pressure (HFP) for a multiphase transmission pipeline. This prediction model is validated based on the experimental data obtained. It was found that the proposed prediction model was in significant compliance with that of the experimental data when CO₂ and deionized water system was used. Similarly, the model that was proposed for the multiphase system was found to be decent as it is within the limit of acceptable error margins. The reason for the inefficiency of the multiphase system was also clearly discussed.

Keywords: *CO₂ hydrate, multiphase flow, temperature for hydrate formation (HFT), pressure for hydrate formation (HFP), statistical regression analysis*

1. INTRODUCTION

Multiphase flow can be characterised as a system of flow containing two or more distinct phases that flow in a mixture or as a mixture simultaneously, and the degree of separation between them is well above the molecular level at a scale. [1]. In many engineering installations, multiphase flow across pipelines is witnessed. In petroleum and chemical manufacturing industries, multiphase flow through pipelines has long been of concern. In the oil & gas industry, multiphase flow is coming across in oil and gas wells, gathering frameworks, numerous funneling frameworks, and critical bits of gear required in processing plants and petrochemical enterprises, for example, boilers, condensers, and separators [2].

In subsea production pipelines, low temperature and high-pressure conditions frequently contribute to the development of gas hydrates, causing blockages and affecting the safety of transmission. In 1810, Sir Humphrey Davy described gas or clathrate hydrates preliminarily.

They are solid compounds containing polyhedral water cavities that clathrate molecules of gas [3]. They are also known as combustible Ice. Industrially, the removal of gas hydrates is important since the presence of them in flowlines poses high commercial losses and environmental hazards, as well as possible safety risks to exploration and transmission workers. [4]. In multiphase flowlines containing gas in major volume in the flow, the principle of gas hydrate development is shown in Figure 1. The depiction of gas hydrate progress at different steps is shown when a multiphase system with gas having the highest volume is observed. They are also of technological significance in separation, fuel transport, and storage processes. [5][6]. They are a possible option for fuel as well. Up until this point, gas hydrates have given a more significant number of issues than answers. The development of gas hydrates in Deepwater production can delay or damage the activities. The gas hydrates prevention, especially for flow assurance, has been a test for a long period, and tending to the presence of gas hydrates in Deepwater production is a noteworthy piece.

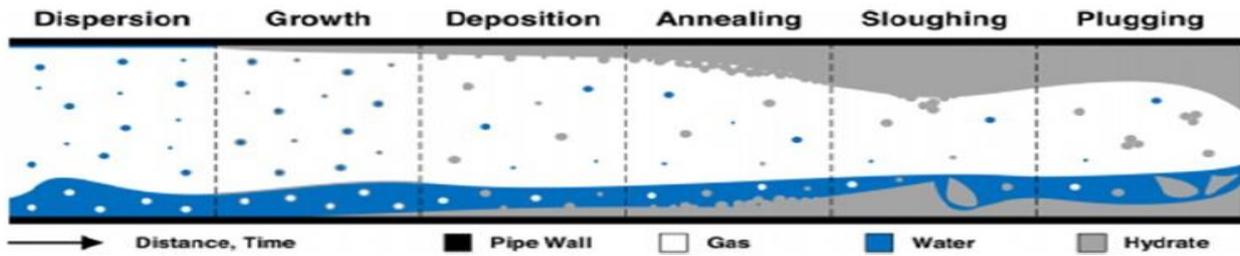


Figure 1 Growth of multiphase gas-dominant transmission pipelines in gas hydrates [7]

Different types and the magnitude of the guest molecule structure result in diverse structures of gas hydrates. The categories of voids that are shaped and the distribution of those voids in a unit cell are used to differentiate the gas hydrates. Currently, there are three common categories of hydrate structures that are known and studied, as displayed in Figure 2. The gas hydrates can be categorized into three

categories based on their structures. The guest molecules define the structure the hydrates tend to form. Natural gas transport is normally done through underground pipelines, and the fortification of gas transport merits our attention. Condensation occurs in the flowlines due to complicated working pressure and temperature changes, contributing to the production of gas hydrates [8][9].

