

**UNIVERSIDADE EDUARDO MONDLANE**

**FACULDADE DE ENGENHARIA**

**ACADEMIC MASTER OF SCIENCE IN PETROLEUM ENGINEERING**

**A SYSTEMATIC EVALUATION OF HYDRATES INHIBITORS FOR FLOW  
ASSURANCE (ECONOMIC AND SCALES – UP). CASE STUDY: Keta Basin of Ghana**

**A Dissertation by**

Edmundo Pedro Mutolo

**Date of Submission:**

**2022**

**Location of Submission:**

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Prof. Doutor Luís Hélder Mendes Lucas, Eng<sup>o</sup>.

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## **DECLARATION OF DOCUMENT ORIGINALITY**

"I declare that this dissertation has never been submitted to obtain any degree or in any other context and is the result of my own individual work. This dissertation is presented in compliance with part of the requirement to obtain the title of Academic Master of Science in Petroleum Engineering granted by Universidade Eduardo Mondlane".

Submitted by:

**EDMUNDO PEDRO MUTOLO**

**Signature of Student:**

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## ABSTRACT

In petroleum industry one of the challenges that is being faced in is the high cost to solve hydrates that plug facilities. Many studies are being developed to enhance new technologies towards the future of reservoirs to be explored in Antarctic and permafrost environment. Since future energy is considered to be stored in the arctic areas, for the near future to explore hydrates in a safer and more economical way, its implementation will need much more improved technologies. During this exploration or production, blockages in facilities will become a serious challenge when hydrates will be formed. The composition of the gas has huge influence in such conditions to form hydrates, such as impurities commonly like H<sub>2</sub>S, N<sub>2</sub> and CO<sub>2</sub>. High pressure, low temperatures, free water and natural gas are the essential conditions to appear hydrates. If one of this four element is upset, no hydrates will be formed and, in this scenario, we are in safe zone. Many commercial softwares like Schlumberger PipeSim, PVTi, Olga, Hydrasoft, and so on, are being developed and enhanced to predict hydrates formation. So, the software used in this study applies temperatures up to 90°F and pressures up to 12,000 psia, in aqueous solutions containing electrolytes as potassium, sodium, and calcium chlorides less than 20 wt% and inhibitors such as methanol less than 20 wt%, ethylene glycol, triethylene glycol, and glycerol less than 40 wt%. In this context, so many inhibitors were experienced and Methanol and NaCl were the best, with much desired degree of performance in inhibition. Once the mixture Methanol & NaCl mixed up to 5% in weight were achieved and from now on, the pressure was doubled, which is what is desired.

## RESUMO

Na indústria do petróleo, um dos desafios que está sendo enfrentado é o alto custo para a resolução de problemas com os hidratos que bloqueiam as instalações. Muitos estudos estão sendo desenvolvidos para melhorar as novas tecnologias em prol à uma enorme tarefa no futuro da exploração dos reservatórios no ambiente antártico e de permafrost. Uma vez que a energia futura é considerada armazenada nas zonas do Ártico, para um futuro próximo da exploração de hidratos de forma mais segura e econômica, a sua efetivação, precisará de tecnologias muito mais melhoradas. Durante essa exploração ou produção, os bloqueios nas instalações serão de maior atenção e será um desafio muito sério quando os hidratos se formarem. A composição do gás tem enorme influência nessas condições para a formação de hidratos, com impurezas comuns tais como  $H_2S$ ,  $N_2$  e  $CO_2$ . Alta pressão, baixas temperaturas, água livre e gás natural são as condições essenciais para o aparecimento dos hidratos. Se um desses quatro elementos estiver ausente, nenhum hidrato será formado, e, nesse cenário, estamos na zona segura. Muitos softwares comerciais como Schlumberger PipeSim, PVTi, Olga, Hydrasoft, etc. estão sendo desenvolvidos e melhorados em prol a prever a formação de hidratos. Portanto, o software utilizado neste estudo, aplica-se a temperaturas até  $90^\circ F$  e pressões até 12.000 psia, em soluções aquosas contendo eletrólitos como cloretos de potássio, sódio e cálcio inferiores a 20% em peso e inibidores como metanol menor que 20% em peso, etileno glicol, trietileno glicol e glicerol inferiores a 40% em peso. Com o uso mundial de metanol como inibidor predileto, tornando-se um imperativo para mitigar a formação de componentes indesejáveis tais como os hidratos, que estão se tornando um objecto de discussão e estudos para futuras explorações na indústria do petróleo e gás. Neste contexto, tantos inibidores foram experimentados e o Metanol e NaCl foram os melhores, com um grau de performance muito desejado em inibição. Feito a mistura Metanol & NaCl, conseguiu-se até 5% de peso e doravante, a pressão duplicou-se, o que é o desejado.

*“After climbing a great hill, one only finds that there are many more hills to climb.”*

*— Nelson Mandela*

## **DEDICATION**

This dissertation is especially dedicated to my Mother Rabelina Nhatsodo, and also to my daughter Euridse Mutolo.

Also not forgetting to my late Dad Pedro Obol from his encouragement to go beyond since I knew to go to school.

My sister Arlinda Mutolo cannot be outside from her patience and worship who always gives me huge effort to my everyday new challenges.

## ACKNOWLEDGEMENTS

For life, realizations, dreams, courage and expertise, I give many thanks to God who guides me to everywhere.

I want to wholeheartedly thank my research advisor, Professor Dr Lucas Mendes by his simplicity compression, availability and encouragement for this Dissertation being done.

Also, for the Former Dear Professors namely Rui Siteo and Alexandre Ali, whose their absence We feel empty their contributions once they were indispensable pillars to the Petroleum Engineering Program in this Faculty.

The acknowledgement is extended to the rest of Professors and Staffs of Petroleum Engineering Program by their teaching and walk in this wonderful student career.

For my classmate: Alberto Mutimuciuo, Salomão Noge, Sidonio Bambo... and we were given the name of '*Dream Team*' from Core program in 2017 to the Master's Program - 2018, I say *Many Thanks!*



## NOMENCLATURE (LIST OF ABBREVIATIONS)

### Abbreviations - Description

AA - Anti-Agglomerates

AAE - Average Absolute Error

BOP - Blowout Preventer

CNG - Compressed Natural Gas

CSI - Cubic Structure I

DEG - Diethylene Glycol

EG – Ethylene Glycol

FLNG - Floating Liquefied Natural Gas

INP - Instituto Nacional do Petróleo

KHI - Kinetic Hydrate Inhibitors

KI - Kinetic Inhibitors

LDHI - Low Dosage Hydrate Inhibitors

LNG - Liquefied Natural Gas

MEG – Mono ethylene glycol

Mt – Metric tonne

M<sup>3</sup> – Cubic meter

MCF – Millions of Cubic Feet

MP – Millions of pounds

N/A - Not Applicable

nm - Nanometre

PVT - Pressure, Volume and Temperature

p<sup>h</sup> - Hydrogen Potential

SH - Structure of type H

SI - Structure I

SII - Structure II

TCF - Trillion Cubic Feet

TEG - Triethylene Glycol

TI - Thermodynamic Inhibitors

UK - United Kingdom

US - United States

ISO - International Organization for Standardization

OHSA - Occupational Safety and Health Administration

Wt – Weight

X Mas tree – Christmas Tree

## **KEY WORDS**

1. Gas hydrate
2. Flow assurance
3. Blockage
4. Inhibitors
5. Methane
6. Methanol
7. NaCl

## **PALAVRAS-CHAVE**

1. Gás Hidratado
2. Segurança no Fluxo
3. Bloqueio
4. Inibidores
5. Metano
6. Metanol
7. NaCl

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# CHAPTER I

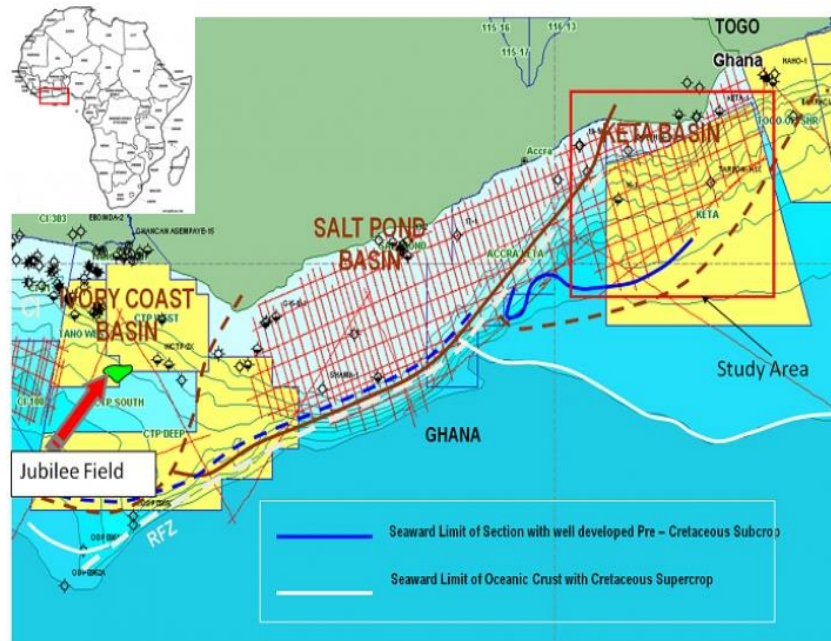
## 1. INTRODUCTION

### 1.1 Introduction

#### i) Overview of hydrocarbons in Ghana

The Keta basin (figure 1) covering approximately 2,200 km<sup>2</sup>, lies along the east coast of Ghana. It is one of the chains of Mesozoic and Tertiary sedimentary basins in the Gulf of Guinea. The basin is filled with 870 m of Paleozoic marine and non-marine sediments that were deposited in an interior basin that once occupied the present site of the Keta basin. These sediments are unconformably overlain by 3,600 m of Mesozoic-Tertiary deposits. Three major Post-Paleozoic depositional cycles are recognized in the basin (Akpati, 1978).

Ghana, which is the first Sub-Saharan African country to gain its independence, discovered their first oil in 1896 but discovery of commercial quantity of petroleum was in 2007. Ghana has four sedimentary basins of which one is inland and the other three are offshore. The inland basin is the Voltaian basin and the offshore basins are Tano, Saltpond and Accra-Keta basins. Currently, the most prolific basin in Ghana which has huge accumulations of hydrocarbons is the Tano basin although exploration works are ongoing in the Saltpond and Keta basins for hydrocarbon potential. Ghana witnessed their first oil production in 2007 in the Jubilee field of the Tano basin at rate of about 55,000 barrels per day with an increase to 120,000 within six months. In 2019, production has increased to about 196,089 barrels per day with an expected increase in production to 420,020 barrels per day by 2023, (LAMBON, 2020).



**Figure 1.** Overview of Keta Basin of Ghana in Guinea Gulf – offshore environment.

**Source:**

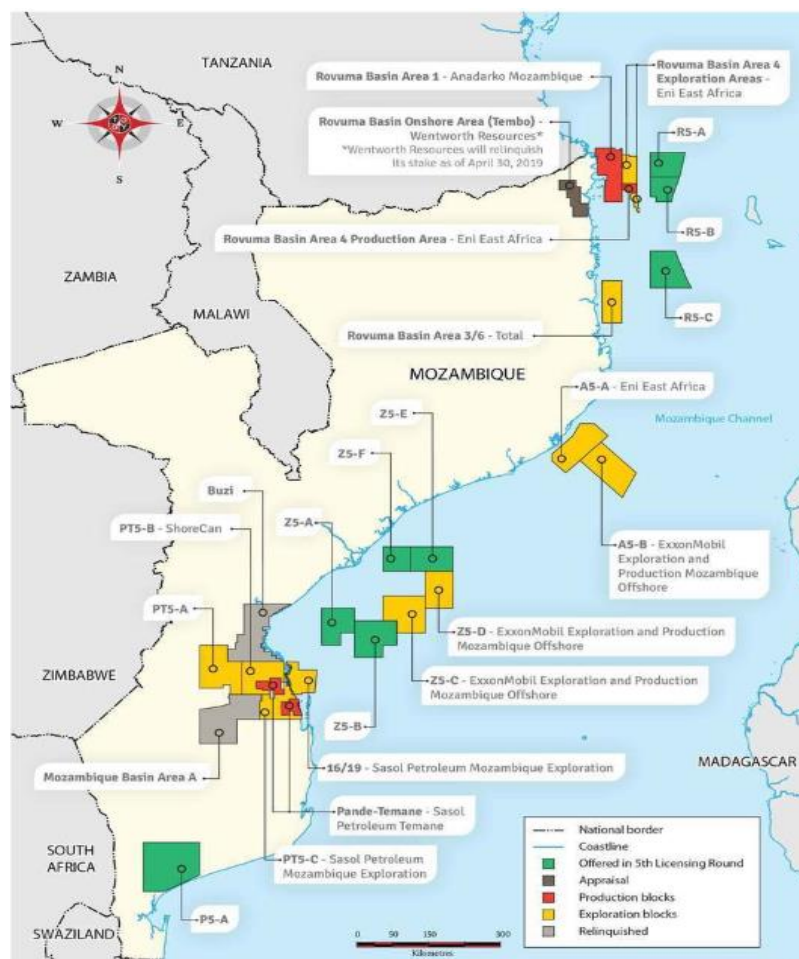
[https://www.google.com/search?sxsrf=ALiCzsY6\\_OhS9ycdI0\\_\\_Y2T1pDPmdVpAzg:1668422076723&source=univ&tbn=isch&q=keta+basin&fi](https://www.google.com/search?sxsrf=ALiCzsY6_OhS9ycdI0__Y2T1pDPmdVpAzg:1668422076723&source=univ&tbn=isch&q=keta+basin&fi)

**ii) Overview of hydrocarbons in Mozambique**

Exploration for hydrocarbons in Mozambique goes back to 1904 when the early explorers discovered thick sedimentary basins onshore Mozambique. Poor technology and lack of funds halted those early exploration attempts. From 1948 onwards international oil companies moved into Mozambique and carried out extensive exploration, mainly onshore with limited activity offshore. As a result, the Pande Gas Field was discovered in 1961 by Gulf Oil followed by the gas discoveries of Búzi (1962) and Temane (1967). Exploration activity declined in the early 1970's due to political unrest. New activity was established in the early 1980's with the enactment of law 3/81 and creation of ENH. In the following years extensive work was carried out to map and appraise the Pande Field.

A breakthrough was made in 1993 when it became clear that the Pande Field could be mapped using direct hydrocarbon indicators (DHI) from seismic data and it turned out that there was a giant bright spot at the top of the reservoir. The method was later also used to map the Temane field with good result. From 1970 to 1980 there have only been drilled 6 wildcat wells in Mozambique 3 of them offshore. An extensive drilling campaign conducted by Sasol in 2003 which included exploration and production wells in the Pande/Temane Block allowed the expansion of gas reserves and the discovery of Inhassoro Gas Field, making total of 5.504 trillion cubic feet, (INP, 2010).

A total of 97 wells were drilled to date in Mozambique. See the Mozambique aggregate map in figure 2, where 61 wildcats, 24 appraisals and 12 production wells. A total of 15 wells located offshore, 16 wells over the Pande Gas Field and 18 wells in the Temane Gas Field, 6 wells over the Inhassoro Gas Field, 4 wells located offshore Zambezi Delta, 1 well drilled in the Rovuma Basin onshore.



**Figure 2.** Exploration for hydrocarbons in Mozambique goes back to 1904 when the early explorers discovered thick sedimentary basins onshore Mozambique.

**Source:** <http://shop.theoilandgasyear.com/mozambique-concession-areas-and-operators-2019/> 02.09.2019

### iii) Floating Liquefied Natural Gas (FLNG) in Mozambique

Coral Sul (figure 3) Floating Liquefied Natural Gas (Coral Sul - FLNG) project located offshore Mozambique, in the southern part of Area 4 of Rovuma Basin, is the first FLNG project in Africa. It is the world’s first deepwater FLNG facility to operate at water depth of 2,000m (6,562 feet).

(ENI, 2021) the developer and operator of Coral Sul FLNG, announced financial closure for the project in December 2017 and started construction in September 2018. The production estimation is 3.4 million tonnes (Mt) a year, over its estimated design life of 25 years, started this mid-2022.

The Coral Sul FLNG project comprises six subsea wells tied-back using three cluster manifolds to a permanently anchored FLNG vessel that is capable of producing and offloading 3Mt of LNG and 480,000t of gas condensate a year, (Coral Sul FLNG Project, 2020).



**Figure 3.** Coral Sul FLNG vessel view.

**Source:** Eni: <https://mz.linkedin.com/company/coralflng>

Measuring 1440 feet long, 213 feet wide, 126 feet tall and 463 MP heavy FLNG vessel was permanently moored with large diameter internal turret to withstand cyclonic weather and oceanic waves, (Samsung Heavy Industries, 2022). The vessel reached at Rovuma Basin in January 2022, and from it, miscellaneous production equipment's were installed including certifications. From June 2022, Coral Sul FLNG began the production.

Samsung Heavy Industries (SHI) was the company the constructed this vessel at Geoje Shipyard in South Korea. The hull of the Coral Sul FLNG is house four turbo compression trains equipped with aero derivative gas turbines and four turbo generation units, and driven by aero derivative gas turbines, for gas refrigeration and power generation.

The FLNG vessel is using dual mixed refrigerant technology for gas liquefaction. It offers a total LNG storage capacity of more than 8 MCF and gas condensate storage capacity of 2 MCF. Boil off gas (BOG) and booster compressors is being used to re-liquefy excessive boil-off gas evaporating out of the LNG storage tanks. The FLNG vessel is also housing quarters for 350 staff on board.

#### **iv) Flow assurance in Coral Sul - FLNG**

Deepwater exploration requires more challenge in all upstream facilities in purpose of mitigate hydrates formation. The depth 6,562 feet that gas will be lifted, the possibilities to form hydrates is a reality. So, new technologies must be explored to monitor hydrocarbon exploration in real time.

Many inhibitors are used in petroleum industry from thermodynamic, environmental and kinetic inhibitors. After many analyses, it is possible to choose the best one that economically have to be practicable to prevent blockage in the facilities to assure the flow.

In 1930, hydrates started to become the biggest challenge in pipelines. Pipelines blocked by ice like plugs which are crystalline compounds which occur when water forms a cage like structure around smaller guest molecule, by (Sloan, 2000).

Natural gas hydrates commonly called gas hydrates, is the crystalline compounds formed when the pressure and temperature of most ocean environment offer appropriate conditions for methane hydrate stability. But considerable amounts of hydrate are formed at the continental shelf due to the effect of geothermal gradient, argues (Remped, 1997).

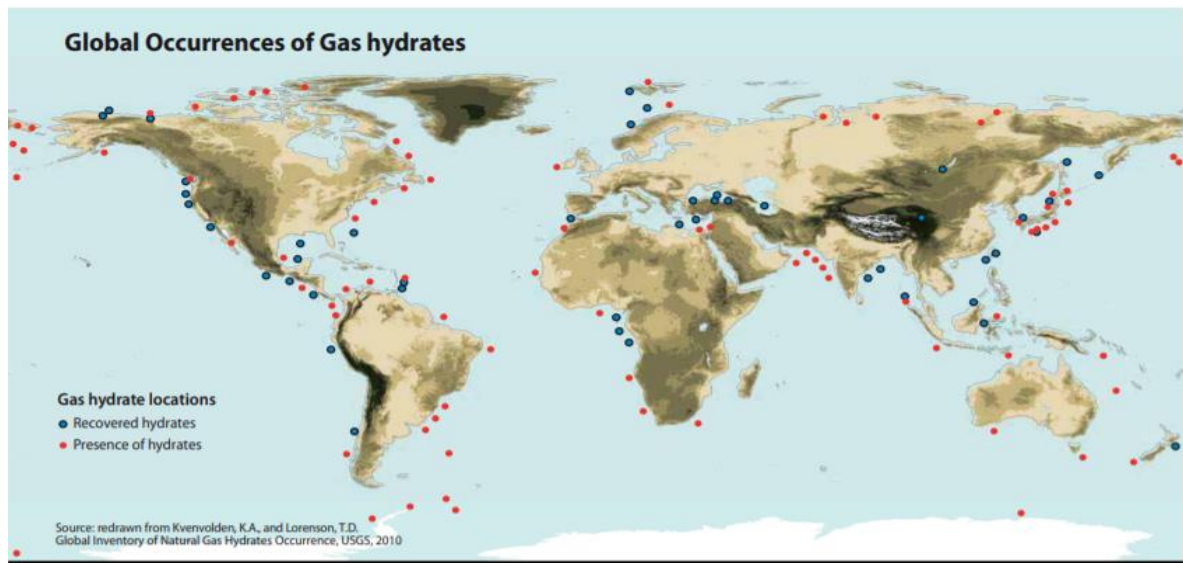
According to (Bahman, 1990) transportation of oil and gas in the pipeline is a common way of transporting oil and gas from wellhead to production site. If the temperature and pressure in pipelines falls within hydrate zone in phase diagram, gas hydrate particles start to form. These particles could eventually plug the pipelines.

