

# **CORRELATION FOR PREDICTING HYDRATE FORMATION**

by

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Dissertation submitted in partial fulfilment of  
the requirements for the  
Bachelor of Engineering (Hons)  
(Petroleum)

MAY 2015

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# CERTIFICATION OF APPROVAL

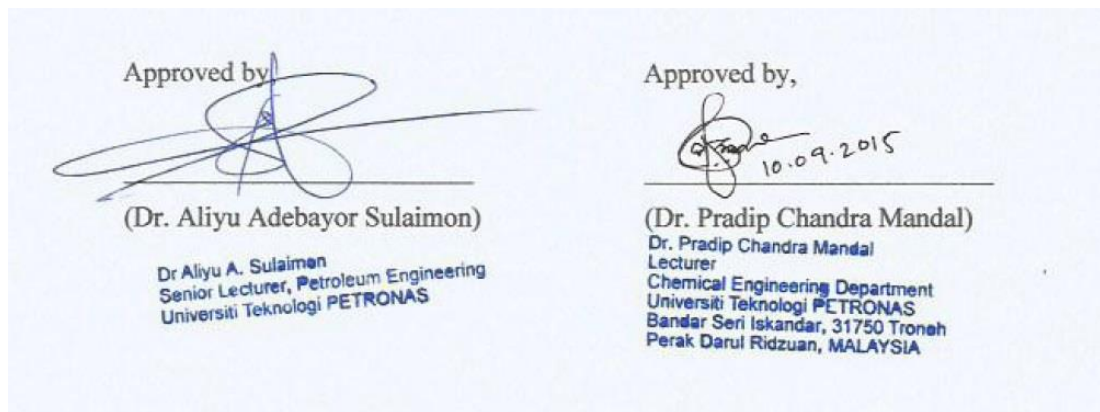
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A project dissertation submitted to the  
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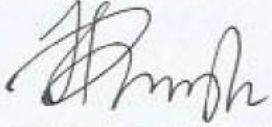
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May 2015

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



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(FATMA JANNA)

## ABSTRACT

One of the common issues occurred with gas production or transmission is the formation of gas hydrates, which can result in an expensive remedial when they plug the oil and gas pipelines. Therefore, knowing the noteworthy conditions at which hydrate gas perform and prevent the hydrate structure to form is a critical deal to manage. Somehow, the most ideal approach to know the hydrate development temperature and pressure is by doing laboratory experiment. Since this practice requires extensive amount of time and money, predicting hydrate development by utilizing correlations is the answer of knowing at which conditions hydrate to form and to prevent it.

There are several methods to develop hydrate formation prediction. The two methods include gas specific gravity and gas compositional. The correlation developed on this study is based on specific gravity method retrieved from literature, where it includes pressure and temperature of hydrate formation as input and output data. The results are then compared with the existing correlations. MATLAB software is utilized to develop the correlations. In the gas compositional method, some existing correlations are reviewed to analyze the performance and the best performance was chosen. The fundamental of gas compositional method is by utilizing K-values, which is the gas constants or equilibrium ratio.

The correlation developed on this study shows the most accurate results as compared to other correlations. Meanwhile, among the existing correlations, Makogon correlation is the closer results to the experimental data. On the gas compositional method, the results showed that Sloan correlation is the most accurate as compared to other correlations to determine K-values and predict hydrate formation pressure at certain temperature.

In conclusion, study comparison of different correlations using specific gravity and gas compositional methods were performed. The results show that computer algorithm can be utilized to develop hydrate correlation and predict at which specific pressure and temperature the hydrate will form.

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## TABLE OF CONTENTS

CERTIFICATION OF APPROVAL ... ..	i
CERTIFICATION OF ORIGINALITY ... ..	ii
ABSTRACT ... ..	iii
ACKNOWLEDGEMENT ... ..	iv
TABLE OF CONTENTS ... ..	v
LIST OF FIGURES ... ..	viii
LIST OF TABLES ... ..	ix
ABBREVIATIONS AND NOMENCLATURE ... ..	x

### CHAPTER ONE: INTRODUCTION

1.1 Background study... ..	1
1.2 Problem statement... ..	2
1.3 Objectives... ..	3
1.4 Scope of Study... ..	3

### CHAPTER TWO: LITERATURE REVIEW AND THEORY

2.1 Hydrates... ..	4
2.1.1 Turbulence... ..	5
2.1.2. Nucleation sites... ..	5
2.1.3. Free water... ..	5
2.2 Gas hydrate compositions... ..	6
2.3 Formation of hydrate ... ..	6
2.4 Determination of the conditions for hydrate to form ... ..	8
2.5 Methods to determine the composition of hydrates ... ..	9
2.6 Correlation... ..	9
2.7 Existing correlation to predict hydrate formation temperature... ..	9
2.7.1 Makogon's correlation... ..	10
2.7.2 Hammerschmidt's correlation... ..	10
2.7.3 Motiee's Correlation ... ..	11
2.7.4 Towler and Mokhatab's correlation ... ..	11
2.7.5 Oestergaard's correlation... ..	12
2.8 Existing correlations on gas compositional study... ..	14

2.8.1	Wilson’s Correlation	...	...	...	...	...	...	15
2.8.2	Whitson and Torp’s Correlation...	...	...	...	...	...	...	16
2.8.3	Sloan’s correlation...	...	...	...	...	...	...	17
2.8.4	Standing’s Correlation...	...	...	...	...	...	...	19
<b>CHAPTER THREE: METHODOLOGY / PROJECT WORK</b>								
3.1	Research Methodology...	...	...	...	...	...	...	20
3.2	Key Milestones	...	...	...	...	...	...	20
3.3	Gantt Chart	...	...	...	...	...	...	22
3.4	Project activities...	...	...	...	...	...	...	24
3.5	Specific gravity method...	...	...	...	...	...	...	24
3.6	Interpretation of specific gravity method chart...	...	...	...	...	...	...	25
3.7	Correlation developed in this study...	...	...	...	...	...	...	26
3.8	Comparison of experimental data with this study	...	...	...	...	...	...	27
3.9	Comparison of different correlations to predict hydrate formation	...	...	...	...	...	...	29
<b>CHAPTER FOUR: RESULTS AND DISCUSSION</b>								
4.1	Results on specific gravity method...	...	...	...	...	...	...	30
4.2	Study comparison of different correlations...	...	...	...	...	...	...	36
4.3	Pressure-Temperature Profile at different specific gravity	...	...	...	...	...	...	41
4.4	Results on gas compositional method	...	...	...	...	...	...	42
<b>CHAPTER FIVE: CONCLUSION AND RECOMMENDATION</b>								
5.1	Conclusion...	...	...	...	...	...	...	48
5.2	Recommendation...	...	...	...	...	...	...	49
REFERENCES	...	....	...	...	...	...	...	50
APPENDIX	...	....	...	...	...	...	...	52
A1.	MATLAB source code of correlation on this study...	...	...	...	...	...	...	52
A2.	MATLAB source code of Oestergaard et al. correlation	...	...	...	...	...	...	53
A3.	MATLAB source code of Makogon to predict pressure	...	...	...	...	...	...	54
A4.	MATLAB source code of Makogon to predict Temperature	...	...	...	...	...	...	54
A5.	MATLAB source code of Hammerschmidt to predict hydrates temperature	...	.....	...	...	...	...	54

A6. MATLAB source code of Hammerschmidt to predict hydrates pressure... ..	54
A7. MATLAB source code of Sloan on gas sample A... ..	55



## LIST OF FIGURES

1.1:	Solid crystalline compound of hydrates formed inside the pipeline	2
1.2:	Removal of hydrates from pipeline during work-over operation	3
2.1:	Hydrate formation conditions criteria	4
2.2:	Process of hydrate formation	7
2.3:	Quadruple point / phase diagram of hydrate	8
3.1:	Key milestones	20
3.2:	Specific gravity method chart	25
3.3:	Phase behavior of water/hydrocarbon system	26
3.4:	Specific gravity method chart developed on this study	28
4.1:	Pressure-temperature profile for gas gravity 0.6	36
4.2:	Pressure-temperature profile for gas gravity 0.7	37
4.3:	Pressure-temperature profile for gas gravity 0.8	38
4.4:	Pressure-temperature profile for gas gravity 0.9	39
4.5:	Pressure-temperature profile for gas gravity 1.0	40
4.6:	Pressure temperature profile of this study	42
4.7:	Correlation result on gas sample A	45
4.8:	Correlation result on gas sample B	47

## LIST OF TABLES

2.1:	Visual coefficients $A_0$ to $A_{17}$ in Sloan's equation	18
3.1:	Gantt Chart of FYP1	22
3.2:	Gantt Chart of FYP2	23
3.3.a:	Correlations of specific gravity method developed on this study	26
3.3.b:	Correlations of specific gravity method developed on this study	26
4.1.a:	Pressure temperature data of different correlations on SG 0.6	31
4.1.b:	Pressure temperature data of different correlations on SG 0.6	31
4.2.a:	Pressure temperature data of different correlations on SG 0.7	32
4.2.b:	Pressure temperature data of different correlations on SG 0.7	32
4.3.a:	Pressure temperature data of different correlations on SG 0.8	33
4.3.b:	Pressure temperature data of different correlations on SG 0.8	33
4.4.a:	Pressure temperature data of different correlations on SG 0.9	34
4.4.b:	Pressure temperature data of different correlations on SG 0.9	34
4.5.a:	Pressure temperature data of different correlations on SG 1.0	35
4.5.b:	Pressure temperature data of different correlations on SG 1.0	35
4.6:	Pressure-temperature data at different specific gravity on this study	41
4.7:	Composition of gas sample A	43
4.8:	Pressure-temperature data of gas sample A	44
4.9:	Composition of gas sample B	45
4.10:	Pressure-temperature data of gas sample B	46

## ABBREVIATIONS AND NOMENCLATURE

$C_1$	= Methane
$C_2$	= Ethane
$C_3$	= Propane
$C_4$	= Butane
$C_{5+}$	= Pentane plus
$CO_2$	= Carbon dioxide
$E_{CO_2}$	= Correction factor due to $CO_2$ gas on Oestergaard's correlation
$E_{N_2}$	= Correction factor due to $N_2$ gas on Oestergaard's correlation
$f_h$	= Hydrate forming components
$F_m$	= Molar ratio between non-hydrate forming and hydrate forming components
$f_{nh}$	= Non-hydrate forming components
FYP	= Final Year Project
$H_2S$	= Hydrogen sulfide
HC	= Hydro Carbon
i- $C_4$	= Isobutene
$K_i$	= K-value or gas constant at component i
n- $C_4$	= Normal-butane
$N_2$	= Nitrogen
P	= Pressure, psia or MPa
$P_{c_i}$	= Critical pressure of component i, psia
Ph	= Hydrate dissociation pressure, psia
$P_{corr}$	= Corrected pressure on Oestergaard's correlation, psia
SG	= Specific Gravity
SSSV	= Sub-surface Safety Valve
T	= Temperature, °F or °R
$T_{c_i}$	= Critical temperature, °F or °R
$\omega_i$	= Acentric factor of component i, dimensionless
$y_i$	= Number of mole fraction of component i in gas / vapor state

# CHAPTER ONE

## INTRODUCTION

### 1.1 Background study

When combined with water, at the specific temperature and pressure, a lot of hydrocarbon components present in natural gas form hydrates. Gas hydrates are common problem occurred in oil and gas industry, specifically in production, processing and transportation of hydrocarbon. The plugging of hydrates cost high amount of extensive of capital to do a remedial action and ensure the flow of hydro carbon inside the pipeline is well maintained. Approximately, single incident can cost \$ 1,000,000 or even more subjective to the inflicted damage. In addition, Carroll (2014) had mentioned an unfortunate event that hydrates occurrence incident were reported also to cause deaths of the people working on the particular incident well, due to mishandling of hydrates.

Natural gas hydrates are solid compound with crystalline structure that composed of water and gas. Sloan and Koh (2008) founded that there are two types of molecules in the hydrate formation, which are water cavities that acts as the “host” of trapped gas molecules, that is known as “guests”. There are certain natural gas that can form hydrates, such as methane, propane, ethane, carbon dioxide and nitrogen. Meanwhile,  $C_{5+}$  gas does not contribute to gas hydrate formation and they are called as non-forming hydrates composition.

The importance of predicting hydrate formation is that whenever hydrate form, the solid crystalline structure that forms like ice will plug the oil and gas pipelines, either during production or transmission of gas. This causes a highly cost problem to the company as for performing a remedial action, it also requires more amount of time. Laboratory experiments are required to determine at which conditions for hydrate to perform. Nevertheless, the lab study can only provide limited data and also the measurement itself is very expensive. Thus, the best practice is to predict hydrates forming condition by using correlation.

## 1.2 Problem statement

Predicting hydrate formation is critical and valuable in the oil and gas industries. It is due to the formation of hydrates in the oil and gas pipelines could cause an extensive amount of capital to perform a remedy of the problem occurred. Available data of which hydrates could develop are only from laboratory experimental measurement, as it requires amount of time and money, a correlation to predict hydrate formation is the best practice to prevent hydrate formation before they plug the oil and gas pipelines.

Figure 1.1 shows hydrate formation inside gas pipeline. It can be observed that hydrate formation in the pipeline causes severe problem in the flow assurance of gas transportation.



Figure 1.1: Solid crystalline compound of hydrates formed inside the pipeline  
(Alberta Analytical Ltd, 2013)

Figure 1.2 also shows hydrate growth inside pipeline, it occupies the whole volume of the pipeline. Flow assurance is at highest risk once this occurred inside the pipeline. Once this occurs, more severe problem can happen, such as explosion in the pipeline, due to high pressure that caused by the hydrate plug, thus remedial action is highly required to remove hydrate plug, even though it costs extensive amount of capital.



Figure 1.2: Removal of hydrates from pipeline during work-over operation (Heriot Watt Institute of Petroleum Engineering, 2015)

### 1.3 Objectives

The objectives of the study are the aim or the purpose of the work or the overall study. Therefore, it should be clearly defined. In this study, the objectives are:

- To develop a new correlation for predicting hydrate formation using experimental data.
- To develop a computer algorithm to predict onset conditions for hydrate formation using gas compositional data.
- To compare the performance of the new correlation with the existing correlations.

### 1.4 Scope of Study

Correlation for predicting hydrate formation includes several studies such as identifying common properties that hydrate will likely to form, comparison study of different existing correlations of predicting hydrate formation pressure and temperature, chemistry of hydrates, natural gas engineering, gas field engineering, and also MATLAB programming language as a method to create problem in order to solve each of different correlation to predict hydrate formation conditions.