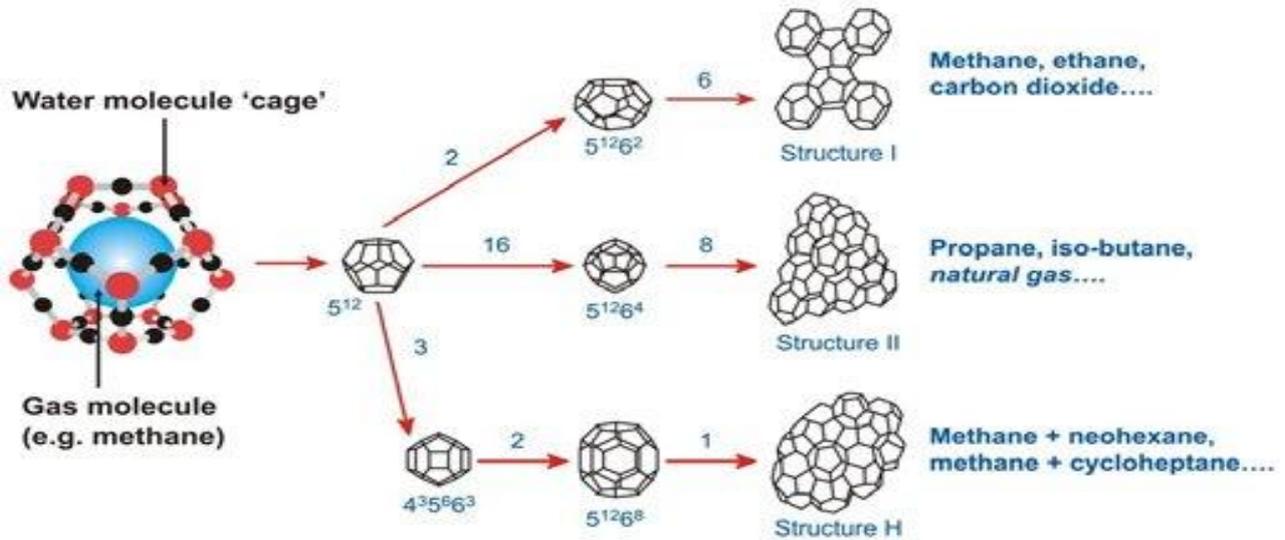


Figure 2 Conventional gas hydrate structures (sI, sII, sH)[10]

The work reported presents the formation of gas hydrates in multi-phase systems under different circumstances of pressure and temperature. Many researchers have developed various kinds of thermodynamic and kinetic models that can forecast the output of gas hydrates and the efficiency of different inhibitors of gas hydrate. Most of them depend on the values of reaction kinetics, mass transfer, heat transfer, fluid flow, etc.[11]. Such research has played a crucial part in hydrate formation and growth analysis. There are various investigations on hydrate formation and flow in gas dominant flowlines to examine the formation of gas hydrates in flowlines and the growth mechanism in the saturated water comprising structure on the pipe wall. However there is limited research focused on explaining the development of hydrates and the extent of obstruction in multiphase gas-dominant flowlines[12] [13]. In the 1980s, the initial argument of the formation of gas hydrates in multiphase flowlines was done. A theoretical study was conducted on gas hydrates in the system

containing multiple phases with the focus in the in-phase behaviour of the formation of hydrate, temperature, pressure and volume of fluid to form gas hydrates in a gas pipeline[14]. Other investigators have proposed that the kinetics of gas hydrates are also influenced by flow parameters such as velocity and fuel discharge in the pipelines. In a research on the influence of different flow velocities varying from 0-5 m/sec on the formation of gas hydrate proved that higher velocity results in quicker blockage of the flowlines due to hydrates [15]. In addition, research was also conducted on the effects of different flow regimes in multiphase flows. [16]. Study of the inhibition of kinetic gas hydrate using economical surfactants, trichlorofluoromethane (CC13F) in water-in-oil blends [17]. Recently research has become more valiant due to the rise in simulation advancements and software, and the estimation of gas hydrates by theoretical modelling has improved. To estimate the particle deposition on the walls of the flow lines due to gas hydrate formation by CFD, a

prediction model has been developed.[18]. In order to experimentally find the phase behaviour environments of gas hydrates in the flowlines containing multiple phases, various investigators also examined blend flowlines with various water cuts. In the work on the formation of gas hydrate in the mixture system containing crude oil with 50-80 percent water cut differences with the Methane, Ethane, and Propane mixed gas system, it was evaluated that the formation of gas hydrate was high at 50 percent water cut as compared to 80 percent water cut[19].