### **1.2 Motivation**

There are several published estimates of the total amount of methane stored in gas hydrates worldwide shown in figure 4, and these estimates range over several orders of magnitude. Generally based on an estimation of the volume of continental margins and arctic permafrost basins that fall within the gas hydrate stability zone and their assumed gas hydrate content. A widely cited estimate



suggest that gas hydrate may account for  $1.87 \times 10^{16} \text{ m}^3$ , an amount approximately gas resources (Lorenson, 2001).



**Figure 4.** Map of the locations at which gas hydrates have been recovered and or confirmed.

**Source:**<https://wedocs.unep.org/bitstream/handle/20.500.11822/9355/GasHydratesSumscreen.pdf?sequence=5&isAllowed=y>

It is important to note that hydrates likely have a much broader distribution. Based on seismic and other remote-sensing techniques, it has also been inferred that gas hydrates exist extensively in sub-permafrost, continental-slope, and continental-rise sediments. But the lack of inferred or recovered gas hydrates in the abyssal plains, indicates that gas-hydrate formation is restricted not just by pressure and temperature requirements, but by the need for the elevated methane concentrations available near the continents, (Obanijesu, 2011).

Once the production begins, blockages can be caused by a variety of sources including scale, paraffin, asphaltenes and hydrates. All of these lead to costly issues like production loss, downtime, equipment repairs and more, according to (Obanijesu, 2011).

Gas hydrate formation during deepwater offshore drilling and production is a well-recognized operational hazard, plugging the Blowout Preventer (BOP) stack, chokes and can kill lines and cause a serious well control problem, as mentioned (Ami at al, 2010). Hydrates are one of the issues in this environment which can be caused in many situations as follows below:

- a) Wax Deposition;
- b) Asphaltenes;
- c) Slugging;

- d) Naphthalene;
- e) Scales;
- f) Corrosion;
- g) Erosion; and
- h) Emulsions.

Economic management of the resources in oil and gas industry becomes nowadays a big challenge. Cheaper and efficient inhibitors are needed to insure flow in production environment.

### **1.3 Research Problem**

Mokhatab and Wilkens, R.J., 2017, says that problems associated with gas hydrates in the production and transportation of unprocessed well streams can be avoided by either preventing hydrate formation or allowing the formation of hydrates.

According to (Leontaritis, 2006) the first approach, which is the current practice in this industry, can be made more cost effective by determining the hydrate phase boundary more reliably. For the second approach, it is necessary to determine the amount of hydrates to be transported as slurry. In this research, the first approach was taken in consideration owing its facility for modelling and results analysis.

The basic idea of this research project will illustrate how hydrates are formed and flow assurance of fluid flow from the wellhead until the facilities environment. Economic and scales up of different kinds of inhibitors will be considered in order to minimize high costs that can be faced for remedy, blockage in pipelines or other equipment during the transportation of the fluid.

### **1.4 Research Objectives**

The present research will be concerned to Systemize and Evaluate Hydrate Inhibitors for Flow Assurance (Economic and Scale-Up Analysis) in Keta Basin-Ghana. Therefore, the specific objectives under this context problem are the following:

- i. To analyse PVT data from one of the field ‘Keta Basin’ in order to predict hydrate formation using different kinds of inhibitors to assure flow;
- ii. To predict and show in a phase diagram whether the field being researched can form hydrate so that production is not interrupted;
- iii. To analyse economically which kind of inhibitor is suitable to be used for flow assurance; and

- iv. To give an idea to mitigate formation of gas hydrate in Mozambique at Rovuma Basin from Keta Basin of Ghana study.

## **1.5 Research Methodology**

The methodology used in this research is analytical models and simulation. Using PVT data, we are able to simulate multiple scenarios in order to model which situation hydrates can become undesired in oil and gas industry.

In the first approach, it was assumed that it is possible to predict hydrates using data from the field in study. In other hand was discussed what kind of inhibitor to be used considering the profitable reason. For the computations, we considered from single inhibitors in different weights and also middling inhibitors in order to see which has the best efficiency. Although we varied the weight of each inhibitor, we assumed that this variation according to its effect in phase behaviour diagram. We also assumed the cost of different kinds of inhibitors chosen according to the efficiency and economic cost in the market.

## **1.6 Summary**

In oil and gas industry, high costs can be spent if hydrates could not be prevented as well as it must be well recognized. In such facilities from upstream to downstream environment. The correct inhibitor must be well analysed first by making some models to predict hydrates formation so that selecting the best inhibitors will match with minimising high costs that are engaged with.

## CHAPTER II

### 2. LITERATURE REVIEW AND THEORETICAL FRAMEWORK

#### 2.1 Introduction

This chapter will discuss petroleum concepts in general, especially items related to hydrates forms for assurance in flow, its structure and kinds of inhibitors used to avoid hydrates formation.

Gas hydrates also known as clathrate hydrates, are solid inclusion compounds that are formed when water and gas come into contact at high pressure and low temperature. This host guest system comprises a host lattice of hydrogen-bonded water molecules that forms cages, which encapsulate guest gas molecule such as methane, carbon dioxide, and propane (Caroly, 2011). Gas hydrate formation is also a key issue in deepwater oil and gas production from a safety perspective. As recently witnessed by Watts, 2010, gas hydrates were a major problem in the containment of oil leak following deepwater oil and gas well blowout in many wells.

Although gas hydrates are considered a nuisance when they occur in oil and gas flowlines, they are considered a potential asset when present in large natural deposits in arctic regions under the permafrost and in oceanic sediments along the continental margins. The global of the amount of energy (methane gas) in figure 3, trapped within natural gas hydrates deposits to be twice that of all fossil fuel reserves available worldwide. Upper estimates of gas hydrate deposits are orders of magnitude greater than those for natural gas reserves that an explored now (Dallimore et al, 2010).

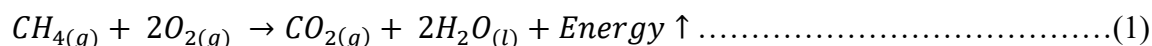
#### 2.2 Formation of gas hydrate

When water molecules come in contact with gas molecules at low temperature and high pressure, different geometric structures contrary to that of a hexagonal ice are formed. The water molecules serve as host molecules and create cage lattices that can hold gas molecules as guest molecules. These cage-like crystalline structures are less dense than crystalline water structure because of the presence of the gas molecules. The gas hydrate formed is held together by the hydrogen bonds of the water molecules and also, stabilized by Vander Waals forces holding the gas and water molecules together. The Vander Waals<sup>1</sup> force is responsible for the stable nature of the gas hydrate and even makes the hydrate more stable than normal ice formed by water. There are different structures of gas hydrate and the shape of their cages characterizes them. Natural gas

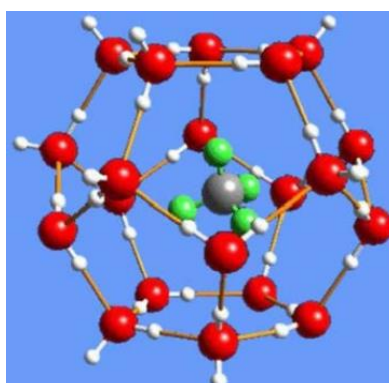
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<sup>1</sup> Johannes Diderik van der Waals was a Dutch theoretical physicist and thermodynamicist famous for his work on an equation of state for gases and liquids. His name is primarily associated with the van der Waals equation of state that describes the behaviour of gases and their condensation to the liquid phase.

composed mainly of methane gas and the complete combustion of methane gas gives water, carbon dioxide, and energy, as shown in the Equation below.



The energy liberated from this process can serve different purposes. This makes natural gas more environmentally friendly than other fossil fuels because more energy is liberated and less CO<sub>2</sub> produced. The pictorial view of the lattice structure of gas hydrate is shown in Figure 5. Methane gas is the guest in the middle in green while water molecule is the host (Pink).



**Figure 5.** Cages structure of gas hydrate (Source: USGS - Science for a Changing World 2014).

Flow assurance problems caused by gas hydrates occur because of slow cooling of oil and gas in pipeline, or rapid cooling due to depressurizing across the valves installed with the pipeline or distribution systems. Recent studies on gas hydrate showed that there are three primary conditions that influence hydrate formation in oil and gas pipelines and in petrochemical processes, there are:

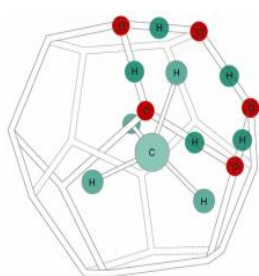
- i. The presence of water and gas components;
- ii. Low temperatures; and
- iii. High pressures.

There are also secondary factors which influencing hydrate formation such as high fluid velocities, agitation, pressure, pulsations or any source of fluid turbulence, the presence of CO<sub>2</sub> and H<sub>2</sub>S, (Gabitto at al., 2010).

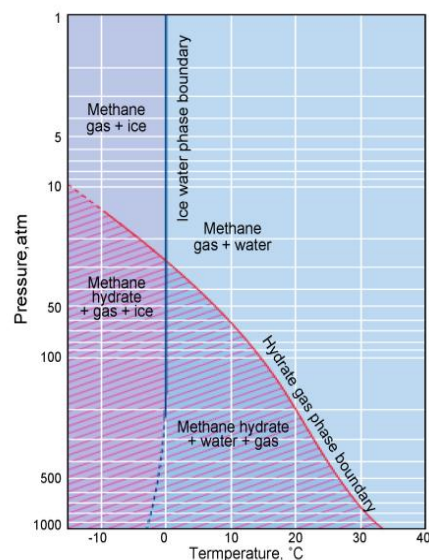
### **2.3 Gas hydrates structure**

Hydrates are formed by hydrogen bond among water molecules. Results of this compounds molecule align to stabilize and precipitate into solid mixture. Formation of gas hydrates cause by contacting of small guest molecule less than 0.9nm such as methane or carbon dioxide (C<sub>2</sub>O) with host under optimum temperatures and pressure. The host and guest molecules are defined as water

molecules and the other compounds those stabilize the crystal. Individual small guest molecule is entrapped in a cage of water molecules that has hydrogen bond between them as shown in Figure 6. A guest molecule is free to rotate within the cavity of water molecules because they have no bonding between host and guest molecule.



**Figure 6.** Molecule structure of gas hydrate



**Figure 7.** Phase diagram of gas hydrate stability

**Source:**

[https://www.google.com/search?q=phase+diagram+of+hydrates&&tbm=isch&ved=2ahUKEwjrtv\\_MvK37AhUMYRoKHcQ1BQYQ2-cC](https://www.google.com/search?q=phase+diagram+of+hydrates&&tbm=isch&ved=2ahUKEwjrtv_MvK37AhUMYRoKHcQ1BQYQ2-cC)

Gas hydrate can be stored or transported at equilibrium conditions with either its saturation temperature or pressure as shown in Figure 7. At the saturation temperature and pressure, hydrates are usually stable. Some factors affect the saturation pressure and temperature of the hydrate. Factors such as cost and weight of material for hydrate storage vessel as well as the environment of the sediments containing the hydrate deposits. Hydrates are usually stable at moderate temperatures and pressures when compared to the conditions required for LNG and CNG, (Aregbe, 2017).

Gas hydrates can form in three different crystalline structures depending on the composition of natural gas implicated during forming. These three structures are discussed in the sections below.

**2.3.1 Structure I**

Structure I (SI) or Type I, and cubic structure I (CSI) are the same structure. SI holds small guest molecules (0.4-0.55 nm) or gases smaller than propane. SI predominates in natural environments. Figure 8 illustrates SI that is 6 large  $5^{12}6^4$  water cages and 2 small  $5^{12}$  water cages per unit cell.  $A^n$  can be interpreted as,  $A$  is the face sides number of a cage and  $n$  is the number of faces in the cage holding (Guan, 2010).

### 2.3.2 Structure II

This structure is sometimes called Type II or cubic structure II (CSII). SII contains gas guest molecule that are larger than SI (0.6-0.7 nm). SII typically occurs with a few percent of molecules larger than ethane. This kind of structure is the most plentiful structure in the oil field environment that has 8 large  $5^{12}6^8$  water cages and 16 small units of  $5^{12}$  water cages per unit cell. This is probably because larger hydrocarbons are present such as pentane and can fill in larger  $5^{12}6^8$  cages, whereas smaller hydrocarbons for example  $\text{CO}_2$  and  $\text{H}_2\text{S}$  can fill in smaller  $5^{12}$  cages. Molecules which are less than 0.35 nm in size are too small to stabilize into any cavities, while molecules size that are larger than 0.75 nm are too large to fill within any cages to form structure I and II. The other smallest gas molecules such as Ar, Kr,  $\text{O}_2$  and  $\text{N}_2$  those have diameter lower than 0.44 nm form SII as well. The guest molecule size with SI and SII are shown in Figure 8.

### 2.3.3 Structure H

Structure H (SH), Type H, or Hexagonal structure H (HSIII) is more complex than SI and SII. In the oil and gas industry, this structure is rarely found. They form only when gas (guest molecules) are consisting of both small and large in sizes (0.8-0.9 nm). All of three structures commonly contain only one non-polar guest molecule within each cage. A size of guest molecule has to be big enough to stabilize in cavity, but not too big to fill the cavity. However, under unusual conditions such as at very high pressure they can have multiple cage occupancy with unusually small guest molecules e.g., hydrogen and noble gasses.

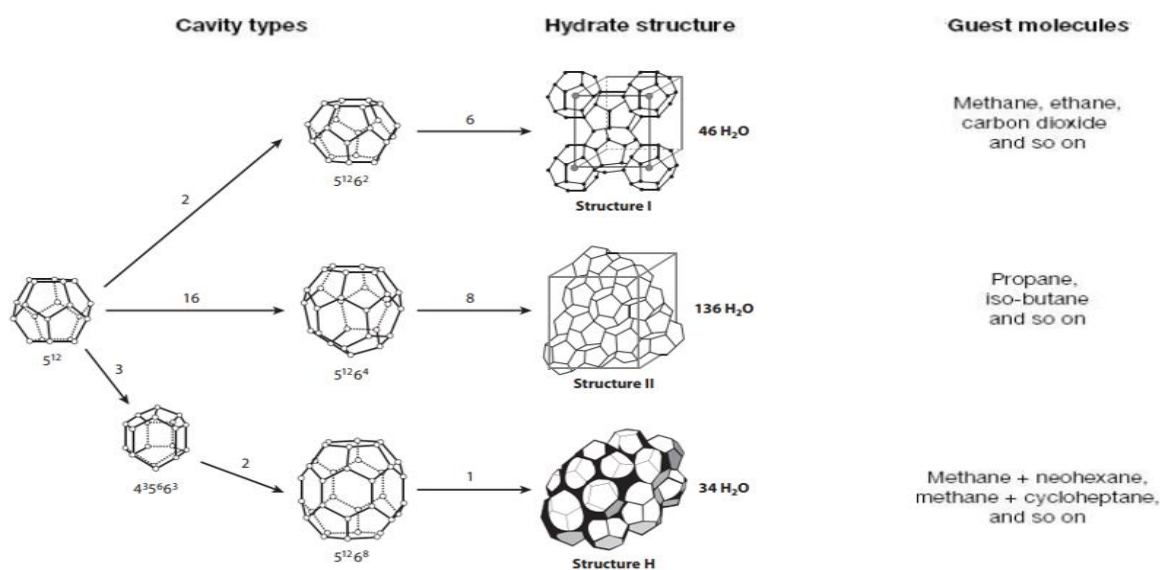


Figure 8. Common gas hydrate structures (SI, SII, SH) and the water cage types that compose the hydrate structures.

**Table 1.** The three-hydrate crystal structure (Sloan, E.D., 2003).

Hydrate crystal structure	I		II		H		
	Small	Large	Small	Large	Small	Medium	Large
Description	5 <sup>12</sup>	5 <sup>12</sup> 6 <sup>2</sup>	5 <sup>12</sup>	5 <sup>12</sup> 6 <sup>4</sup>	5 <sup>12</sup>	4 <sup>3</sup> 5 <sup>6</sup> 6 <sup>3</sup>	5 <sup>12</sup> 6 <sup>8</sup>
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91*	4.06*	5.71*
Coordination Number <sup>2</sup>	20	24	20	28	20	20	36
Number of waters per unit cell	46	-	136	-	34	-	-

\* Estimates of structure H cavities from geometric models.

## 2.4 The effect of the natural gas hydrates (NGH) in flow assurance

### 2.4.1 Blockage in the facilities

Flow assurance can be defined as an operation that provides a reliable and controlled flow of fluids from the reservoir to the sales point (upstream to downstream). Flow assurance operation deals with formation, depositions and blockages of gas hydrates, waxes, emulsions, paraffin, asphaltenes, and scales that can reduce flow efficiency of oil and gas facilities (Nakarit, 2012). Due to significant technical difficulties and challenges, providing safe and efficient flow assurance needs interdisciplinary focus on the issue and joined efforts of scientists, engineers and operation engineers to solve or avoid these troubles, thus, we can describe this situation below.

### 2.4.2 Hydrates formation

It was mentioned by (Guo et al., 2009) that as a rule of thumb, methane caged NGH will form if the temperature is as under as 4.5<sup>0</sup>C and pressures are as above as 11.7 bars. Hydrates are crystalline materials similar to ice in structure and form, at high-pressure and low-temperature conditions. When light hydrocarbons (e.g., methane, ethane, propane, isobutene and inorganic molecules such as CO<sub>2</sub> and H<sub>2</sub>S) meet with water, crystalline molecular complexes form that and can cause blockages in gas flow lines (Johal, 2012) as shown in figure 9. These crystalline compounds of water and low boiling gases are forming a special form of molecular structure.

<sup>2</sup> This is the number of oxygen's of the periphery of each cavity.



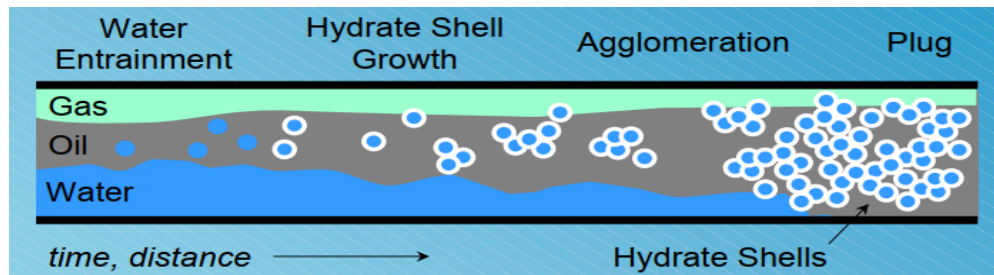


**Figure 9.** Hydrate Plug Formed in a Subsea Hydrocarbon.

**Source:**

[[http://www.uio.no/studier/emner/matnat/math/MEK4450/h11/undervisningsmateriale/modul5/MEK4450\\_Flow assurance\\_pensum-2.pdf](http://www.uio.no/studier/emner/matnat/math/MEK4450/h11/undervisningsmateriale/modul5/MEK4450_Flow assurance_pensum-2.pdf)].

As stated, in oil-dominated systems, water is present in the form of dispersed droplets along with a free gas phase. At high pressure and low temperature conditions, hydrate shells are formed around the dispersed water droplets, thus converting the water droplets to hydrate particles as shown in Figure 10.



**Figure 10.** Conceptual Picture Illustrating Hydrate Formation, Growth, Agglomeration and Plugging Phenomena in Water Dispersed Oil Continuous Systems (Chaudhari PN - 2015).

**Source:** <https://cdnsiencepub.com/doi/10.1139/cjc-2014-0608>

## 2.5 Gas hydrate inhibitors

Understanding the key requirements and the likely location at which gas hydrates form are crucial for the successful gas hydrates mitigation and remediation in drilling, production and transportation. (Lavallie et al., 2009), based on the three key criteria of hydrate formation, the possible means of mitigation may be:

- i. *Removal of hydrate formers;*
- ii. *Dehydration* - removal of water from the system either by separation or dehydration;
- iii. *Increasing the system temperature (Insulation and Heating)* - maintaining high temperatures through insulation and pipe bundling or introducing heat using hot fluids or electrical heating;

- iv. *Decrease the system pressure* - Operating at reduced pressure, although this will decrease transportation efficiency;
- v. *Chemical Inhibitors* - injection of a chemical components to alter the fugacity of water and move the hydrate formation conditions to lower temperatures and higher pressures:
  - *Thermodynamic inhibitors (TI)*
    - Methanol, ethanol and glycols.
  - *Low dosage hydrate inhibitors (LDHI)*
    - Kinetic hydrate inhibitors (KHI); and
    - Anti-Agglomerates (AA).