## CHAPTER TWO

### LITERATURE REVIEW AND THEORY

#### 2.1 Hydrates

Carroll (2014) mentioned in his book that the first invention of hydrate was made by Sir Humprey Davy. He reported hydrate of chlorine in the early 19<sup>th</sup> century. Prevalently, in his depiction, water entraps the gas particles under suitable temperature and pressure, whereas hydrate favors to form in the low temperature and high pressure environment. Figure 2.1 shows the illustration of the condition criteria for hydrates to form.

As shown in Fig. 2.1, there are certain criteria for hydrates to form:

1. The right combination of hydrates forming condition, which is high pressure and low temperature.
2. Hydrate formers must exist, Fig. 2.1 illustrates this as the gas, hydro carbon components that can form hydrates are including methane, ethane, propane, carbon dioxide, hydrogen sulfide and nitrogen.
3. A sufficient amount of water, the water molecule entraps the gas and form hydrates.

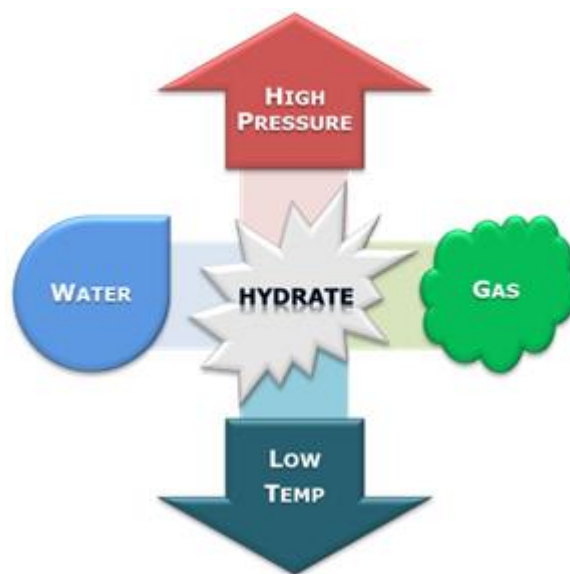


Figure 2.1: Hydrate formation conditions criteria (Gate Inc, 2012)

Carroll (2014) had found out that hydrate formation is caused by the hydrogen bond in water. Hydrogen bond makes the water molecules align in regular pattern. The presence of hydrate forming hydrocarbon components causes the aligned molecules to stabilize and then a solid mixture precipitates.

Other occurrence that improve hydrate formation also found by Carroll (2014):

### **2.1.1 Turbulence**

Turbulence flow can be impacted by high velocity and agitation.

- **High velocity**

Formation of hydrate favors regions in which the fluid velocity is high. This phenomenon causes choke valves particularly susceptible for hydrate to form. Firstly, there is commonly an extensive amount of temperature drop when natural gas is choked through a valve, caused by Joule-Thompson effect. Second, the velocity is high when the fluid flow through the narrowing of the valve.

- **Agitation**

What enhances hydrate formation is also the mixing of different state of fluid in pipeline, process vessel, heat exchanger, etc. The mixing might not be caused by the actual mixer, but due to a tortuous routing of the line instead.

### **2.1.2 Nucleation sites**

Nucleation site is a state where a phase transition is likely to occurred, and in this case is the formation of solid from a fluid phase. Good nucleation site for hydrate to form includes the imperfection in pipeline, a pipeline fitting (elbow, valve, tee, etc) and also a weld spot. Corrosion caused by products, scales, dirt, silts and sand utilized good nucleation as well.

### **2.1.3 Free water**

The existence of free water improves hydrate formation, it also assures that there is plenty of water at which more likely to form plug or clog inside pipeline. Moreover, the interface between water and gas is a good nucleation site for hydrate formation.



Establishment of gas hydrate study is given by Hammerschmidt in 1940. By characterizing the ideal state of hydrate arrangement, four basic means are acquainted with avert hydrate development by keeping the framework outside of the hydrate conditions to form.

1. Expel water from the framework
2. Expand the temperature until above the hydrate temperature
3. Reduce pressure until the framework is out of hydrate pressure formation
4. Infuse inhibitor, for example, Mono Ethylene Glycol (MEG) to move thermodynamic soundness district with the goal that hydrate won't structure in the current temperature and pressure.

## **2.2 Gas hydrate compositions**

Gas hydrate composition is determined by the initial parameters of a hydrate crystal formation, by the compositions of gas and water, and by pressure and temperature. Most accurate way to obtain the composition of hydrates under different conditions can be determined using physical or physicochemical experimental method of study (Makogon, 1997).

Generally hydrate consists of water as the host molecule and hydrocarbon light components that are trapped in the water as the guest molecule. Hydrates that formed without the water as the host molecule are considered not so problematic, because it can easily be removed by utilizing pigging tool (Carroll, 2014). In the other hand, they also are less stable compared to hydrates formed by entrapment of gas hydrate component inside molecule of water.

## **2.3 Formation of hydrate**

Figure 2.2. shows how hydrate form in the flow line. The gas water immiscible fluid forms emulsion. Then, the water molecule forms a cage that traps gas hydrate inside, this process is call shell formation. At the specific hydrate pressure and temperature, more water will forms shell with gas hydrate in it and then agglomeration occurred.

The deposition of these particular hydrate will then form plug and cause severe problem of the flow assurance.

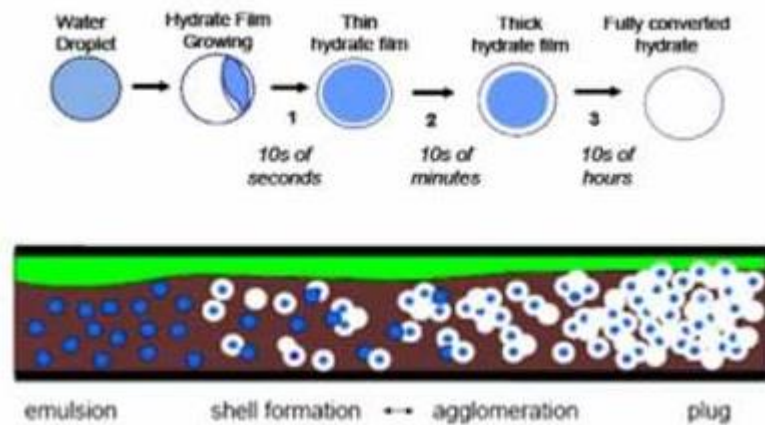


Figure 2.2: Process of hydrate formation (The Pennsylvania State University, 2014)

Formation of hydrate can cause an extensive risk in oil and gas industry, especially the high pressure natural gas transport lines including the connecting lines and manifold systems in subsea transportation of compressed natural gas. Given the importance of safety and reliability in any high pressure natural gas transport framework, it is exceptionally critical to have an accurate analysis of such systems from the safety outlook.

The variation in pressure and temperature of the system is one of the most important factors which lead to the formation of hydrate. These circumstances can also be commonly found in exploration and production systems when fluids flow through various types of equipment along the production tubing or transportation pipelines. Components of upstream oil and gas industry, such as chokes, velocity-controlled subsurface safety valves (SSSV) and fittings (piping segments) can all act as restriction to the flowing fluid causing changes in the flow conditions (Jassim, 2011).

The location at which hydrate forms is usually in the offshore subsea facilities, especially inside the multiphase line where water and gas exist at the same time. Some example of fields where hydrate commonly occurs are Gullfaks field, Asgard field and Kristin field in the North Sea.

## 2.4 Determination of the conditions for hydrate to form

Regularly, the determination of hydrate conditions to form is performed at the stage of designing production technology, processing, and transportation of gas, by the time the development of measures for preventing hydrates to form and removal of the hydrate plugs (Makogon, 1997).

The most rigorous parameters of hydrate formation from a real gas of complex composition usually can be retrieved by experimental work in a defined range of temperature and pressure (Makogon, 1997). Experimental investigations have been performed for almost all of the common components in natural gas (Carroll, 2014). The author noticed that not all components of hydrocarbon can form hydrates. Thus, there are hydrate forming hydrocarbon components and non-hydrate forming hydrocarbon components.

Figure 2.3 presents a typical phase diagram for a mixture of water with a light, pure hydrocarbon (HC), similar to that presented by McCain (1990).

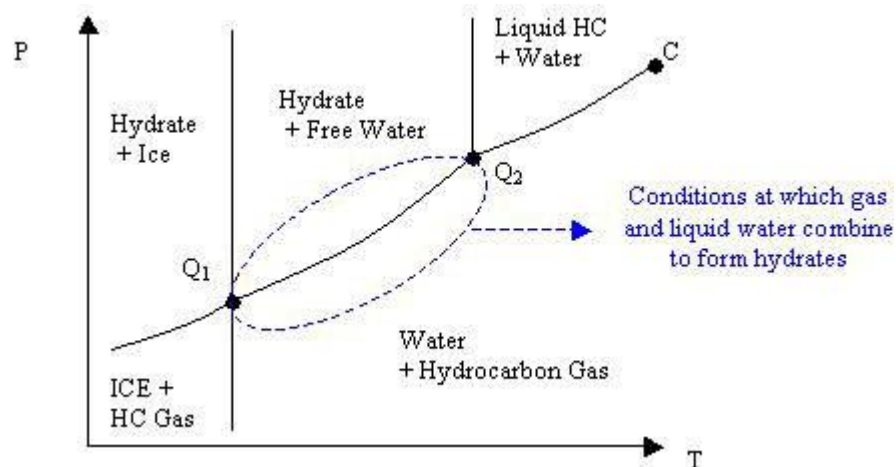


Figure 2.3: Quadruple point / phase diagram of hydrate  
(The Pennsylvania State University, 2014)

## **2.5 Methods to determine the composition of hydrates**

At the early time, researchers used the direct measurement of water to gas ratio of hydrates, whereas many types of solids such as carbon dioxide precipitate in a moderately pure structure, or a form of fixed composition. Gas hydrate composition is variable with temperature, pressure and composition of the associated fluid phases.

The advance of modern microscopic technology enables the direct determination of hydrate state properties. The hydration number can be justified from single crystal or powder using x-ray and neutron diffraction (Sloan and Koh, 2008).

## **2.6 Correlation**

Correlation is a factual measure that demonstrates the degree to which two or more variables vary with each other. For instance, a positive interrelationship shows the degree to which those variables build or reduction in parallel; a negative connection demonstrates the degree to which one variable increments as alternate abatements.

At the point when the vacillation of one variable dependably predicts a comparative variance in another variable, there's regularly an inclination to imagine that implies that the change in one causes the change in the other. Notwithstanding, connection does not suggest causation. There may be, for instance, an obscure variable that impacts both variables comparably (Wigmore, 2013).

## **2.7 Existing correlation to predict hydrate formation temperature**

Most of these correlations use pressure and gas gravity as their input and predict the hydrate formation. Some of the widely used existing correlations are introduced below (Ghayyem, Izadmehr et al., 2014).

### 2.7.1 Makogon's correlation

Makogon (1981) invented a simple correlation to predict hydrate formation pressure by using temperature and specific gravity for paraffin hydrocarbons.

$$\text{Log}P = \beta + 0.0497 (T + kT^2) - 1 \quad \dots \quad \dots \quad \dots \quad (2.1)$$

Where P is the pressure in MPa unit, while T is temperature in °C unit. The equation can be rearranged to become temperature explicit as given below:

$$T = \sqrt{\frac{\log P + 1 - \beta}{0.0497k} + \frac{0.25}{k^2}} - k \quad \dots \quad \dots \quad \dots \quad (2.2)$$

Makogon provided a chart to obtain the values of constant  $\beta$  and k. (Elgibaly and Elkamel 1998) provided simple correlation for the constant  $\beta$  and k.

$$\beta = 2.681 - 3.811 SG + 1.6779 SG^2 \quad \dots \quad \dots \quad \dots \quad (2.3)$$

$$k = -0.006 + 0.011 SG + 0.011 SG^2 \quad \dots \quad \dots \quad \dots \quad (2.4)$$

SG is the specific gravity of gas, which is dimensionless.

### 2.7.2 Hammerschmidt's correlation

Hammerschmidt (1934) presented the following correlation as the results of his experiments which can predict HFT (Hydrate Formation Temperature) only as a function of pressure, in which pressure is stated in psi and temperature is calculated in °F. This correlation describes T as a function of pressure:

$$T = 8.9 P^{0.285} \quad \dots \quad \dots \quad \dots \quad (2.5)$$

Due to its simplicity, this correlation does not provide accurate predictions in average temperatures. However, in contrast with most of the other complicated models it doesn't show large deviations from experimental values in elevated temperature and pressure.

### 2.7.3 Motiee's Correlation

This equation provides a relationship to estimate T as a function of pressure and gas gravity, where the temperature is in °C and pressure is in MPa:

$$T = b_1 + b_2 \log P + b_3 \log P^2 + b_4 SG + b_5 SG^2 + b_6 SG \log P \quad \dots \quad \dots \quad \dots \quad (2.6)$$

where

$$\begin{aligned} b_1 &= -253.24469 \\ b_2 &= 78.99667 \\ b_3 &= -5.352544 \\ b_4 &= 349.473877 \\ b_5 &= -150.854675 \\ b_6 &= 27.604065 \end{aligned}$$

### 2.7.4 Towler and Mokhatab's correlation

Towler and Mokhatab (Carroll, 2014) provided a correlation that is specific for light alkanes and sweet natural gas. In their correlation T is given by:

$$T = 13.47 \ln P + 34.27 \ln SG - 1.675 \ln P \ln SG - 20.35 \quad \dots \quad \dots \quad \dots \quad (2.7)$$

Where T is temperature in Reamur and P is pressure in psia.

