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-THEME –

Preventing hydrate formation in gas pipelines

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Bismi Allah Alrahman Alrahim

Dedication

This work is dedicated to my parents for their endless love, unwavering support, and constant encouragement throughout my life and studies. Your sacrifices and belief in me have been the foundation of all my achievements. I am forever grateful for your guidance and care.

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For my friends especially my friend wissem thank you for the moral support, understanding and patience. Your companionship and the moments of joy and sadness helped me maintain my balance during this journey. Thank you for always being there for me.

Abd elmoumen

Dedication

This thesis is dedicated to my parents whose unwavering love, encouragement, and sacrifices have been my guiding light throughout this journey. Your belief in me has fueled my determination, and I am forever grateful for your endless support. I dedicate this thesis to my dear friends and invaluable colleagues, Abd elmoumen Baroud and zakaria Hoggas, whose combined dedication, expertise, and unwavering support have been instrumental in bringing this project to fruition. Your collaborative spirit, insightful contributions, and tireless efforts have significantly enriched the quality of this work.

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Abdelaziz

Dedication

There is no joy like sharing my happiness with the people I love

. After completing my studies, I am honored to dedicate this humble work:

✓To my dear father, for all the sacrifices and advice he gave me.

✓To my dear mother who was patient and worked hard to see me succeed.

✓To my dear brothers and sisters Haroune, Amal and Khadidja.

✓To my colleagues Abd elmoumen and abd elAziz who contributed to the completion of this work.

Zakaria

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LIST OF SYMBOLES:

T: temperature

Xm: Amont of gas absorbed by unit mass of absorbent

M: Molecular weight of inhibitor

C: Physical constant of inhibitor

q_x: the rate of heat transfer in the x direction where is [W]

A: the area normal to the direction of heat flow [m2]

dT/dx :the temperature gradient in the x direction [K/m]

K: the thermal conductivity.

h : heat transfer coefficient,[W=m2 K]

TEG: Triethylene glycol

MEG: Monoethylene glycol

DEG: Diethylene glycol

MeOH: Methanol

Abstract:

Gas hydrates, solid crystalline compounds formed under high-pressure and low-temperature conditions, present substantial challenges in the oil and gas industry by causing blockages in pipelines and processing equipment. Our study investigates various methods to prevent hydrate formation, focusing on traditional techniques such as thermal management, dehydration, and chemical inhibition, as well as innovative approaches involving advanced materials and pipeline design enhancements. Through a comprehensive review of current technologies and methodologies, the findings from our internship and HYSYS models simulation aim to offer a holistic understanding of hydrate prevention strategies, providing industry professionals with practical insights to enhance operational safety and efficiency. Ultimately, this research is to evaluate the most used hydrate formation prevention methods in the industry which are Triethylene glycol at concentration of 98,62% and 1,38% H_2O, methanol with composition of 30% and 70% H_2O and heat exchanger with 0.13 m^3/h gain of production.

Keywords: Triethylene glycol, methanol, hydrate, HYSYS.

Résumé

Les hydrates de gaz, composés cristallins solides formés dans des conditions de haute pression et de basse température, posent des problèmes considérables à l'industrie du pétrole et du gaz en provoquant des blocages dans les pipelines et les équipements de traitement. Notre étude porte sur diverses méthodes de prévention de la formation d'hydrates, en se concentrant sur les techniques traditionnelles telles que la gestion thermique, la déshydratation et l'inhibition chimique. Grâce à l'examination complet des technologies et des méthodologies actuelles, les résultats de notre stage et la simulation des modèles HYSYS visent à offrir une compréhension globale des stratégies de prévention des hydrates, en fournissant aux professionnels de l'industrie des idées pratiques pour améliorer l'efficacité des opérations. En fin de compte, cette recherche est pour évaluer les méthodes de prévention des hydrates les plus utilisés dans l'industrie qui sont Triéthylène glycol avec une concentration 98,62% et 1,38% H_2O, méthanol de concentration de 30% et 70% H_2O, l'échangeur de chaleur de 0.13 m^3/h gain de production.

Mots clés : Triéthylène glycol, méthanol, hydrate, HYSYS

تلخيص:

هيدرات الغاز، وهي مركبات بلورية صلبة تتشكل في ظروف الضغط العالي ودرجة الحرارة المنخفضة، تنتج عنها مشاكل كبيرة في إنتاج النفط والغاز من خلال التسبب في انسداد خطوط الأنابيب ومعدات المعالجة. وتبحث دراستنا في الطرق المختلفة لمنع تكون الهيدرات، مع التركيز على التقنيات التقليدية مثل الإدارة الحرارية والتجفيف والتثبيط الكيميائي. من خلال مراجعة شاملة للتقنيات والمنهجيات الحالية، تهدف نتائج المأخوذة من التربص ومحاكاة نماذج HYSYS إلى تقديم فهم شامل لاستراتيجيات منع تكون الهيدرات، وتزويد المتخصصين في الصناعة بأفكار عملية لتحسين الكفاءة التشغيلية. وفي نهاية المطاف، يهدف هذا البحث إلى تقييم طرق منع الهيدرات الأكثر استخدامًا في الصناعة وهي التريثيلين جلايكول بتركيز 98.68% و 1.38% تركيز الماء والميثانول بتركيز 30% و70% تركيز الماء والمبادل الحراري بـ0.13 م^3/سا فائض انتاج.

كلمات المفتاحية: التريثيلين جلايكول، الميثانول، الهيدرات، HYSYS.

GENERAL INTRODUCTION

General Introduction

Gas hydrate, crystalline compounds formed when water molecules encase gas molecules under high pressure and low temperature conditions. Hydrate formation in natural gas pipelines and processing facilities poses significant operational problems, including blockages, pressure drops. Preventing hydrate formation is critical for maintaining efficient and safe operations. This thesis aims to assess and compare various strategies for mitigating hydrate risks using the process simulation software HYSYS.

The focus of this study is twofold. First, it examines the use of heat exchangers as a method to prevent hydrate formation by controlling the temperature of the gas stream. By maintaining the gas temperature above the hydrate formation threshold, heat exchangers can effectively inhibit hydrate formation. This approach is analyzed in terms of its practicality, efficiency, and operational feasibility.

Second, the thesis explores chemical inhibition methods, specifically the use of Triethylene Glycol (TEG) and Methanol, which are commonly employed to prevent hydrate formation. Both TEG and Methanol lower the hydrate formation temperature, thereby allowing the gas to remain in a flowable state under typical pipeline conditions. The mechanisms by which TEG and Methanol inhibit hydrate formation are investigated, including their interaction with water and gas molecules and their effects on the phase behavior of the gas mixture.

A detailed comparison between TEG and Methanol is conducted to evaluate their effectiveness, and operational considerations. HYSYS is utilized to simulate various scenarios, enabling a comprehensive analysis of each method's performance under different operating conditions. This simulation-based approach provides valuable insights into the optimal strategies for hydrate prevention, balancing technical efficiency with economic factors.

By combining the theoretical foundations of hydrate formation and prevention with practical simulation results, this thesis aims to contribute to the broader understanding of effective hydrate management in natural gas processing. The findings will assist industry professionals in selecting and implementing the most appropriate hydrate prevention techniques, thereby enhancing the safety and reliability of gas transportation and processing systems.

The main objective of our work is:

- Evaluation of hydrate formation prevention methods
- The use of HYSYS to know the mechanisms and characterize the optimum operating conditions for inhibitors.
- Compare between TEG and Methanol in terms of efficiency, mechanisms, dosage.

We have structured our thesis on three main chapters:

ChapterI will be literature review on natural gas generally and we will elaborate more gas lift and define gas hydrate problem.

ChapterII it will be divided into two parts, PartI we will continue our literature review on hydrate formation condition, phase equilibrium and hydrate formation inhibition and prevention methods.

PartII we will examine a case study on the use of heat exchanger to prevent hydrate formation on HMD field.

ChapterIII it will be focused on HYSYS simulation, first we will simulate models to explain how each inhibitor works, second, we will do the comparison between TEG and Methanol.

In conclusion, we will resume the highlighted results obtained from our research.

CHAPTER I:

GENERALITIES ABOUT GAS AND GAS HYDRATES

I.1 Introduction:

Even though all terrestrial gases (air, volcanic emissions, swamp gas, etc.) are natural, the term "natural gas" is customarily reserved for the mineral gases found in subsurface rock reservoirs. These gases are often associated with crude oil. Natural gas is a mixture of hydrocarbons (such as methane, ethane, propane, etc.) and a few nonhydrocarbons (hydrogen sulfide, carbon dioxide, nitrogen, etc., and water).

I.2 Natural Gas globally:

Although limited, these reserves are very substantial, and estimates of their size continue to improve as new exploration and extraction techniques are discovered. Natural gas resources are abundant and widely distributed around the world, as shown in Figure I. 1. It is estimated that a significant quantity of natural gas remains to be discovered.**[1]**
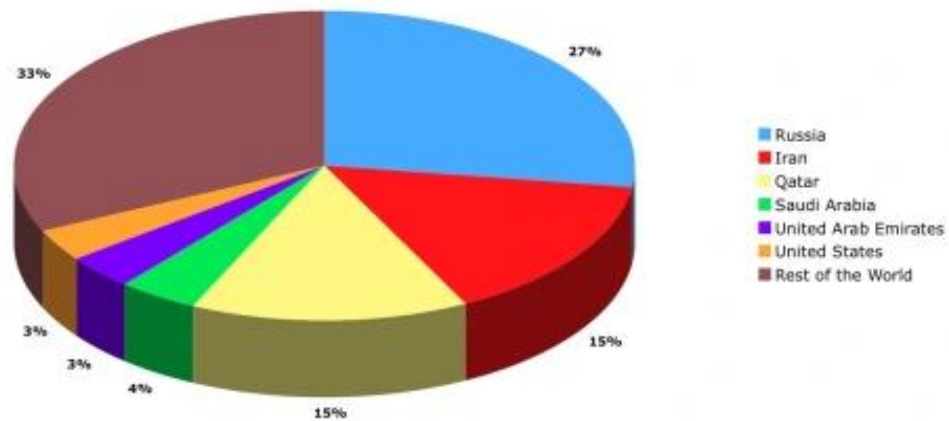
Figure I. 1: Global distribution of proven Natural gas reserves (2009) **[1]**

Europe countries and middle east share more than 74% of proven natural gas reserves globally on 2009.