### **2.5.1 Removal of hydrate formers**

Preventing the formation of hydrates by removing the supply of hydrate forming molecules is not practical as most of the hydrate formers are the primary species in natural gas and petroleum systems. However, this approach may be useful for subsea operation where gas and liquids are separated in subsea, and are transported to the processing facilities in separate pipelines. The gas pipeline still requires hydrate inhibition (through chemical inhibitors) but the liquids line (containing oil and water) is able to operate satisfactorily without forming hydrates due to the absence of hydrate formers. It is not known whether such a system has yet been installed and operated in this way (Lavallie et al., 2009).

### **2.5.2 Dehydration**

According to (Lavallie et al, 2009), dehydration is a therefore common method for hydrates prevention and has the additional engineering benefits of reducing the risk of corrosion and increasing transportation efficiency by reducing liquid accumulation in gas lines. If water could be removed completely then hydrates could not form. On the other hand, if it can be reduced significantly, then the formation of hydrates will be less likely. The amounts formed will be much smaller not to cause any dangerous damages. Glycol dehydration, molecular sieves or refrigeration may achieve dehydration. Glycols are usually used for gas dehydration as:

- i. Water is highly soluble in glycols;
- ii. Hydrocarbons, in contrast, are not soluble in glycols, minimising loss of product;
- iii. Glycols have low vapour pressures, reducing solvent losses due to vaporisation;
- iv. Glycols are thermally stable, allowing regeneration of the solvent by heating to drive off water;

- v. Glycols do not react with CO<sub>2</sub> or H<sub>2</sub>S and are generally non-corrosive. The glycols most often considered for use are mono-ethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) which is the most popular. Often, water content of the gas leaving the contactor will be specified. It should be low enough to avoid hydrate formation at later points in the process as when gases are cooled through gas expansion. Problems may occur if the gas is not dried sufficiently or there is water carry over.

### **2.5.3 Increasing the system temperature**

The initial high reservoir temperatures may be retained by some degree by insulation. Pipelines burial are one means of providing insulation and protection. The degree of insulation depending on the thermal gradient along the pipeline route, the pipeline depth and the environment temperature.

Pipelines burial may be economic on land but very expensive in deepwater. Temperature control by passive insulation only offers hydrate control during normal operation when hot production fluids are continually heating the system. Subsea and buried pipelines will inevitably lose heat to their surroundings, especially following a shutdown the production fluids will cool down and can enter the hydrate envelope. Additional heating can be supplied by either line heaters or heat tracing, although may be neither practical nor economic in all circumstances. A heater has to supply sufficient heat to maintain the fluid temperature outside the hydrate forming region until the next point where heat is supplied.

Alternatively, heat tracing may be used to inject heat continuously along a line, using electrical or fluid mediums. Common means of supplying heat are bundling hot water lines, induction heating with current flowing through cables outside the pipe. Although, within insulation and direct electrical heating in which the pipe acts as a conductor with a current return line in parallel. Supplying heat is usually limited to strategic points in a process, such as valves. Heating tools were later introductions for pipelines and, to be economic, may be available only when the line is most vulnerable, e.g. during shut-in, (Lavallie et al., 2009).

### **2.5.4 Decrease the system pressure**

Much of the process may be controlled by pressure including transportation, compression and expansion. Depressurisation is not used as much in hydrate prevention as hydrate remediation.

## 2.5.5 Chemical inhibitors

The final, and probably the most frequent and effective chemical inhibitor, means of hydrate prevention is by injecting a hydrate inhibitor, such as methanol or MEG (Mono-Ethylene Glycol), which acts as an antifreeze and decreases the hydrate formation temperature to below the operating temperature. These inhibitors are known as thermodynamic inhibitors. Ionic salts also act as inhibitors. These ionic salts are usually present in the formation or production water that must be considered in hydrate inhibition.

### 2.5.5.1 Thermodynamic inhibitors (TI)

The mechanism for thermodynamic hydrate inhibition is the inhibitor dissolving in the free water phase thereby reducing the fugacity of water. As water is the principal component of hydrates, reducing the fugacity of water also reduces the tendency of hydrates to form. It is also important to realise that thermodynamic inhibitors modify the properties of the fluid phases, not the solid gas hydrate phase, and as a result, they have a number of other effects. The presence of inhibitors raises the solubility of gases and hydrocarbons in the water phase thereby inhibiting the formation of hydrates further.

Inhibitors also depresses the ice point and reduces the vapour pressure of water, i.e. it has a dehydrating effect on the vapour and hydrocarbon liquid phases. The weight of methanol provides a greater inhibiting effect than the glycols. Methanol is the most frequently used inhibitor for pipelines and process equipment and it can have some adverse effects:

- ❖ In subsequent processing of the hydrocarbon stream, the methanol may concentrate in the liquefied petroleum gas (LPG). LPG consists largely of propane and butanes, and both propane and n-butane form azeotropes with methanol, making it impossible to separate the systems using binary distillation;
- ❖ Methanol may also cause problems in relation to corrosion. As some corrosion inhibitors are alcohol based, methanol dissolves the inhibitor leading to unexpected corrosion problems. Moreover, if stored on site in tanks open to the atmosphere, it dissolves air, adding to the long-term corrosion effects;
- ❖ Another reported finding is that under inhibition with methanol is worse than no inhibition because under inhibited systems form hydrates faster than systems without inhibitors; and
- ❖ Hydrates stick to pipe walls more aggressively when insufficient methanol is injected. Methanol is relatively volatile, so significant amounts of injected methanol are lost to the hydrocarbon gas, oil or condensate phases. Methanol can be recovered from the free water

phase to reduce concentration such that the water can be dumped overboard. Methanol recovery from the vapour phase, while possible, is seldom done due to considerations of cost and safety.

The use of methanol has become so expensive in terms of capital cost. Storage and operational costs that alternatives to methanol injection have been implemented, particularly in the North Sea. MEG is the most frequently used of the glycols as it has a lower viscosity and is more effective per unit weight. It is also less volatile than methanol, so it is more easily recovered and recycled on platforms and less is lost to the hydrocarbon phases. One potential complication in MEG is that it is recovered with water, and salt concentrates in it to regenerator bottoms. The salt solubility limit in MEG is often exceeded leading to salt precipitation and consequent fouling of exchangers and other equipment, (Lavallie et al., 2009).

**Table 2.** Advantages and disadvantages between Methanol and MEG during their performance.

<b>Methanol and MEG attributes</b>		
	<b>Methanol</b>	<b>MEG</b>
<b>Advantages</b>	Vaporises easily	Easy to recover
	No problems with salt	Low gas and condensate solubility
	Used for flow lines and topside plugs	Used for plugs in wells and risers
<b>Disadvantages</b>	Costly to recover	Flow problems from high viscosity
	High losses to hydrocarbon phases	Salt precipitation and fouling
	May have problems if under inhibition	Remains in water phase

### 2.5.5.2 LDHI - Kinetic inhibitors and anti-agglomerates

Kinetic hydrate inhibitors are injected in much smaller quantities compared to thermodynamic inhibitors. Therefore, offer significant potential cost savings, depending on the pricing policies of major chemical suppliers. They are also typically non-toxic and environmentally friendly. Moreover, considerable field experience is now available following a number of successful trials. However, they have some important limitations, including restrictions on the degree of sub-cooling (typically only guaranteed for less than 10°C) and problems associated with residence times (implications for shutdowns). In addition, the effectiveness of kinetic inhibitors appears to be system specific, meaning that testing programmes are required prior to implementation. Unfortunately, adequate testing can require appreciable quantities of production fluids, which may not be available, particularly for new field developments. Furthermore, they can interact with other chemical inhibitors (e.g. corrosion inhibitors). Finally, there are no established models for

predicting the effectiveness of the kinetic inhibitors, which presents difficulties for field developers considering the application of these chemicals.

The benefits and limitations of anti-agglomerates are largely similar to those for kinetic inhibitors, although they have not the same sub-cooling limitations. However, there is uncertainty about the effectiveness of anti-agglomerates under shutdown or low flow rate conditions and it is postulated that agglomeration may still proceed. In addition, they are limited to lower water cuts due to the requirement for a continuous hydrocarbon liquid phase and field experience with anti-agglomerates appears to be lacking which the relatively small number of publications available in the open literature reflects.

## **2.6 Summary**

Natural gas contains mainly methane, which is colourless, odourless, and combusts completely to generate carbon dioxide, water and significant amount of energy. Therefore, when hydrates are formed, we can see several options to remove it and even to avoid. The economic status and the efficiency of inhibitors in many cases determine what kind of method to be applied to this undesired situation. In such operations, much money may be spent to solve these issues once are well known over the world in terms of being expensive.

Flow assurance can be called in this case as successful operations when undesired elements do not appear, avoided or are removed in facilities of oil and gas industry. Profitable in their cost will insure flow of fluids from the reservoir to the sales point or plant.

## CHAPTER III

### 3. RESEARCH METHODS AND STRATEGIES

#### 3.1 Introduction

In this chapter, we will discuss all the methodologies, principles, methods and strategies that were used for the present research. An analytical method was used to this research to predict the formation of gas hydrate, which can also be done by any type of commercial software available in the market like HydraFlash, Hyd-Predic, PVTsim and others. It is up to the economic rate and the purpose of the research to be done that can make a good decision of which software can be applied to model hydrates for flow assurance.

#### 3.2 Analytical methods to predict hydrates formation

The data were obtained from Keta Basin in Ghana and used to model whether in this field which scenario can have hydrates according to the data given in ‘*The Open Petroleum Engineering Journal*’ which shows this basin modelled using PVTsim with two kinds of gas namely:

- ❖ Synthetic Natural Gas System; and
- ❖ Natural Gas System.

In PVTsim, the natural gas hydrate phase condition predictions are modelled as proposed by (Munck *et al.* 2017), which is derived from the Van Der Waals<sup>3</sup> and Platteeuw model and adapts the Langmuir adsorption theory for determining natural gas molecule occupying a cavity in the hydrate structure. The modified Peng-Robinson (PR) Equation of State (EOS)<sup>4</sup> with volume correction parameter is used by PVTsim to calculate the fugacity parameter in the Langmuir equation.

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<sup>3</sup> *Johannes Diderik van der Waals* was born on November 23, 1837 in Leyden, The Netherlands, the son of Jacobus van der Waals and Elisabeth van den Burg. After having finished elementary education at his birthplace he became a schoolteacher. Although he had no knowledge of classical languages, and thus was not allowed to take academic examinations, he continued studying at Leyden University in his spare time during 1862-65. In this way he also obtained teaching certificates in mathematics and physics.

<sup>4</sup> *The Peng-Robinson EOS* has become the most popular equation of state for natural gas systems in the petroleum industry. During the decade of the 1970’s, D. Peng was a PhD student of Prof. D.B. Robinson at the University of University of Alberta (Edmonton, Canada). The Canadian Energy Board sponsored them to develop an EOS specifically focused on natural gas systems.

We used Natural Gas System data to model hydrates formation, in purpose to see whether the results of the scientific paper where we took the data for simulations could be the same using different software as we did.

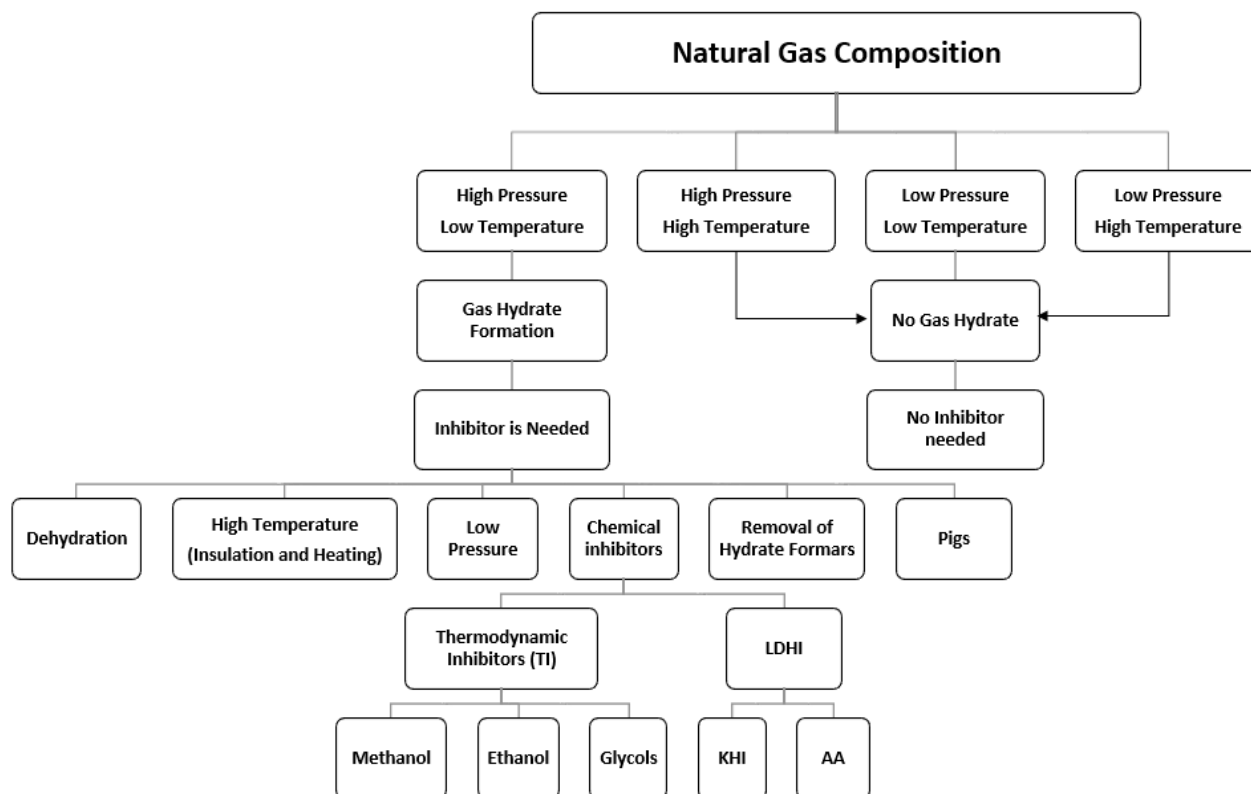


Figure 11. Adapted schematic showing conditions to form hydrates, their Mitigation forms or Solutions.

### 3.3 The research strategies: Data and simulation procedures

In the scientific paper ‘*The Open Petroleum Engineering Journal*’ of Keta Basin in Ghana, PVTSim was used to predict the hydrate formation phase boundary of a synthetic natural gas reservoir. Pressure and temperature ranges from 55 - 81 °F respectively. In this study, we used a software developed by S. Ameripour and M. Barrufet.

The effects of changes in natural gas composition (N<sub>2</sub> and H<sub>2</sub>S) and the presence of thermodynamic gas hydrate inhibitors on the hydrate formation phase boundary are presented in the scientific paper where we took the data. This study is relevant to flow assurance and economics scales-up purpose, where gas hydrate formation at the Keta basin of Ghana was predicted.



### 3.3.1 Experimental data

The entire experimental data gathered and used in this study, see below table 3, we only use composition of Natural Gas once Synthetic one was studied in the source of the scientific paper deeply (This was the key research from the scientific paper).

**Table 3.** Natural Gas composition from Keta Basin in Ghana. Source: DOI: 10.2174/1874834101701010064.

ID	Gas	Synthetic Natural Gas	Natural Gas
		Composition (%)	Composition (%)
1	N2	1.016	0.04
2	CO2	0.853	0
3	H2S	1.191	0
4	C1	59.339	89.86
5	C2	6.752	6.4
6	C3	7.768	2.71
7	iC4	1.659	0.48
8	nC4	4.077	0.49
9	iC5	2.032	0
10	nC5	2.324	0.02
11	C6	1.437	0
12	C7	2.266	0
13	C8	3.177	0
14	C9	3.154	0
15	C10	2.955	0
<b>Sum</b>		<b>100</b>	<b>100</b>

### 3.3.2 Simulation procedures

Many simulations were done considering single inhibitors and cocktail of inhibitors with their weight. The purpose of this methodology was to study the suitable model of the inhibitor(s) to be used according to economic prices in the market of oil and gas industry. Therefore, the simulations procedures sequences were carried out using the table below:

**Table 4.** Adapted table of economics parameters used for simulation analysis.

Inhibitor	Wt									
	1.25%	2.50%	3.75%	5.00%	7.50%	10.00%	15.00%	20.00%	25.00%	30.00%
NaCl	✓	✓	✓	✓	✓	✓	X	X	X	X
Methanol	✓	✓	✓	✓	✓	✓	X	X	X	X
E. Glycol	✓	✓	✓	✓	✓	✓	✓	✓	X	X
Nacl & Methanol	✓	✓	✓	✓	X	X	X	X	X	X

**Where:**

- ✓ - Experience done successfully; and
- X - Experience not done due to limitation of software, Wt. or P allowed to Gas production.

These experiments were done from a software developed by S. Ameripour<sup>5</sup> and M. Barrufet<sup>6</sup>, where the correlations are applicable to a range of temperatures up to 90°F and pressures up to 12,000 psi. The capability of these correlations has been tested for aqueous solutions containing electrolytes such as sodium, potassium and calcium chlorides (NaCl, KCl and CaCl<sub>2</sub>) lower than 20 wt. %. Inhibitors such as methanol lower than 20 wt.%, ethylene glycol (EG), triethylene glycol (TEG) and glycerol (GL) lower than 40 wt.%. Since the use of higher amounts of these inhibitors is neither practical nor economic viability (Barrufet, 2016).

**3.3.2.1 Pseudo-reduced temperature and pressure**

Gas compositions play an important role in the determination of hydrate formation pressure or temperature. By calculating the pseudo-reduced temperature and pressure, we can take into account the effect of each component in the mixture. The pseudo-reduced temperature and pressure are defined as temperature or pressure of a system divided by pseudo-critical temperature or pressure of the mixture of gas:

$$T_{pr} = \frac{T}{T_{pc}} \dots\dots\dots (2)$$

$$P_{pr} = \frac{P}{P_{pc}} \dots\dots\dots (3)$$

**Where:**

T<sub>pr</sub> , P<sub>pr</sub> - Are the pseudo-reduced temperature and pressure in °K and Psia; and

T<sub>pc</sub>, P<sub>pc</sub> - Are pseudo-critical temperature and pressure of gas mixtures in °K and Psia.

---

<sup>5</sup> **Sharareh Ameripour** is currently working at Canadian Natural Resources Limited. Prior to this, she worked for Schlumberger Oil Services in Thailand. She has ten years of work experience as a Process Engineer with the Petroleum Engineering Department of the National Iranian Oil Company in Ahwaz. Her technical interests include gas processes, gas hydrates, gas gathering production planning and production optimization. Sharareh holds a B.Sc. degree in chemical engineering from the Amirkabir University of Technology (Tehran Polytechnic) in Iran, an M.Sc. degree in petroleum engineering and a Certificate in Reserves Estimate and Evaluation, both from Texas A&M University in College Station, TX. She won first place in the Master’s division of the SPE Regional Student Paper Contest (Gulf Coast Region, March 2005) for presenting this paper. She is a member of the Society of Petroleum Engineers (SPE).

<sup>6</sup> **Dr. Maria A. Barrufet** is a Professor in the Harold Vance Department of Petroleum Engineering at Texas A&M University and the holder of the Baker Hughes Chair. She is also the Director of the Distance Learning Program in the Petroleum Engineering Department and the Assistant Department Head for Administration. Dr. Barrufet is an expert in compositional modelling. She has developed fluid models for compositional simulation from near-critical fluids, black oil systems and heavy oils. She has worked extensively in the characterization of fluids for compositional simulation of several fields. Dr. Barrufet has over 100 publications in the area of reservoir simulation, experimental and theoretical prediction of fluid properties, equations of state and neural networks, among other areas, including optimization and algorithm development.

To calculate  $T_{pc}$  and  $P_{pc}$ , we use the relations:

$$T_{pc} = \frac{K^2}{J} \dots\dots\dots (4)$$

$$P_{pc} = \frac{T_{pc}}{J} \dots\dots\dots (5)$$

The range of data for the mixing rules is summarized as follows:

**Table 5.** Range of data for the mixing rules

Source: PIPER, L.D., MCCAIN, W.D. and CORREDOR, J.H., Houston, TX, 3-6 October 1993.