### 2.7.5 Oestergaard's correlation

Oestergaard et al (Carroll, 2014) proposed a correlation to predict hydrate pressure. In the correlation, the N<sub>2</sub> and CO<sub>2</sub> components are considered to affect the hydrate dissociation pressure. Thus, he created a factor to consider these two components.

$$f_h = y_{C1} + y_{C2} + y_{C3} + y_{i-C4} + y_{n-C4} \quad \dots \quad \dots \quad \dots \quad (2.8)$$

This is the sum of mole fraction of all hydrate forming hydrocarbons, like methane, ethane, propane and butanes.

$$f_{nh} = y_{C5+} \quad \dots \quad \dots \quad \dots \quad (2.9)$$

f<sub>nh</sub> is the submission of mole fraction of all non-hydrate forming hydrocarbons, including pentanes and heavier components.

$$Fm = \frac{f_{nh}}{f_h} \quad \dots \quad \dots \quad \dots \quad (2.10)$$

Fm is the molar ratio between non-hydrate forming and hydrate forming components.

$$SG_h = \frac{\sum_{i=C1}^{n-C4} y_i M_i}{28.96} \quad \dots \quad \dots \quad \dots \quad (2.11)$$

$$P_h = 0.1450377 \exp \left\{ \left[ \frac{a_1}{(SG_h + a_2)^3} + a_3 Fm + a_4 FM^2 + a_5 \right] T + \frac{a_6}{(SG_h + a_7)^3} + a_8 FM + a_9 FM^2 \right\} \quad \dots \quad \dots \quad \dots \quad (2.12)$$

where

- P<sub>h</sub> = hydrate dissociation pressure, psia
- T = temperature, °R
- SG<sub>h</sub> = Specific gravity of hydrates

The constants of a1 to a9 are provided below:

$a_1 = 2.50744 \times 10^{-3}$	$a_6 = 3.6625 \times 10^{-4}$
$a_2 = 0.46852$	$a_7 = -0.485054$
$a_3 = 1.214644 \times 10^{-2}$	$a_8 = -5.44376$
$a_4 = -4.676111 \times 10^{-4}$	$a_9 = 3.89 \times 10^{-3}$
$a_5 = 0.0720122$	$a_{10} = -29.9351$

In the existence of CO<sub>2</sub> and N<sub>2</sub> gas, Oestergaard made correction factor as follow:

$$E_{CO_2} = 1 + \frac{(b_1 F m + b_2) * y_{CO_2}}{(1 - y_{N_2})} \quad \dots \quad \dots \quad \dots \quad (2.13)$$

$$E_{N_2} = 1 + \frac{(b_3 F m + b_4) * y_{N_2}}{(1 - y_{CO_2})} \quad \dots \quad \dots \quad \dots \quad (2.14)$$

where

$E_{CO_2}$  = correction factor due to CO<sub>2</sub> gas

$E_{N_2}$  = correction factor due to N<sub>2</sub> gas

$y_{CO_2}$  = mole fraction of CO<sub>2</sub>

$y_{N_2}$  = mole fraction of N<sub>2</sub>

$$b_1 = \frac{-2.0943 \times 10^{-4} \times (T/1.8 - 273.15)^3 + 3.809 \times 10^{-3} \times (T/1.8 - 273.15)^2 - 2.42 \times 10^{-2} \times (T/1.8 - 273.15) + 0.423}{\dots \quad \dots \quad \dots} \quad (2.15)$$

$$b_2 = \frac{2.3498 \times 10^{-4} \times (T/1.8 - 273.15)^3 - 2.086 \times 10^{-3} \times (T/1.8 - 273.15)^2 + 1.63 \times 10^{-2} \times (T/1.8 - 273.15) + 0.65}{\dots \quad \dots \quad \dots} \quad (2.16)$$

$$b_3 = \frac{1.1374 \times 10^{-4} \times (T/1.8 - 273.15)^3 + 2.61 \times 10^{-4} \times (T/1.8 - 273.15)^2 + 1.26 \times 10^{-2} \times (T/1.8 - 273.15) + 1.123}{\dots \quad \dots \quad \dots} \quad (2.17)$$

$$b_4 = \frac{4.335 \times 10^{-5} \times (T/1.8 - 273.15)^3 - 7.7 \times 10^{-5} \times (T/1.8 - 273.15)^2 + 4 \times 10^{-3} \times (T/1.8 - 273.15) + 1.048}{\dots \quad \dots \quad \dots} \quad (2.18)$$



Then, the formula to calculate the corrected pressure is

$$P_{corr} = P_h E_{CO_2} E_{N_2} \dots \dots \dots (2.19)$$

Where  $P_{corr}$  is the corrected pressure, the final predicted pressure of hydrate formation.

## 2.8 Existing correlations on gas compositional study

The main method for analyzing correlation of hydrate forming condition using gas composition is the K-value method. Carson and Katz (Ahmed, 2007) proposed that hydrates are the equilibrium-state of solid solutions instead of mixed crystals, therefore, estimate that hydrate forming conditions could be predicted empirically from determined vapor/solid equilibrium ratios.

K is denoted as the equilibrium ratio that represents the number of mole fraction of component  $i$  in the vapor (gas) phase over the amount of mole fraction of component  $i$  in the solid phase (Ahmed, 2007).

The equilibrium ratio is defined as:

$$K_{i(v-s)} = \frac{y_i}{x_{i(s)}} \dots \dots \dots (2.20)$$

where

- $K_{i(v-s)}$  = equilibrium ratio of component  $i$  between vapor and solid
- $y_i$  = the number of mole fraction of component  $i$  in the vapor (gas) phase
- $x_{i(s)}$  = the amount of mole fraction of component  $i$  in the solid phase on a water free basis

The calculation on prediction of the hydrate forming conditions in term of pressure and temperature is related to the dew-point calculation of gas mixtures. In general, gas hydrate will form when the following term is satisfied.

$$\sum_{i=1}^n \frac{y_i}{K_{i(v-S)}} = 1 \quad \dots \quad \dots \quad \dots \quad (2.21)$$

The closer the value of submission of  $y_i$  over  $K_i$ , the more accurate it is.

### 2.8.1 Wilson's Correlation

One of the correlations to calculate K-value is Wilson's Correlation (Ahmed 2007). Wilson had proposed a simplified thermodynamic equation for estimating K-values, in the following form:

$$K_i = \frac{P_{c_i}}{P} \exp \left[ 5.37 (1 + \omega_i) \left( 1 - \frac{T_{c_i}}{T} \right) \right] \quad \dots \quad \dots \quad \dots \quad (2.22)$$

where

- $K_i$  = Equilibrium ration of component i, dimensionless
- $P_{c_i}$  = critical pressure of component i, psia
- $P$  = system pressure, psia
- $T_{c_i}$  = critical temperature of component i, ° R
- $T$  = system temperature, °R
- $\omega_i$  = acentric factor of component i

This correlation generates reasonable values for the equilibrium ratio when applied at low pressure. As hydrates are likely to form at low temperature and high pressure, it is required to utilize a correlation that can generate K-values at high pressure.

## 2.8.2 Whitson and Torp's Correlation

Whitson and Torp (Ahmed, 2007) reformulated Wilson's equation to yield accurate results at higher pressures. Wilson's equation was modified by incorporating the convergence pressure into the correlation, the correlation then becomes:

$$K_i = \left(\frac{P_{c_i}}{P_k}\right)^{A-1} \left(\frac{P_{c_i}}{P}\right) \exp \left[ 5.37 (1 + \omega_i) \left(1 - \frac{T_{c_i}}{T}\right) \right] \quad \dots \quad \dots \quad \dots \quad (2.23)$$

$$A = 1 - \left(\frac{P}{P_k}\right)^{0.7} \quad \dots \quad \dots \quad \dots \quad (2.24)$$

where

- $K_i$  = Equilibrium ration of component i, dimensionless
- $P_{c_i}$  = critical pressure of component i, psig
- $P$  = system pressure, psig
- $T_{c_i}$  = critical temperature of component i, °R
- $T$  = system temperature, °R
- $P_k$  = convergence pressure, psig
- $\omega_i$  = acentric factor of component i

Edmister's equation (Ahmed, 2007) is used to calculate the acentric factor of a gas component:

$$\omega_i = \frac{3 \log\left(\frac{P_{c_i}}{14.7}\right)}{7 \left(\frac{T_{c_i}}{T_{b_i}} - 1\right)} - 1 \quad \dots \quad \dots \quad \dots \quad (2.25)$$

where

- $T_{b_i}$  = normal boiling temperature of component i, °R

The acentric factor “ $\omega$ ” is a concept that was introduced by Pitzer in 1955, and has proven to be very useful in the characterization of substances. It has become a standard for the proper characterization of any single or pure component, along with

other common properties, such as molecular weight, critical temperature, critical pressure, and critical volume.

### 2.8.3 Sloan's correlation

Sloan provides a correlation that involves pressure and temperature parameter to determine the value of K. The Sloan's correlation is as below.

$$\ln(K_{i(v-s)}) = A_0 + A_1 T + A_2 P + \frac{A_3}{T} + \frac{A_4}{P} + A_5 P T + A_6 T^2 + A_7 P^2 + A_8 \frac{P}{T} + A_9 \ln\left(\frac{P}{T}\right) + \frac{A_{10}}{P^2} + A_{11} \frac{T}{P} + A_{12} \frac{T^2}{P} + A_{13} \frac{P}{T^2} + A_{14} \frac{T}{P^3} + A_{15} T^3 + A_{16} \frac{P^3}{T^2} + A_{17} T^4 \quad \dots \quad \dots \quad \dots \quad (2.26)$$

where

- A = constants
- P = pressure, psia
- T = temperature, °F

The constants of Sloan's equation are provided in the Table 2.1, where it presents each constant A for each gas component. It means that the values of A are different to calculate K-values of different gas component.

**Table 2.1: Visual coefficients  $A_0$  to  $A_{17}$  in Sloan's equation**

	<b>CH<sub>4</sub></b>	<b>C<sub>2</sub>H<sub>6</sub></b>	<b>C<sub>3</sub>H<sub>8</sub></b>	<b>i-C<sub>4</sub>H<sub>10</sub></b>	<b>n-C<sub>4</sub>H<sub>10</sub></b>	<b>N<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>H<sub>2</sub>S</b>
<b>A<sub>0</sub></b>	1.63636	6.41934	-7.8499	-2.17137	-37.211	1.77857	9.0242	-4.7071
<b>A<sub>1</sub></b>	0	0	0	0	0.86564	0	0	0.06192
<b>A<sub>2</sub></b>	0	0	0	0	0	-0.00136	0	0
<b>A<sub>3</sub></b>	31.6621	-290.283	47.056	0	732.2	-6.187	-207.033	82.627
<b>A<sub>4</sub></b>	-49.3534	2629.1	0	0	0	0	0	0
<b>A<sub>5</sub></b>	$5.31 \times 10^{-6}$	0	$-1.17 \times 10^{-6}$	0	0	0	$4.66 \times 10^{-5}$	$7.39 \times 10^{-6}$
<b>A<sub>6</sub></b>	0	0	$7.145 \times 10^{-4}$	$1.251 \times 10^{-3}$	0	0	-0.006992	0
<b>A<sub>7</sub></b>	0	$9 \times 10^{-8}$	0	$1 \times 10^{-8}$	$9.37 \times 10^{-6}$	$2.5 \times 10^{-7}$	$2.89 \times 10^{-6}$	0
<b>A<sub>8</sub></b>	0.128525	0.129759	0	0.166097	-1.07657	0	-0.006223	0.240869
<b>A<sub>9</sub></b>	-0.78338	-1.19703	0.12348	-2.75945	0	0	0	-6.4405
<b>A<sub>10</sub></b>	0	-84600	$1.669 \times 10^4$	0	0	0	0	0
<b>A<sub>11</sub></b>	0	-71.0352	0	0	-66.221	0	0	0
<b>A<sub>12</sub></b>	0	0.596404	0.23319	0	0	0	0.27098	0
<b>A<sub>13</sub></b>	-5.3569	-4.7437	0	0	0	0	0	-12.704
<b>A<sub>14</sub></b>	0	$7.82 \times 10^4$	-44800	-884	$9.17 \times 10^5$	$5.87 \times 10^5$	0	0
<b>A<sub>15</sub></b>	$-2.3 \times 10^{-7}$	0	$5.5 \times 10^{-6}$	0	0	0	$8.82 \times 10^{-5}$	$-1.3 \times 10^{-6}$
<b>A<sub>16</sub></b>	$-2 \times 10^{-8}$	0	0	$-5.7 \times 10^{-7}$	$4.98 \times 10^{-6}$	$1 \times 10^{-8}$	$2.25 \times 10^{-6}$	0
<b>A<sub>17</sub></b>	0	0	0	$-1.0 \times 10^{-8}$	$-1.26 \times 10^{-6}$	$1 \times 10^{-7}$	0	0

### 2.8.4 Standing's Correlation

Standing provides a correlation to determine the value of K, as follows.

$$F_i = b_i \left( \frac{1}{T_{bi}} - \frac{1}{T} \right) \quad \dots \quad \dots \quad \dots \quad (2.27)$$

where

$F_i$  : component characterization factor of component i

$T_{bi}$  : normal boiling point of component i, °R

T : temperature of the gas, °R

$$b_i = \frac{\log\left(\frac{P_{ci}}{14.7}\right)}{\left(\frac{1}{T_{bi}} - \frac{1}{T_{ci}}\right)} \quad \dots \quad \dots \quad \dots \quad (2.28)$$

where

$P_{ci}$  : critical pressure of component i, psia

$T_{ci}$  : critical temperature of component i, °R

Finally, to determine the value of K, the following equation is utilized.

$$\log (K_i P) = a + c F_i \quad \dots \quad \dots \quad \dots \quad (2.29)$$

where

$K_i$  : gas constant or K value of component i

The values of a and c can be obtained from the following equations.

$$a = 1.2 + 0.00045 P + 15 \times 10^{-8} P^2 \quad \dots \quad \dots \quad \dots \quad (2.30)$$

$$c = 0.89 - 0.00017 P - 3.5 \times 10^{-8} P^2 \quad \dots \quad \dots \quad \dots \quad (2.31)$$

# CHAPTER THREE

## METHODOLOGY / PROJECT WORK

### 3.1 Research Methodology

In order to achieve the objectives that have been highlighted, a complete methodology has been set up in this project. This methodologies show the procedures and steps on how the project been conducted within the given timeframe.