Global natural gas reserves got doubled during the last 20 years and raised 187.5 trillion cubic meters on 2009.

I.3   Natural gas in Algeria:

Algeria is the tenth largest in terms of market size with proven natural gas reserves, is the world's fourth-largest gas exporter, and is home to the world's third-largest untapped reserves. The proven oil reserves make it sixteenth, while about sixty percent of the total production is exported. The only reserves to date are onshore. The Sonatrach survey estimates that two-thirds of the Algerian territory are underdeveloped or unexplored. More than 100 undeveloped discoveries can be distinguished.

Algeria has immense natural gas reserves. The Hassi R'Mel field is the world's largest, and the Ain Salah field was tapped in 2002. Algeria ranks fourth, with around 10% of the world's reserves.

Algeria's natural gas production reached 80 billion m3 in 2010 (figure I. 2). In other words, Algeria has become the world's leading exporter in this sector.

In January 2003, proven natural gas reserves were estimated at $4,077*10^9$ m3, with the Berkine and Illizi basins recording the highest exploitation success rates, at 51% and 50% respectively for several years.**[2]**
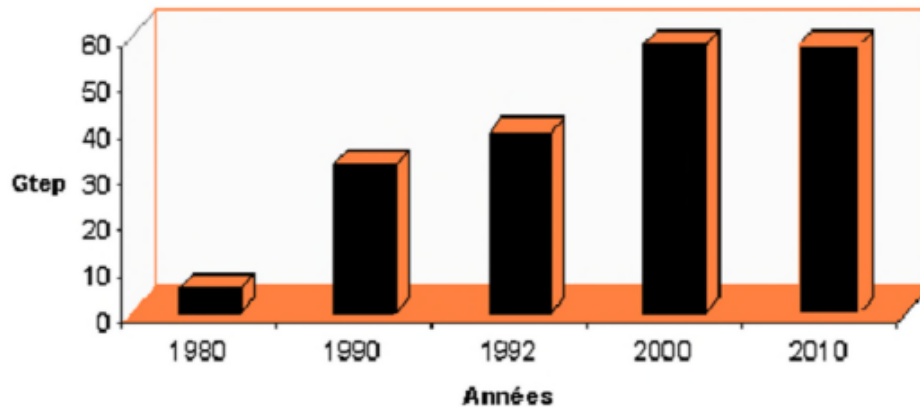
Figure I. 2: Natural gas production in Algeria **[2]**

According to OPEC Annual Statistical Bulletin Algeria's total estimated local production in 2023 around 112838 MMc , However, the total estimated exports around 68802 MMc.

Sonatrach and its subsidiaries roughly control 80 percent of hydrocarbon production while IOC's account for the remaining 20 percent.

I.4   Problems caused by natural gas:

Natural gas transportation and storage systems can create various pollution and safety problems and should be monitored, inspected, and controlled carefully in order to avoid the escape and emission of dangerous natural gas. Gas storage facilities may undergo significant variation in the gas pressure and storage stress conditions as a result of frequent injection and production under different scenarios associated with various services.

The main problems that can occur during gas transportation and storage are:

I.4.1   Corrosion:

Corrosion can be defined as the damage or deterioration of materials by chemical components. The main material affected by corrosion can be concrete, wood and plastic as well as polymers and metal. Because of their particular characteristics and physical properties such as durability, strength, ductility, electrical conductivity, wear resistance and production environment, metals are the most important useful material and more exposited to corrosion.

The carbon steel corrosion rate and corrosion behavior will be studied in the presence of CO_2 at various pH levels and pressure variation using classical electrochemical techniques. **[3]**

I.4.2   Gas explosions:

Gas explosions constitute a major hazard for offshore gas and oil producing installations. A gas explosion is the consequence of an accidental release of a flammable gas, the mixing with air and a subsequent ignition. Under appropriate boundary conditions the resulting flame propagation process may develop explosive combustion and damaging blast loadings.

I.4.3   Hydrate formation:

Natural-gas hydrates are ice-like solids that form when free water and natural gas combine at high pressure and low temperature. This can occur in gas and gas/condensate wells, as well as in oil wells. Location and intensity of hydrate accumulations in a well vary.

Shut-in gas wells are particularly prone to serious hydrate problems, if the well has been producing some water. Subsequent equilibration of the tubular and its contents with cold zones of the rock can lower the temperature into the hydrate-formation region. Hydrate nuclei form from the films

of water on the tubular walls. The subsequent crystallization can result in large plugs of hydrate tens or hundreds of meters long. **[4]**

I.5 Gas lift:

The gas-lift is one of the most widely used and effective well stimulation techniques. Its objective is to reduce the bottom hole flowing pressure from the reservoir by decreasing the fluid density, as the injected gas is less dense than the fluid coming out of the reservoir.

I.5.1 Principle:

The principle is to inject gas as deep as possible to lighten the column of fluid in the tubing. This is similar to adding power at the bottom of the hole to help the reservoir produce the effluent it contains up to the separator.
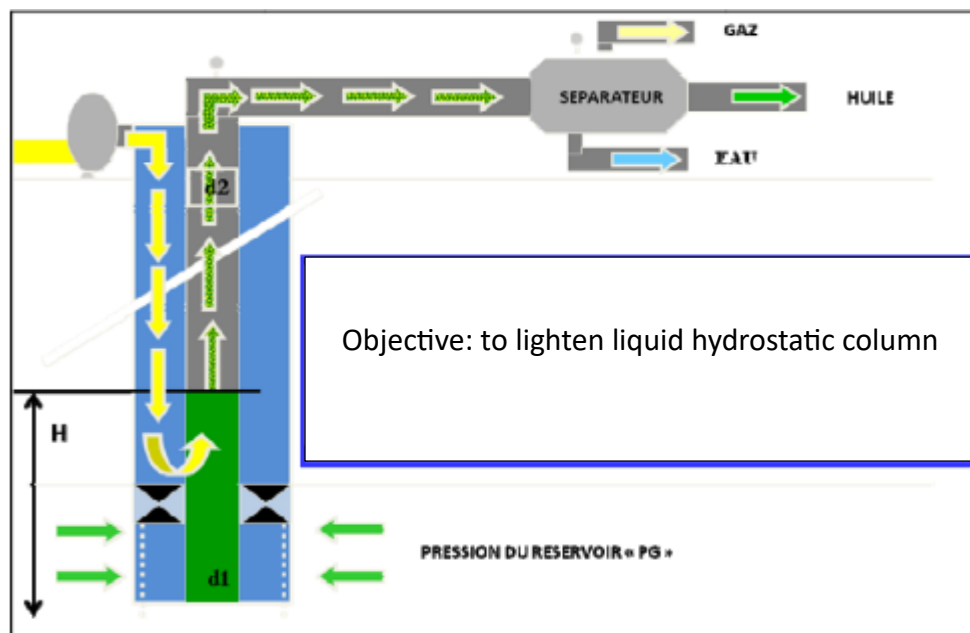
Figure I. 3: The process of gas lift **[5]**

I.5.2 Applications of gas lift:

More than 20% of the wells in production worldwide are affected by gas lift. The numerous applications of gas lift are:

- **The oil wells:** The main application of gas-lift in these wells is to increase production from depleted fields. Increasingly, it is also used in still eruptive wells and even new wells.

- **Water wells:** These wells produce aquifers for various uses such as reinjection into an oil reservoir or domestic use. It also happens that gas lift is used to produce seawater. Shallow wells often use air instead of gas.

- **Well Kick-off:** In some cases, gas lift is used solely to start a dead well that can do without activation once its eruptivity is restored. There are gas wells equipped with a gas lift mandrel to restart them after the tubing has been filled with water.

- **Cleaning of injector wells:** Injector wells need to be periodically put into production to remove particles that clog the perforations or the formation.**[5]**

I.6 Hydrates formation:

I.6.1 Hydrates formation definition:

It is a result of the hydrogen bond that water can form hydrates. The hydrogen bond causes the water molecules to align in regular orientations. The presence of certain compounds causes the aligned molecules to stabilize and a solid mixture precipitate. The water molecules are referred to as the "host" molecules, and the other compounds, which stabilize the crystal, are called the "guest" molecules.

The hydrate crystals have complex, three-dimensional structures where the water molecules form a cage, and the guest molecules are entrapped in the cages. The stabilization resulting from the guest molecule is postulated to be due to van der Waals forces, which is the attraction between molecules not due to electrostatic attraction. As described earlier, the hydrogen bond is different from the van der Waals force because it is due to strong electrostatic attraction, although some classify the hydrogen bond as a van der Waals force.

Indeed, the diameter of the molecule must be smaller than that of the cavity for the molecule to enter the cavity, but it must be just as large to ensure stability of the crystalline structure. The most widely studied hydrates are natural gas hydrates, such as CH_4, C_2H_6, C_3H_8, H_2S and CO_2, all of which are in a gaseous state under ambient conditions.**[6]**
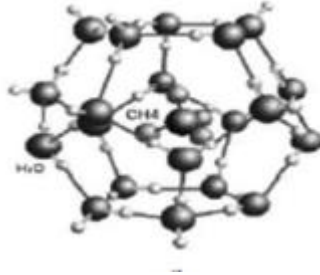
Figure I. 4: Structure of hydrate unit. **[6]**

Liquide particles can also be inserted into the cavities and form hydrate, but they are typically in cyclic nature like cyclo hexane and methyl-cyclohexane.