<b>Variables</b>	<b>Mean</b>	<b>Minimum</b>	<b>Maximum</b>
H <sub>2</sub> S	2.45	0.00	51.37
CO <sub>2</sub>	3.38	0.00	67.16
N <sub>2</sub>	1.87	0.00	15.68
C1	71.15	19.37	94.73
C2	8.21	2.30	18.40
C3	4.04	0.06	12.74
iC4	0.90	0.00	2.60
nC4	1.55	0.00	6.04
iC5	0.64	0.00	2.24
nC5	0.88	0.00	3.92
nC6	0.65	0.00	4.78
Temperature, °F	243.8	78	326
Pressure, Psia	3758.6	514	12814
Gas Specific Gravity ( $\gamma_{air} = 1$ )	0.972	0.613	1.821

Where J and K are defined:

$$J = \alpha_0 \sum_{i=1}^3 \alpha_i y_i \left( \frac{T_c}{P_c} \right) + \alpha_4 \sum_j y_j \left( \frac{T_c}{P_c} \right) j \dots\dots\dots (6)$$

$$K = \beta_0 \sum_{i=1}^3 \beta_i y_i \left( \frac{T_c}{\sqrt{P_c}} \right) + \beta_4 \sum_j y_j \left( \frac{T_c}{\sqrt{P_c}} \right) j \dots\dots\dots (7)$$

Where:

- ❖  $y_i$  - is the mole fraction of non-hydrocarbon and  $y_j$  is the mole fraction of hydrocarbon components in %;

- ❖ J = Another term for pseudo geometrical factor, the response of a logging measurement as a function of distance from the tool;
- ❖ K= Reference to the spontaneous potential log, the coefficient, K, in the equation relating electrochemical potential to the chemical activity of the mud filtrate and formation water; and
- ❖  $\alpha_0 - \alpha_4$  and  $\beta_0 - \beta_4$  are constants as given in the following table below.

**Table 6.** Values of constants  $\alpha$  and  $\beta$  for calculating J and K.

**Source:** PIPER, L.D., MCCAIN, W.D. and CORREDOR, J.H., Houston, TX, 3-6 October 1993.

<b>i</b>	<b><math>\alpha_i</math></b>	<b><math>\beta_i</math></b>
0	5.2073E-2	-3.9741E-1
1	1.0160E+0	1.0503E+0
2	8.6961E-1	9.6592E-1
3	7.2646E-1	7.8569E-1
4	8.5101E-1	9.8211E-1

### 3.3.2.2 Gas specific gravity

The specific gravity of the gas mixture is expressed as the molecular weight of the gas mixture divided by the molecular weight of air and is given by:

$$\gamma = \frac{\sum_i y_i MW_i}{MW_{air}} \dots\dots\dots (8)$$

**Where:**

$MW_i, y_i$  - are the molecular weight and mole fraction of component  $i$  in the mixture; and

$\gamma$  - is the specific gravity of the gas mixture.

### 3.3.2.3 Water vapour pressure

The vapour pressure measures the ability of molecules to escape from the surface of a solid or liquid. A common equation to estimate the vapour pressure of a component (in this case, water) is given by (9):

$$\log_{10}(p_w^v) = \frac{a_w^v + b_w^v}{T + c_w^v \log_{10} T + d_w^v T + e_w^v T^2} \dots\dots\dots (9)$$

**Where:**

$T$  - is the temperature of the system in K;

$p_w^v$  - is the vapour pressure of water in mmHg (must be converted from mmHg to psi when used in Equation (10)); and

$a_w^v, b_w^v, c_w^v, d_w^v$  and  $e_w^v$  are constants:

$$a_w^v = 29.8605;$$

$$b_w^v = -3.1522E+3;$$

$$c_w^v = -7.3037;$$

$$d_w^v = 2.4247E-9; \text{ and}$$

$$e_w^v = 1.8090 \text{ E-6.}$$

### 3.3.2.4 Liquid water viscosity

The viscosity measures the resistance of a substance to flow. Viscosity is affected by both temperature and pressure; it will decrease as temperature increases or pressure decreases. Equation (10) calculates the viscosity of a liquid (in this case, water):

$$\log_{10}(\mu_w^l) = a_w^l + b_w^l/T + c_w^l T + d_w^l T^2 \dots\dots\dots (10)$$

**Where:**

- ❖  $T$  is the temperature in °K,
- ❖  $\mu_w^l$  is the viscosity of liquid water in cP; and
- ❖  $a_w^l, b_w^l, c_w^l,$  and  $d_w^l$  are constants:
- ❖  $a_w^l = -10.2158;$
- ❖  $b_w^l = 1.7925E+3;$
- ❖  $c_w^l = 1.7730E-2; \text{ and}$
- ❖  $d_w^l = -1.2631E-5.$

**Table 7.** Values of constants for hydrate formation pressure and temperature correlations.

<b>i</b>	<b>a<sub>i</sub></b>	<b>Standard Error</b>	<b>b<sub>i</sub></b>	<b>Standard Error</b>
0	-2.924729E+0	8.031E-2	3.11137797464E+0	2.39E-2
1	+7.069408E+0	3.424E-1	-6.1218110000E-2	5.4841E-4
2	-6.716740E-1	8.15E-2	-3.4581592000E-2	1.3E-3
3	+2.158912E+0	3.0819E-1	-2.2257841E-2	1.06E-3
4	-1.4446E-2	1.6E-3	-1.61387206E-1	9.5E-3
5	3.367516E+0	9.032E-2	4.644864E-4	3.249E-5
6	-1.68816E-1	3.947E-2	6.0870675E-3	2.101E-5
7	1.3213962E+1	3.0521E-1	-4.9726E-4	4.64E-5
8	2.365031E+0	3.4994E-1	1.682281E-4	1.282E-5
9	-2.5796E-2	3.41E-3	-1.93610096E-1	5.68E-3
10	2.461102E+0	2.3531E-1	1.963793E-4	8.61E-6
11	-7.100059E+0	1.50553E+0	1.324677497E-1	1.1E-2
12	1.820312E+0	1.6222E-1	-7.8512137E-2	4.03E-3
13	7.517561E+0	6.8072E-1	9.232805E-5	4.9397E-4
14	-1.8793E-2	9.1908E-4	-2.32276E-4	2.148E_5
15	1.9029E-2	2.78E-3	8.054836679E-1	3.98E-3
16	-5.307E-3	8.8911E-4	6.3403148E-3	1.04E-3
17	-3.2564E-2	5.44E-3	-	-

### 3.3.2.5 Hydrate formation pressure correlation

The software also applies a regression of model in to find the best relationships among the regression variables. Equation (11) is the result of this regression, the  $p$ -correlation, which predicts the hydrate formation pressure at a given temperature:

$$\begin{aligned}
\ln p_{pr} = & a_0 + a_1 \ln T_{pr} \\
& + a_2 \left[ \left( \sum_i \frac{x_i}{M_i} \right) T_{pr} \right] / \gamma^2 + a_3 \left( \sum_i \frac{x_i}{M_i} \right) T_{pr} \\
& + a_4 \left[ \left( \sum_j \frac{x_j}{M_j} \right) (x_{CO_2} + x_{H_2S} + x_{N_2}) \right] \left( \frac{1}{T_{pr}} \right)^2 \\
& + a_5 \left( \sum_j \frac{x_j}{M_j} \right) \left( \frac{1}{T_{pr}} \right) + a_6 \left[ (\mu_w^l)^4 (T_{pr})^2 (P_w^v) \right] \\
& + a_7 \left[ (P_w^v) \left( \frac{1}{T_{pr}} \right) \right] + a_8 (T_{pr})^2 \\
& + a_9 \left[ \left( 100 - \sum_i x_i \right) (T_{pr})^2 \right] + a_{10} [(\ln \gamma) (T_{pr})] \\
& + a_{11} [(\ln \gamma) (\ln T_{pr}) (P_w^v)] + a_{12} [(\ln \gamma)^2 (T_{pr})^2] \\
& + a_{13} [(\ln \gamma) (T_{pr}) (P_w^v)^2] + a_{14} [(x_{C_3} + x_{iC_4}) (T_{pr})^6] \\
& + a_{15} [(x_{C_3} + x_{iC_4}) (P_w^v) (T_{pr})^6] \\
& + a_{16} [(x_{CO_2} + x_{H_2S}) (\gamma) \left( \frac{1}{T_{pr}} \right)] \\
& + a_{17} \left[ (x_{N_2}) (\gamma) \left( \frac{1}{T_{pr}} \right)^2 \right]
\end{aligned} \tag{11}$$

**Where:**

- ❖  $T_{pr}, P_{pr}$  - are the pseudo-reduced temperature and pressure;
- ❖  $\gamma$  - is the specific gravity of the gas;
- ❖  $x_i$  - variable indicates the concentration of electrolytes, such as sodium chloride, potassium chloride or calcium chloride;
- ❖  $x_j$  - variable indicates concentration of thermodynamic inhibitors, such as methanol, ethylene glycol, triethylene glycol or glycerol, and both are expressed in weight percent;
- ❖  $p_w^v, \mu_l^w$  - are the variables of water vapour pressure and liquid water viscosity;
- ❖  $a_0$  to  $a_{17}$  - are the coefficients of this correlation; and
- ❖  $a_0$  to values of coefficients  $a_{17}$  - are given in Table 3.

### 3.3.2.6 Hydrate formation temperature correlation

Equation (12), the  $T$ -correlation, predicts the hydrate formation temperature when a pressure is given:

$$\begin{aligned}
\ln T_{pr} = & b_0 + b_1 (\ln p)^2 + b_2 \left[ \left( \sum_i \frac{x_i}{M_i} \right) / \gamma^2 \right] \\
& + b_3 \left[ \left( \sum_j \frac{x_j}{M_j} \right) / \gamma^2 \right] + b_4 (\gamma^2) \\
& + b_5 \left[ \left( 100 - \sum_i x_i \right) (\gamma^3) \right] \\
& + b_6 (x_{CO_2} + x_{H_2S} + x_{N_2}) \\
& + b_7 \left[ \left( \sum_j \frac{x_j}{M_j} \right) (x_{CO_2} + x_{H_2S} + x_{N_2}) \right] \\
& + b_8 \left[ (x_{C_3} + x_{C_4}) / \gamma^6 \right] + b_9 [(\ln \gamma)(\ln p)] \\
& + b_{10} [(\ln \gamma)(\ln p)^4] + b_{11} [(\ln p) / \gamma] \\
& + b_{12} [(\ln p)^2 / \gamma] + b_{13} [(\ln p)^3 / \gamma] \\
& + b_{14} [(\ln p)^4 / \gamma] + b_{15} (\ln p_{pr}) \\
& + b_{16} (\ln p_{pr})^2
\end{aligned} \dots\dots\dots (12)$$

Where:

❖  $b_0 - b_{16}$  constants are the coefficients of this correlation and their values are given in Table3.

### 3.4 Economics and Engineering scales-up analysis procedures

#### 3.4.1 Inhibitors at economic analysis

In oil and gas industry, procedures for inhibitors are challenges tasks once its prices are very high. Therefore, in this case to take decision after modelling (we are looking to see which inhibitor(s) has (have) the best performance) not forgetting to see prices of it(s) in the market and try to select the best one in terms of cost and efficiency. Below is presented the prices of different kinds of inhibitors proposed:

**Table 8.** Appreciation of prices of inhibitors in the marked of oil and gas industry – Feb, 2022.

NaCl				Methanol				Glycerol			
Qt (Kg)	Qt (pound)	Price (EUR)	Price (USD)	Qt (L)	Qt (gal)	Price (EUR)	Price (USD)	Qt (L)	Qt (gal)	Price (EUR)	Price (USD)
0.5	1.102	27.2	30.192					0.5	0.132	54.7	60.717
1	2.204	39.7	44.067	1	0.264	30.3	33.633	1	0.264	50.2	55.722
2.5	5.511	87.6	97.236	2.5	0.660	59.2	65.712	3.79	1.001	207	229.77
10	22.046	163	180.93					5	1.320	220	244.2
25	55.115	634	703.74					20	5.283	740	821.4

Source: <https://www.sigmaaldrich.com/programs/research-essentials-products.html?TablePage=102880799>

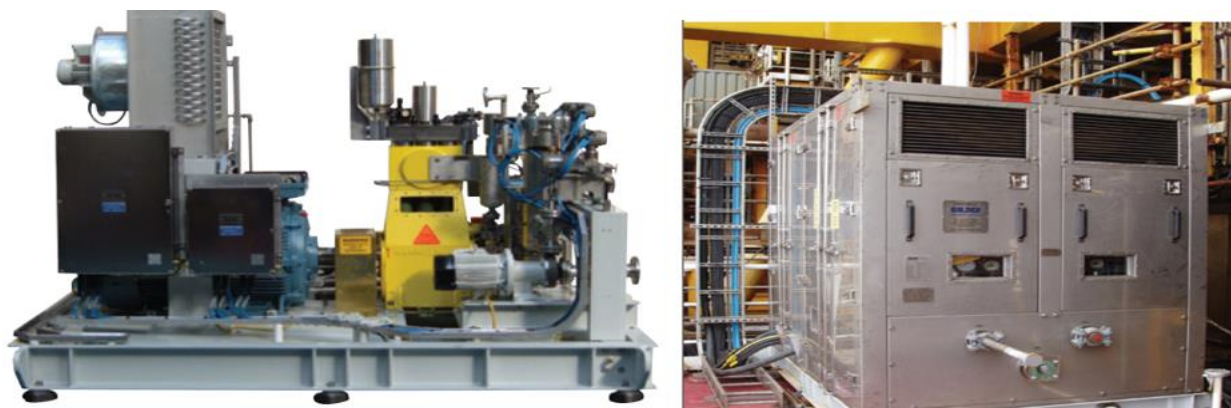


### 3.4.2 Engineering and scales-up analysis (Proposed Equipment)

#### 3.4.2.1 CALDER - A PG flow solution company overview

The Calder range of high-pressure reciprocating plunger pump units figure 12 are designed and built primarily for the Oil & Gas Industry for operation in hazardous and non-hazardous locations; On-shore fields from the Siberian Arctic to Kuwait Desert; Offshore facilities from Northern Norwegian waters to Asian and African tropical oceans. The pump packages are designed to deliver fixed or variable flows at a range of pressures to meet the most challenging field conditions. Below is some important ISO:

- ❖ **ISO 9001** - Quality Standard;
- ❖ **ISO 14001** - Environmental Standard; and
- ❖ **OHSAS 18001** - Safety Record.



*Figure 12.* From left to right: Overview of Methanol Injection Pump Packages -7033 before and after installed.

*Source:* [http://www.calderltd.com/pdf/7033\\_CHEMICAL\\_INJ\\_PUMPS.pdf](http://www.calderltd.com/pdf/7033_CHEMICAL_INJ_PUMPS.pdf)

#### 3.4.2.2 Applications in engineering projects

- Methanol & MEG Injection;
- Glycol circulation (dehydration);
- Injection of corrosion inhibitors;
- General chemical injection; and
- Water & Gas condensate injection.

#### 3.4.2.3 Operation & control systems

- Simple controls to fully integrated unmanned control systems;
- Pump flow rate controls allow fixed or variable flow rates using variable frequency or hydraulic drives;

- Single or Multiple pump unit control systems which can be operated from a remote location;
- Local control systems available which can be skid mounted;
- Full integration & interface with client control systems Dashboard;
- Use of latest communication protocols;
- Comprehensive instrumentation with health/status monitoring functions; and
- Full data acquisition and logging capabilities.

#### 3.4.2.4 Engineering and technical specifications

##### ❖ Temperature, Containerised/Noise Enclosure with Blast

- Noise attenuated: 85, 83 or 78 DBs at 1M (as required);
- Environmental conditions: -40°C (35°F) to 55°C (130°F);
- Hazardous area: Zone 1, Zone 2, or Safe Area; and
- Driver type: Electric motor, hydraulic motor or air motor.

##### ❖ Pump Types

- Triplex or quintuplex reciprocating plunger pumps. API 674;
- Pressure range: 30 bar (435 psi) to 4000 bar (56,000 psi); and
- Flow range: 6.0 Litres/hr (1.6 gph) to 120Litres/hr (528 gph).



**Figure 13.** Offshore Environment of Methanol Injection Pump Packages -7033 in full operation.

**Source:** [http://www.calderltd.com/pdf/7033\\_CHEMICAL\\_INJ\\_PUMPS.pdf](http://www.calderltd.com/pdf/7033_CHEMICAL_INJ_PUMPS.pdf)

In summary, the equipment proposed is from a well-known service provider company in oil and gas industry as mentioned above and has the summarized characteristics in the following table.

**Table 9.** Adapted Table of comparison of the essential parameters of Calder Methanol Injection Pump Packages - 7035 and the field environment to be used at Keta Basin in Ghana.

<b>Proposed Equipment (Pump)</b>			
<b>Variables</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Units</b>
<b>P =</b>	435	56000	Psi
<b>q =</b>	1.6	528	gal/h
<b>T =</b>	35	130	°F
<b>Keta Basin Environment</b>			
<b>P =</b>	625	5076	Psi
<b>T =</b>	55	81	°F

### 3.5 Research validation plan

As mentioned in this study, the aim of the present study is to optimize the cost of the best inhibitors that can be used, avoiding in this case high costs, which are spent in such situations in the facilities of oil and gas industry. Hence minimized this cost, this may be achieved by minimizing the total amount of inhibitors. The cost function of the inhibitors and their equipment must be seen as optimization process to minimize the total cost invested. So, to validate the results, was compared with the result in ‘*The Open Petroleum Engineering Journal*’ from Keta Basin Offshore Gas Reservoir of Ghana.

### 3.6 Study Limitations

The following aspects below can be considered as the main limitations of this study:

- ❖ This research should be done from data of Mozambique Rovuma Basin, therefore, it was a great challenge to get it. Keta Basin Offshore Gas Reservoir from Ghana, was the option to be studied;
- ❖ Simulations are limited at 12,000 Psia, so the cocktail that were done had limitation from its concentration (5%);
- ❖ Electrolytes like  $\text{CaCl}_2$  and  $\text{KCl}$  their results were not presented here owing its low ability to be the best inhibitors, and in this family  $\text{NaCl}$  was the best to be part of sample, and 20% of concentration is the maximum allowed to be injected;
- ❖ In thermodynamic inhibitors, EG and Methanol were chosen to be part of sample than Glycerol and TEG, and maximum concentration allowed are 20% for Methanol, 40% to EG, TEG and Glycerol;

- ❖ Prices of other equipment for instance injection industrial machine (Methanol Injector, ROV, Dashboard simulator in real time) were big challenge to get them, even with the quotation requested as a service provider; and
- ❖ Additional data like flow rate, environment where the equipment must be installed and other information, was given in many papers that were consulted.

## CHAPTER IV

### 4. RESULTS AND DISCUSSION

#### 4.1 Introduction

From the explanation done in the Section III, it is clear that in this chapter we will present the discussion and results of hydrates inhibitors and how to use the best of them in economic approach. From the data given in the area of study, it will be shown which one will be used according analyses done, from the main objective to reach the specific ones. The following approach explains itself below.

#### 4.2 Description of results

After preparing the data for experiment, here follows the samples from de composition of the natural gas to predict whether these hydrocarbons are being produced in safe zone or in hydrate one. It can be demonstrated in charts Pressure & Temperature with different composition of the inhibitors, and in the first part it will have hydrate phase diagram with one inhibitor in different weights and, for the second approach, in the same phase diagram different inhibitors will be analysed in purpose to find the good one.