### 3.2 Key Milestones

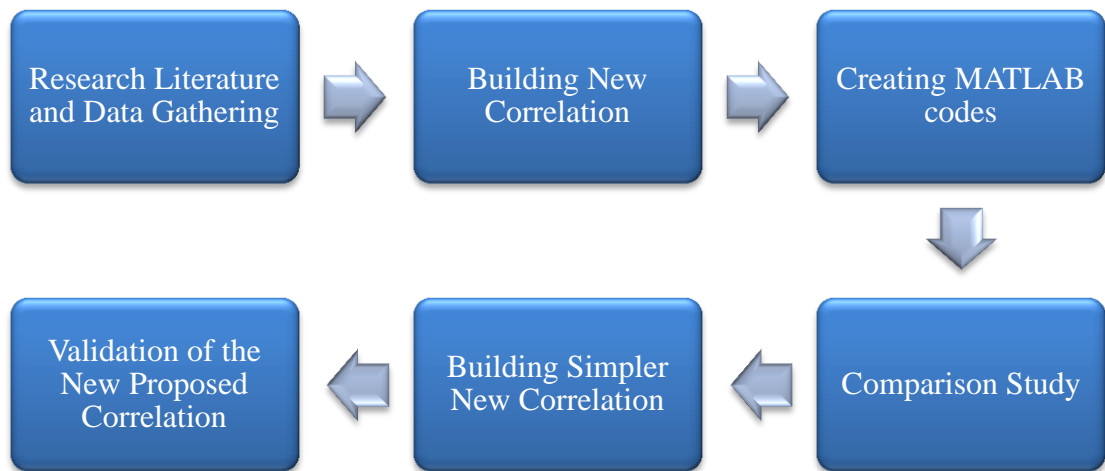


Figure 3.1: Key Milestones

- Research literature  
Literature study of hydrates formation, different correlations to predict hydrates formation pressure and temperature, etc.
- Data gathering from the literatures  
The data retrieved from the literatures are mainly experimental data
- Building and creating new correlation  
Creating new correlation to predict hydrate conditions of pressure and temperature by using computerization of SG method chart.
- Creating MATLAB codes

- ✓ Creating MATLAB codes, testing and running the code to predict hydrate pressure and temperature based on the correlations from computerization of SG method chart.
- ✓ Creating MATLAB codes for current existing correlations, like Makogon and Hammerschmidt to predict hydrate formation pressure and temperature.
- ✓ Creating MATLAB codes on the gas composition method (K-value method)
- Comparison study
  - ✓ Comparison study of computerization of SG method chart with the current existing correlations.
  - ✓ Comparison study of the gas composition method (K-value method) using different correlations to obtain K-value for each gas composition.
- Building simpler correlation
 

After comparing different method of correlations, the author will build a new proposed correlation that is simpler compared to the existing correlation.
- Validation of the new proposed correlation



### 3.3 Gantt Chart

**Table 3.1: Gantt Chart of FYP1**

No	Detail / Week	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Pick an FYP topic													
2	Literature study													
3	Experimental Data Gathering													
4	Preparation and Submission of Extended Proposal													
5	Developing Correlation													
6	Proposal Defence													
7	Comparison of different correlation on specific gravity method													
8	Preparation and submission of draft interim report													
9	Submission of interim report													

**Table 3.2: Gantt Chart of FYP2**

No.	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Literature study	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
2	Data gathering from MATLAB software	■	■	■	■											
3	Comparison of this study with specific gravity method		■	■												
4	Comparison of different trend-lines on existing correlations				■	■	■									
5	Preparation of progress report					■	■	■								
6	Submission of progress report							■								
7	Correlation based on gas compositions							■	■							
8	Phase behavior of gas hydrates with different specific gravity								■	■						
9	Preparation for Pre-SEDEX									■	■					
10	Pre-SEDEX										■					
11	Preparation of final report and technical paper										■	■	■			
12	SEDEX												■			
13	Submission of draft final report and technical paper												■			
14	Viva													■		
15	Submission of project dissertation (hard bound)														■	■

### **3.4 Project activities**

There are several project activities that have been conducted by the author to perform correlation for predicting hydrate forming conditions, in term of pressure and temperature. Somehow, in the current time the project activities are also still in progress, the results are expected to be obtained within 2-3 weeks. The following are the project activities that have been performed, the current progress work are delivered in the subsequence section.

### **3.5 Specific gravity method**

Specific Gravity Method is the most common method being used in oil and gas industry, somehow the practice is still using a graph that the engineers need to read and this practice tends to err in reading the prediction of either temperature or pressure of hydrate formation. Thus, computerization of Specific Gravity Method was the solution to get the prediction of hydrates temperature and pressure.

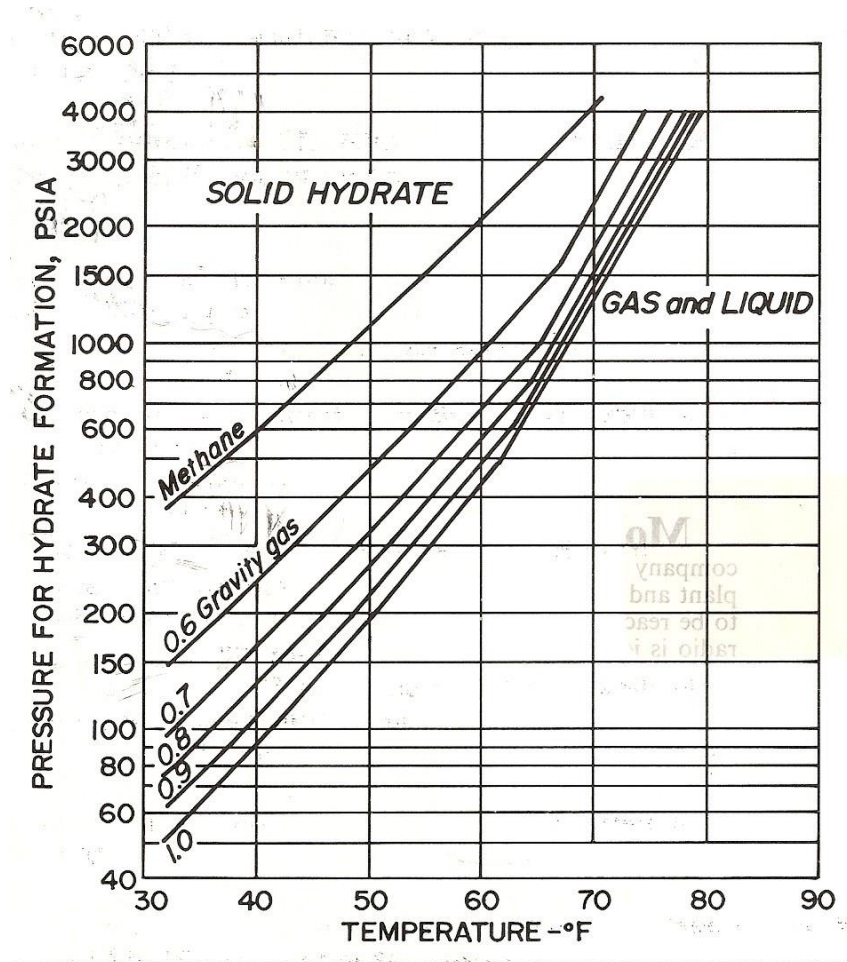


Figure 3.2: Specific gravity method chart (Ahmed, 2007)

### 3.6 Interpretation of specific gravity method chart

Figure 3.3 present how the pressure versus temperature profile of hydrate is described in the specific gravity method chart. At the region below the line, hydrate is not formed, which means that water and gas are immiscible and free. The region at which hydrate forms is located at the above line. The line represents the condition at which hydrate dissociates to release water and gas. The line is the condition at which hydrate will start to form if the pressure increases more.

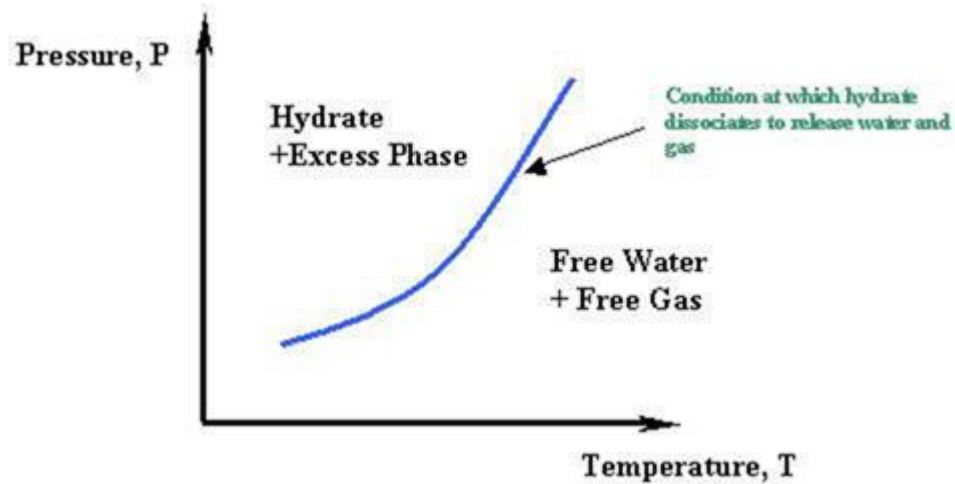


Figure 3.3: Phase behavior of water/hydrocarbon system  
(The Pennsylvania State University, 2014)

The basic interpretation of pressure versus temperature profile is also applied to other results on hydrate correlations. Hydrate forms above the line of hydrate pressure versus temperature profile.

### 3.7 Correlation developed in this study

To develop new correlations from SG Method chart, the author assumed that the lines are straight lines and then three points were picked for each Specific Gravity. By utilizing these points, Microsoft Excel was used to build the correlations. Adding trend-line was the method of showing the correlations of the data points.

**Table 3.3.a: Correlations of specific gravity method developed on this study**

SG	Correlation	Condition
<b>0.6</b>	$P = 16.752 e^{0.0679T}$	Temperature $\leq 66.9^{\circ}\text{F}$
<b>0.7</b>	$P = 9.6466 e^{0.0720T}$	Temperature $\leq 64.5^{\circ}\text{F}$
<b>0.8</b>	$P = 7.2681 e^{0.0738T}$	Temperature $\leq 63.7^{\circ}\text{F}$
<b>0.9</b>	$P = 5.2498 e^{0.0762T}$	Temperature $\leq 62.2^{\circ}\text{F}$
<b>1.0</b>	$P = 3.9293 e^{0.0787T}$	Temperature $\leq 61.5^{\circ}\text{F}$

**Table 3.3.b: Correlations of specific gravity method developed on this study**

<b>SG</b>	<b>Correlation</b>	<b>Condition</b>
<b>0.6</b>	$P = 0.4646 e^{0.1215T}$	Temperature > 66.9°F
<b>0.7</b>	$P = 0.4200 e^{0.1205T}$	Temperature > 64.5°F
<b>0.8</b>	$P = 0.4027 e^{0.1192T}$	Temperature > 63.7°F
<b>0.9</b>	$P = 0.4119 e^{0.1170T}$	Temperature > 62.2°F
<b>1.0</b>	$P = 0.3608 e^{0.1175T}$	Temperature > 61.5°F

Where

- SG = Specific gravity
- P = Hydrate formation pressure (psia)
- T = Hydrate formation temperature (°F)

These correlations were then transferred into MATLAB codes. Then, they were compared with the experimental data obtained from the literature. The consecutive steps of the project were to build the MATLAB codes of the existing correlations reviewed in literature review and then compared with the computerized SG method chart. The source codes of MATLAB of all correlations are provided in the appendices.

### **3.8 Comparison of experimental data with this study**

Figure 6 shows the chart of pressure predicted by using this study correlation. By utilizing a copy carbon, the author has confirmed that the chart on figure 6 is approaching approximately the same as the Specific Gravity Method Chart. The data points retrieved in the SG chart have below 5% different with the ones in this study.

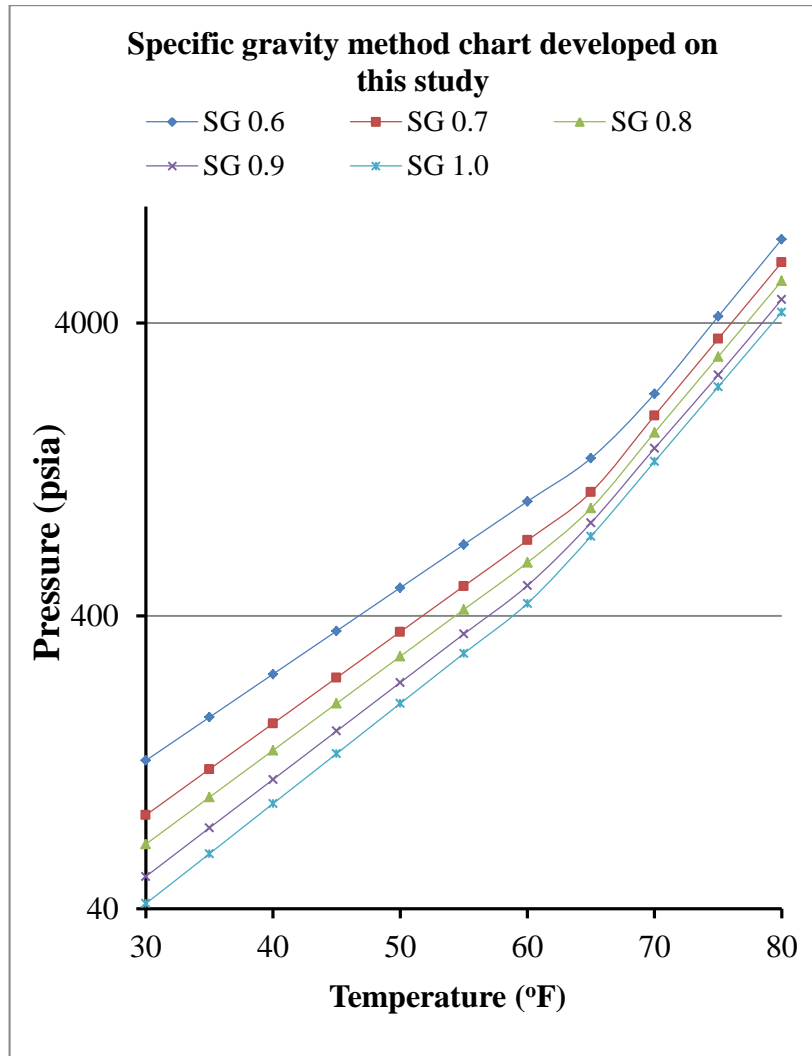


Figure 3.4: Specific gravity method chart developed on this study

### **3.9 Comparison of different correlations to predict hydrate formation**

By utilizing different correlations that were discussed in the literature review section, it could be analyzed how the Specific Gravity Method, correlation developed in this study and other correlations approach each other. This is also to confirm that the study that had been performed has a good outcome.

This activity was performed by building the different existing correlations on MATLAB program. Different data point prediction of temperature with the range of 30 – 80 °F were utilized to obtain the predicted pressure of each respective correlations. The results were then all plotted in the same normal x and y axis.