I.6.2   Discovery history of hydrates:

History discovered natural gas hydrate is divided into three main periods:

First period of interesting phenomena related to the formation of hydrate science. Because the accumulation of water and gas together as a hydrate phase due to lack of compliance with the terms and scientific information at that time (non-mixing of water and gas) is an interesting phenomenon. The exact course of the year 1810 CE the same time discovering the whereabouts hydrate started continues.

The second term is related to the year 1934. With more extensive research on gas hydrate structure reveals the fact that Crick thought the natural gas transmission pipeline route at low temperatures due to freeze Animate and not because of favorable conditions for gas hydrate is formed in other words this part of History devoted to the discovery of natural gas hydrate problems of hydrate formation is an unwanted case.

Third term in 1960 simultaneously with the discovery of large amounts of these molecules in the ground layers contain large amounts of natural gas are much devoted to the fact hydrate History found. So today the confluence of three periods hydrate history is important and that same appeal in certain aspects of the existence of hydrate hydrate this part of history brings.**[6]**

I.6.3   Hydrate structure types:

The petroleum business commonly encounters two types of hydrates. These are known as type I and type II, sometimes referred to as structures I and II. A third type of hydrate that may also be encountered is type H, also known as structureH. However, it is less likely to encounter.
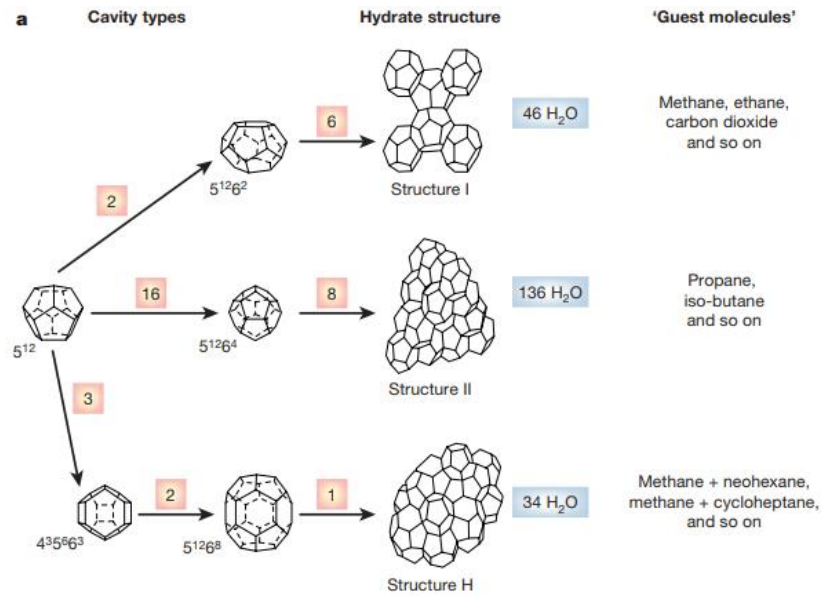
Figure I. 5: The three common hydrate unit crystal structures. Nomenclature: $5^{12}6^4$ indicates a water cage composed of 12 pentagonal and four hexagonal faces. The numbers in squares indicate the number of cage types. For example, the structure I unit crystal is composed of two 512 cages, six $5^{12}6^2$ cages and 46 water molecules.[7]

- Structure SI is composed by 46 water molecules where: $2M_1$ $6M_2$ $46H_2O$.

M_1 designate molecules occupying 5^{12} cavities, M_2 designate molecules occupying $5^{12}6^2$

- Structure SII is composed by 136 water molecules where: $8M_1$ $6M_3$ $136H_2O$.

M_1 designate molecules occupying 5^{12} cavities, M_3 designate molecules occupying $5^{12}6^4$.

- Structure SH is composed by 34 water molecules where: $3M_1$ $2M_4$ $34H_2O$.

M1 designate molecules occupying 5^{12} cavities, M4 designate molecules occupying 4^3 5^6 6^3 cavities, M_5 designate molecules occupying $5^{12}6^8$ cavities.

Table I. 1: Characteristics of three hydrate structures **[7]**

Hydrate crystal structure	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
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	3.9↑	4.06↑	5.71↑
Coordination number*	20	24	20	28	20	20	36
Number of waters per unit cell	46		136		34		

*Number of oxygens at the periphery of each cavity.

↑Estimates of structure H cavities from geometric models

I.6.4   Hydrate Nucleation:

The first stage of any phase transition is a dynamic connection of transport processes and thermodynamic transformations. The free energy modification of the phase conversion has to be negative and large enough to also prevail over the penalizing work needed for providing space for the new phase. The modification of an unstable state over to a stable increased volume is termed nucleation. Nucleation of the hydrate formation may occur along many alternative paths. Heterogeneous nucleation at the interface connecting the fluid or a gas and water is the best known. The distrusted hydrate origins in water could also create a homogenous hydrate.and the hydrate can nucleate toward mineral surfaces in natural sediments or a pipeline (rust).

I.6.5   Hydrate Growth:

The critical size for a hydrate particle is such a particle's size where it can enter the stable growth regime. The associated length and nucleation times are nanoscale processes. The side dynamics of rapid and stable growth can be very slow, given that the hydrate-forming molecules and water must transport across pre-existent hydrate films. However, the induction times can set to zero; the time required reaching a visible, growing hydrate.**[8]**
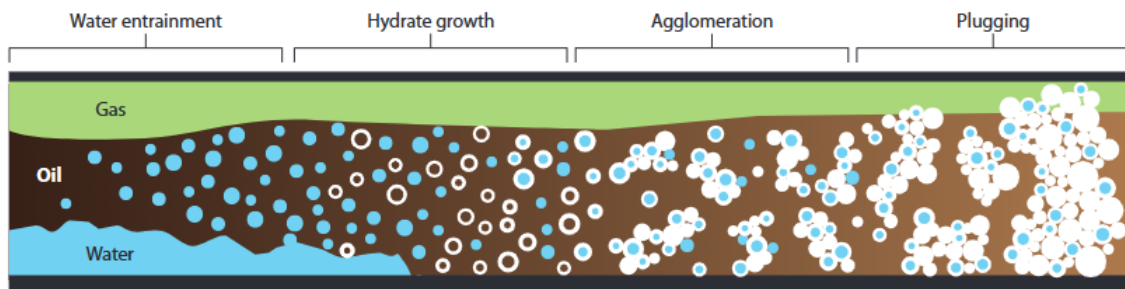
Figure I. 6:conceptual model for hydrate formation [8]

I.6.6   Hydrate formers:

The formation of a hydrate requires the following three conditions:

- The right combination of temperature and pressure. Hydrate formation is favored by low temperature and high pressure.
- A hydrate former must be present. Hydrate formers include methane, ethane, and carbon dioxide.

- Enough amount of water.

Figure I.7 gives a visual of the three criteria for hydrate formation. The three are interconnected if one of them is removed a hydrate does not form. Although this figure gives a quick visual image, it lacks the detail provided by the discussion presented earlier. However, it provides a useful visual.
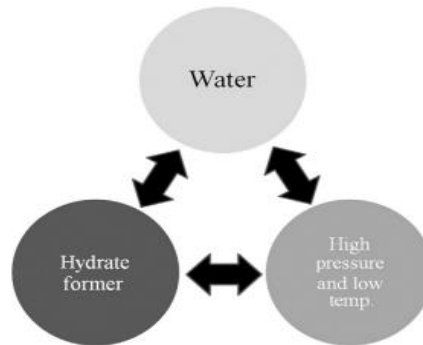
Figure I. 7: Simplified diagram of three criteria for hydrate formation [5]

I.6.7   Hydrate formation enhancers:

phenomena that enhance hydrate formation include the following:

I.6.7.1 Turbulence

- **a. High velocity**

Hydrate formation is favored in regions where the fluid velocity is high. This makes choke valves particularly susceptible to hydrate formation.

- **b. Agitation:**

The mixing may not be due to an actual mixer but perhaps to a tortuous routing of the line.

I.6.7.2 Nucleation sites:

In general terms, a nucleation site is a point where a phase transition is favored, good nucleation sites for hydrate formation include an imperfection in the pipeline, a weld spot, or a pipeline fitting (elbow, tee, valve, etc.).

I.6.7.3 Free-water:

Free-water is not necessary for hydrate formation, but the presence of free-water certainly enhances hydrate formation. The presence of free water also assures that they is plenty of water present, which is more likely to form a plug.**[5]**

I.7   Conclusion:

In summary, this chapter has provided an overview of natural gas, including its significance and application in gas lift techniques. We have delved into the concept of gas hydrates, tracing their discovery history and examining various types. Additionally, we explored the processes of nucleation and growth, along with the substances that form and enhance hydrate formation. This foundational understanding sets the stage for further investigation into the challenges and opportunities presented by gas hydrates in the energy industry. The insights gained here will inform subsequent chapters and contribute to a comprehensive analysis of natural gas utilization and management.

CHAPTER II: HYDRATE FORMATION INHIBITION AND PREVENTION

Part 1: Hydrate formation mitigation

II.1 Introduction:

In this chapter, we will explore the critical aspects of hydrate formation conditions and equilibrium, delving into factors that enhance the formation of gas hydrate in natural gas systems.

We will examine several strategies for inhibiting and preventing hydrate formation, emphasizing both chemical and mechanical methods.

A significant portion of this chapter is dedicated to a study case that demonstrates the application of heat exchangers as an effective solution for preventing hydrate formation. By analyzing this example taken from HMD field, we will illustrate the practical implications and benefits of using heat exchangers in maintaining the integrity and efficiency of natural gas operations.