##### 4.2.1 Inhibitor: NaCl at 2.5; 5.0; 7.5 and 10.0% Wt.

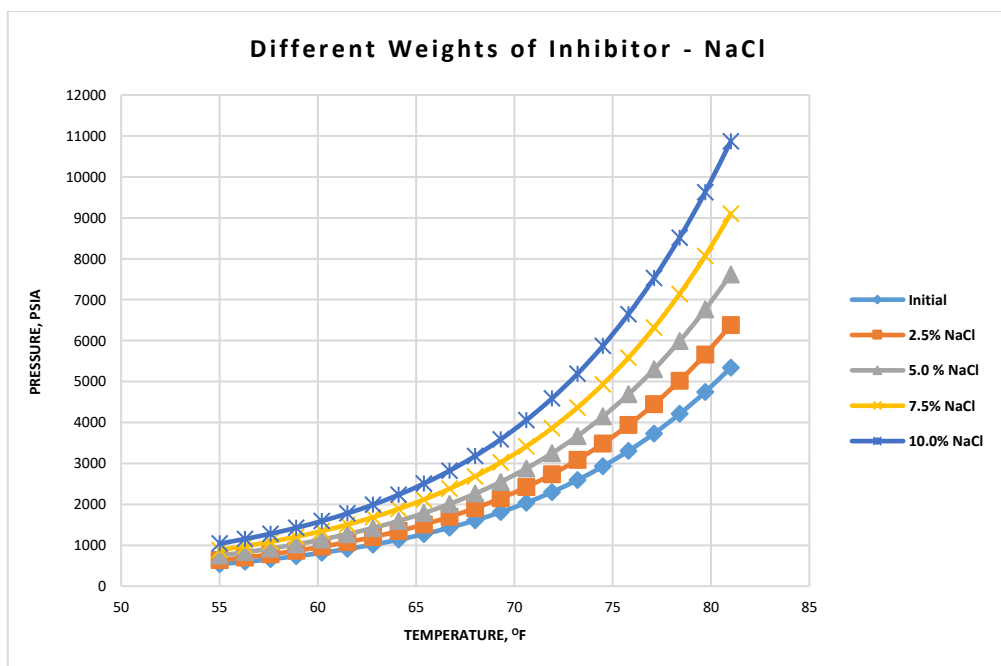
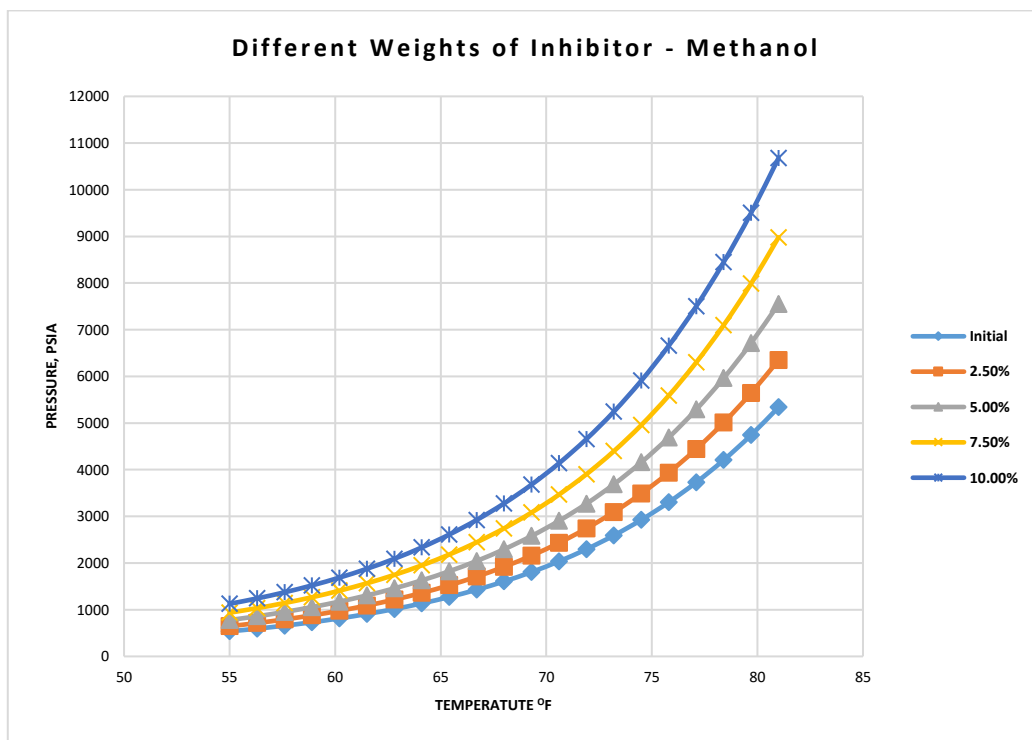


Figure 14. Phase diagram of different weight of the Inhibitor – NaCl.

Electrolytes are good inhibitors as it can be seen in figure 14, NaCl at all weights tries to push the phase boundary to the left side, which means that operational pressure in the field is arising significantly and, in this scenario, it is a good signal for the production that will have no need for artificial lift of hydrocarbon from the reservoir up to upstream.

#### 4.2.2 Inhibitor: Methanol at 2.5; 5.0; 7.5 and 10.0% of Wt.



**Figure 15.** Phase diagram of different weights of Inhibitor – Methanol.

For all these Phase Diagrams, the goal is to turn the *initial* condition (real first situation where the hydrocarbons are produced to left side) so that its can be produced in free zone and in safer condition.

Thermodynamic inhibitors like methanol are one of the better and is worldwide most used for hydrate solution in oil and gas industry. In figure 15 from initial condition, step by step modelling 2.50% in wt up to 10.00%, for each wt, it is clear that P rises significantly showing in this experience the most preferred inhibitor to be used.

### 4.2.3 Inhibitor: Ethylene Glycol (EG) at different weights

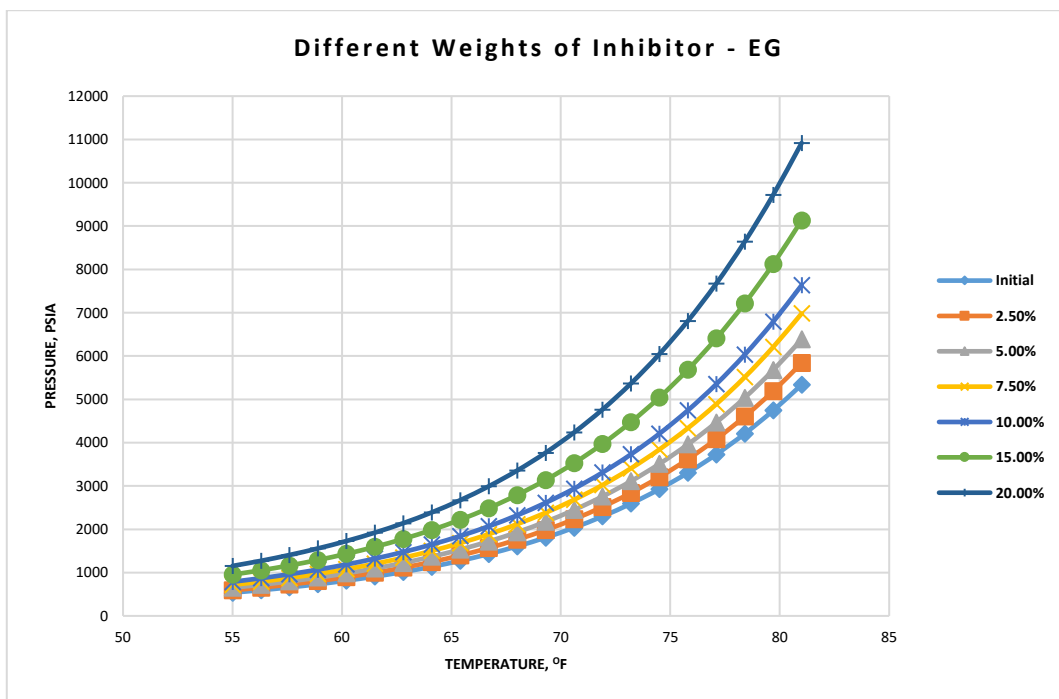


Figure 16. Phase diagram of different weights of Inhibitor - Ethylene Glycol.

In figure 16, this inhibitor (EG) can be used up to 40% and in this experiment, went up to 20% due to high pressure situations seen in the sample (more than 12 000 Psia). Also is considered one of the best inhibitors that can be used in such case once the cost and the efficiency allows us to put it in the top of the best to be recommended in this study.

### 4.2.4 Cocktail of Inhibitors: NaCl & Methanol at 1.25; 2.50; 3.75 and 5.00% of Wt

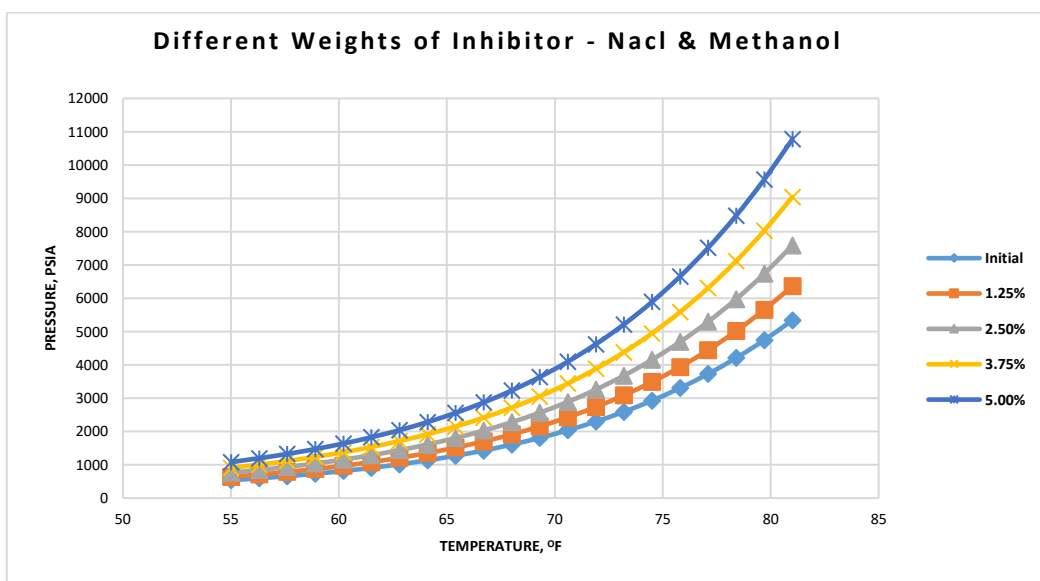
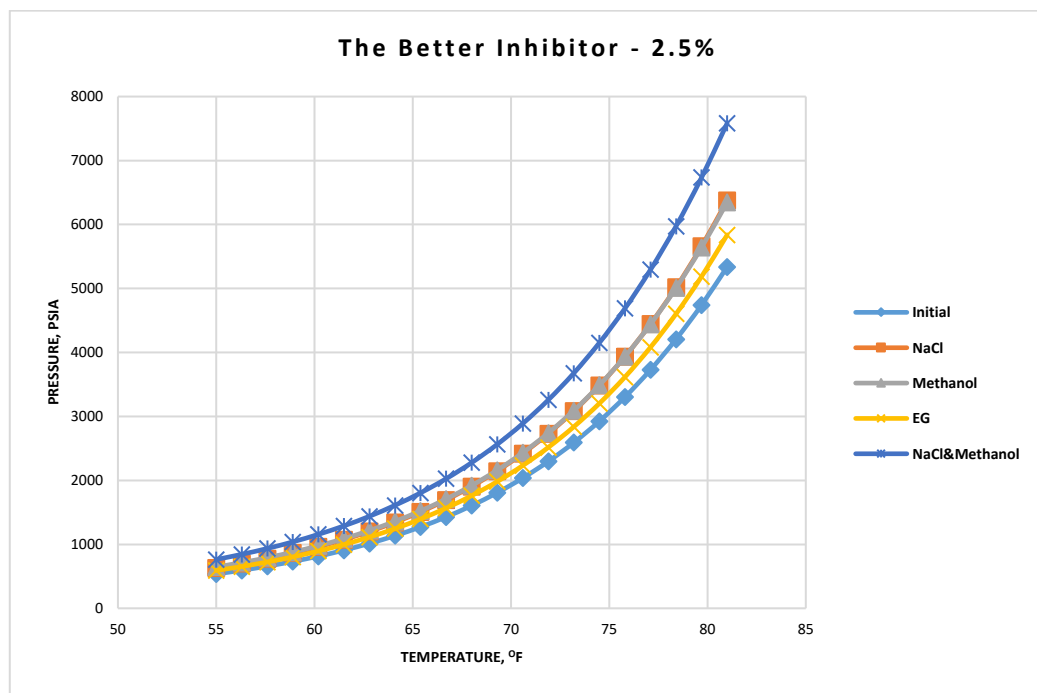


Figure 17. Phase diagram of cocktail Inhibitors in different weight – NaCl & Methanol.

The results can be seen among these miscellaneous experiments of these inhibitors (figure 17), in the cocktail made from Methanol & NaCl. In every percentage of wt. the efficiency from initial situation T for instance, pressure double in only 5% of Wt. More weight it goes at high P environment (more than 12 000 Psia).

#### 4.2.5 Analysis of different Inhibitors at 2.5 and 5.0% of Wt.

At this stage, now is the time for the second approach to be analysed. From many experiments done, combinations of medley inhibitors can be done so that deeper analyses can be seen. Calling all proposed inhibitors at the same weight in the same Phase Diagram, it can be analysed their efficiency among them. Results are shown below at figures 18 up to 21.

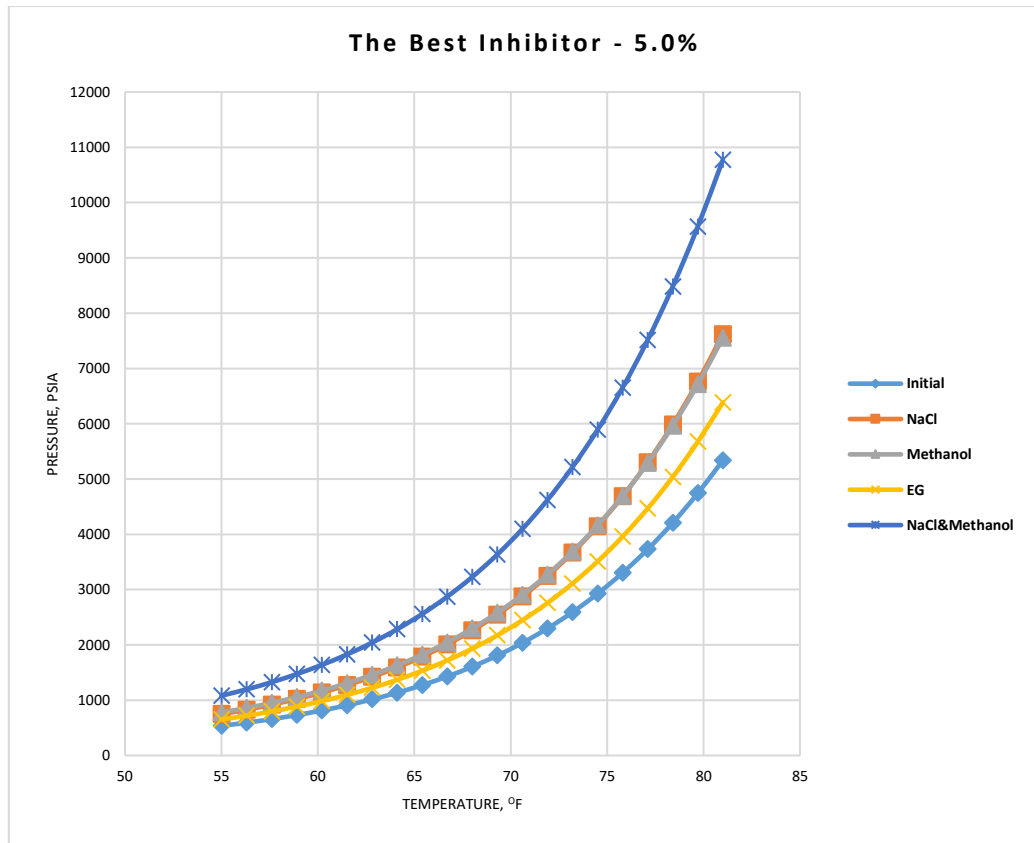


**Figure 18.** Phase diagram of all proposed Inhibitors to be used at 2.5%.

Now, it is time to see which inhibitor(s) is(are) better with their wt in these models. From figure 18, at 2.5% of wt it is clear that we can add more wt to enhance the performance of these inhibitors. The cocktail – NaCl&Methanol is the best among others. P= 12 000 Psia is not desired because blowout may occur, so the actual T is less than 8 000 Psia, therefore, next step is to increase the wt.

NaCl and Methanol, their curves are overlapping themselves showing in this scenario the same behaviour in their efficiency.





**Figure 19.** Phase diagram of all proposed Inhibitors to be used at 5.0%.

According to efficiency of each inhibitor from 2.5 and 5.0% of wt, all experiments were done successfully, while beyond this weight some inhibitors cannot be applied due to high P phase diagram that shows us, e.g., cocktail of Methanol & NaCl. In figure 19, now 5.0% of wt is modelled and still persisting the good efficiency of the cocktail – NaCl&Methanol. NaCl and Methanol are competing in their efficiency, and it can be seen from the overlapping curves.

In this situation, the inhibitor cocktail – NaCl&Methanol is now at the end of its wt to used, owing high P zones that is allowed in oil and gas industry productions facilities.

#### 4.2.6 Analysis of different Inhibitors at 7.5 and 10.0% in weight

At this stage, once the inhibitor cocktail – NaCl&Methanol is out for more modelling, 7.5 an 10.0% of wt will be done for other inhibitors. Phase Diagrams bellow illustrated will show the performance of the rest three inhibitors namely Methanol, NaCl and EG.

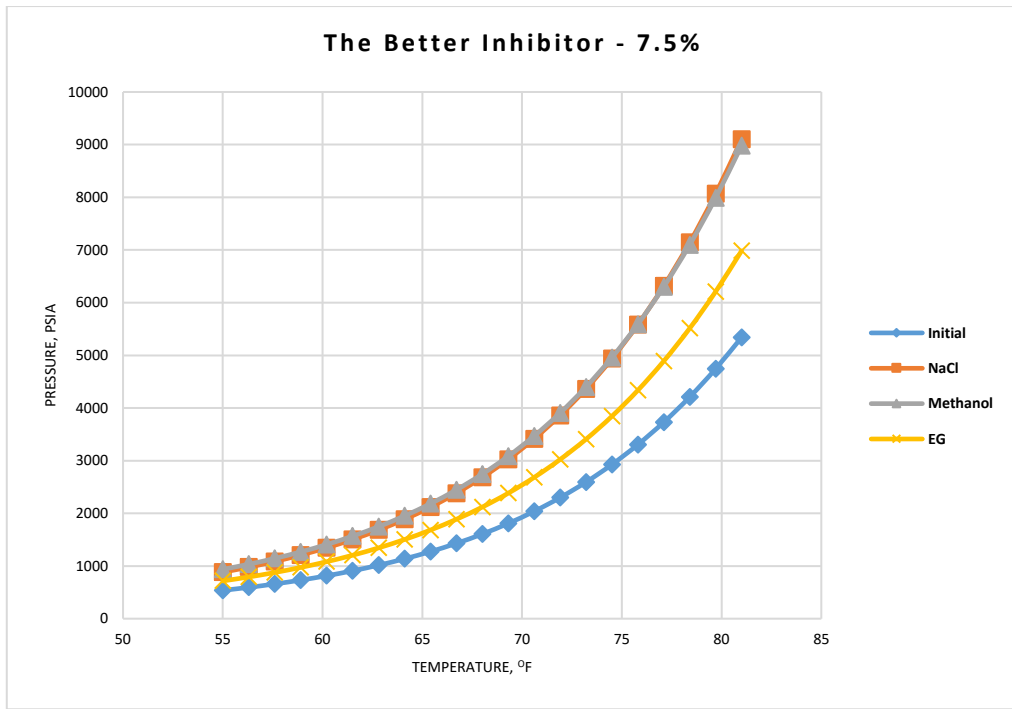


Figure 20. Phase diagram of Inhibitors at 7.5%.