The specific gravity method used semi-log axis, then the correlation itself was determined to be exponential. While other correlations might not always be exponential, thus to utilize a common condition, normal x and y axis was chosen. All the results from this activity are presented in the chapter four, which is Result and Discussion section.



## **CHAPTER FOUR**

### **RESULTS AND DISCUSSION**

Different correlations were developed and solved using MATLAB program, a range of temperature between 30 – 80 °F ( -1.11 – 26.67 °C) were used to predict the corresponding pressure conditions of hydrate formation. The data generated from each correlation then were utilized to plot the pressure vs temperature prediction of hydrate forming conditions for each common specific gravity of gas: 0.6, 0.7, 0.8, 0.9 and 1.0.

#### **4.1 Results on specific gravity method**

Following tables present the prediction of hydrate pressure condition from experimental data, this study and other correlations that were retrieved from the literature. The experimental data is the base case data that being utilized for comparison with other correlations, including correlation in this study. The data are presented for each specific gravity.

Each correlation was developed using MATLAB software. It can be seen that on each table, the results of Hammerschmidt correlation only has one same predicted pressure for each respective temperature. Because Hammerschmidt correlation is very simple, it does not depend on gas hydrate specific gravity. Thus, the prediction is same for each specific gravity. Somehow, the correlation can still be utilized in this study for comparison, because it depends on pressure and temperature of hydrates formation (equation 2.5).

Makogon and Hammerschmidt's correlation utilize temperature as input data to predict the pressure of formation hydrate. While Berge, Motiee, Towler and Mokhatab's correlations use pressure as the input data to predict temperature. Furthermore, correlation on this study was set to use temperature as input to predict hydrate formation pressure. The prediction of temperature by using hydrate formation pressure is also possible by performing reverse calculation.

**Table 4.1.a: Pressure temperature data of different correlations on SG 0.6**

<b>Temperature (°F)</b>	<b>Pressure (psia)</b>			
	<b>Experiment</b>	<b>This Study</b>	<b>Makogon</b>	<b>Hammer- schmidt</b>
<b>30</b>	130	128.4	127.5	71.1
<b>35</b>	185	180.4	175.3	122.1
<b>40</b>	258	253.3	243	195
<b>45</b>	359	355.7	339.7	294.8
<b>50</b>	510	499.5	478.6	426.7
<b>55</b>	709	701.4	679.8	596.1
<b>60</b>	990	984.9	973.4	809
<b>65</b>	1400	1383	1405	1071.3
<b>70</b>	2300	2294.8	2044.3	1389.4
<b>75</b>	4220	4213	2998.7	1770
<b>80</b>	7800	7734.3	4434.2	2219.8

**Table 4.1.b: Pressure temperature data of different correlations on SG 0.6**

<b>Pressure (psia)</b>	<b>Temperature (°F)</b>		
	<b>Berge</b>	<b>Motiee</b>	<b>Towler and Mokhatab</b>
<b>500</b>	-	34.97	51.17
<b>1000</b>	6.53	52.27	61.1
<b>1500</b>	25.1	61.58	66.91
<b>2000</b>	36.23	67.83	71.03
<b>2500</b>	43.64	72.46	74.23
<b>3000</b>	48.93	76.12	76.84
<b>3500</b>	52.9	79.11	79.05
<b>4000</b>	55.98	81.64	80.96
<b>4500</b>	58.45	83.81	82.65
<b>5000</b>	60.46	85.71	84.16

**Table 4.2.a: Pressure temperature data of different correlations on SG 0.7**

Temperature (°F)	Pressure (psia)			
	Experiment	This Study	Makogon	Hammer- schmidt
30	85	83.6	87.6	71.1
35	123	119.9	120.6	122.1
40	175	171.8	168	195
45	249	246.3	237	294.8
50	358	353	338.6	426.7
55	510	506	489.9	596.1
60	729	725.3	717.6	809
65	1063	1058.9	1064.4	1071.3
70	1937	1934.3	1598.7	1389.4
75	3539	3533.3	2431.4	1770
80	6500	6454.3	3744.6	2219.8

**Table 4.2.b: Pressure temperature data of different correlations on SG 0.7**

Pressure (psia)	Temperature (°F)		
	Berge	Motiee	Towler and Mokhatab
500	-	49.16	54.85
1000	22.89	64.97	64.6
1500	38.47	73.41	70.31
2000	47.43	79.03	74.35
2500	53.25	83.18	77.49
3000	57.33	86.44	80.06
3500	60.35	89.11	82.22
4000	62.68	91.34	84.1
4500	64.52	93.26	85.76
5000	66.03	94.94	87.24

**Table 4.3.a: Pressure temperature data of different correlations on SG 0.8**

<b>Temperature (°F)</b>	<b>Pressure (psia)</b>			
	<b>Experiment</b>	<b>This Study</b>	<b>Makogon</b>	<b>Hammer- schmidt</b>
<b>30</b>	68	66.5	65.1	71.1
<b>35</b>	98	96.2	89.6	122.1
<b>40</b>	143	139.1	125.5	195
<b>45</b>	209	201.2	178.9	294.8
<b>50</b>	299	291	259.5	426.7
<b>55</b>	423	420.9	383	596.1
<b>60</b>	611	608.8	575	809
<b>65</b>	940	933	878.6	1071.3
<b>70</b>	1709	1693.3	1365.9	1389.4
<b>75</b>	3080	3073.1	2160.8	1770
<b>80</b>	5650	5577.2	3478.1	2219.8

**Table 4.3.b: Pressure temperature data of different correlations on SG 0.8**

<b>Pressure (psia)</b>	<b>Temperature (°F)</b>		
	<b>Berge</b>	<b>Motiee</b>	<b>Towler and Mokhatab</b>
<b>500</b>	-	57.93	58.04
<b>1000</b>	27.95	72.24	67.63
<b>1500</b>	42.44	79.8	73.25
<b>2000</b>	50.67	84.8	77.23
<b>2500</b>	55.98	88.48	80.32
<b>3000</b>	59.69	91.34	82.84
<b>3500</b>	62.43	93.67	84.98
<b>4000</b>	64.54	95.62	86.82
<b>4500</b>	66.21	97.28	88.45
<b>5000</b>	67.56	98.73	89.91

**Table 4.4.a: Pressure temperature data of different correlations on SG 0.9**

<b>Temperature (°F)</b>	<b>Pressure (psia)</b>			
	<b>Experiment</b>	<b>This Study</b>	<b>Makogon</b>	<b>Hammer- schmidt</b>
<b>30</b>	55	51.6	52.3	71.1
<b>35</b>	77	75.6	72	122.1
<b>40</b>	115	110.6	101.4	195
<b>45</b>	170	161.9	146.1	294.8
<b>50</b>	240	237	215.4	426.7
<b>55</b>	350	347	324.8	596.1
<b>60</b>	510	507.9	500.9	809
<b>65</b>	840	832.6	790.2	1071.3
<b>70</b>	1500	1495.2	1275.1	1389.4
<b>75</b>	2700	2658.2	2104.6	1770
<b>80</b>	5000	4822.4	3553.4	2219.8

**Table 4.4.b: Pressure temperature data of different correlations on SG 0.9**

<b>Pressure (psia)</b>	<b>Temperature (°F)</b>		
	<b>Berge</b>	<b>Motiee</b>	<b>Towler and Mokhatab</b>
<b>500</b>	-	61.26	60.85
<b>1000</b>	30.41	74.08	70.31
<b>1500</b>	44.34	80.76	75.84
<b>2000</b>	52.22	85.14	79.76
<b>2500</b>	57.28	88.34	82.81
<b>3000</b>	60.82	90.81	85.3
<b>3500</b>	63.42	92.81	87.4
<b>4000</b>	65.42	94.47	89.22
<b>4500</b>	67	95.88	90.83
<b>5000</b>	68.28	97.1	92.27

**Table 4.5.a: Pressure temperature data of different correlations on SG 1.0**

Temperature (°F)	Pressure (psia)			
	Experiment	This Study	Makogon	Hammer- schmidt
30	45	41.7	45.3	71.1
35	62	61.7	62.4	122.1
40	90	91.5	88.5	195
45	127.13	135.6	129.1	294.8
50	190	201	193.6	426.7
55	299	298	298.8	596.1
60	424.53	441.6	474.3	809
65	720	748.5	774.3	1071.3
70	1280.25	1346.9	1300.5	1389.4
75	2400	2423.7	2246.8	1770
80	4265	4361.5	3992.9	2219.8

**Table 4.5.b: Pressure temperature data of different correlations on SG 1.0**

Pressure (psia)	Temperature (°F)		
	Berge	Motiee	Towler and Mokhatab
500	1.13	59.16	63.36
1000	31.87	70.48	72.7
1500	45.46	76.29	78.16
2000	53.12	80.06	82.03
2500	58.04	82.77	85.04
3000	61.47	84.85	87.5
3500	64	86.51	89.57
4000	65.93	87.88	91.37
4500	67.46	89.04	92.96
5000	68.7	90.03	94.38

## 4.2 Study comparison of different correlations

Figure 4.1 shows the pressure vs temperature prediction of hydrate forming conditions with gas specific gravity of 0.6. It is observed that the experiment data trend-line of pressure vs temperature of hydrate forming condition is overlapped by the correlation on this study. That means the correlation on this study has very close prediction with the experiment.

Other correlations, namely Makogon, Hammerschmidt, Berge, Motiee as well as Towler and Mokhatab are seen to have close behavior of prediction of hydrate forming pressure and temperature, while the Berge method has a quite far away prediction among others.

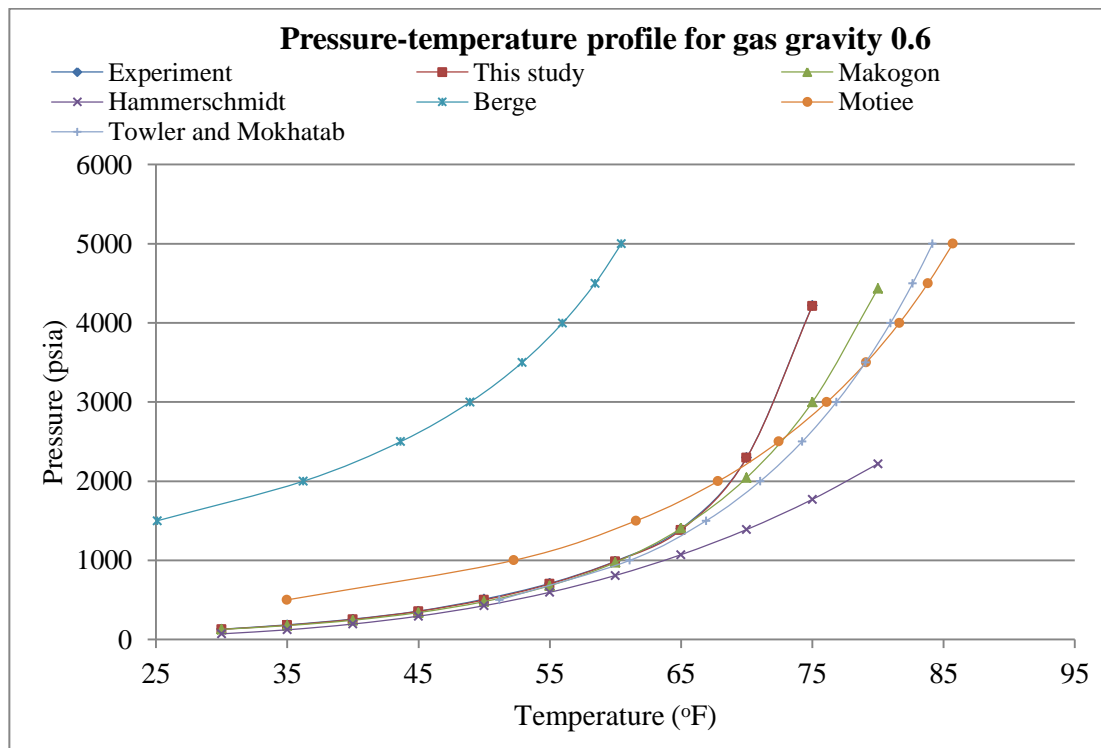


Figure 4.1: Pressure-temperature profile for gas gravity 0.6

In a deeper observation, at the temperature range of 30 – 50 °F, the experiment, this study correlation, Makogon, Towler and Mokhatab, as well as Hammerschmidt has a very close prediction between each other. This fact shows that at lower temperature, different correlations predict almost the same approximation. The results support the

theory that hydrate is likely to form at lower temperature. At a greater temperature, the trend-lines of pressure vs temperature prediction of different correlations vary among each other.

Figure 4.2 shows the pressure vs temperature prediction of hydrate forming conditions with gas specific gravity of 0.7. It is observed that the experimental data trend-line of pressure vs temperature of hydrate forming condition is overlapped by the correlation on this study. That means the correlation on this study has very close prediction with the experimental data.

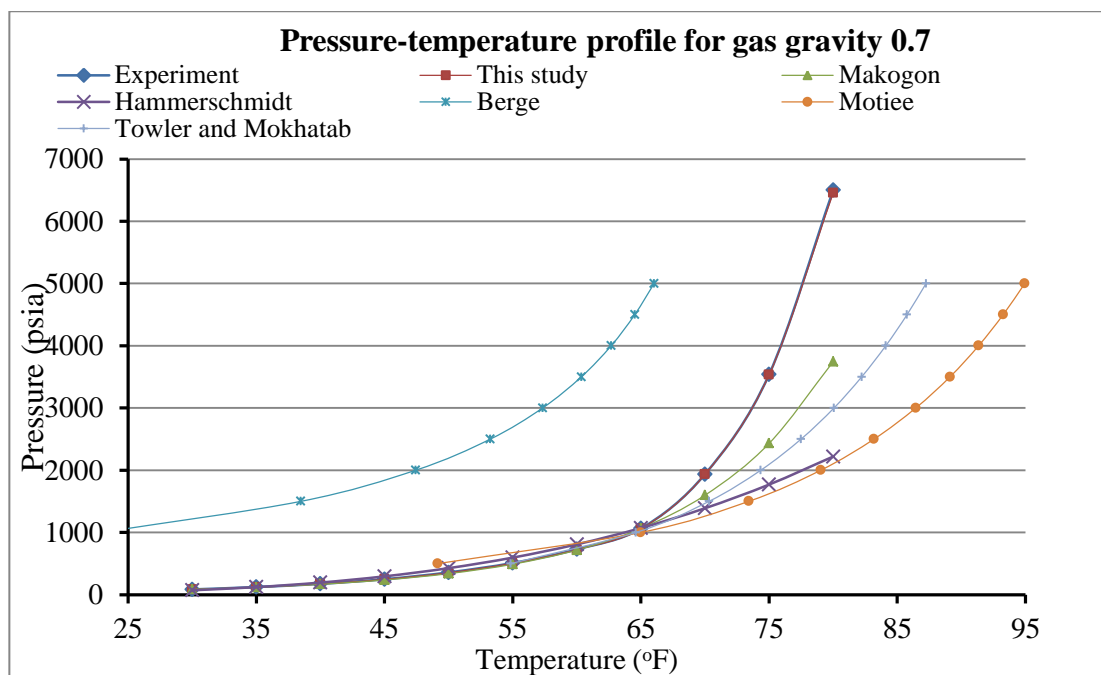


Figure 4.2: Pressure-temperature profile for gas gravity 0.7

Below the temperature of 65°F, the experiment, this study, Makogon, Towler and Mokhatab, and also Hammerschmidt have quite similar trend. The trends vary at temperature above 65°F. Motiee and Berge correlations are observed to be separated away from other correlations.