II.2 Hydrate formation conditions:

Gas hydrates are formed when water and gas (having lower molecular weight) combine at low temperature and generally high pressure (e.g. temperatures below 25 °C and pressures greater than 1.5MPa for natural gas hydrates), precise conditions vary depending on the composition of the fluid. They exist onshore beneath the permafrost or offshore in shallow depths in the ocean. The gases that can form gas hydrates include methane (predominantly), propane, ethane, butane, chlorine, CO2, nitrogen even oxygen can create hydrates. At high pressure, gas hydrates can exist at temperatures greater than the freezing point of water. The solid hydrate compounds form with the aforementioned gases at elevated pressures in the presence of water. At equilibrium conditions the hydrates cause a higher amount of water to be removed from the vapor phase than in the case of liquid water at the same pressure and temperature, this is due to the lower vapor pressure of the hydrates [9]
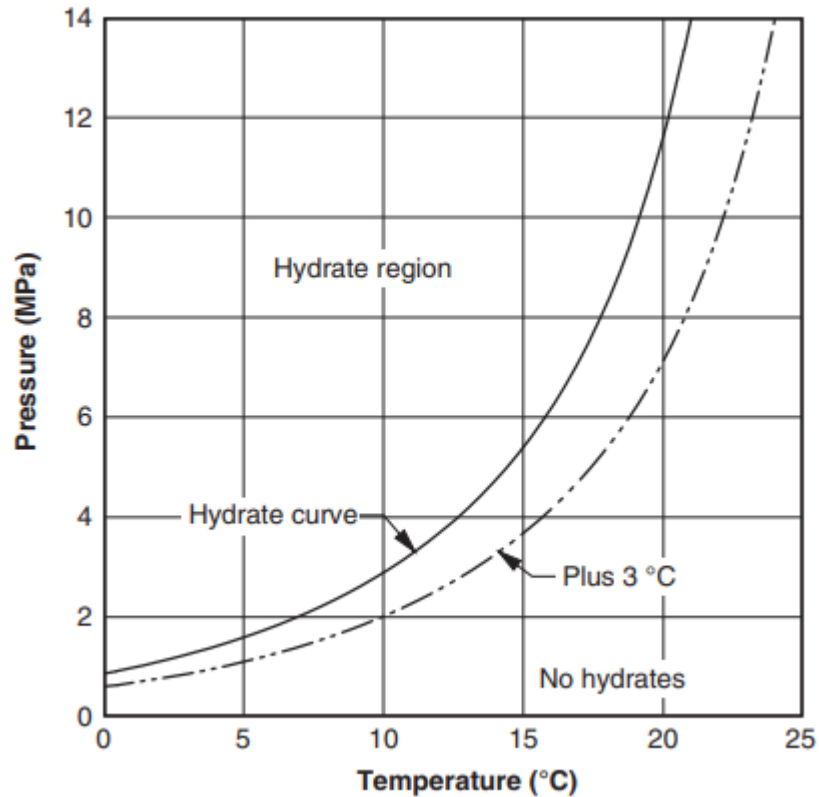
Figure II. 1: Pressure-Temperature Diagram Showing the Hydrate Region, the Region with no hydrate and safety margin **[9]**

II.3   Phase equilibrium:

Figure II.2 shows the hydrate equilibrium curve (I-H-V), (LW-H-V), (LW-H-LHC) for several components. The letters H, I, V, LW, and LHC represent hydrate, ice, hydrocarbon vapor, liquid water, and hydrocarbon liquid respectively. The lower quadruple point, Q1 indicates the point at which the four-phase ice, liquid water, hydrocarbon vapor and hydrate (I-LW-H-V) are in equilibrium. The temperature at this point approximates the ice point.
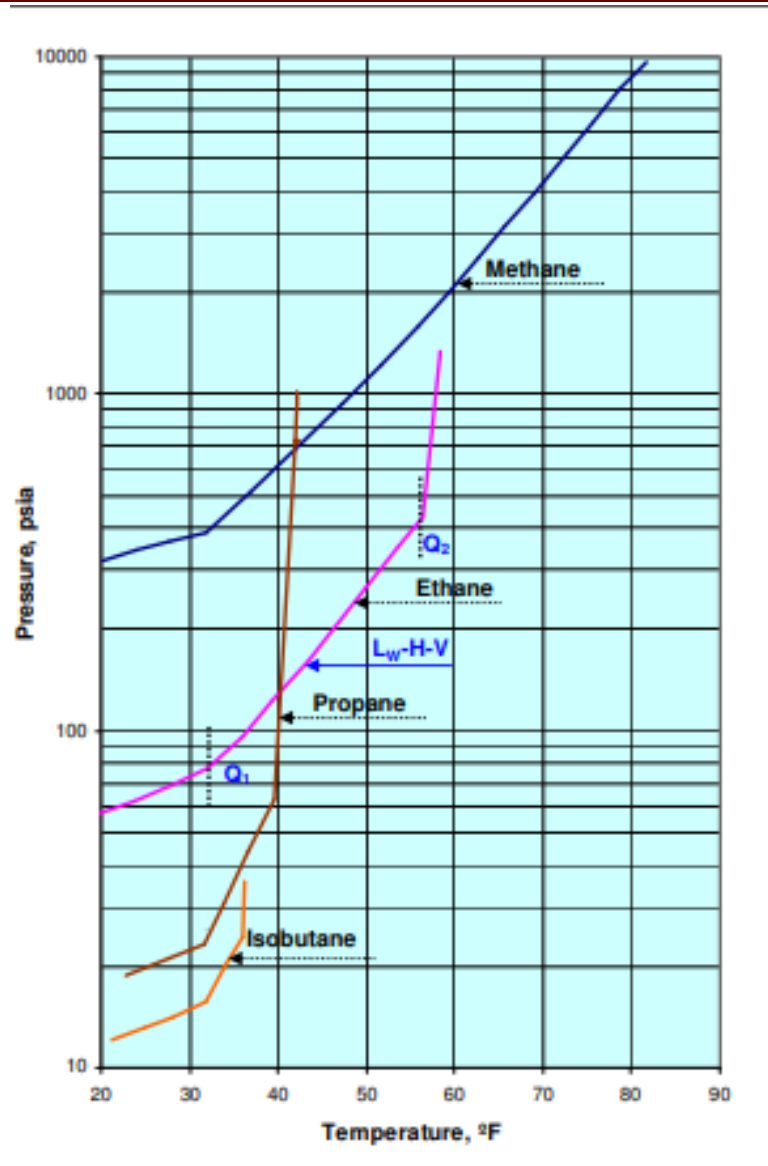
Figure II. 2: Phase diagram for natural gas hydrocarbons which form hydrate **[10]**

The point Q2 is the upper quadruple point at which the four-phase water liquid, hydrocarbon liquid, hydrocarbon vapor, and hydrate (LW-LHC-V-H) are in equilibrium. The pressures and temperatures at the Q1Q2 line represent the conditions that three-phase liquid water, hydrocarbon vapor and hydrate are in equilibrium. Therefore, at the right side of this line no hydrates form; however, hydrates begin to form at this line and become more stable at a higher pressure and/or lower temperature.

II.4   Hydrate Formation inhibition and prevention:

Hydrate formation could be avoided before it will happen by knowing thermodynamic conditions of its formation. This could be realized by rising the temperature on a giving pression or lowering the pression (depressurization) on a giving temperature. If this is not possible, we should remove hydrate formation by reducing water content on gas using inhibitors to dry gas.

II.4.1   Chemical inhibitors:

The most common way to inhibit hydrates is to inject chemical inhibitors. Instead of removing the water to avoid creating hydrates. The inhibitors prevent the water from structuring the way it must become hydrates; therefore, at a specific temperature, the pressure needed to form a hydrate increases. Two main types of chemical inhibitors used are:

- **Alcohols:**

Alcohols such as methanol, glycols, and diethylene glycol (DEG) and triethylene glycol (TEG) are widely used in the oil and gas industry to avoid the formation of gas hydrates. FigureII.3 below shows the three-dimensional structures of the primary alcohols applied (methanol, monoethylene glycol (MEG) , and diethylene glycol). At least to thermodynamically inhibit a gas hydrate, an extensive amount of alcohol content is necessary and to modify the hydrate thermodynamic curve to attain lower temperature and higher-pressure region.
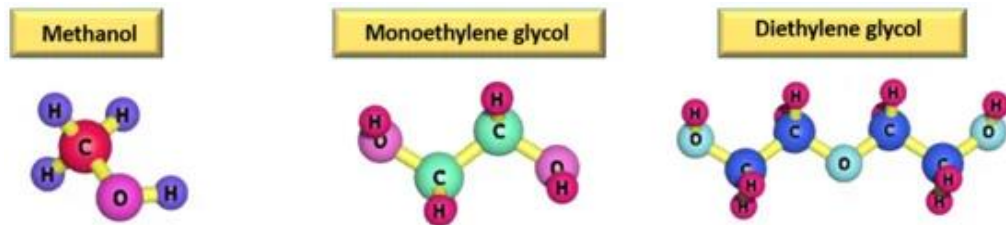
Figure II. 3: Three-dimensional structures of primary alcohols **[12]**

Table II. 1: Inhibitors parameters[13]

INHIBITOR	M	Xm	C
MEOH	32	0.612	2335
EGLYCOL	62.07	0.6423	2700
DEGLYCOL	106.12	0.7231	4000
TEGLYCOL	150.17	0.7634	5400

Among glycols, monoethylene glycol (MEG) is very efficient and suitable for hydrate inhibition, due to its lower molecular weight.

- **Electrolytes:**

The use of electrolyte salts to prevent the formation of gas hydrates is based on the contact between the electrolyte molecules and the dipole of the water molecules because the attraction between the water molecules and ions is more favorable than the attraction between the hydrate structures.