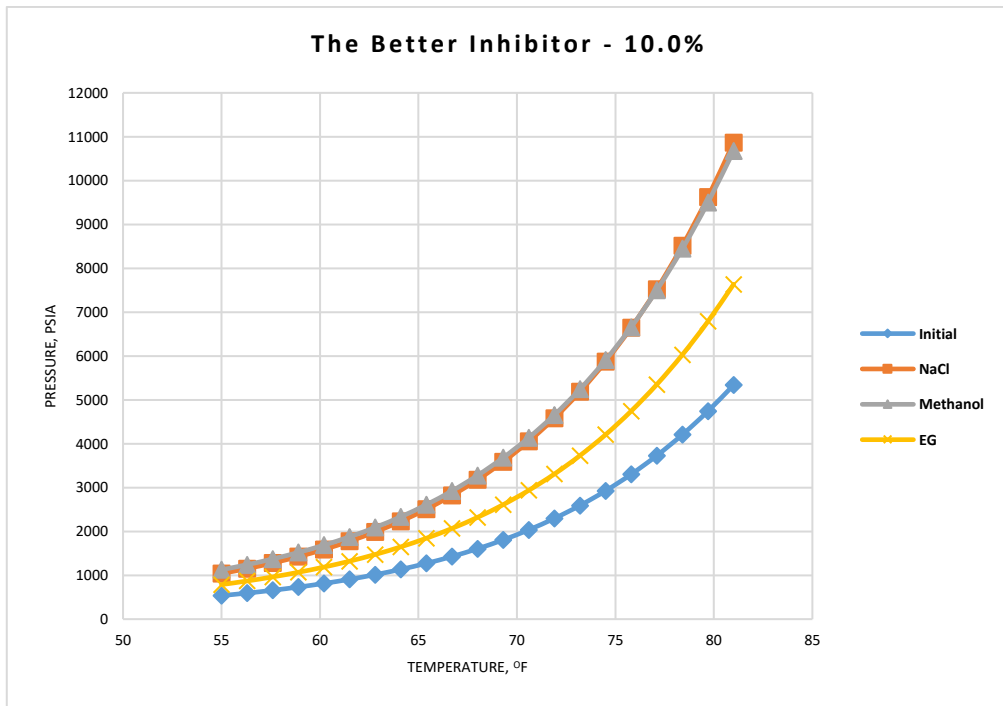
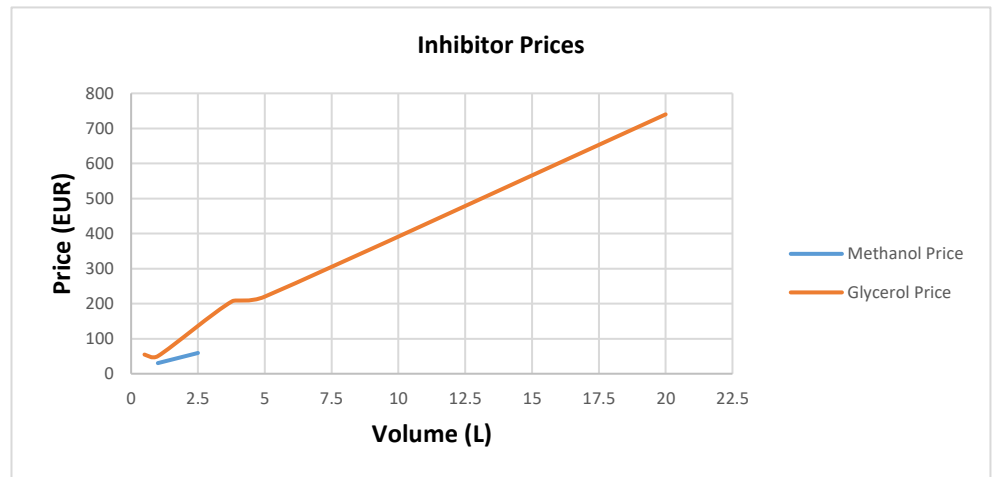


Figure 21. Phase diagram of Inhibitors at 10.0%.

In figures 20 and 21, the same efficiency is seen from inhibitors Methanol and NaCl, their curves are overlapping at all wt (7.5 and 10.0% of wt). At this wt (10%) it is enough wt to be modelled. More wts implies high P zones which means blowout scenario. Methanol and NaCl are better inhibitors in these models.

### 4.3 Results of economic analysis and Engineering scales-up

This section presents the economic analysis results from the project alternative decision chosen. After many simulations from several inhibitors of different weights, now it is time to set the best one among all simulations taking an account the economic sensitive analysis from the cost of the inhibitors that are illustrated in Table 8.



**Figure 22.** View of prices for inhibitors at the market of oil and gas industry supply. Source:

<https://www.sigmaaldrich.com/programs/research-essentialsproducts.html?TablePage=102880799>

Before a good decision from what kind of inhibitor to be used, we can simulate the real environment where and how much will be applied. In figure 23, are two scenarios that Methanol Injector can be installed.



**Figure 23.** FLNG vessel or platform (Jack up Rig) are the samples where the proposed equipment can be installed.

**Source:** [www.flexlngproducer.com](http://www.flexlngproducer.com)

**Table 10.** Environmental analyse between proposed equipment at Keta Basin.

<b>Proposed Equipment (Methanol Injector)</b>			
<b>Variables</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Units</b>
<b>P =</b>	435	56000	Psi
<b>q =</b>	1.6	528	gal/h
<b>T =</b>	- 40	130	°F
<b>Keta Basin Environment</b>			
<b>P =</b>	625	5076	Psi
<b>T =</b>	55	81	°F

**Table 11.** Economic analyse of cocktail inhibitors prices and production rate.

<b>q (gal/h)</b>	<b>q (gal/d)</b>	<b>Production/Day</b>		<b>Qt/day</b>		<b>Price/Day (USD)</b>	
		<b>gal</b>	<b>ft<sup>3</sup></b>	<b>5% NaCl (pound)</b>	<b>5% Methanol (gal)</b>	<b>Cost NaCl</b>	<b>Cost Methanol</b>
250 <sup>7</sup>	6 000	74 805 <sup>8</sup>	10 000	500	500	18,012.7	49,781.82
				<b>Total Cost (USD)</b>	<b>67,794.52</b>		

#### 4.3.1 Economic analyse of sensibility

Once the prices in market can vary any time without a pre-announcement. In the oil industry, the final sale price of gas, in addition to several variants of production costs, inhibitors directly affect the final sale price on the international market. The total cost showed in table 11, demonstrates the inevitable cost of gas production. This cost may vary depending on market prices as well as currency inflation or international market demand.

The price in cubic feet of gas on the market varies depending on production costs. Hence, the increase in the cost of purchasing inhibitors, it will directly affect production costs, and thus, the variable price of gas sales will directly suffer from this oscillation. In this context, this project, as it is an economic analysis of these inhibitors, for its implementation, it will always be necessary to reassess the economic stability of the prices of the inhibitors (Methanol & NaCl) at 5% wt proposed.

<sup>7</sup> These values were chosen arbitrary for simulate the cost of inhibitors during the production, once we have no data of Keta Basin.

<sup>8</sup> In addition, these ones were chosen in random for having an idea.

For the same study in Mozambique, having data such as  $q$  and the amount of production per day, it will have a real mirror from what it can be spent on inhibitors (not forgetting to add this cost with the cost of the ROV Software, methanol injector and the ROV which will be explained later).

### **4.3.2 Ethylene Glycol Injection**

In a Methanol injector system, glycol is injected into a gas stream at a point upstream of hydrate prone areas such as high pressure or low temperature regions (this is normally injected by umbilical, see figure 24 and controlled remotely by ROV, see figures 25 and 26). Glycol in gas stream prevents hydrate forming conditions by absorbing the free water in the system.

The glycol and water mixture may be separated by regeneration, allowing the glycol to be recycled. Ethylene glycol is generally preferred to DEG or TEG for this type of operation due to its low solubility in hydrocarbons. EG also possesses a low viscosity and is more effective on a weight basis for hydrate inhibition (Kohl, 1985).

### **4.3.3 Methanol Injection**

Methanol is also used to control hydrate formation. The methanol injection process is sufficiently similar to the glycol injection process previously discussed (Kohl, 1985). Unlike the glycol process, methanol is typically not regenerated in gas processing systems. Therefore, BTEX (xylenes) emissions are not a consideration in the non-regenerated methanol system.

## **4.4 Fundamental subsea equipment for inhibitors injection**

In figures 23 and 24, we can see clearly offshore environment, production stage, and flow assurance and in all the facilities are essential task for hydrate remediation and consequently minimizing the costs. Many kinds of pipes or equipment's are used:

- ❖ Jumpers;
- ❖ Risers;
- ❖ Flowlines;
- ❖ Pipelines;
- ❖ X - Mas tree;
- ❖ Umbilical;
- ❖ Flying leads;
- ❖ Manifold;
- ❖ PLET (Pipeline End Termination); and

- ❖ UTA.

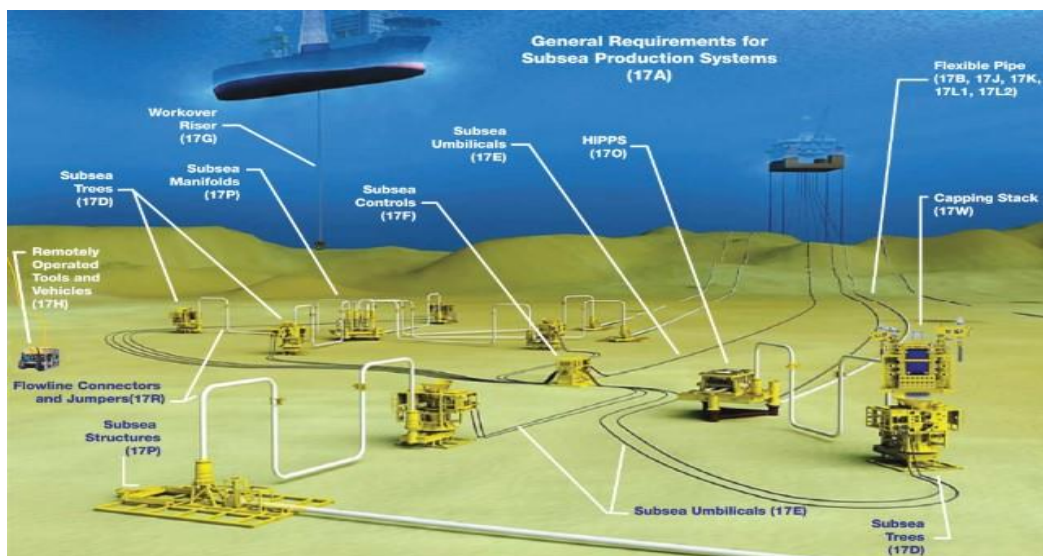
The above pipes are used for the special purpose according to the work that are designed for, and here we have some equipment below that can be appreciated in subsea environment, see figure 23:

- ❖ FPSO;
- ❖ CPF;
- ❖ LNG, LPG Plant; and
- ❖ Offtake tanker.



**Figure 24.** Generalised facilities in offshore (upstream) and onshore environment for gas production.

**Source:** <https://www.upstreamonline.com/field-development/subsea-race-for-abadi/2-1-770100>

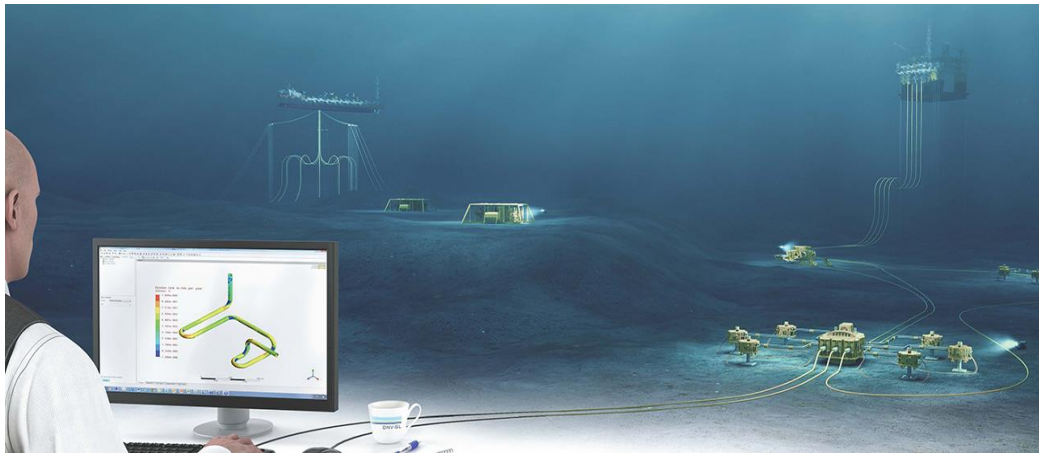


**Figure 25.** Generalised facilities in offshore environment (Upstream) for gas production.

**Source:** <https://mycommittees.api.org/standards/ecs/sc17/default.aspx>

In this environment, umbilical (in red) is used to inject inhibitors which is put at downstream flowing to UTA, Flying Leads in blue, X-Mas tree, manifolds, i.e., it runs from all subsea facilities (see figure 25) to ensure the flow and is returned in pipelines as a production. At downstream in separators, these inhibitors must be taken off or recycled for another injection. Methanol is not recyclable.

With the advancement of technology, all these processes can be monitored remotely in real time of the actions, see figure 26.



**Figure 26.** Typical environment for facilities (Pipes) management controlled remotely in order to monitor hydrate formation daily.

**Source:** Subsea-ill-w1288xh500px1\_tcm8-141407.

Remotely operated vehicles (ROVs), figure 26, is a safe and widely used type of underwater vehicle serving a range of military, commercial, and scientific needs. ROVs are unoccupied, highly manoeuvrable underwater robots operated by a person on the surface as we can see below. An intelligent submarine capable of inspecting wellheads and pipelines over tens of kilometres, in 3,000 meters (9843 feet) of depth. Capable, too, of detecting anomalies independently, providing real-time warnings and transmitting large amounts of data so that his innovation would allow performing the same tasks four times faster, improving both safety and costs.





**Figure 27.** ROV - Last and high technology from Total for monitor subsea facilities (pipes) for flow assurance.

**Source:** <https://www.total.com/en/media/news/news/linnovation-total-3-000-metres-sous-les-mers>

## 4.5 Temperature and pressure drop during injection

### 4.5.1 Temperature variation

In injection, environment drops of temperatures or pressure are issues that always engineers must deal with. For many reasons, T drop is an issue that must have a constant look in production environment and Total technologies has developed such technology to monitoring it in real time. T and P of the fluid (see figure 25 and 26) and this ROV can work in depth of between 2000 to 9000 feet.

**Table 12.** SARSHAR, Sacha. *SPE London meetings in subsea production and flow assurance*, CALTEC, 2013.

Pipe Length (miles)	Temperature Drop (°F)	
	Flowlines	Risers
3	1.2	16.6
6	2.9	16.6
15	9.2	16.5

The graph below, illustrates the drop of T according to the distance in miles that the gas is travelling. In this case, it is noted that the Risers in terms of the T drop tends to be more stable in relation to the flowlines.



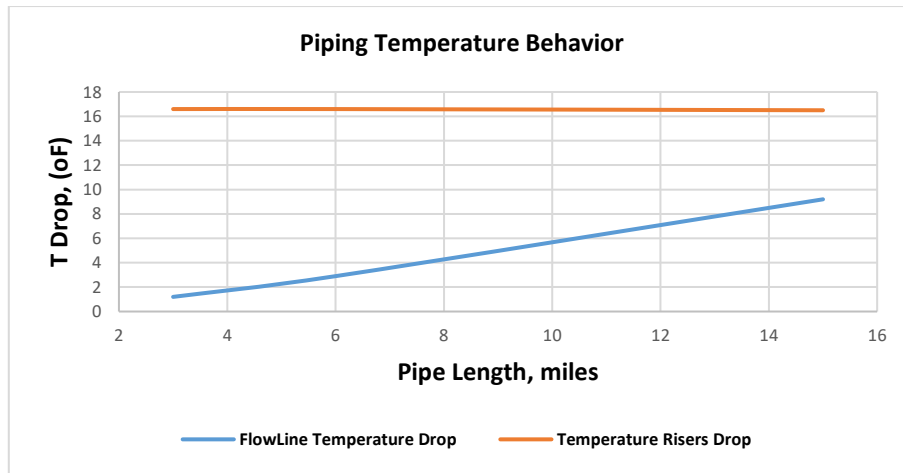


Figure 28. Temperature profile along the Gas export line for various flow rates.

### 4.5.2 Pressure drop

One of the big challenges in production engineering and facilities is the pressure drop during the production. Here is the general equation for calculating gas flow drop:

$$w^2 = \left[ \frac{144gA^2}{V_1' \left( \frac{fL}{D} + 2 \log_e \frac{P_1}{P_2} \right)} \right] \times \left[ \frac{(P_1)^2 - (P_2)^2}{P_1} \right] \dots\dots\dots (13)$$

Where:

w = Rate of flow dropped in lbm/sec;

g = Acceleration of gravity, 32.2 ft/sec<sup>2</sup>;

A = Cross-sectional area of pipe, ft<sup>2</sup>;

V<sub>1</sub>' = Specific volume of gas at upstream conditions, ft<sup>3</sup>/lbm;

f = Friction factor, dimensionless;

L = Length, ft;

D = Diameter of the pipe, ft;

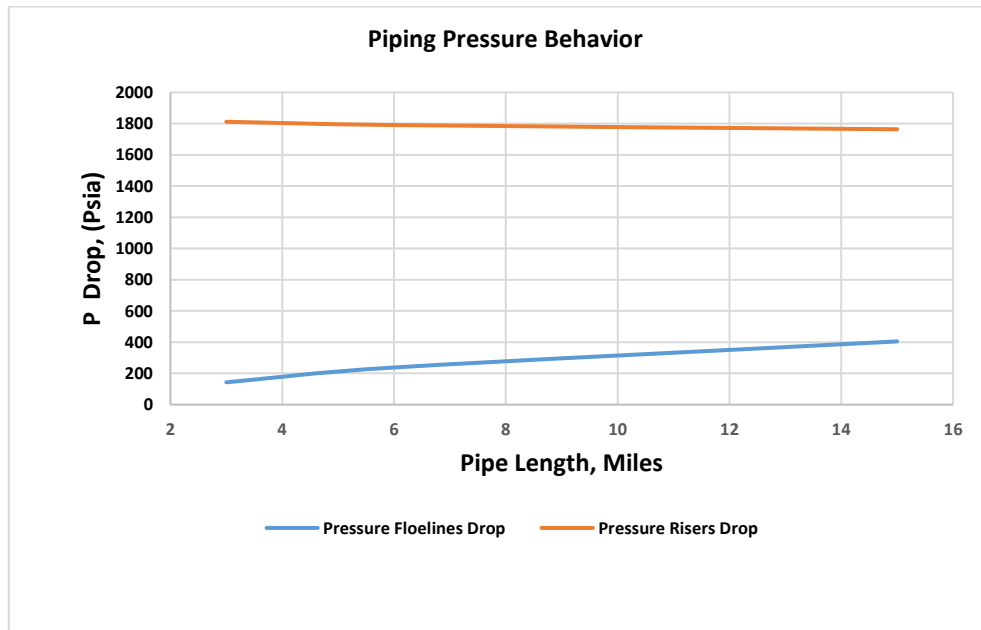
P<sub>1</sub> = Upstream pressure, psia; and

P<sub>2</sub> = Downstream pressure, psia.

Assumptions: no work performed, steady-state flow, and f = constant as a function of the length.

Table 13. SARSHAR, Sacha. SPE London meetings in subsea injection and flow assurance, CALTEC, 2013.

Pipe Length (miles)	Pressure Drop (Psia)	
	Flowlines	Risers
3	143	1812
6	238	1791
15	405	1764



**Figure 29.** Typical pressure profile along the gas export line for various flow rates and upstream pressures.

The same analysis can be done on the P fall according to the distance that the gas travels. The same conclusion is done for Risers tend to be more stable in relation to Flowlines. In this case it will depend on the total fulfilment of the Flowlines so that there is a given distance<sup>9</sup> a pump can be mounted so that the P is increased so that the gas reaches to the next treatment step (facilities).

#### 4.6 Challenges for Subsea Equipment

Most of subsea equipment are very expensive and for their installation for high production in oil and gas industry. It is recommended that previous studies must be analysed in purpose of minimizing huge costs that can be spent. Nevertheless, here are some points to be considered:

- ❖ Reliability - 5 to 8 years or longer and acceptance criteria-approvals;

<sup>9</sup> In this scenario a full Production Engineering study must be done to monitor or to model the P drop so that pumps can be stalled to increase the pressure.

- ❖ Collaboration between operators and suppliers of equipment/system is needed to share costs/risks/rewards; and
- ❖ Standardisation are needed to improve reliability and simplify qualification or approvals.

#### 4.7 Discussion of Results

For several inhibitors namely Methanol, NaCl at (2.5, 5.0, 7.5 and 10% of wt.), EG at (2.5, 5.0, 7.5, 10, 15 and 20% of wt.) and cocktail of Methanol & NaCl at (1.25, 2.25, 3.75 and 5.00% of wt.) were done experiments as shown in figures 13 to 20. KCl, NaCl<sub>2</sub>, TEG and Glycerol were not done due to low efficiency to become the best inhibitor in this study. Methanol and NaCl were better among others tested, but the cocktail of Methanol & NaCl was the best than all inhibitors according to experiments and price in oil and gas market.

From the previous research in this Basin of Keta, Methanol showed also the efficient than many other inhibitors used, although the component cost was not taken in account.

After many analyses from different kinds of chemical inhibitors, we can assume that thermodynamic inhibitor (Methanol) is the most used worldwide than EG. In terms of efficiency, Methanol and NaCl showed good results (Figure 19) in mixing them at 5% for each. For instance, at wt. = 5%, T = 75 °F the results before and after put the inhibitor can be appreciated in the table below:

**Table 14.** Comparison of inhibitor efficiency at the same T and wt. before and after.

T (°F)	Wt. (%)	Inhibitor	Pressure (Psi) (Without Inhibitor)	Pressure (Psi) (With Inhibitor)
75	5	Cocktail (Methanol & NaCl)	3000	6300

Notwithstanding, the model to be used is this cocktail at this wt. and T, it means, P can arise from 3000 to 6300 Psia! Therefore, at this situation we can produce hydrocarbons easily without any worry about some mechanism of lifting it, which normally need additional cost.