Formation and dissociation of gas hydrates with fuel oils such as Diesel has been carried out in multiphase systems. Hydrodynamic models are also proposed to forecast the formation of gas hydrate in flowlines containing multiple phases, paving the path for comprehensive analysis in multiphase deep-water flowlines[20]. In addition, study on the formation of methane hydrate in dispersed mixtures with oil by experimental and simulation is gained consideration [21]. Investigation on the formation of gas hydrate in flowlines containing multiple phases with black oil or crude oil containing gas dominant or dominant oil system is later carried out vibrantly to evaluate real-time subsea environments and gas hydrate kinetics.[22]. So, these days, with the existence of crude oil and numerous water cuts, the gas dominant multiphase pipelines are the research theme. Intelligent methods of optimization in the prediction of hydrate formation in Deepwater flowlines are popular approaches. To optimise the unidentified variables of established correlation models, the optimization algorithms are malleable. Intelligent Optimization techniques are conspicuous methodologies in the forecast of hydrate formation or occurrence in Deepsea flowlines. The

optimization processes are flexible to enhance the unidentified factors of advanced correlation models.

In this work, a prediction model has been proposed based on statistical regression analysis and is validated with the experimental data. In the pressure range of 2.5-3.5MPa using gas hydrate rocking cell equipment, the gas hydrate formation experiments were performed on Deionized water + CO₂ and Gasoline + CO₂ + Deionized Water system.

2. EXPERIMENTAL

2.1. Material

The constituents utilized for the experimental analysis of multiphase pipelines gas hydrate formation are CO₂ Gas, Gasoline and Deionized water. The CO₂ gas with a concentration of 99.99% molarity is given by Linde Malaysia Sdn. Bhd. Deionized water, which is usable at the research laboratory for gas hydrates, is used. The fuel is obtained from the adjacent accessible filling station. So, this gasoline is a general fuel used in daily life in Automobiles.

2.2. Experimental setup

The illustration of the experimental equipment used for the inquiry is displayed in Figure 3. The experiments are carried out in the 6-reactor rocking cell equipment. The description of the equipment is mentioned in the literature[23]

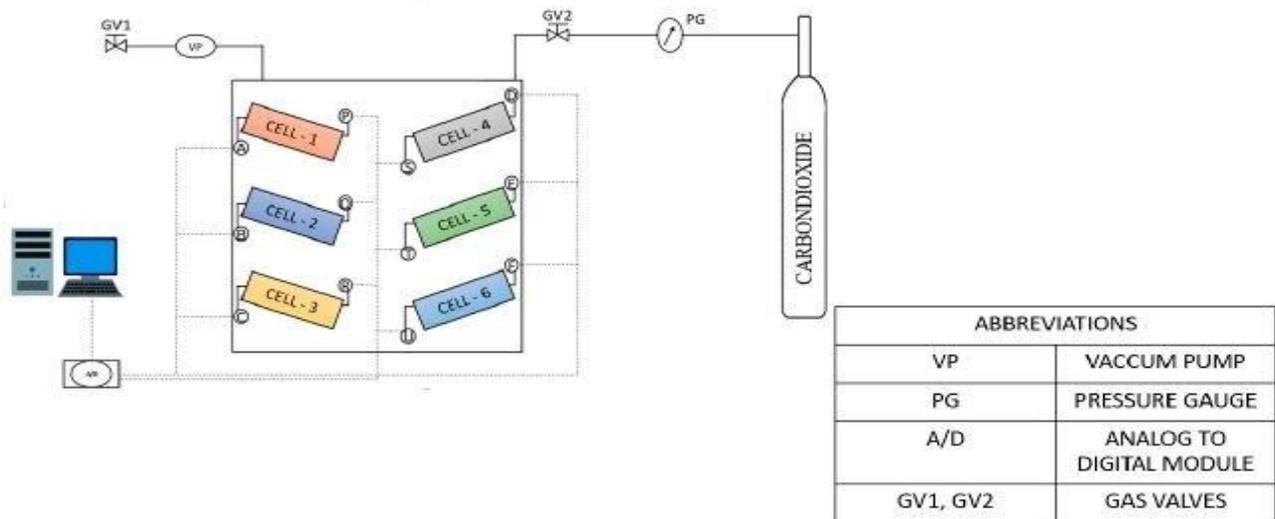


Figure 3 Schematic representation of experimental setup

2.3. Experimental procedure

The experimental procedure is adapted from the literature and is clearly mentioned how the experiments are done and the HLVE curves are drawn[24].

3. RESULTS AND DISCUSSION

3.1. Multiphase system behaviour

The thermodynamic equilibrium conditions were captured with the T- Cycle method and the Hydrate Liquid-Vapor Equilibrium (HLVE) curve has been plotted. The plot is

displayed in Figure 4. From this, it can be drawn that the HLVE curve of the multiphase system has a swing towards the lower temperature at a defined pressure condition when analyzed to that of a pure system with deionized water. This can be due to chemical additives that are added in treated fuel as the fuel sample has been collected from a daily usage location.