Calcium chloride ($CaCl_2$) is frequently chosen for its effectiveness and low cost. On the other hand, because of the risk of corrosion and deposit formation, salts are not commonly used as inhibitors in practice.[7]

II.4.2 Mechanical inhibition:

- **Pressure reduction:**

A pressure drop at a fixed temperature is one way of leaving the hydrate formation zone. However, gas expansion is generally accompanied by a drop in temperature, which runs counter to the desired effect.

Depressurization can only remove a hydrate plug if it is carried out almost isothermally, which implies that the pipe is well insulated and that the process is sufficiently slow. If, however, the pressure drop (loss of head for the flow) is isothermal, hydrate formation will be avoided.

- **Heating:**

Active heating includes electrical heating and heating by fluid circulation in a bundle. At flow lines and production columns, active heating must be applied with thermal insulation to minimize energy requirements.

Hot upstream

Insulation

downstream

a. heating through hot fluid circulation

Electric heating cable

Thermal insulation

line
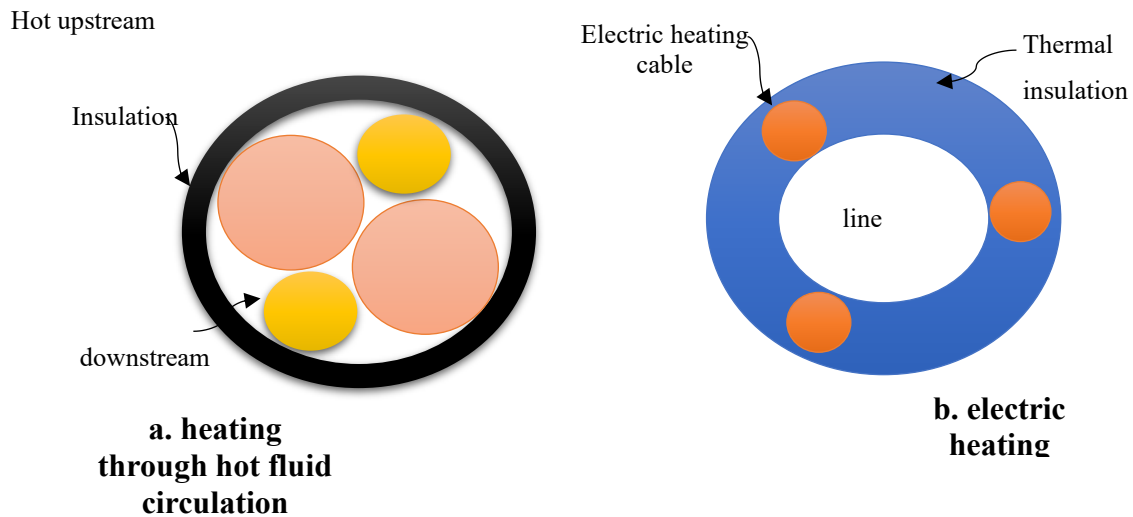
b. electric heating

Figure II. 4: Technics of pipe heating

Electric heating (Figure II.4. b) is a rapidly developing technology with applications in offshore fields. In contrast, hot fluid heating (Figure II.4.a) offers the same advantages as electric heating. Instead of using electricity to supply heat, hot fluid, typically inhibited water, circulates through the bundles to supply heat to the production fluid. **[14]**

Part 2: Hydrate formation inhibition using heat exchanger:

II.5   Heat transfer:

We call something that flows from hot object to cold object a heat flow, which has different modes and processes that mainly exist throughout earth.

The only conceivable domain free from heat flow would have to be isothermal and totally isolated from any other region. It would be "dead" in the fullest sense of the word – devoid of any process of any kind.

II.5.1   Heat transfer modes:

II.5.1.1   Conduction:

Conduction refers to the transfer of heat from the hotter to the colder part of a body by direct molecular contact, not by gross movement of clumps of hot material to the cold region. At steady state the rate of heat transfer depends on the nature of the material and the temperature differences and is expressed by Fourier's law as.

$$q_x = -k.A.\frac{dT}{dn} \quad \left(\frac{J}{S} = W\right)$$

II.5.1.2   Convection:

When hot fluid moves past a cool surface, heat goes to the wall at a rate which depends on the properties of the fluid and whether it is moving by natural convection, by laminar flow, or by turbulent flow. To account for this form of heat transfer.

$$q = h.A.\Delta T$$

II.5.1.3   Radiation:

It is a mode of transfer by which heat is transmitted from one body to another without this touching, the two layers can be separated by the thermal radiation is held continuously in all bodies and in all directions, it is electromagnetic radiation, the best-known example is radiation from the sun. **[15]**

$$\phi = \sigma.ST^4$$

II.6 Heat exchangers:

II.6.1 Definition of heat exchanger:

A heat exchanger is a piece of equipment built for efficient heat transfer from one medium to another. The media may be separated by a solid wall, so that they never mix, or they may be in direct contact. They are widely used in space heating, refrigeration, air conditioning, power plants, chemical plants, petrochemical plants, natural gas processing, and sewage treatment. The classic example of a heat exchanger is found in petroleum refineries. Oil Refinery is an industry which refines crude oil into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas by fractional distillation.

Heat exchangers may be classified according to the following main criteria.

- Recuperators/regenerators
- Transfer processes: direct contact and indirect contact
- Geometry of construction: tubes, plates, and extended surfaces
- Heat transfer mechanisms: single phase and two phase
- Flow arrangements: parallel flows, counter flows, and cross flows.
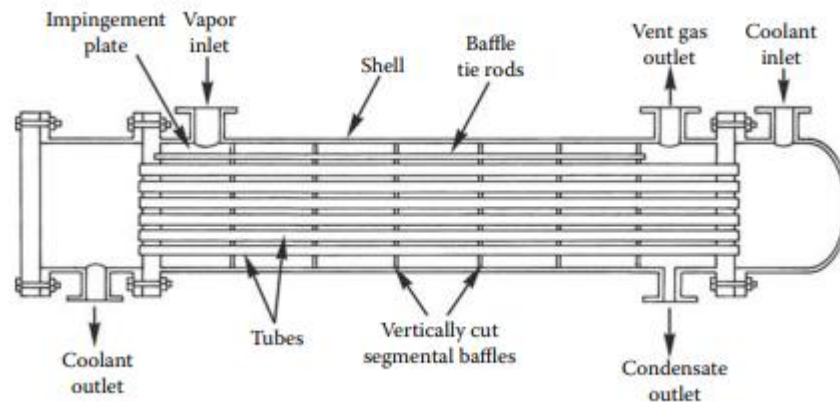
Figure II. 5: Typical shell and tube heat exchanger **[16]**

As shown in figure II.5 The simplest form of a horizontal shell-and-tube type condenser with various components. Shell-and-tube heat exchangers are built of round tubes mounted in large cylindrical shells with the tube axis parallel to that of the shell. They are widely used as oil

coolers, power condensers, preheaters in power plants, steam generators in nuclear power plants, in process applications, and in general in oil and gas industry.

II.6.2 Heat exchanger application;

- Cooling – Cooling using water or air, without phase change.
- Chilling – Refrigerating below that obtainable with water.
- Condensing – Condensing vapor/ vapor mixture.
- Steam Heating – Using steam for heating.
- Steam Generating – Producing steam from water.
- Reboiler – Using steam/hot fluid to heat, for
- distillation column.

II.6.3 Heat exchangers used in petroleum industry:

In oil refineries and petrochemicals, we generally use shell and tube type of heat exchangers which are classified under TEMA (Tubular Exchanger Manufacturers Association) to transfer heat between two fluids. Heat Exchangers here generally find their application in preheating of the fluids More than 35-40 % of heat exchangers are of the shell and tube type due to their robust geometry construction, easy maintenance and possible upgrades.

II.6.4 Heat exchanger types:

II.6.4.1 U-TUBE Heat exchanger:

generally, it is taken less under consideration for heat exchanging because in case of any leakage or testing the tubes are difficult to clean. Here the tube expansion is independent of other tubes. This is used in oil refinery in crude distillation unit for heat exchange between crude and medium pressure steam.

II.6.4.2 Fixed tube sheet heat exchanger

is the cheapest and most economical type of heat exchanger used in any oil refinery for heat exchanging because the mechanism of its operation is simple and also the testing and repair of the same is easy to perform

II.6.4.3 floating head heat exchanger

is the most efficient type of heat exchanger used in an oil refinery. It has a floating head attached to one of its ends which helps in the proper heat transfer between fluids. The floating heat permits the free expansion and contraction. Also, this type of heat exchanger is easy to clean and test for performance enhancement's purpose. This is used in oil refinery in crude distillation unit for heat exchange between crude and naphtha. It increases the temperature of crude. It is used to preheat the heat exchanger before sending it to crude distillation column.

II.6.4.4 Kettle heat exchanger:

Is a special type of heat exchangers which is used when the fluids used consist of high-pressure gases and this heat exchanger has a specially designed shell that gives expansion space to the heat exchanger. This heat exchanger can handle large amount of load fluctuation. This is used in oil refinery in crude distillation unit for heat exchange between naphtha and diesel or between kerosene (light and heavy) and heavy atmospheric gas oil (HAGO). **[16]**

II.7 Case Study:

- **Field description:**

The HASSI MESAOUD reservoir was discovered by two separate companies - CFPA at the northern part and SN-REPAL at the southern part of the field.

In 1946 SN-REPAL began its research across the ALGERIAN Sahara, three years later geophysical prospecting started with a- gravity recognition.

The HASSI MESSAOUD field was discovered on 16th of January , 1956 by the SN- REPAL which initiated the first MD 1 drilling, this drilling discovered oil-producing Cambrian sandstones at a depth of 3338.

In May 1957, seven kilometers northwest of MD1, the CFPA confirmed the existence of a deposit by drilling OM1. Drillings which was then ten per year, has continued to multiply since 1967 and especially from the nationalization measures of the hydrocarbons on 24th February 1971.