Figure 4.3 shows the pressure vs temperature prediction of hydrate forming conditions with gas specific gravity of 0.8. It is observed that the experiment data trend-line of pressure vs temperature of hydrate forming condition is overlapped by



the correlation on this study. That means the correlation on this study has very close prediction with the experiment.

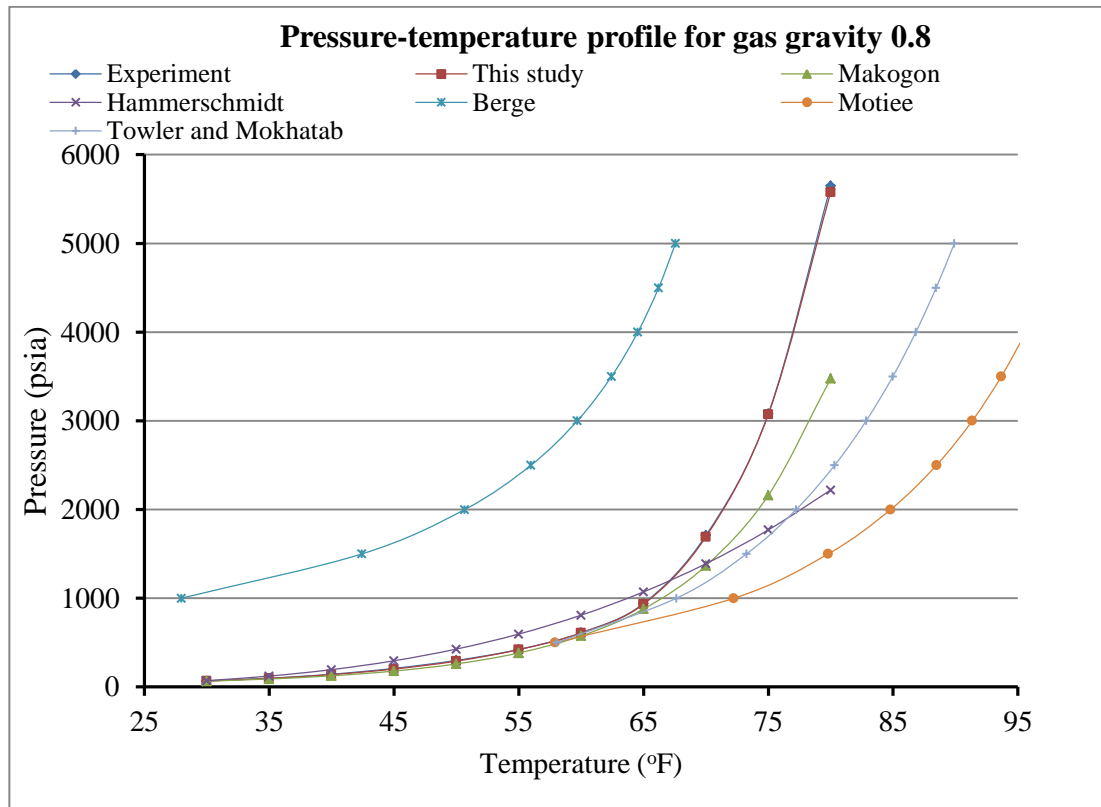


Figure 4.3: Pressure-temperature profile for gas gravity 0.8

These correlations, namely experiment, this study, Makogon, Towler and Mokhatab, are still having similar trend at low temperature, which is below 65°F. However, Hammerschmidt appears differently. Actually, in each plot the Hammerschmidt correlation trend-line is exactly the same, it is because its correlation does not depend on specific gravity, only pressure and temperature.

Berge and Motiee correlations still stay separated from other correlations. It seems that these two correlations are the boundaries of pressure temperature behavior of hydrate formation.

Figure 4.4 shows the pressure vs temperature prediction of hydrate forming conditions with gas specific gravity of 0.9. At the temperature range of 30 - 60 °F, the experiment, correlation on this study, Makogon and Towler and Mokhatab

trendlines are quite similar. At higher temperature, Makogon correlation does not approximate the experiment and correlation on this study trend-line closely anymore. Towler and Mokhatab correlation also has relatively different behavior at higher temperature.

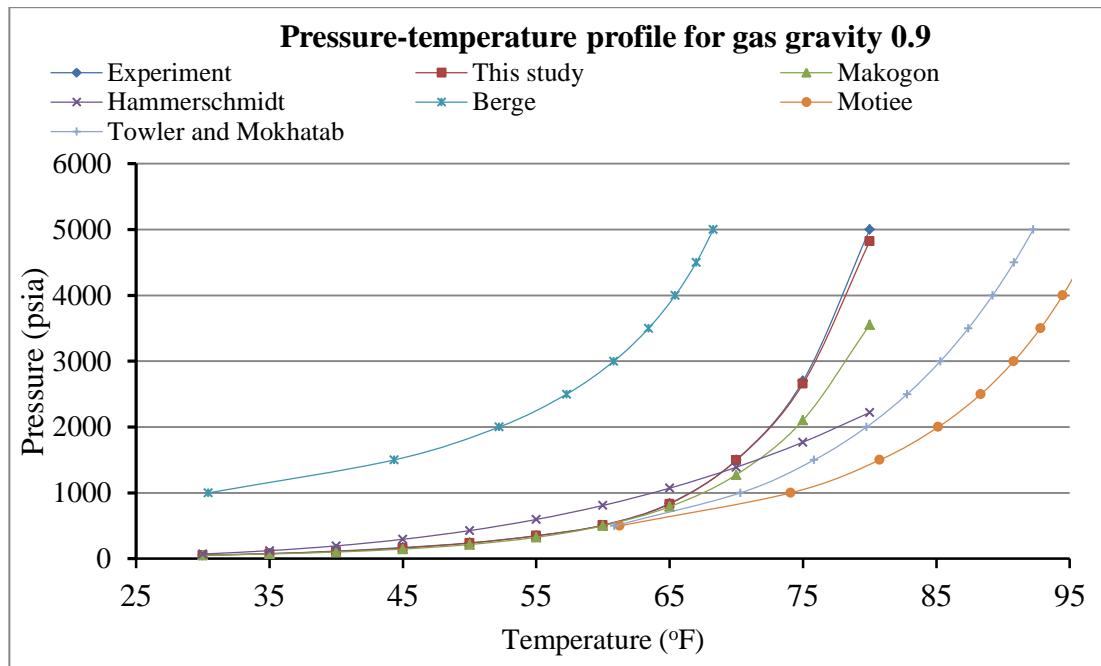


Figure 4.4: Pressure-temperature profile for gas gravity 0.9

At temperature above 60°F, the experiment and correlation on this study are showing that a little increase of temperature makes a lot of higher pressure required to form hydrate. While Towler and Mokhatab trendline shows that increase of temperature gradually increase the pressure required to form hydrate.

Figure 4.5 shows the pressure vs temperature prediction of hydrate forming conditions with gas specific gravity of 1.0. It is observed that the experiment data trend-line of pressure vs temperature of hydrate forming condition is overlapped by the correlation on this study. That means the correlation on this study has very close prediction with the experiment.

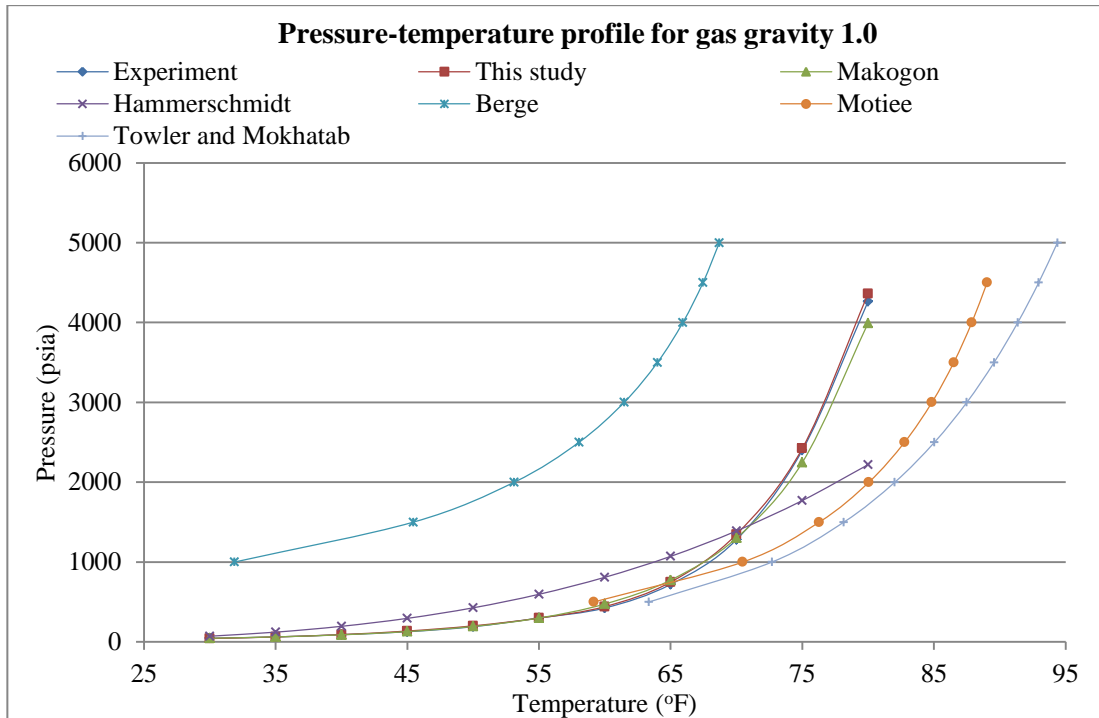


Figure 4.5: Pressure-temperature profile for gas gravity 1.0

The only correlation that is still on the same trend-line with correlation on this study is Makogon at a temperature range of 30 – 60 °F. At the temperature above 60°F, Makogon’s correlation trendline still follows closely to the experiment and SG trendlines, while the other correlations vary accordingly from low to high temperature.

All the results show that at low temperature, most correlations predict similar pressure of hydrate formation. This supports the theory that hydrate formation is likely to form at low temperature and high pressure. At higher temperature, higher pressure is required for hydrate to form.

### 4.3 Pressure-Temperature Profile at different specific gravity

Table below provides the prediction of pressure at different temperature corresponds to each specific gravity. The specific gravity was set to be different for each with a range of 0.05. It is aimed to analyze the prediction of hydrate at different specific gravity. The data from table below are then plotted on x and y axis, which is pressure versus temperature, to be analyzed.

**Table 4.6: Pressure-temperature data at different specific gravity on this study**

Temperature (°F)	Pressure (psia)								
	Specific Gravity								
	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00
30	128.4	106	83.6	75.1	66.5	59.1	51.6	46.7	41.7
35	180.4	150.2	119.9	108.1	96.2	85.9	75.6	68.7	61.7
40	253.3	212.6	171.8	155.5	139	124.9	111	101.1	91.5
45	355.7	301	246.3	233.8	201	181.6	162	148.8	135.6
50	499.5	426.3	353	322	291	264	237	219	201
55	701.4	603.7	506	463.5	421	384	347	322.5	298
60	984.9	855.1	725.3	667.1	609	558.4	508	474.8	441.6
65	1383	1221	1059	996	933	882.8	833	790.6	748.5
70	2295	2115	1934	1813.8	1693	1594	1495	1421.1	1347
75	4213	3873	3533	3302	3073	2865.6	2658	2540.9	2424
80	7734	7094	6454	6015.8	5577	5199.8	4822	4591.9	4362

Figure 4.6 shows the pressure vs temperature of correlation on this study with specific gravity range of 0.05. It is observed that the distance between each plot is not the same, even though the range of SG is constant. Figure 4.6 also shows that the higher the specific gravity of the gas, the closer the distance between each plot. That means the change of temperature affects greatly on predicted pressure for hydrates to form at gas with lower specific gravity (0.6 - 0.7).

From Fig. 4.6, the author also finds out that at the same amount of temperature, a gas with lower specific gravity requires higher amount of pressure to form hydrates, compared to gas with higher specific gravity.

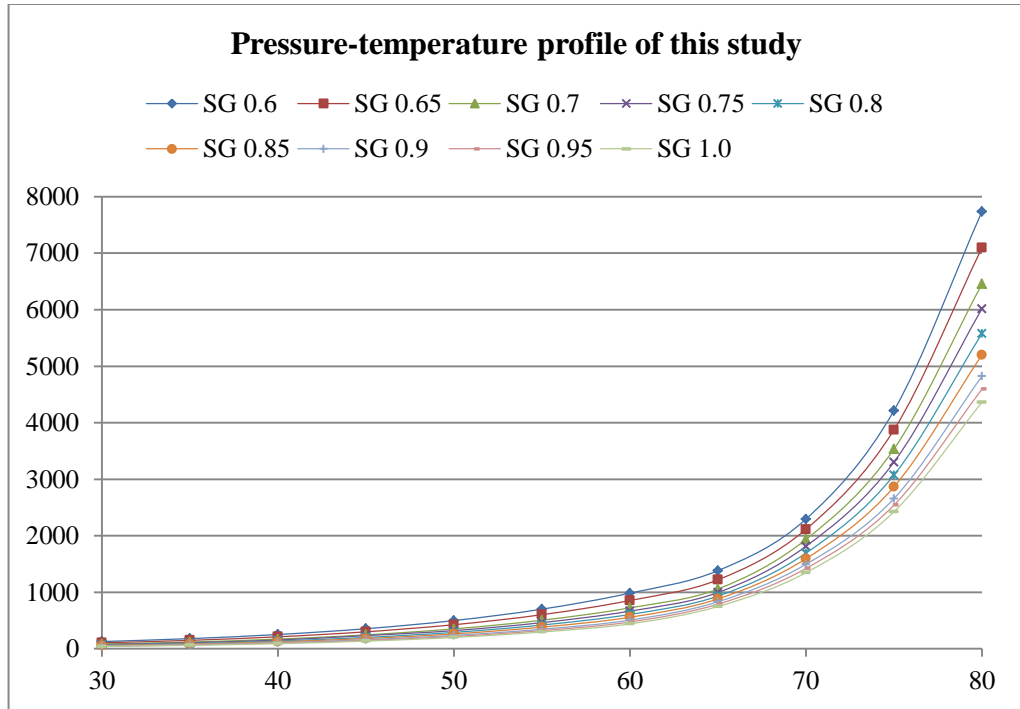


Figure 4.6: Pressure temperature profile of this study

#### 4.4 Results on gas compositional method

Comparison study of existing correlations, correlation on this study and experiment data have been performed. These methods are focused on the prediction of hydrate forming condition, which are pressure and temperature, using the specific gravity of gas. In fact, some natural gas with same amount of SG might have different gas composition.