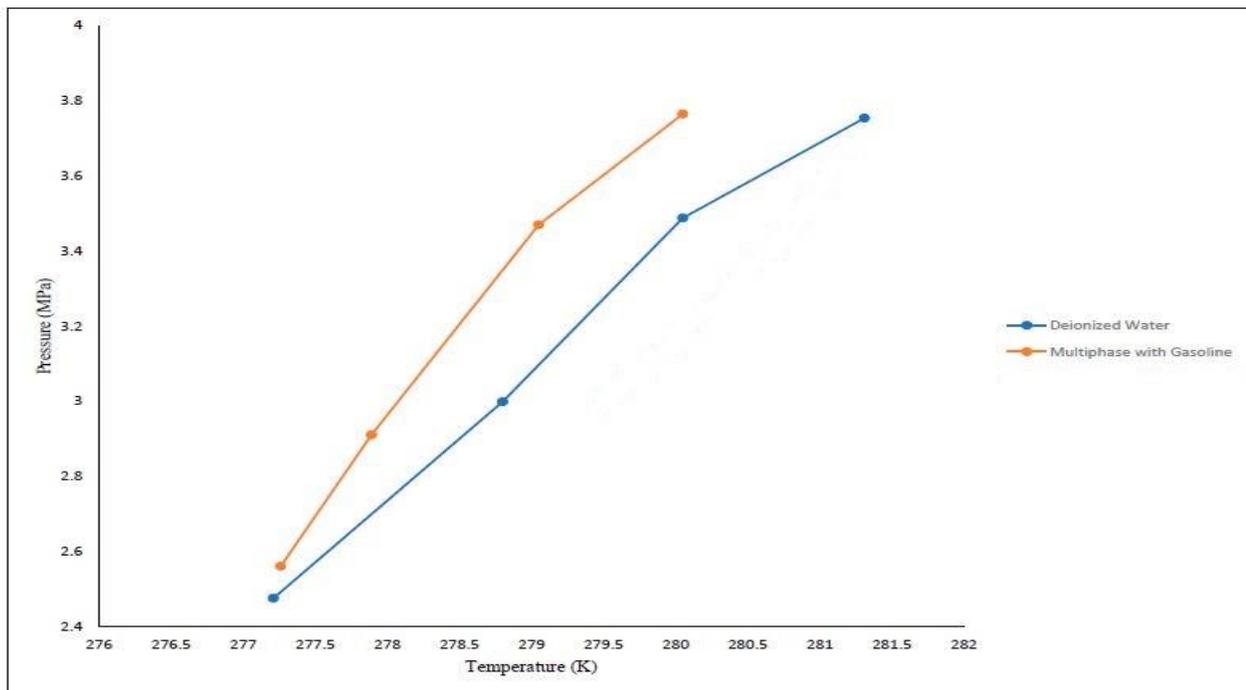


Figure 4 HLVE curves comparison between multiphase system and deionized water

3.2. Statistical regression model

Theoretically, reliable statistical regression investigation is also performed for the estimation of hydrate formation temperature (HFT) and hydrate formation pressure (HFP). A validation model was built based on the experimental results on the basis of the Optimization process that assists in the calculation of HFT and HFP. The eventual R2 values are obtained, and to show the critical points of each system, the most important HFT and HFP are established. The regression investigation data of deionized water are presented in Table 1 and Table 2.

Table 1 Regression analysis of deionized water

REGRESSION STATISTICS	
Multiple R	0.989615573
R ²	0.979338983
Adjusted R ²	0.969008474
Standard Error	0.322951006
No. of Observations	4

The regression model estimated 0.979338983 to be the R².

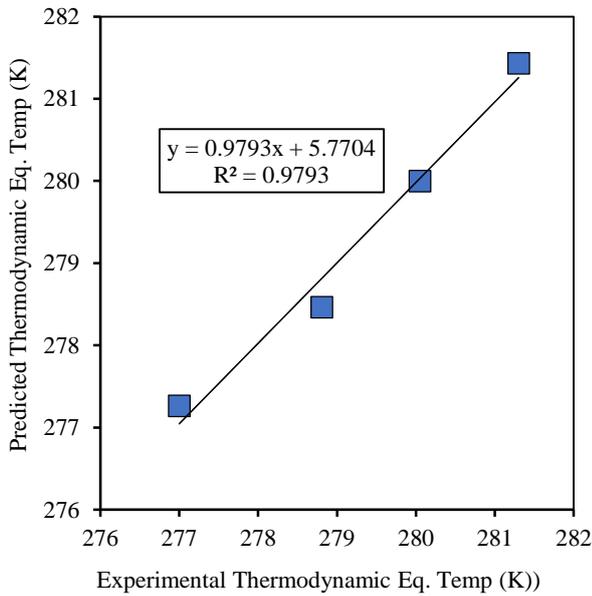


Figure 5 Predicted vs actual of deionized water.