- **Geographical situation:**

The Hassi Messaoud field occupies the central part of the TRIASIC province it is limited:

- To the North by the structures of Djamaa -Touggourt
- To the West by the Oued Mya depression.
- To the South by the Amguid d'Elbio

To the east by the high seas of Dahar Rhourd EL Baguel and the depression of Gadames.

- **Reservoir characteristics:**

At Hassi Messaoud, it is the Cambrian sediments which are saturated with oil. They are protected by a good cover formed by thick salt layers and clay from the Triassic.

The upper surface of water was initially at a depth of approximately 3380m, given the significant depletion of the field, the water somewhat invaded a good part of R2.

Essentially constituted anisometrical sandstone, except the Ra; zone of around a hundred meters presents the best petrophysical characteristics. She is the most productive of the Cambrian reservoir located approximately between 3300m and 3500m depth.

- The oil is light Density, average surface 0.8 allowing to increase the recovery rate by gas reinjection.
- field pressure is variable. 400 to 120 kg/cm^2
- The temperature is around 118°C.
- The porosity is low 5 to 10%.
- permeability is very low
- the viscosity is 0.2CP
- The volumetric factor of fender is1.7
- Porosity very low 5 to 10%

- **The structure of the field:**

The field of Hassi Messaoud constitutes a vast bald cambro Ordovician anticline. The reservoir is covered by the clay-sandstone and salt complex of the Triassic discordant on the erosion surface of the Ordovician Cambro. Saturation develops into a vast anticline with a general direction NNE -SSW, but whose dips rarely exceed 1 degree.

II.7.1 Description of the problem:

From our internship in Hassi Messaoud field and regarding the growing number of Gas lift wells (500 wells plus) and their contribution of the overall production of crude oil (40% contribution) which become more important to assure the right optimization and permanent monitoring of continued gas lift injection.

It is important to note that during winter, Sonatrach always confronted with a considerable icing at the level of Gas Lift line which has a negative impact on the realization of the prevision of the production expected.

Knowing that 90% of the icing is eliminated by the commissioning of the new Gas lift loop, Nevertheless, double injection wells (Water, Gas lift) are still getting impacted by icing effect resulting a lack of production estimated at **400 tons/day**.

Besides this, many solutions have been tested in order to overcome this problem without any noticed results [heater /Export], Skid methanol (SH), reheater of the injected water of desalting [GPS energy], Glycol injection [Trans Algerie].

Following to this, a study of heat exchanger sizing has been elaborated by DEP engineers and executed by technical direction based on thermal energy transfer principle of produced oil, filling the exchanger neck towards the gas lift which runs through the coil.

II.7.2   Summary report on gas lift wells:

376 PPHGL   144 PPHSGL

Number of wells including Total down time due to icing > 100 hours: 28

Number of Wells including Total down time < 100 heures : 78

Deficit T/d : 250 to 300
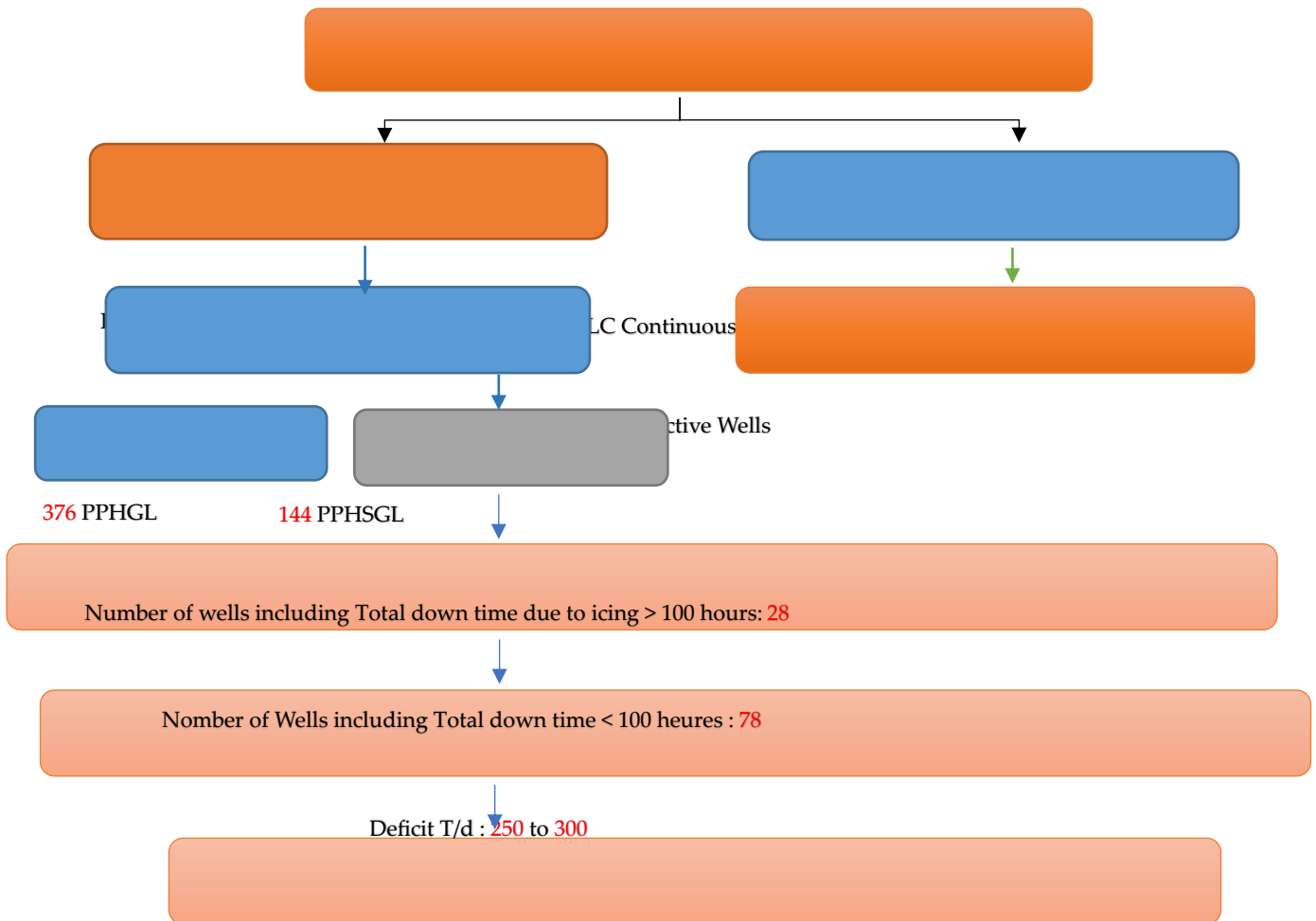
Figure II. 6: Summary report on gas lift wells

II.7.3   Gas properties

II.7.3.1 Chemical composition

Components	Composition (%molar)
Nitrogen	3.32
CO_2	2.29
Methane	72.67
Ethane	20.73
Propane	0.99

II.7.3.2 Molar Weight:

$$MW = Yi \times Mi$$

MW= 20.27

II.7.3.3 Gas density:

$$d = \frac{MW}{29}$$

d= 0.6999

II.7.4 Heat exchanger sizing:
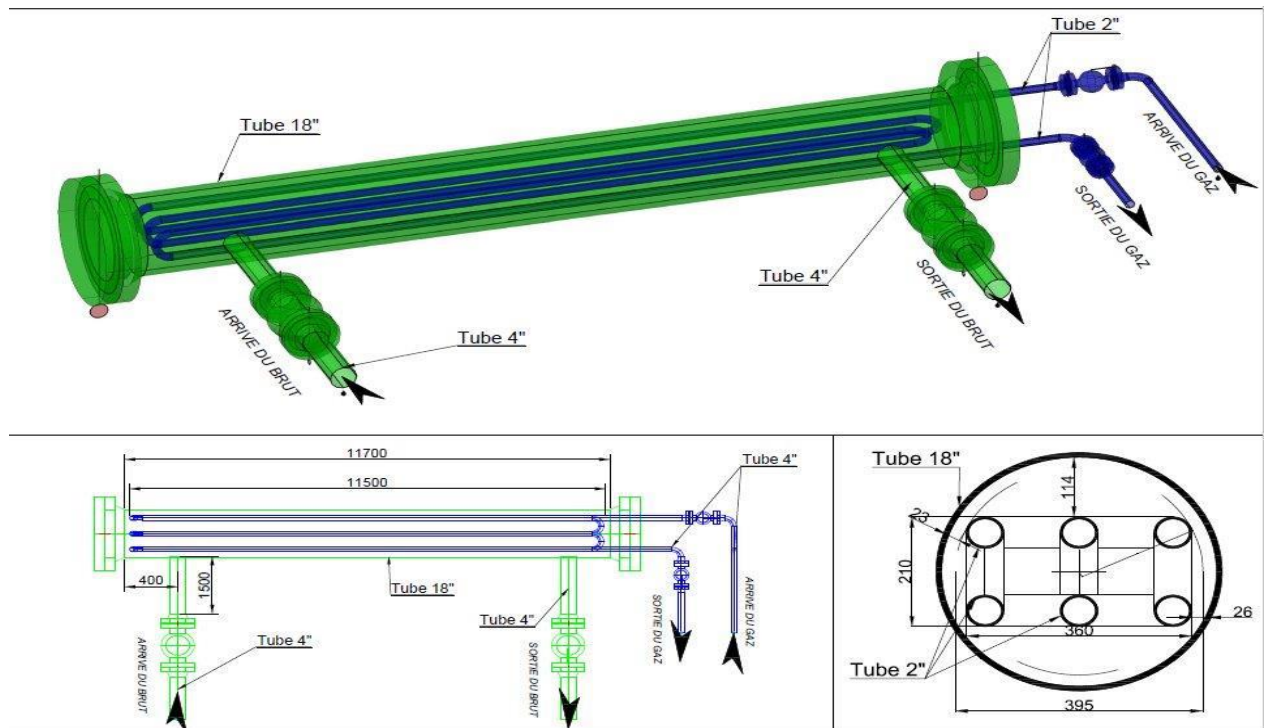
Figure II. 8: Heat exchanger size and dimensions**.**

Figure II.7 shows the design that has been obtained from pilot test and model simulation of the problem, further optimization will be considered based on the wellhead temperature and gas lift choke situation.