The main method for analyzing correlation of hydrate forming condition using gas composition is the K-value method. Carson and Katz proposed that hydrates are the equilibrium-state of solid solutions instead of mixed crystals, therefore, estimate that hydrate forming conditions could be predicted empirically from determined vapor/solid equilibrium ratios.

Table below provides the data of gas hydrate component being utilized for correlation to predict hydrate formation on gas compositional method. It was retrieved from the literature, which is Tarek Ahmed's book.

**Table 4.7: Composition of gas sample A**

Component	$y_i$
CO <sub>2</sub>	0.002
N <sub>2</sub>	0.094
C <sub>1</sub>	0.784
C <sub>2</sub>	0.06
C <sub>3</sub>	0.036
i-C <sub>4</sub>	0.005
n-C <sub>4</sub>	0.019

Table 4.8 shows the results of correlation on gas compositional method by utilizing gas sample A. The sum of  $y_i$  over  $K_i$  are all really close to one, which means that the predicted pressure is very accurate for that particular correlation.

**Table 4.8: Pressure temperature data of gas sample A**

Correlation	Temperature (°F)	Pressure (psi)	$\sum \frac{y(i)}{K(i)}$
Sloan	30	76	1.0215
	40	165.5	1.0001
	50	308.5	1.0004
	60	583.3	1.0001
	70	1198.15	1.0000
	80	4741	1.0002
Wilson	30	402.4	1.0001
	40	479.5	1.0001
	50	566.6	1.0000
	60	664.3	1.0000
	70	773.1	1.0000
	80	893.5	1.0002
Standing	30	911.5	1.0000
	40	1154	1.0001
	50	1440	1.0001
	60	1830	1.0001
	70	2625	0.9791
	80	2583	0.9111

Figure 4.7 shows the results of correlation on sample 6-13 by using gas compositional method. The most accurate results is Sloan because it can predict the same as the example in Tarek Ahmed's book. Somehow, the literature does not provide the complete prediction of each respective temperature and pressure of hydrate formation.

It can be seen from Fig. 4.7 that Wilson's correlation predicts better than Standing's correlation. The prediction of Wilson is almost accurate as Sloan at the temperature of 60°F. The Standing's correlation shows a deviation of result, which is at the temperature of 80°F, it is depleted. All the correlations from specific gravity method

are observed to have elevation trend from lower temperature to higher temperature, meaning that the hydrate pressure is higher at higher temperature.

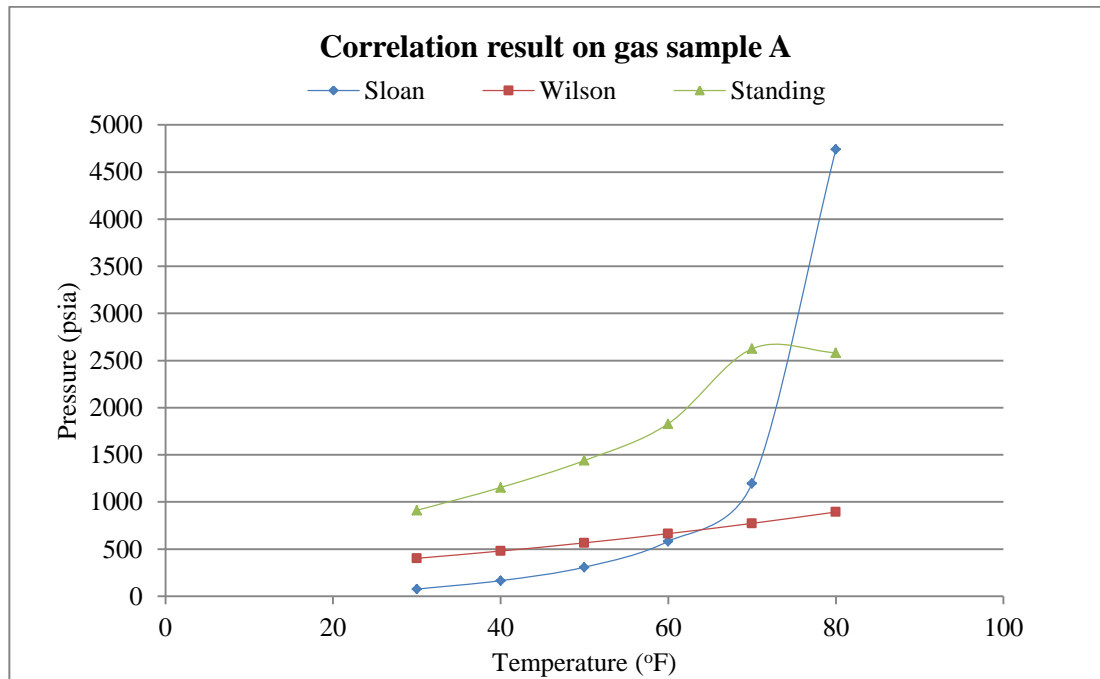


Figure 4.7: Correlation result on gas sample A

Another gas sample was retrieved from the literature, which is gas sample B and being analyzed. The table below provides the gas composition of gas sample B.

**Table 4.9: Composition of gas sample B**

Component	$y_i$
CO <sub>2</sub>	0.04
N <sub>2</sub>	0.06
C <sub>1</sub>	0.78
C <sub>2</sub>	0.06
C <sub>3</sub>	0.03
i-C <sub>4</sub>	0.01
C <sub>5+</sub>	0.02



**Table 4.10: Pressure temperature data of gas sample B**

Correlation	Temperature (°F)	Pressure (psi)	$\sum \frac{y(i)}{K(i)}$
Sloan	30	76	1.0215
	40	165.5	1.0002
	50	306.6	1.0001
	60	2648.5	1.0000
	70	3961.5	1.0004
	80	4740.85	1.0001
Wilson	30	716	1.0001
	40	834.6	1.0000
	50	965.5	1.0000
	60	1109.1	1.0000
	70	1265.6	1.0000
	80	1435	1.0000
Standing	30	2665	0.9195
	40	1154	1.0001
	50	1440	1.0001
	60	1830	1.0001
	70	2625	0.9791
	80	2583	0.9111

Figure 4.8 shows the results of correlation on gas sample B by using gas compositional as input data. The most accurate results is Sloan also because it can predict the same as the example in Tarek Ahmed's book. Somehow, the literature does not provide the complete prediction of each respective temperature and pressure of hydrate formation.

It can be seen from Fig. 4.8 that Wilson's correlation predicts better than Standing's correlation. The prediction of Wilson is almost accurate as Sloan at the temperature of 57°F. The Standing's correlation shows a deviation of result, which is at the temperature of 80°F, it is depleted. All the correlations from specific gravity method

are observed to have elevation trend from lower temperature to higher temperature, meaning that the hydrate pressure is higher at higher temperature.

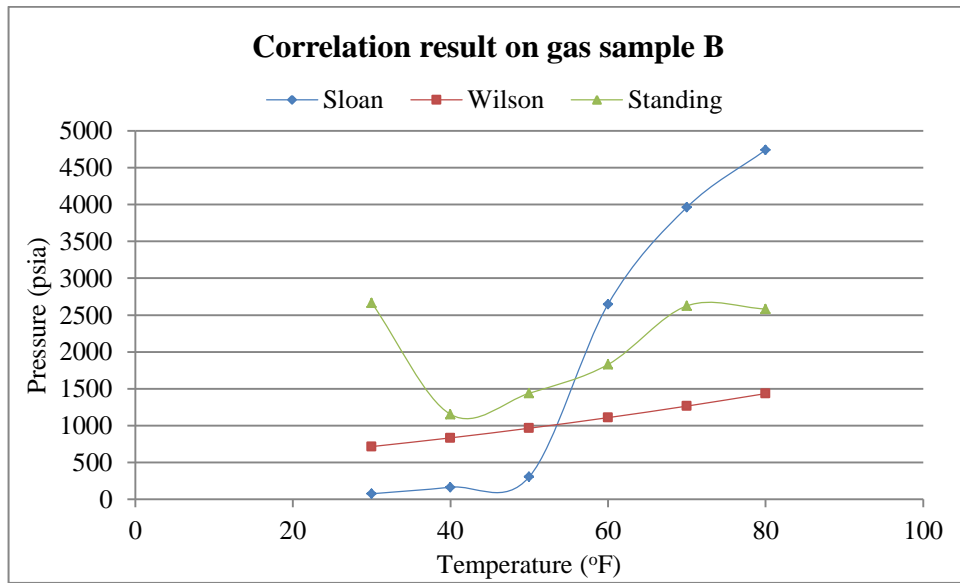


Figure 4.8: Correlation result on gas sample B

## **CHAPTER FIVE**

### **CONCLUSION AND RECOMMENDATION**

#### **5.1 Conclusion**

Hydrates are natural occurrence in the oil and gas industry and once occurred, it costs millions of dollars to the company to do remedial action and maintain the flow assurance. High pressure and low temperature are the two main criteria for hydrates to form, besides the existence of water and hydrate forming hydrocarbon components. In order to prevent and avoid hydrates to form, experimental work is the best practice to predict hydrates formation pressure and temperature. Somehow, the practice requires extensive amount of money to perform and also time consuming. Thus, predicting hydrates formation condition by using correlation is a better solution.

The gas specific gravity method and gas compositional method were utilized to develop correlation to predict hydrate formation pressure and temperature. The existing correlations are obtained from the literature to compare the author developed correlation as well as the experiment experimental data. The K-values method was utilized to develop the study comparison of hydrate prediction on gas compositional method.

After performing the project, the results show that the developed correlation by the author shows the most accurate results. Meanwhile, Makogon is the second best results. In the gas compositional method, Sloan's correlation shows the most accurate results. The study also shows that computer algorithm can be utilized to develop correlation on predicting hydrate formation conditions.

In conclusion, the study has met its objectives, which are to develop new correlation on predicting hydrate formation and perform study comparison on different correlations to predict hydrate formation.

## 5.2 Recommendation

This study is a good example for researchers who want to develop correlation on predicting hydrate formation. It provides several correlations to predict hydrate formation conditions, in terms of pressure and temperature. The correlation developed by the author can also be utilized.

It is recommended that the gas compositional method to be develop further, because it gives more accurate impact on the results. As well as, gas compositional study differentiates gas more accurately. For example, when there are two different gas mixtures with same number of specific gravity, gas compositional study can distinguish the two gas mixtures.

The problem with gas compositional is that it has complicated correlation and requires iteration to obtain one K-value for each gas component, and the procedure needs to be repeated for other gas components in the mixture. Thus, it is also recommended to be more careful and precise on the gas composition study.

Another recommendation is that researcher needs to add more parameters in developing correlations for predicting hydrate formation. Water molecule and fugacity are some examples that the estimated to be also utilized to predict hydrate formation conditions. Furthermore, location of hydrate formation condition that was utilized in this study is focused on gas transportation on offshore field. Further study can be developed for hydrate that forms in the upstream line, either in the reservoir or in the production well.

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# APPENDIX

## A1. MATLAB source code of correlation on this study

```
SG = input('SG = ');
predict = input('What would you like to predict? \n press t for temperature and p for pressure \n t/p? = ','s');
if strcmp(predict,'p')
    Temp = input('Temperature (degF) = ');
elseif strcmp(predict,'t')
    Press = input('Pressure (psia) = ');
else
    disp('wrong input')
end
if strcmp(predict,'p')

    if SG == 0.6 & (Temp > 66.9)
        Pressure = 0.4646 * exp(0.1215*Temp)
    elseif (SG == 0.6 & (Temp <= 66.9))
        Pressure = 16.752 * exp(0.0679*Temp)

    elseif (SG == 0.7 & (Temp > 64.5))
        Pressure = 0.42 * exp(0.1205*Temp)
    elseif (SG == 0.7 & (Temp <= 64.5))
        Pressure = 9.6466 * exp(0.072*Temp)

    elseif (SG == 0.8 & (Temp > 63.7))
        Pressure = 0.4027 * exp(0.1192*Temp)
    elseif (SG == 0.8 & (Temp <= 63.7))
        Pressure = 7.2681 * exp(0.0738*Temp)

    elseif (SG == 0.9 & (Temp > 62.2))
        Pressure = 0.4119 * exp(0.1171*Temp)
    elseif (SG == 0.9 & (Temp <= 62.2))
        Pressure = 5.2498 * exp(0.0762*Temp)

    elseif (SG == 1.0 & (Temp > 61.54))
        Pressure = 0.3608 * exp(0.1175*Temp)
    elseif (SG == 1.0 & (Temp <= 61.54))
        Pressure = 3.9293 * exp(0.0787*Temp)

    end

elseif strcmp(predict,'t')

    if SG == 0.6 & (Press > 1570)
        Temperature = (log(Press/0.4646)) / 0.1215
    elseif (SG == 0.6 & (Press <= 1570))
        Temperature = (log(Press/16.752)) / 0.0679

    elseif (SG == 0.7 & (Press > 1000))
        Temperature = (log(Press/0.42)) / 0.1205
    elseif (SG == 0.7 & (Press <= 1000))
        Temperature = (log(Press/9.6466)) / 0.072

    elseif (SG == 0.8 & (Press > 800))
        Temperature = (log(Press/0.4027)) / 0.1192
    elseif (SG == 0.8 & (Press <= 800))
        Temperature = (log(Press/7.2681)) / 0.0738

    elseif (SG == 0.9 & (Press > 600))
        Temperature = (log(Press/0.4119)) / 0.1171
    elseif (SG == 0.9 & (Press <= 600))
        Temperature = (log(Press/5.2498)) / 0.0762

    elseif (SG == 1.0 & (Press > 500))
        Temperature = (log(Press/0.3608)) / 0.1175
```

```

elseif (SG == 1.0 & (Press <= 500))
    Temperature = (log (Press/3.9293) ) / 0.0787
end

end