This is also strongly compatible with the modified value of R². The normal regression error is estimated to be 0.322951006. This means the regression model is valid and the statistics predicted are precise [25]. ANOVA statistical analysis is conducted on the basis of the regression results to evaluate the approximation amongst the real vs. the expected data. The graph that shows the real vs. forecast is shown in Figure 5.

Table 2 ANOVA statistics

MODEL	df	Sum of Squares	Mean Square	F	Significant F
Regression	1	9.888	9.888	94.80	0.010
Residual	2	0.209	0.104		
Total	3	10.096052			

The graph shows a linear regression, which suggests that the temperature is influenced or basically the pressure and the temperature are dependent on each other with varying pressure. Similarly, the regression analysis and ANOVA statistical prediction for the gasoline is presented in Table 3 and Table 4.

The regression model projected that the R² is 0.764666918. But, when an adjusted R² value is defined, it tends to show less effectiveness compared to that of the deionized water system. According to [26], the model can be still effective forecast model with R² value > 0.75 and adjusted R² value > 0.5. therefore, this regression study can be utilized to express the HFT and HFP. The typical error for the regression is projected as 0.628907311. This indicates that the model is not so substantial as the error margin is greater.

Table 3 Regression Analysis of Multiphase System

REGRESSION STATISTICS	
Multiple R	0.874452353
R ²	0.764666918
Adjusted R ²	0.529333835
Standard Error	0.628907311
No. of Observations	5

This is due to the variance of concentration of gasoline and water simultaneously on the same experiments. This affects the clear prediction as the error margin is considered of both parameters. ANOVA statistical analysis is conducted on the basis of the regression results to evaluate the error between the real vs. the expected data. The graph that suggests actual vs. predicted is displayed in Figure 6. The plot suggests a polynomial plot.

Table 4 ANOVA statistics

MODEL	df	Sum of Squares	Mean Square	F	Significant F
Regression	2	2.570	1.285	3.249	0.235
Residual	2	0.791	0.396		
Total	4	3.361			

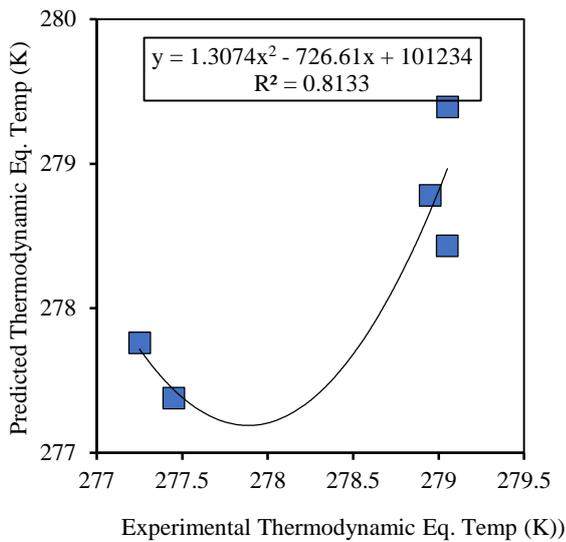


Figure 6 Predicted vs Actual of multiphase system

4. CONCLUSION

In this research, an experimental investigation was carried out on the CO₂ hydrate in the presence of gasoline to replicate and understand the gas hydrate behaviour in multiphase flowlines. It was displayed from the results that the thermodynamic phase behaviour of multiphase pipelines is different from that of the pure system. Also, when gasoline has been included as the new phase, it displayed an inhibition effect. Then, a forecast model has been proposed to determine the gas hydrate formation conditions of pressure and temperature in multiphase Deepwater transmission pipelines. The model is validated by a set of experiments that are performed with a simple system as well as a multiphase system. From this work, it can be concluded that the proposed model is in high accordance with the experimental results of the pure system. Also, from the statistical regression analysis, it was found that the prediction performance is linear. Similarly, the model proposed for the multiphase system was an unacceptable range and can be used for an initial prediction. This is because of the variance of concentration of gasoline and water simultaneously on the same experiments. The regression plot suggests for the multiphase system as polynomial regression. From these results, it can be drawn that the component variation must be singular when developing a prediction model for the better accuracy of the prediction. Also, there is a scope of improvement for the speculation of gas hydrates formation in flowlines containing multiple phases as the regression models display the difference in prediction when an additional phase is included.

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