II.7.5 Pilot test:

The pilot test of the heat exchange has been very conclusive and reveal its efficiency on the well, gas temperature increased from -6 to 38 degree Celsius.

Furthermore, based on the simulation, wells whose well-head temperature varies between 28°C and 50°C, showed good results and especially double injection wells (water and gas)

On the other hand, wells whose well-head temperature lower than 25°C, showed that the outlet temperature of the heat exchanger was very critical to the hydrate formation temperature.
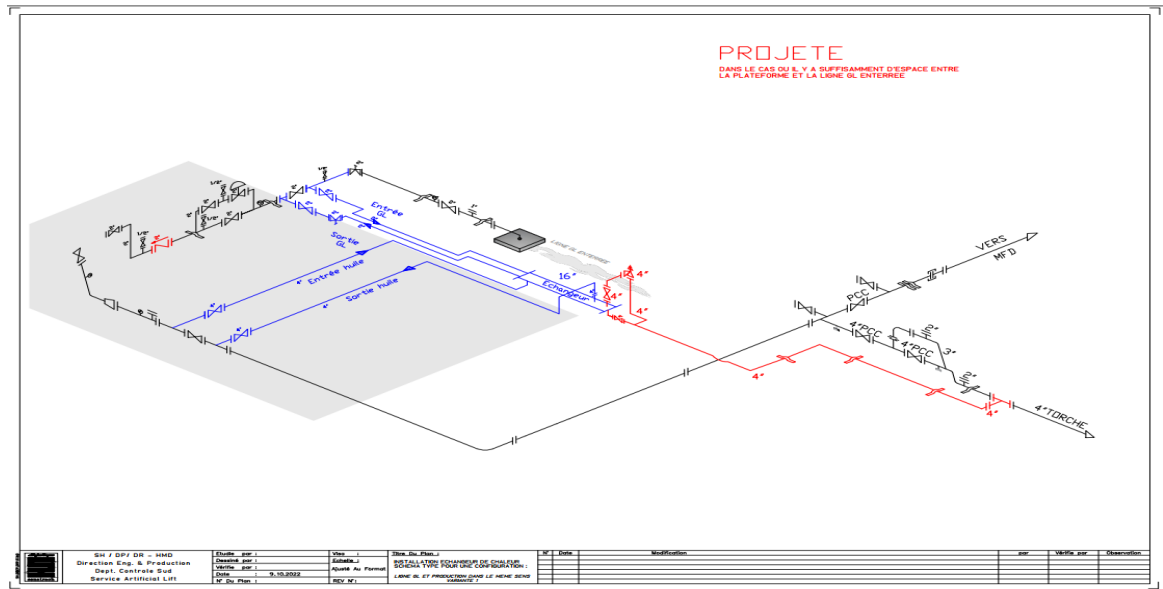
Figure II. 9: Variable diagram of the heat exchanger installationFigure II.8 shows a typical diagram of the heat exchanger installation; this installation will be suitable if there are sufficient

space between the platform and gas lift inlet line.

Figure II. 10: image of the heat exchanger

II.7.6 Well performance after heat exchanger commissioning:
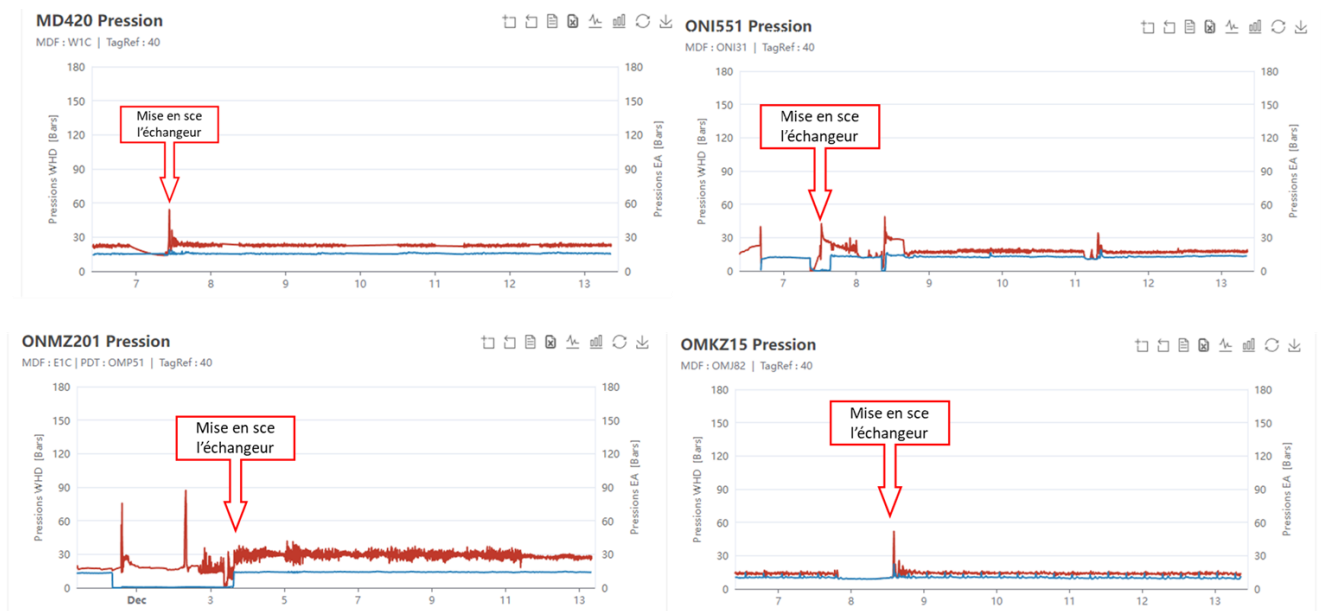
Figure II. 11: WHP of four wells observation

- **Observation and interpretation:**

After the commissioning of the heat exchanger on the four wells the well head pressure tend to be more stable than before.

The pressure instability before the commissioning of the heat exchanger is because of the hydrate plug on the well heat surrounding.

That means that the hydrate plug will be unlikely to form due thermal exchange from the hot oil and cold gas

II.7.7 Evaluation of the first phase:

Table II. 2: heat exchanger first phase evaluation

Wells	Oil Flowrate (m³/h)	Water Flowrate (m³/h)	Gas injection flowrate (m³/j)	WHT (C°)	Temp before The exchanger	Temp after The exchanger	ΔT (C°)
OMJZ633	2.9	1.2	25000	31	14	23	9
OMGZ81	6.43	1.54	17000	44	16	26	10
ONMZ201	4.16	1.2	31000	30	5	20	15
MD660	4.99	0.92	35000	29	18	29	11
MD179	1.1	0.67	26000	22	15	22	7
MD322	3.29	1.15	35000	35	-2	18	20
ONMZ513	1.98	1.7	33000	28	16	27	11
OMKZ103	3.69	0.9	13000	46	15	30	15
ONM61	2.45	1.2	25000	28	0	10	10
OMNZ102	5.9	0.86	12000	59	12	35	23

- **Observations deducted:**

The gas expansion at the GL choke is the main cause of the temperature drop

GL Choke upstream the heat exchanger:

- Very satisfactory results
- GL outlet temperature after exchanger (18 °C to 35 °C)
- ΔT ranges from 07 to 23 °C

GL choke downstream the heat exchanger:

- Unsatisfactory results
- GL outlet temperature after exchanger (10 °C to 16 °C)
- ΔT ranges from -04°C to -14°C