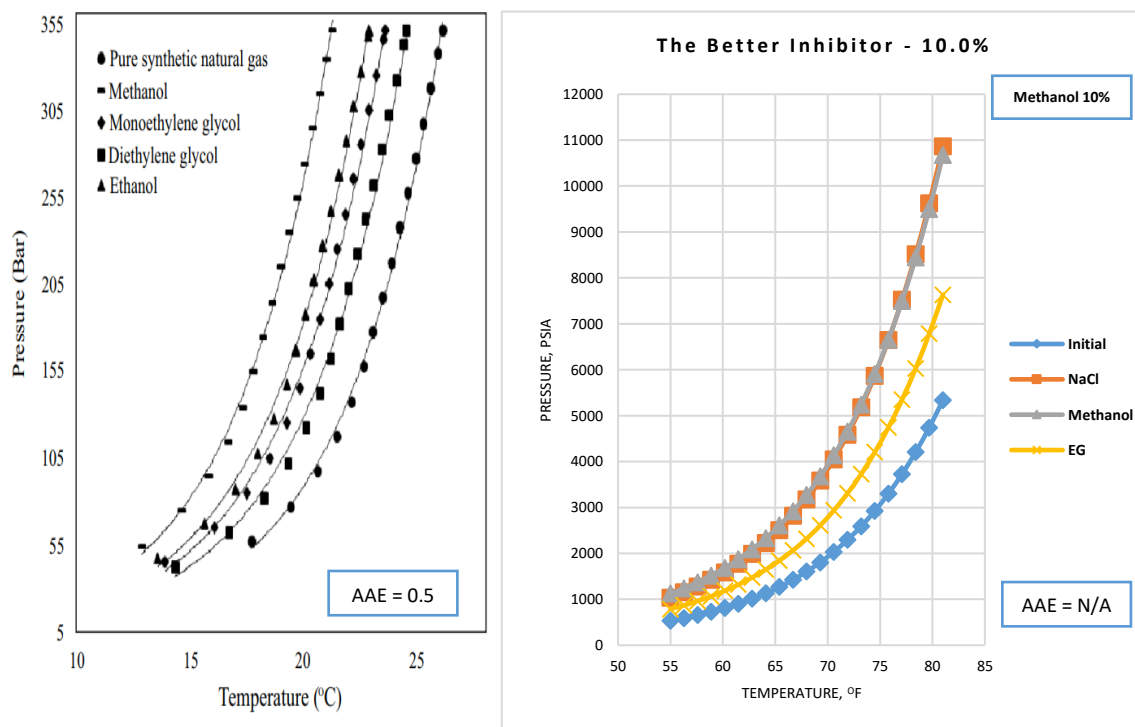
To choose an inhibitor for hydrate prevention for flow assurance, it was done after many experiments from thermodynamic inhibitors (Methanol and Glycerol) and from LDHI - NaCl.

#### 4.8 Research results and validation

Clearly, after the study done from the Paper in Keta Basin in Ghana as mentioned before by commercial software PVTsim, we reached at the same point by using different software. Methanol

is a good inhibitor owing its impact of duplicating the pressure from initial condition in phase behaviour boundary of hydrate to the actual pressure.

The Average Absolute Error found in PVTsim was 0.5 while in Ameripour & Barrufet software's is not applicable. The same result were found using different software's as it can be appreciated in the figures 30 and 31.



**Figure 30 and 31.** From left to right: Comparison of Results “PVTsim from *The Open Petroleum Engineering Journal* and Ameripour & Barrufet software's”

#### 4.8 Summary

In this chapter, we discussed the main part of the research from different kinds of inhibitors to be used and their weight to its efficiency for flow assurance in oil and gas facilities. Methanol and NaCl were seen clearly in phase boundary of hydrates their performance in arising P, and in most of the time could be in double comparing at the initial condition.

Using only Methanol to reach the same results as a good inhibitor for flow assurance, it is not practicable owing high costs of the inhibitor (Methanol) at 10%. Also using simply NaCl we are in trouble about speeding up corrosion in tubing. Nevertheless, we found a good technique of making cocktail of (Methanol & NaCl) at 5% of Wt.

## CHAPTER V

### 5. CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

- ❖ Methanol or NaCl at 2.5, 5 and 10% of wt. has the same impact in arising pressure in double. In Economic rate we did not choose simply NaCl owing high capability for corrosion of the facilities. Methanol is very expensive, although has good results like NaCl;
- ❖ Choosing only Methanol or NaCl at 10%, could be made but it would not be economically practicable, although these inhibitors also have the same behaviour like the best cocktail that was chosen;
- ❖ There is a great advantage using EG than Methanol owing its capacity of being recycled at the end of the process;
- ❖ All the facilities in subsea environment, for best operation, inhibitors must circulate in them and a ROV (which is a remote system of control that) must be installed for best results.
- ❖ It is worth spending the cost simulated in Table 11, ROV in figure 25, Methanol injector in figure 10 and integrated system for control remotely in figure 24 than stopping production and trying to solve plunging facilities (mostly in pipes) from hydrates.

#### 5.2 Recommendations

From this study, here are the recommends for further researchers:

- i. Effect of Methanol and NaCl in Gas production after injection in facilities;
- ii. From Mozambique data (Rovuma Basin), the same study can be done;
- iii. Evaluation and scales up of Removal of hydrate formers as mitigate form of the hydrate formation;
- iv. Evaluation of corrosion in subsea facilities from cocktail of inhibitors (NaCl &EG) during the production; and
- v. Mitigate flow assurance from hydrates using heating method.

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## **APPENDICES**

### **SUPPLEMENTAL MATERIAL**

## APPENDIX A

### A.1 Exhaustive and Extensive Data – Initial Condition

Table A.1 Initial Condition for simulation data (input). Table A.2 Initial Condition for simulation data output

<b>Input</b>		
<b>Temperature</b>		
<b>Min</b>	55.166	°F
<b>Max</b>	81.122	°F
<b>Gas Composition</b>		
<b>Gas</b>	<b>mol(%)</b>	
<b>C<sub>1</sub></b>	89.86	
<b>C<sub>2</sub></b>	6.40	
<b>C<sub>3</sub></b>	2.71	
<b>iC<sub>4</sub></b>	0.48	
<b>nC<sub>4</sub></b>	0.49	
<b>iC<sub>5</sub></b>	0.00	
<b>nC<sub>5</sub></b>	0.02	
<b>nC<sub>6</sub></b>	0.00	
<b>nC<sub>7</sub></b>	0.00	
<b>nC<sub>8</sub></b>	0.00	
<b>C<sub>2</sub>H<sub>4</sub></b>	0.00	
<b>C<sub>3</sub>H<sub>6</sub></b>	0.00	
<b>H<sub>2</sub>S</b>	0.00	
<b>CO<sub>2</sub></b>	0.00	
<b>N<sub>2</sub></b>	0.04	
<b>Total</b>	100.00	
<b>Water Composition</b>		
	<b>wt %</b>	
	<b>Initial</b>	<b>Modified</b>
<b>NaCl</b>	0.00	0.00
<b>KCl</b>	0.00	0.00
<b>CaCl<sub>2</sub></b>	0.00	0.00
<b>Methanol</b>	0.00	0.00
<b>EG</b>	0.00	0.00
<b>TEG</b>	0.00	0.00
<b>Glycerol</b>	0.00	0.00

<b>Output</b>		
<b>Gas Properties</b>		
<b>MW</b>	18.12	
<b>Gravity</b>	0.625	
<b>T<sub>pc</sub></b>	355.9	°R
<b>P<sub>pc</sub></b>	677.5	psia
<b>Hydrate Conditions</b>		
	<b>Pressure (psia)</b>	
<b>T (°F)</b>	<b>Initial</b>	<b>Modified</b>
<b>55.17</b>	544	544
<b>56.46</b>	602	602
<b>57.76</b>	667	667
<b>59.06</b>	741	741
<b>60.36</b>	825	825
<b>61.66</b>	920	920
<b>62.95</b>	1028	1028
<b>64.25</b>	1150	1150
<b>65.55</b>	1289	1289
<b>66.85</b>	1447	1447
<b>68.14</b>	1627	1627
<b>69.44</b>	1831	1831
<b>70.74</b>	2063	2063
<b>72.04</b>	2326	2326
<b>73.34</b>	2625	2625
<b>74.63</b>	2963	2963
<b>75.93</b>	3344	3344
<b>77.23</b>	3774	3774
<b>78.53</b>	4257	4257
<b>79.82</b>	4797	4797
<b>81.12</b>	5397	5397

## A.2 Hydrate Formation Phase Boundary Zone - Keta Basin in Ghana

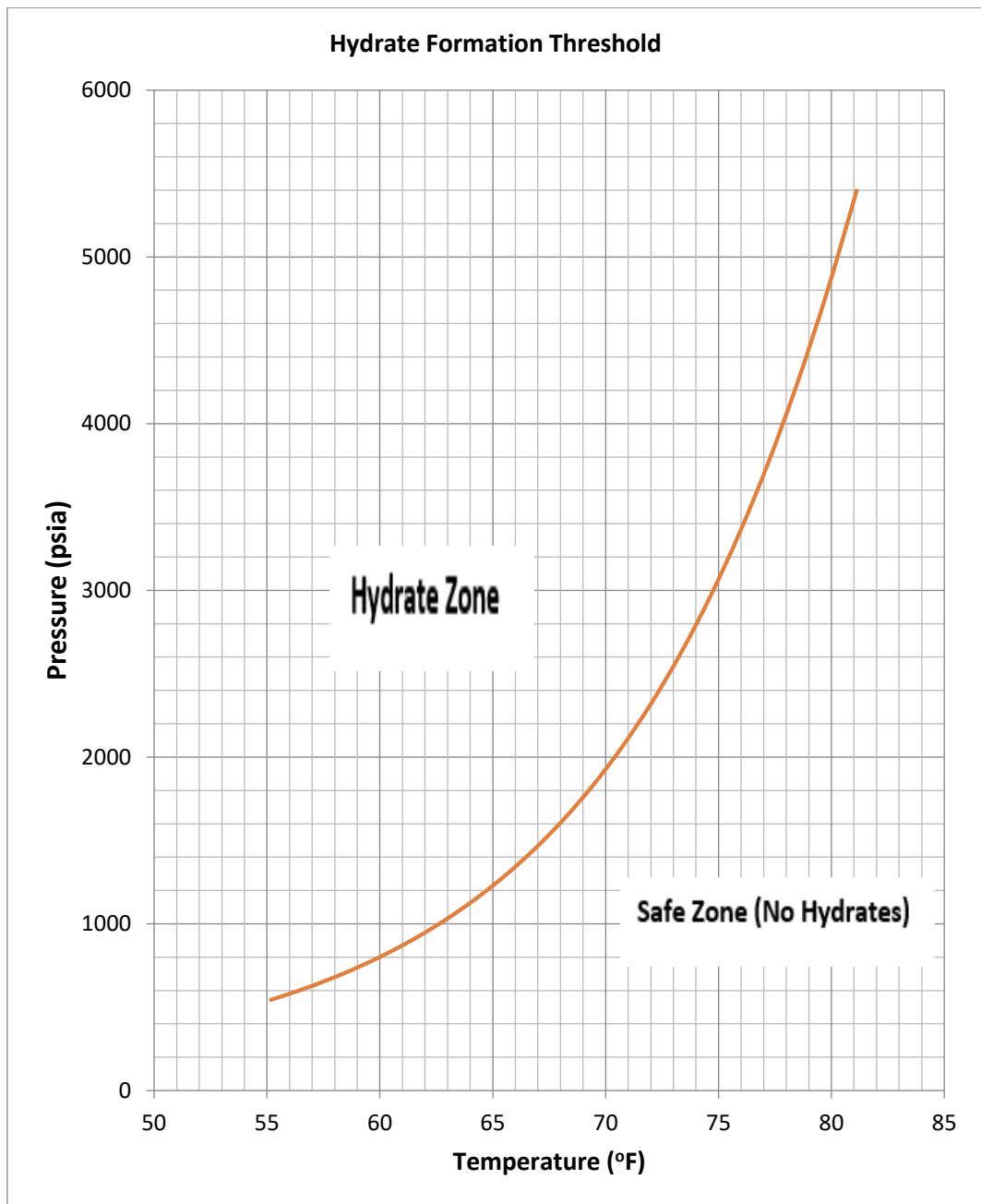


Figure A.2 Phase boundary for safety zone and hydrate one at initial conditions.

## APPENDIX B

### B.1 Hydrate Formation Critical Pressure and Temperature Computation

*Table B.1* Hydrate formation critical pressure and temperature computations

Natural Gas				P <sub>c</sub> Psia	T <sub>c</sub>	
H <sub>c</sub>	Comp				°F	°R
C <sub>1</sub>	0.8986	16.040	14.414	666.40	-116.67	343.33
C <sub>2</sub>	0.064	30.070	1.924	706.50	89.92	549.92
C <sub>3</sub>	0.0271	44.100	1.195	616.00	206.06	666.06
iC <sub>4</sub>	0.0048	58.120	0.279	527.90	274.46	734.46
nC <sub>4</sub>	0.0049	58.120	0.285	550.60	305.62	765.62
iC <sub>5</sub>	0	72.150	0.000	490.40	369.10	829.10
nC <sub>5</sub>	0.0002	72.150	0.014	488.60	385.80	845.80
nC <sub>6</sub>	0	86.180	0.000	436.90	453.60	913.60
nC <sub>7</sub>	0	100.260	0.000	396.80	512.70	972.70
nC <sub>8</sub>	0	114.230	0.000	360.70	564.22	1024.22
C <sub>2</sub> H <sub>4</sub>	0	28.050	0.000	729.80	48.58	508.58
C <sub>3</sub> H <sub>6</sub>	0	42.080	0.000	669.00	196.90	656.90
<b>Non-Hydrocarbons</b>						
H <sub>2</sub> S	0	34.08	0.000	1300.00	212.45	672.45
CO <sub>2</sub>	0	44.01	0.000	1071.00	87.91	547.91
N <sub>2</sub>	0.0004	28.01	0.011	493.10	-232.51	227.49
Sum	1		18.123			

*Table B.2* Constants used to compute P<sub>c</sub> and T<sub>c</sub>

i	a	b
0	0.05207	-0.39741
1	1.01600	1.0503
2	0.86961	0.96592
3	0.72646	0.78569
4	0.85101	0.98211
J		
J	0.525297	
K		
K	13.67308	
T <sub>pc</sub>		
T <sub>pc</sub>	355.8999	
P <sub>pc</sub>		
P <sub>pc</sub>	677.5214	

## APPENDIX C

### C.1 Viscosity Properties

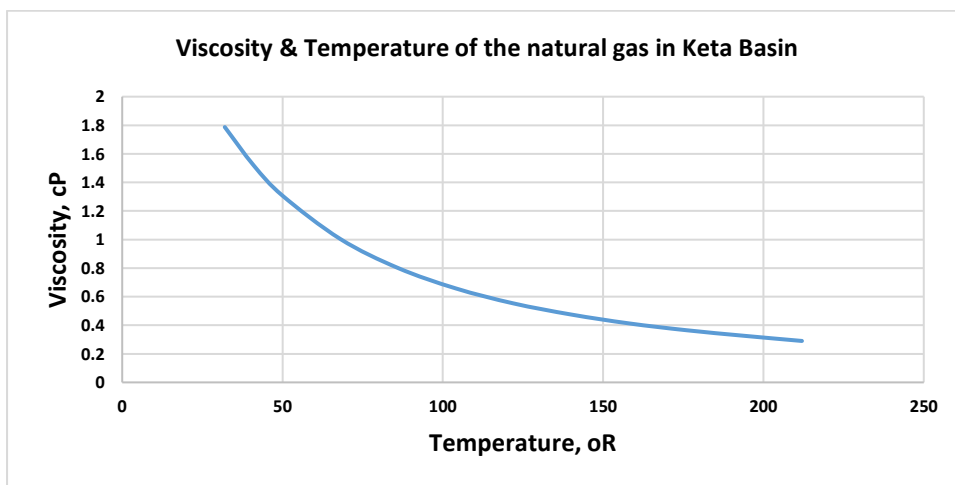
*Table C.1 Viscosity properties at several temperature of natural gas*

°F	°R	°K	Log <sub>10</sub> (m <sup>l</sup> <sub>w</sub> )	m <sup>l</sup> <sub>w</sub>
55.17	514.84	286.02	0.081	1.206
56.46	516.13	286.74	0.073	1.183
57.76	517.43	287.46	0.065	1.161
59.06	518.73	288.18	0.057	1.140
60.36	520.03	288.90	0.049	1.119
61.66	521.33	289.63	0.041	1.099
62.95	522.62	290.35	0.033	1.079
64.25	523.92	291.07	0.025	1.060
65.55	525.22	291.79	0.018	1.041
66.85	526.52	292.51	0.010	1.023
68.14	527.81	293.23	0.002	1.005
69.44	529.11	293.95	-0.005	0.988
70.74	530.41	294.67	-0.013	0.971
72.04	531.71	295.39	-0.020	0.954
73.34	533.01	296.11	-0.028	0.938
74.63	534.30	296.84	-0.035	0.923
75.93	535.60	297.56	-0.042	0.907
77.23	536.90	298.28	-0.049	0.892
78.53	538.20	299.00	-0.057	0.878
79.82	539.49	299.72	-0.064	0.864
81.12	540.79	300.44	-0.071	0.850

Temperature (°C)	Temperature (°R)	Viscosity (P)	Viscosity (cP)
0	32	1.787	1.787
5	41	1.519	1.519
10	50	1.307	1.307
20	68	1.002	1.004
30	86	0.798	0.801
40	104	0.653	0.658
50	122	0.547	0.553
60	140	0.467	0.475
70	158	0.404	0.413
80	176	0.355	0.365
90	194	0.315	0.326
100	212	0.282	0.29

a	-10.2158
b	1792
c	0.0177
d	-0.0000126

Const av As Double = -10.2158
Const bv As Double = 1792
Const cv As Double = 0.0177
Const dv As Double = -0.0000126



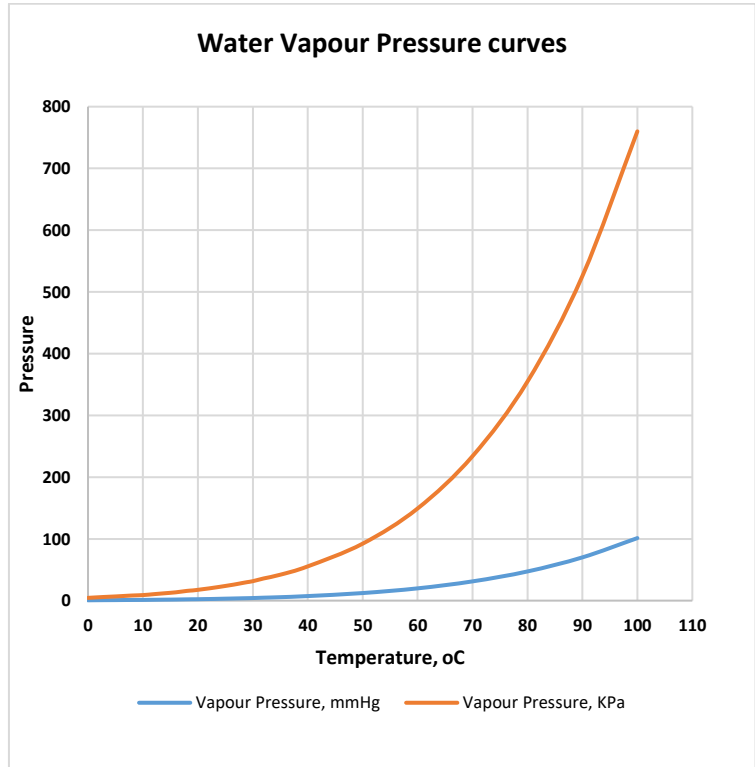
*Figure C.1 Viscosity & Temperature of the natural gas in Keta Basin*

## APPENDIX D

### D.1 Water Vapour Pressure Analysis

*Table D.1* Water vapour pressure analysis

T (°C)	T (°K)	Vapour Pressure (kPa)	Vapour Pressure (mmHg)
0	273	0.6	4.5
3	276	0.8	6.0
5	278	0.9	6.8
8	281	1.1	8.3
10	283	1.2	9.0
12	285	1.4	10.5
14	287	1.6	12.0
16	289	1.8	13.5
18	291	2.1	15.8
19	292	2.2	16.5
20	293	2.3	17.5
21	294	2.5	18.7
22	295	2.6	19.8
23	296	2.8	21.1
24	297	3.0	22.4
25	298	3.2	23.8
26	299	3.4	25.2
27	300	3.6	26.7
28	301	3.8	28.4
29	302	4.0	30.0
30	303	4.2	31.5
32	305	4.8	36.0
35	308	5.6	42.0
40	313	7.4	55.5
50	323	12.3	92.3
60	333	19.9	149.3
70	343	31.2	234.1
80	353	47.3	354.9
90	363	70.1	525.9
100	373	101.3	760.0



*Figure D.1* Water vapour pressure analysis.