```

## A2. MATLAB source code of Oestergaard et al. correlation

```

Yco2 = 2.38 / 100; % Yco2, Yn2, Y1 and so on are the mole fraction of each component
Yn2 = 0.58 / 100;
y1 = 73.95 / 100; y2 = 7.51 / 100; y3 = 4.08 / 100; yi4 = 0.61 / 100; yn4 = 1.58 / 100; yi5 = 0.5 / 100;
yn5 = 0.74 / 100; y6 = 0.89 / 100; y7 = 7.18/100;

M1 = 16.04; M2 = 30.07; M3 = 44.1; Mi4 = 58.12; Mn4 = 58.12;
% M1, M2, M3, and so on are the molar mass of the hydrates components

Fh = y1 + y2 + y3 + yi4 + yn4; % mole fraction of methane, ethane, propane, butane, isobutane
Fnh = yi5 + yn5 + y6 + y7; % mole fraction of C5+ components

Fm = Fnh / Fh; %Fm : molar ration between hydrate n non hydrate foming comp.

Mh = y1 * M1 + y2 * M2 + y3 * M3 + yi4 * Mi4 + yn4 * Mn4;
%Molecular weight of hydrate forming condition

y1norm = y1 / Fh; y2norm = y2 / Fh; y3norm = y3 / Fh; yi4norm = yi4 / Fh; yn4norm = yn4 / Fh;
Mhnorm = y1norm * M1 + y2norm * M2 + y3norm * M3 + yi4norm * Mi4 + yn4norm * Mn4;
% mole fraction of hydrates components are being normalized to disregard the non-hydrate components

SGh = Mhnorm / 28.96;

a1 = 2.50744 * 10^(-3); a2 = 0.46852; a3 = 1.214644 * 10^(-2); a4 = -4.676111 * 10^(-4);
a5 = 0.0720122; a6 = 3.6625 * 10^(-4); a7 = -0.485054; a8 = -5.44376; a9 = 3.89 * 10^(-3); a10 = -29.9351;

T = 505; %temperature in Reamur unit
dalem = (T*( a1/(SGh + a2)^3 + a3*Fm + a4*Fm^2 + a5) )+ (a6 / (SGh + a7)^3) + a8*Fm + a9 * Fm^2 + a10;
Ph = 0.1450377 * exp ( dalem );
% Ph : hydrate dissociation pressure

b1 = -2.0943 * 10^(-4) * (T/1.8 - 273.15)^3 + 3.809 * 10^(-3) * (T/1.8 - 273.15)^2 - 2.42*10^(-2) * (T/1.8 -
273.15) + 0.423 ;

b2 = 2.3498 * 10^(-4) * (T/1.8 - 273.15)^3 - 2.086 * 10^(-3) * (T/1.8 - 273.15)^2 + 1.63*10^(-2) * (T/1.8 -
273.15) + 0.65 ;

b3 = 1.1374 * 10^(-4) * (T/1.8 - 273.15)^3 + 2.61 * 10^(-4) * (T/1.8 - 273.15)^2 + 1.26*10^(-2) * (T/1.8 -
273.15) + 1.123 ;

```



$b4 = 4.335 * 10^{(-5)} * (T/1.8 - 273.15)^3 - 7.7 * 10^{(-5)} * (T/1.8 - 273.15)^2 + 4 * 10^{(-3)} * (T/1.8 - 273.15) + 1.048$  ;

$Eco2 = 1 + ((b1 * Fm + b2) * Yco2 / (1 - Yn2))$ ;  $En2 = 1 + ((b3 * Fm + b4) * Yn2 / (1 - Yco2))$ ;

% Yco2 : mole fraction of CO2; % Yn2 : mole fraction of n2;

$Pcorr = Ph * Eco2 * En2$

%Pcorr is the corrected pressure, the final predicted pressure of hydrate formation

### A3. MATLAB source code of Makogon to predict pressure

SG = input ('SG = ');

T = input ('Temp in degF = ');  $Tc = (T - 32) * 5/9$ ; %Tc is temperature in degC

$Beta = 2.681 - 3.811 * SG + 1.679 * SG^2$ ;

$k = -0.006 + 0.011 * SG + 0.011 * SG^2$ ;

$result = Beta + 0.0497 * (Tc + k * Tc^2) - 1$ ;

$P = 10 ^ result$ ;

%P is pressure in MPa

$Ppsia = P * 145.0377$

%now is pressure in Psia

### A4. MATLAB source code of Makogon to predict Temperature

SG = input ('SG = ');

Psia = input ('Pressure in psia = ');

$Beta = 2.681 - 3.811 * SG + 1.679 * SG^2$ ;

$k = -0.006 + 0.011 * SG + 0.011 * SG^2$ ;

$Pmpa = Psia / 145.0377$ ;

%now is pressure in MPa

$a = k$ ;  $b = 1$ ;

$result = \log_{10}(Pmpa)$ ;

$c = -((result - Beta + 1) / 0.0497)$ ;

$x = (-b + (b^2 - 4 * a * c)^{0.5}) / (2 * a)$ ; %x is temperature in degC

$Tf = x * 9/5 + 32$  %Tf is temperature in degF

### A5. MATLAB source code of Hammerschmidt to predict hydrates temperature

P = input ('Pressure in psia = ');

$T = 8.9 * P ^ 0.285$  %Temperature is in degree Fahrenheit

### A6. MATLAB source code of Hammerschmidt to predict hydrates pressure

T = input ('Temperature in degF = '); power = 1/0.285;

$P = (T/8.9)^power$  %Pressure is in psia

## A7. MATLAB source code of Sloan on gas sample A

```
y = [0.002, 0.094, 0.784, 0.06, 0.036, 0.005, 0.019];  
K = [0,0,0,0,0,0];  
P = 325 %P = Psi/14.7; %P must be in degF  
SG = 0.728;
```

```
b = 2.681 - 3.811 * SG + 1.679 * SG^2; k = -0.006 + 0.011*SG + 0.011*SG^2;
```

```
T = 50
```

```
Ac1 = [ 1.63636, 0, 0, 31.6621, -49.3534, 5.31*10^-6, 0, 0, 0.128525, -0.78338, 0,0,0, -5.3569, 0, -2.3*10^-7, -  
2*10^-8, 0];
```

```
Ac2 = [6.41934, 0,0, -290.283, 2629.1, 0,0, 9*10^-8, 0.129759, -1.19703, -8.46*10^4, -71.0352, 0.596404, -  
4.7437, 7.82*10^4, 0, 0, 0];
```

```
Ac3 = [-7.8499, 0,0, 47.056, 0, -1.17*10^-6, 7.145*10^-4, 0,0, 0.12348, 1.669*10^4, 0, 0.23319, 0, -4.48*10^4,  
5.5*10^-6, 0, 0];
```

```
Aic4 = [-2.17137, 0,0,0,0,0, 1.251*10^-3, 1*10^-8, 0.166097, -2.75945, 0,0,0,0, -8.84*10^2, 0, -5.7*10^-7, -  
1*10^-8];
```

```
Anc4 = [-37.211, 0.86564, 0, 732.2, 0,0,0, 9.37*10^-6, -1.07657, 0,0, -66.221, 0,0, 9.17*10^5, 0, 4.98*10^-6, -  
1.26*10^-6];
```

```
An2 = [1.77857, 0, -0.001356, -6.187, 0,0,0, 2.5*10^-7, 0,0,0,0,0,0, 5.87*10^5, 0, 1*10^-8, 1*10^-7];
```

```
Aco2 = [ 9.0242, 0,0, -207.033, 0, 4.66*10^-5, -6.992*10^-3, 2.89*10^-6, -6.223*10^-3, 0,0,0, 0.27098, 0,0,  
8.82*10^-5, 2.25*10^-6, 0];
```

```
Ah2s = [ -4.7071, 0.06192, 0, 82.627, 0, 7.39*10^-6, 0, 0, 0.240869, -6.4405, 0,0,0, -12.704, 0, -1.3*10^-6, 0, 0];
```

```
sum1co2 = Aco2(1) + Aco2(2)*T + Aco2(3)*P + Aco2(4) / T + Aco2(5) / P;
```

```
sum2co2 = Aco2(6)*P*T + Aco2(7)*T^2 + Aco2(8)*P^2 + Aco2(9)*P/T + Aco2(10)*log(P/T);
```

```
sum3co2 = Aco2(11)/P^2 + Aco2(12)*T/P + Aco2(13)*T^2/P + Aco2(14)*P/T^2 + Aco2(15)*T/P^3;
```

```
sum4co2 = Aco2(16)*T^3 + Aco2(17)*P^3/T^2 + Aco2(18)*T^4 ;
```

```
answerco2 = sum1co2 + sum2co2 + sum3co2 +sum4co2;
```

```
Kco2 = exp(answerco2);
```

```
K(1) = Kco2;
```

```
sum1n2 = An2(1) + An2(2)*T + An2(3)*P + An2(4) / T + An2(5) / P;
```

```
sum2n2 = An2(6)*P*T + An2(7)*T^2 + An2(8)*P^2 + An2(9)*P/T + An2(10)*log(P/T);
```

```
sum3n2 = An2(11)/P^2 + An2(12)*T/P + An2(13)*T^2/P + An2(14)*P/T^2 + An2(15)*T/P^3;
```

```
sum4n2 = An2(16)*T^3 + An2(17)*P^3/T^2 + An2(18)*T^4 ;
```

```
answern2 = sum1n2 + sum2n2 + sum3n2 +sum4n2;
```

```
Kn2 = exp(answern2);
```

```
K(2) = Kn2;
```

```
sum1 = Ac1(1) + Ac1(2)*T + Ac1(3)*P + Ac1(4) / T + Ac1(5) / P;
```

```
sum2 = Ac1(6)*P*T + Ac1(7)*T^2 + Ac1(8)*P^2 + Ac1(9)*P/T + Ac1(10)*log(P/T);
```

```
sum3 = Ac1(11)/P^2 + Ac1(12)*T/P + Ac1(13)*T^2/P + Ac1(14)*P/T^2 + Ac1(15)*T/P^3;
```

```
sum4 = Ac1(16)*T^3 + Ac1(17)*P^3/T^2 + Ac1(18)*T^4 ;
```

```
answer = sum1 + sum2 + sum3 + sum4;
```

```
Kc1 = exp(answer); K(3) = Kc1;
```

```
sum1_c2 = Ac2(1) + Ac2(2)*T + Ac2(3)*P + Ac2(4) / T + Ac2(5) / P;
```

```
sum2_c2 = Ac2(6)*P*T + Ac2(7)*T^2 + Ac2(8)*P^2 + Ac2(9)*P/T + Ac2(10)*log(P/T);
```

```
sum3_c2 = Ac2(11)/P^2 + Ac2(12)*T/P + Ac2(13)*T^2/P + Ac2(14)*P/T^2 + Ac2(15)*T/P^3;
```

```
sum4_c2= Ac2(16)*T^3 + Ac2(17)*P^3/T^2 + Ac2(18)*T^4 ;
```

```
answer_c2 = sum1_c2 + sum2_c2 + sum3_c2 + sum4_c2;
```

```
Kc2 = exp(answer_c2); K(4) = Kc2;
```

```
sum1_c3 = Ac3(1) + Ac3(2)*T + Ac3(3)*P + Ac3(4) / T + Ac3(5) / P;
```

```
sum2_c3 = Ac3(6)*P*T + Ac3(7)*T^2 + Ac3(8)*P^2 + Ac3(9)*P/T + Ac3(10)*log(P/T);
```

```
sum3_c3 = Ac3(11)/P^2 + Ac3(12)*T/P + Ac3(13)*T^2/P + Ac3(14)*P/T^2 + Ac3(15)*T/P^3;
```

```
sum4_c3= Ac3(16)*T^3 + Ac3(17)*P^3/T^2 + Ac3(18)*T^4 ;
```

```
answer_c3 = sum1_c3 + sum2_c3 + sum3_c3 + sum4_c3;
```

```
Kc3 = exp(answer_c3); K(5) = Kc3;
```

```
sum1_ic4 = Aic4(1) + Aic4(2)*T + Aic4(3)*P + Aic4(4) / T + Aic4(5) / P;
```

```
sum2_ic4 = Aic4(6)*P*T + Aic4(7)*T^2 + Aic4(8)*P^2 + Aic4(9)*P/T + Aic4(10)*log(P/T);
```

```
sum3_ic4 = Aic4(11)/P^2 + Aic4(12)*T/P + Aic4(13)*T^2/P + Aic4(14)*P/T^2 + Aic4(15)*T/P^3;
```

```
sum4_ic4= Aic4(16)*T^3 + Aic4(17)*P^3/T^2 + Aic4(18)*T^4 ;
```

```
answer_ic4 = sum1_ic4 + sum2_ic4 + sum3_ic4 + sum4_ic4;  
Kic4 = exp(answer_ic4); K(6) = Kic4;
```

```
sum1_nc4 = Anc4(1) + Anc4(2)*T + Anc4(3)*P + Anc4(4) / T + Anc4(5) / P;  
sum2_nc4 = Anc4(6)*P*T + Anc4(7)*T^2 + Anc4(8)*P^2 + Anc4(9)*P/T + Anc4(10)*log(P/T);  
sum3_nc4 = Anc4(11)/P^2 + Anc4(12)*T/P + Anc4(13)*T^2/P + Anc4(14)*P/T^2 + Anc4(15)*T/P^3;  
sum4_nc4 = Anc4(16)*T^3 + Anc4(17)*P^3/T^2 + Anc4(18)*T^4 ;  
answer_nc4 = sum1_nc4 + sum2_nc4 + sum3_nc4 + sum4_nc4;  
Knc4 = exp(answer_nc4); K(7) = Knc4;
```

```
sum_y_overK = 0;
```

```
for i = 1:7  
    yoverK(i) = y(i)/K(i);  
    sum_y_overK = sum_y_overK + y(i)/K(i);  
end
```

```
sum_y_overK
```