## D.2 Water Analysis

Table D.2 Water Analysis weight.

Components	Wt Percent	MW				
Electrolytes Inhibitors						
NaCl	5	58.44	0.085558	5	58.44	0.085558
KCl	0	74.55	0	0	74.55	0
CaCl <sub>2</sub>	0	110.98	0	0	110.98	0
(x <sub>i</sub> )=	<b>5</b>	(x <sub>i</sub> /MW <sub>i</sub> )=	<b>0.085558</b>	<b>5</b>	(x <sub>i</sub> /MW <sub>i</sub> )=	<b>0.085558</b>
<b>Alcohol Inhibitors</b>						
Methanol	5	32.04	0.156055	5	32.04	0.156055
EG	0	62.07	0	0	62.07	0
TEG	0	150.20	0	0	150.20	0
Glycerol	0	92.09	0	0	92.09	0
(x <sub>j</sub> )=	<b>5</b>	(x <sub>j</sub> /MW <sub>j</sub> )=	<b>0.156055</b>	<b>5</b>	(x <sub>j</sub> /MW <sub>j</sub> )=	<b>0.156055</b>

## D.3 Pressure, initial water

Table D.3 Water Analysis at initial conditions.

<b>Gas Molecular Weight</b>	18.123	
<b>Gas Gravity</b>	0.625	
<b>T<sub>pc</sub></b>	355.900	<b>°R</b>
<b>P<sub>pc</sub></b>	677.521	<b>psia</b>
(x <sub>i</sub> /MW <sub>i</sub> )	0.85557837	%
(x <sub>j</sub> /MW <sub>j</sub> )	0.156054931	%
(x <sub>i</sub> )	5	%
(x <sub>j</sub> )	5	%

## APPENDIX E

### E.1 Pseudo Critical Temperature and Pressure Computations

**Table E.1** Pseudo critical temperature and pressure of natural gas

**Table E.2** Constant for hydrates formation.

composition in Keta Basin – Ghana.

Temperature			T <sub>pr</sub>	P <sub>w</sub> <sup>v</sup>	□ <sub>w</sub> <sup>l</sup>	P <sub>pr</sub>	P (psia)
°F	°R	°K		Psia	Cps		
55.17	514.84	286.02	1.447	0.215	1.206	1.639	1110.67
56.46	516.13	286.74	1.450	0.225	1.183	1.811	1226.83
57.76	517.43	287.46	1.454	0.236	1.161	2.004	1358.02
59.06	518.73	288.18	1.458	0.248	1.140	2.223	1506.42
60.36	520.03	288.90	1.461	0.259	1.119	2.471	1674.48
61.66	521.33	289.63	1.465	0.271	1.099	2.753	1865.04
62.95	522.62	290.35	1.468	0.284	1.079	3.072	2081.33
64.25	523.92	291.07	1.472	0.297	1.060	3.435	2327.03
65.55	525.22	291.79	1.476	0.311	1.041	3.847	2606.32
66.85	526.52	292.51	1.479	0.326	1.023	4.316	2923.93
68.14	527.81	293.23	1.483	0.340	1.005	4.849	3285.19
69.44	529.11	293.95	1.487	0.356	0.988	5.455	3696.06
70.74	530.41	294.67	1.490	0.372	0.971	6.145	4163.18
72.04	531.71	295.39	1.494	0.389	0.954	6.928	4693.83
73.34	533.01	296.11	1.498	0.406	0.938	7.817	5295.96
74.63	534.30	296.84	1.501	0.424	0.923	8.823	5978.10
75.93	535.60	297.56	1.505	0.443	0.907	9.962	6749.24
77.23	536.90	298.28	1.509	0.463	0.892	11.245	7618.64
78.53	538.20	299.00	1.512	0.483	0.878	12.687	8595.53
79.82	539.49	299.72	1.516	0.504	0.864	14.300	9688.69
81.12	540.79	300.44	1.520	0.526	0.850	16.097	10905.87

i	a <sub>i</sub>	b <sub>i</sub>
0	-2.924729	3.111380
1	7.069408	-0.061218
2	-0.671674	-0.034582
3	2.158912	-0.022258
4	-0.014440	-0.161387
5	3.367516	0.000464
6	-0.168816	0.006087
7	13.213962	-0.000497
8	2.365031	0.000168
9	-0.025796	-0.193610
10	2.461102	0.000196
11	-7.100059	0.132468
12	1.820312	-0.078512
13	7.517561	0.009233
14	-0.018793	-0.000232
15	0.019029	0.805484
16	-0.005307	0.006340
17	-0.032564	-



## APPENDIX F

### PHASE DIAGRAM INHIBITOR COMPUTATIONS

#### F.1 Computations for all inhibitors at different weights

##### F.1.1 Inhibitor: NaCl at 2.5, 5, 7.5 and 10%

*Table F.1.1* Range of pressure at different weights of the inhibitor NaCl.

T (°F)	Pressure (Psia)				
	Initial	2.5% NaCl	5% NaCl	7.5% NaCl	10% NaCl
55.17	543.80	642.09	757.68	893.62	1053.48
56.46	601.84	710.90	839.24	990.28	1168.04
57.76	667.37	788.62	931.42	1099.60	1297.68
59.06	741.45	876.53	1035.75	1223.41	1444.60
60.36	825.30	976.11	1154.00	1363.82	1611.32
61.66	920.31	1089.02	1288.16	1523.24	1800.73
62.95	1028.09	1217.18	1440.55	1704.43	2016.15
64.25	1150.45	1362.77	1613.78	1910.54	2261.36
65.55	1289.46	1528.28	1810.84	2145.15	2540.67
66.85	1447.44	1716.51	2035.11	2412.33	2858.98
68.14	1627.01	1930.62	2290.38	2716.67	3221.80
69.44	1831.11	2174.14	2580.92	3063.31	3635.34
70.74	2062.98	2451.01	2911.49	3457.98	4106.52
72.04	2326.22	2765.54	3287.31	3907.00	4643.00
73.34	2624.70	3122.46	3714.09	4417.30	5253.12
74.63	2962.59	3526.82	4197.96	4996.30	5945.92
75.93	3344.29	3983.94	4745.41	5651.88	6730.97
77.23	3774.28	4499.33	5363.12	6392.20	7618.20
78.53	4257.05	5078.44	6057.77	7225.42	8617.58
79.82	4796.83	5726.49	6835.78	8159.40	9738.77
81.12	5397.33	6448.07	7702.82	9201.17	10990.43

### F.1.2 Inhibitor: Methanol at 2.5, 5, 7.5 and 10%

*Table F.1.2* Range of pressure at different weights of the inhibitor Methanol.

T (°F)	Pressure (Psia)				
	Initial	2.5% Methanol	5% Methanol	7.5% Methanol	10% Methanol
<b>55.17</b>	543.80	655.03	788.41	948.36	1140.16
<b>56.46</b>	601.84	724.30	871.07	1047.00	1257.86
<b>57.76</b>	667.37	802.47	964.32	1158.24	1390.55
<b>59.06</b>	741.45	890.81	1069.67	1283.86	1540.36
<b>60.36</b>	825.30	990.76	1188.83	1425.91	1709.69
<b>61.66</b>	920.31	1104.00	1323.77	1586.71	1901.31
<b>62.95</b>	1028.09	1232.39	1476.72	1768.92	2118.37
<b>64.25</b>	1150.45	1378.11	1650.25	1975.56	2364.44
<b>65.55</b>	1289.46	1543.59	1847.24	2210.06	2643.58
<b>66.85</b>	1447.44	1731.58	2070.95	2476.27	2960.36
<b>68.14</b>	1627.01	1945.20	2325.06	2778.54	3319.92
<b>69.44</b>	1831.11	2187.90	2613.65	3121.71	3727.97
<b>70.74</b>	2062.98	2463.52	2941.28	3511.14	4190.86
<b>72.04</b>	2326.22	2776.30	3312.93	3952.73	4715.54
<b>73.34</b>	2624.70	3130.83	3734.01	4452.86	5309.55
<b>74.63</b>	2962.59	3532.00	4210.31	5018.35	5980.93
<b>75.93</b>	3344.29	3985.00	4747.93	5656.38	6738.11
<b>77.23</b>	3774.28	4495.11	5353.07	6374.26	7589.71
<b>78.53</b>	4257.05	5067.59	6031.92	7179.23	8544.23
<b>79.82</b>	4796.83	5707.39	6790.28	8078.10	9609.64
<b>81.12</b>	5397.33	6418.86	7633.21	9076.78	10792.81

### F.1.3 Inhibitor: EG at 2.5, 5, 7.5, 10, 15 and 20%

Table F.1.3 Range of pressure at different weights of the inhibitor EG.

T (°F)	Pressure (Psia)						
	Initial	2.5% EG	5% EG	7.5% EG	10% EG	15% EG	20% EG
<b>55.17</b>	543.80	598.69	658.98	725.19	797.91	965.50	1167.65
<b>56.46</b>	601.84	662.28	728.65	801.51	881.53	1065.85	1288.08
<b>57.76</b>	667.37	734.06	807.26	887.63	975.85	1179.01	1423.84
<b>59.06</b>	741.45	815.18	896.11	984.93	1082.40	1306.80	1577.09
<b>60.36</b>	825.30	906.99	996.64	1095.00	1202.93	1451.29	1750.32
<b>61.66</b>	920.31	1011.01	1110.51	1219.66	1339.40	1614.86	1946.34
<b>62.95</b>	1028.09	1128.99	1239.64	1361.00	1494.11	1800.19	2168.38
<b>64.25</b>	1150.45	1262.89	1386.18	1521.37	1669.61	2010.37	2420.08
<b>65.55</b>	1289.46	1414.99	1552.60	1703.45	1868.83	2248.87	2705.59
<b>66.85</b>	1447.44	1587.81	1741.65	1910.27	2095.08	2519.62	3029.59
<b>68.14</b>	1627.01	1784.21	1956.47	2145.23	2352.06	2827.03	3397.32
<b>69.44</b>	1831.11	2007.40	2200.54	2412.12	2643.91	3176.02	3814.63
<b>70.74</b>	2062.98	2260.92	2477.71	2715.16	2975.22	3572.05	4288.00
<b>72.04</b>	2326.22	2548.66	2792.24	3058.97	3351.04	4021.09	4824.53
<b>73.34</b>	2624.70	2874.87	3148.75	3448.59	3776.84	4529.65	5431.92
<b>74.63</b>	2962.59	3244.07	3552.16	3889.38	4258.47	5104.65	6118.39
<b>75.93</b>	3344.29	3661.05	4007.68	4386.99	4802.08	5753.38	6892.56
<b>77.23</b>	3774.28	4130.69	4520.62	4947.22	5413.96	6483.27	7763.21
<b>78.53</b>	4257.05	4657.85	5096.26	5575.80	6100.34	7301.68	8739.03
<b>79.82</b>	4796.83	5247.14	5739.60	6278.15	6867.10	8215.52	9828.15
<b>81.12</b>	5397.33	5902.58	6454.99	7058.97	7719.34	9230.78	11037.59

#### F.1.4 Inhibitor: Cocktail (NaCl & Methanol) at 1.25, 2.50, 3.75 and 5%

*Table F.1.4* Range of pressure at different weights of the Cocktail inhibitor (NaCl & Methanol).

T (°F)	Pressure (Psia)				
	Initial	1.25% Cocktail (NaCl & Methanol)	2.50% Cocktail (NaCl & Methanol)	3.75% Cocktail (NaCl & Methanol)	5.00% Cocktail (Na Cl& Methanol)
<b>55.17</b>	543.80	648.53	772.90	920.59	1095.97
<b>56.46</b>	601.84	717.57	855.01	1018.25	1212.13
<b>57.76</b>	667.37	795.51	947.73	1128.54	1343.32
<b>59.06</b>	741.45	883.64	1052.58	1253.28	1491.72
<b>60.36</b>	825.30	983.41	1171.28	1394.52	1659.78
<b>61.66</b>	920.31	1096.48	1305.84	1554.65	1850.34
<b>62.95</b>	1028.09	1224.76	1458.53	1736.38	2066.63
<b>64.25</b>	1150.45	1370.42	1631.92	1942.78	2312.33
<b>65.55</b>	1289.46	1535.92	1828.95	2177.36	2591.62
<b>66.85</b>	1447.44	1724.03	2052.95	2444.09	2909.23
<b>68.14</b>	1627.01	1937.89	2307.65	2747.43	3270.49
<b>69.44</b>	1831.11	2181.01	2597.24	3092.37	3681.36
<b>70.74</b>	2062.98	2457.26	2926.35	3484.46	4148.48
<b>72.04</b>	2326.22	2770.92	3300.10	3929.80	4679.13
<b>73.34</b>	2624.70	3126.64	3724.04	4435.04	5281.26
<b>74.63</b>	2962.59	3529.41	4204.13	5007.31	5963.40
<b>75.93</b>	3344.29	3984.47	4746.67	5654.13	6734.54
<b>77.23</b>	3774.28	4497.22	5358.09	6383.22	7603.94
<b>78.53</b>	4257.05	5073.01	6044.83	7202.29	8580.83
<b>79.82</b>	4796.83	5716.93	6812.99	8118.65	9673.99
<b>81.12</b>	5397.33	6433.45	7667.94	9138.76	10891.17

## APPENDIX G

### COMPUTATIONS FOR ANALYSE OF THE INHIBITOR TO BE USED

#### G.1 Analysis of the better Inhibitor at 2.50 %

*Table G.1* Range of pressure at different weights for the better inhibitor at 2.50%.

T (°F)	Pressure (Psia)				
	Initial	2.5% NaCl	2.5% Methanol	2.5% EG	2.50% Cocktail (NaCl & Methanol)
<b>55.17</b>	543.80	642.09	655.03	598.6909	772.90
<b>56.46</b>	601.84	710.90	724.30	662.2829	855.01
<b>57.76</b>	667.37	788.62	802.47	734.0587	947.73
<b>59.06</b>	741.45	876.53	890.81	815.1839	1052.58
<b>60.36</b>	825.30	976.11	990.76	906.9933	1171.28
<b>61.66</b>	920.31	1089.02	1104.00	1011.013	1305.84
<b>62.95</b>	1028.09	1217.18	1232.39	1128.986	1458.53
<b>64.25</b>	1150.45	1362.77	1378.11	1262.894	1631.92
<b>65.55</b>	1289.46	1528.28	1543.59	1414.987	1828.95
<b>66.85</b>	1447.44	1716.51	1731.58	1587.807	2052.95
<b>68.14</b>	1627.01	1930.62	1945.20	1784.213	2307.65
<b>69.44</b>	1831.11	2174.14	2187.90	2007.402	2597.24
<b>70.74</b>	2062.98	2451.01	2463.52	2260.92	2926.35
<b>72.04</b>	2326.22	2765.54	2776.30	2548.663	3300.10
<b>73.34</b>	2624.70	3122.46	3130.83	2874.867	3724.04
<b>74.63</b>	2962.59	3526.82	3532.00	3244.071	4204.13
<b>75.93</b>	3344.29	3983.94	3985.00	3661.045	4746.67
<b>77.23</b>	3774.28	4499.33	4495.11	4130.686	5358.09
<b>78.53</b>	4257.05	5078.44	5067.59	4657.852	6044.83
<b>79.82</b>	4796.83	5726.49	5707.39	5247.14	6812.99
<b>81.12</b>	5397.33	6448.07	6418.86	5902.575	7667.94

## G.2 Analysis of the best Inhibitor at 5 %

*Table G.2* Range of pressure at different weights for the best inhibitor at 5%.

<b>T (°F)</b>	<b>Pressure (Psia)</b>				
	<b>Initial</b>	<b>5% NaCl</b>	<b>5% Methanol</b>	<b>5% EG</b>	<b>5% Cocktail (NaCl &amp; Methanol)</b>
<b>55.17</b>	543.80	757.68	788.41	658.98	1095.97
<b>56.46</b>	601.84	839.24	871.07	728.65	1212.13
<b>57.76</b>	667.37	931.42	964.32	807.26	1343.32
<b>59.06</b>	741.45	1035.75	1069.67	896.11	1491.72
<b>60.36</b>	825.30	1154.00	1188.83	996.64	1659.78
<b>61.66</b>	920.31	1288.16	1323.77	1110.51	1850.34
<b>62.95</b>	1028.09	1440.55	1476.72	1239.64	2066.63
<b>64.25</b>	1150.45	1613.78	1650.25	1386.18	2312.33
<b>65.55</b>	1289.46	1810.84	1847.24	1552.60	2591.62
<b>66.85</b>	1447.44	2035.11	2070.95	1741.65	2909.23
<b>68.14</b>	1627.01	2290.38	2325.06	1956.47	3270.49
<b>69.44</b>	1831.11	2580.92	2613.65	2200.54	3681.36
<b>70.74</b>	2062.98	2911.49	2941.28	2477.71	4148.48
<b>72.04</b>	2326.22	3287.31	3312.93	2792.24	4679.13
<b>73.34</b>	2624.70	3714.09	3734.01	3148.75	5281.26
<b>74.63</b>	2962.59	4197.96	4210.31	3552.16	5963.40
<b>75.93</b>	3344.29	4745.41	4747.93	4007.68	6734.54
<b>77.23</b>	3774.28	5363.12	5353.07	4520.62	7603.94
<b>78.53</b>	4257.05	6057.77	6031.92	5096.26	8580.83
<b>79.82</b>	4796.83	6835.78	6790.28	5739.60	9673.99
<b>81.12</b>	5397.33	7702.82	7633.21	6454.99	10891.17

### G.3 Analysis of the best Inhibitor at 7.5 % and 10%

Tables G.3 and G.4 Ranges of pressures at different weights for the better inhibitors at 7.50% and 10%.

T (oF)	Pressure (Psia)			
	Initial	7.5% NaCl	7.5% Methanol	7.5% EG
55.17	543.80	893.62	948.36	725.19
56.46	601.84	990.28	1047.00	801.51
57.76	667.37	1099.60	1158.24	887.63
59.06	741.45	1223.41	1283.86	984.93
60.36	825.30	1363.82	1425.91	1095.00
61.66	920.31	1523.24	1586.71	1219.66
62.95	1028.09	1704.43	1768.92	1361.00
64.25	1150.45	1910.54	1975.56	1521.37
65.55	1289.46	2145.15	2210.06	1703.45
66.85	1447.44	2412.33	2476.27	1910.27
68.14	1627.01	2716.67	2778.54	2145.23
69.44	1831.11	3063.31	3121.71	2412.12
70.74	2062.98	3457.98	3511.14	2715.16
72.04	2326.22	3907.00	3952.73	3058.97
73.34	2624.70	4417.30	4452.86	3448.59
74.63	2962.59	4996.30	5018.35	3889.38
75.93	3344.29	5651.88	5656.38	4386.99
77.23	3774.28	6392.20	6374.26	4947.22
78.53	4257.05	7225.42	7179.23	5575.80
79.82	4796.83	8159.40	8078.10	6278.15
81.12	5397.33	9201.17	9076.78	7058.97

T (°F)	Pressure (Psia)			
	Initial	10% NaCl	10% Methanol	10% EG
55.17	543.80	1053.48	1140.16	797.91
56.46	<b>601.84</b>	1168.04	1257.86	881.53
57.76	<b>667.37</b>	1297.68	1390.55	975.85
59.06	741.45	1444.60	1540.36	1082.40
60.36	825.30	1611.32	1709.69	1202.93
61.66	920.31	1800.73	1901.31	1339.40
62.95	1028.09	2016.15	2118.37	1494.11
64.25	1150.45	2261.36	2364.44	1669.61
65.55	1289.46	2540.67	2643.58	1868.83
66.85	1447.44	2858.98	2960.36	2095.08
68.14	1627.01	3221.80	3319.92	2352.06
69.44	1831.11	3635.34	3727.97	2643.91
70.74	2062.98	4106.52	4190.86	2975.22
72.04	2326.22	4643.00	4715.54	3351.04
73.34	2624.70	5253.12	5309.55	3776.84
74.63	2962.59	5945.92	5980.93	4258.47
75.93	3344.29	6730.97	6738.11	4802.08
77.23	3774.28	7618.20	7589.71	5413.96
78.53	4257.05	8617.58	8544.23	6100.34
79.82	4796.83	9738.77	9609.64	6867.10
81.12	5397.33	10990.43	10792.81	7719.34

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