For this technique to be reliable, WHT must be at least 30°C

Table II. 3: Observation of shutdowns and SIP before and after heat exchanger

	Wells	Restoring GL (ICING) 21-22 Before HE			Restoring GL (ICING) 22-23 After HE			GAIN		GAIN/DAY		Moy Temp	Qgl optimum
		Down time	SIP (T)	Shutdown frequency	Down time	SIP (T)	Shutdown Frequency	Down time	SIP (T)	Down time	LAP (T)		
1	OMJZ633	225	487	25	70	157	8	155	330	2,12	4,52	31,10	22000
2	ONI551	146	171	14	30	52	3	116	119	1,84	1,89	27,51	24000
3	ONMZ201	102	317	12	0	0	0	102	317	1,50	4,66	29,42	31000
4	OMGZ81	120	735	16	19	98	2	101	637	1,28	8,06	51,88	17000
5	MD322	88	105	10	0	0	0	88	105	0,96	1,14	35,27	23000
6	MD660	80	412	10	0	0	0	80	412	1,14	5,89		20500
7	OMKZ15	84	228	10	7	17	1	77	211	1,17	3,20	32,92	23000
8	MD420	78	212	9	18	34	2	60	178	0,91	2,70	27,01	34500
9	MD179	66	47	9	12	7	3	54	40	0,79	0,59	25,14	29000
10	ONMZ513	31	77	4	0	0	0	31	77	0,55	1,38	25,53	25000
11	OMKZ103	45	81	8	22	68	2	23	13	0,43	0,25	44,11	11100
12	ONM61	36	35	8	20	44	3	16	-9	0,29	-0,16	15,96	45000
13	OMNZ102	17	36	1	3	17	1	14	19	0,26	0,36	53,46	27000
14	MDZ717	36	84	4	29	136	3	7	-52	0,11	-0,84		24000
15	OMGZ801	189	470	24	208	489	25	-19	-19	-0,24	-0,24	23,21	20000
	TOTAL	1343	3497	164	438	1119	53	905	2378	0,88	2,40		
										Moyen par Puits (m3/h)	0,13		
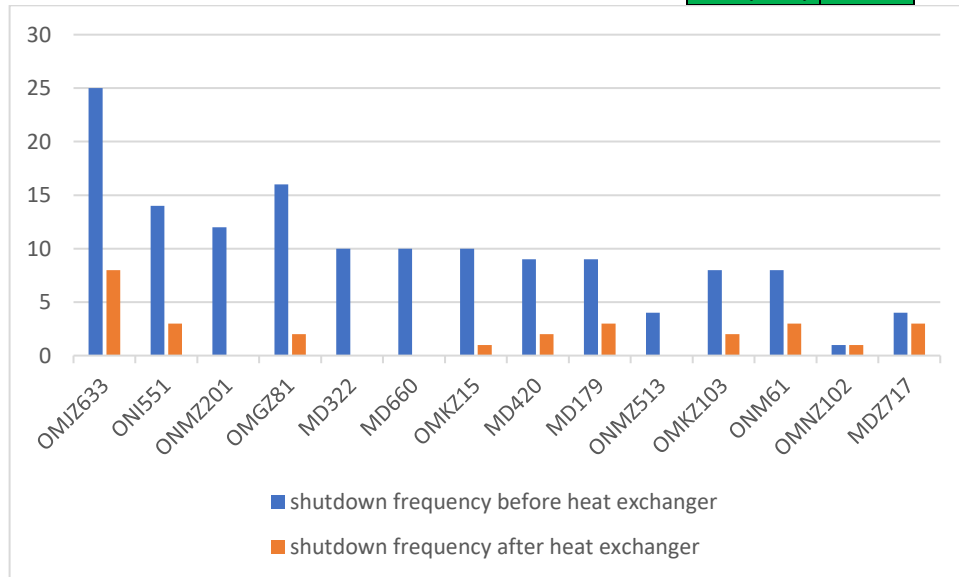
Figure II. 12: WH blockage frequency before and after heat exchanger

The table II.3 showing the noticeable difference in the shortfall in production (SIP) before and after the commissioning of the heat exchanger, this illustrates the effectiveness of the heat exchanger as a solution of the hydrate problem plug.

The graph on the figure II.11 shows that heat exchanger helps to decrease the number of well shutdowns due Well head blockage because of hydrate plug.

II.7.8 Recommendations:

- GL Choke must always be upstream of the heat exchanger.
- The best candidates for this solution are:
  - Wells that produce with High Oil Temperature.
  - Wells that produce in a steady flow regime.
- A Rotation of the GL Choke located downstream the heat exchanger
- The Auto-GL valve position must be upstream to keep the gas expanding before the heat exchanger.

II.8 Conclusion

In conclusion, the understanding of the hydrate formation conditions and phase equilibrium is crucial in order to predict and prevent hydrate formation and blockage, also for safe operation of natural gas systems.

By exploring both chemical and mechanical methods for inhibiting and preventing hydrate formation, we can develop comprehensive strategies tailored to specific operational needs.

The case study highlights the effectiveness of heat exchanger in hydrate prevention, by increasing gas temperature above HFT using hot oil from production line.

The case study also demonstrates the capability of heat exchangers to mitigate risks associated to hydrate formation, and also decrease the number of shutdowns and reduce the down time due to hydrate plugs and icing.

Through this analysis, we have shown that a well-designed prevention strategy not only enhances system reliability but also contributes to overall operational efficiency, safety and production gain.

CHAPTER III: HYSYS SIMULATION OF HYDRATE FORMATION PRIVENTION METHODS

III.1 . Introduction:

Modeling is an approach that allows, from experimental facts, to build a mathematical tool linking the outputs of a system to its inputs.

In this chapter we will investigate chemical inhibition techniques, focusing on two widely used inhibitors Triethylene glycol and methanol. These chemicals work by altering the thermodynamic conditions necessary for hydrate formation. We will examine the mechanisms by which TEG and Methanol inhibit hydrate formation, including their interaction with water and gas molecules.

The chapter culminates in a comparative analysis of TEG and methanol, evaluating their mechanisms, efficiency and dosage. By leveraging simulation data from HYSYS, we provide a detailed assessment of each method's performance under various operating conditions..

III.2 HYSYS Presentation

It is the most widespread; It is mainly found in commercial static or dynamic simulation software. This extremely powerful software is based on thermodynamic models calculating the mixing properties from those of pure bodies (phase equilibrium, enthalpy, entropy) and on intensive variables (temperature, pressure and composition).

HYSYS is not the most flexible simulation software, nor the most widely used in the industry, but it has the advantage of being user-friendly and easy to use once the basic elements are understood.

HYSYS has been developed for the petroleum industry, it has been designed to enable the treatment of a wide range of problems from simple bi- and tri-phase separations, compression to distillation and chemical transformation, although it is used for other types of chemical processes.

Simulations are accomplished using the menu tools. In addition, it has a graphical interface for the construction of process flow diagrams (PDFs). A large database on pure bodies is incorporated with the HYSYS software, these bodies are grouped into several families:

- ✓ Hydrocarbons: normal paraffins and iso-paraffins, olefins, naphthenes, aromatics
- ✓ Hydrocarbons oxygens, azotes et sulfurés (amine, alcohols, nitriles, aldéhydes…
- ✓ Halogen
- ✓ Solides (soufre)

- ✓ Corps hypothèques (pures, complexes, solides)
- ✓ Diverses (O 2, N 2, CO 2, H2O, HCL…………....)

HYSYS presents several thermodynamic models with their field of application we can have:

Special models for amines;

- ✓ Models using vapor pressure (Antoine's equation, NK10 and Esso table);
- ✓ Special models for water vapor (ASTM stream, NBS stream);
- ✓ Semi-empirical models;
- ✓ Hybrid models (for systems with high polarity, high deviation from ideality, azeotropes)
- ✓ Models based on equations of state; such as Peng-Robinson (PR), Soave – Redlick-Kwong (SRK), the field of application of these models to the between phases and limited to normal fluids;

- ✓ To the equations SRK, PR, it is necessary to add the Lee-Kesler-Plücker EDE (LKP) them
- ✓ The preferred area is the refining, petrochemical and processing industries. gas.

The HYSYS Simulator is a set of mathematical models of unit operations

(Flask, distillation column, compressor, valve... etc.), these operations are connected

in a PFD process diagram by the current of information generated in these operations.

So, the HYSYS is a computer program for the simulation of

the gas, refining and petrochemical industries,

- In a steady state.
- In a dynamic situation.

III.3 . Uses of HYSYS

The HYSYS can be used for

- ➢ Engineering.
- ➢ Establishment of material and energy balances of an industrial process.

   Equipment sizing.

- ➢ Readjustment of operating parameters in the event of a change in Composition of the diet.
- ➢ Determination of equipment performance.

To use the HYSYS, the user must:

- ➢ Choose a thermodynamic model and the constituents.
- ➢ Establish the PFD process flowsheet.
- ➢ Specify the necessary parameters of each operation. **[17]**

III.4 . Tri ethylene glycol absorption mechanism using hysys:

III.4.1 TEG theoretical mechanism:

In dehydration by absorption water is removed by a liquid with strong affinity for water, glycols being the most common. The lean (dry) glycol removes the water from the gas in an absorption column known as a contactor. After the contactor the rich (wet) glycol must be regenerated before it can be reused in the contactor. With glycol absorption it is possible to lower the water contents down to approximately 10 ppm, depending on the purity of the lean glycol. Gas dehydration by glycol absorption will be treated more thoroughly in section.

III.4.2 Hysys simulation for TEG mechanisms illustration:

III.4.2.1 Gas field and TEG conditions:

Table III. 1: Gas field composition used in the absorber

Composition	Chemical formula	Mole fraction
Methane	CH4	0.9099
Ethane	C2H6	0.0447
Propane	C3H8	0.0186
I-Butane	C4H10	0.0019
n-Butane	C5H12	0.0041
I-Pentane	C5H12	0.0010
n-Pentane	C5H12	0.0010
n-Hexane	C6H14	0.0009
n- Heptane	C7H16	0.0008
n-Octane	C8H18	0.0008
n-Nonane	C9H20	0.0004
n-Decan	C10H22	0.0003
n-C11	C11H24	0.0001
n-C12	C12H26	0.0001
Hydrogen	H2	0.0007
Helium	He	0.0002
Nitrogen	N2	0.0022
Carbone dioxide	CO2	0.0098
Water	H2O	0.0025

The input gas constituents in the absorption column are taken from a gas treatment unit of Ain Salah are given above.

we took the same operating conditions of gas and actual solvent TEG from the Ain-Salah gas processing unit to Temperature, pressure, and molar flow.

Table III. 2: Gas and TEG input conditions

	Gas Enter	TEG Enter
	Conditions	
T (°C)	53.20	59.07
P (KPa)	8361	8360
Q (Kgmol/h)	14230.004	113.2

For the TEG solvent we used a solvent with the Characteristics given in the table:

Table III. 3: TEG Inhibitor concentration

Composition	Chemical formula	Mole fraction %
Water	H2O	1.38%
Triethylene glycol	C6H14O4	98.62%

For the absorber we used the same characteristics from the absorber in the Ain salah unit

Table III. 4: Absorber characteristics**.**

	T100: Absorber	
	1_Main Tower	3_Main Tower
	Condition	
T (°C)	54.73	54.72
P (KPa)	8185	8360
Q (Kgmol/h)	14230.004	153.5

III.4.2.2 Simulation steps:

- Open the HYSYS software
- Create a new box
- Put in the Natural Gas and Solvent Component (**TEG**)
- The choice of thermodynamic model: **Peng- Robinson**
- Open to the simulation box
- Entre GAS and TEG Condition
- Entre composition
- Choose absorber column and click RUN.

III.4.2.3 . Simulation Diagram
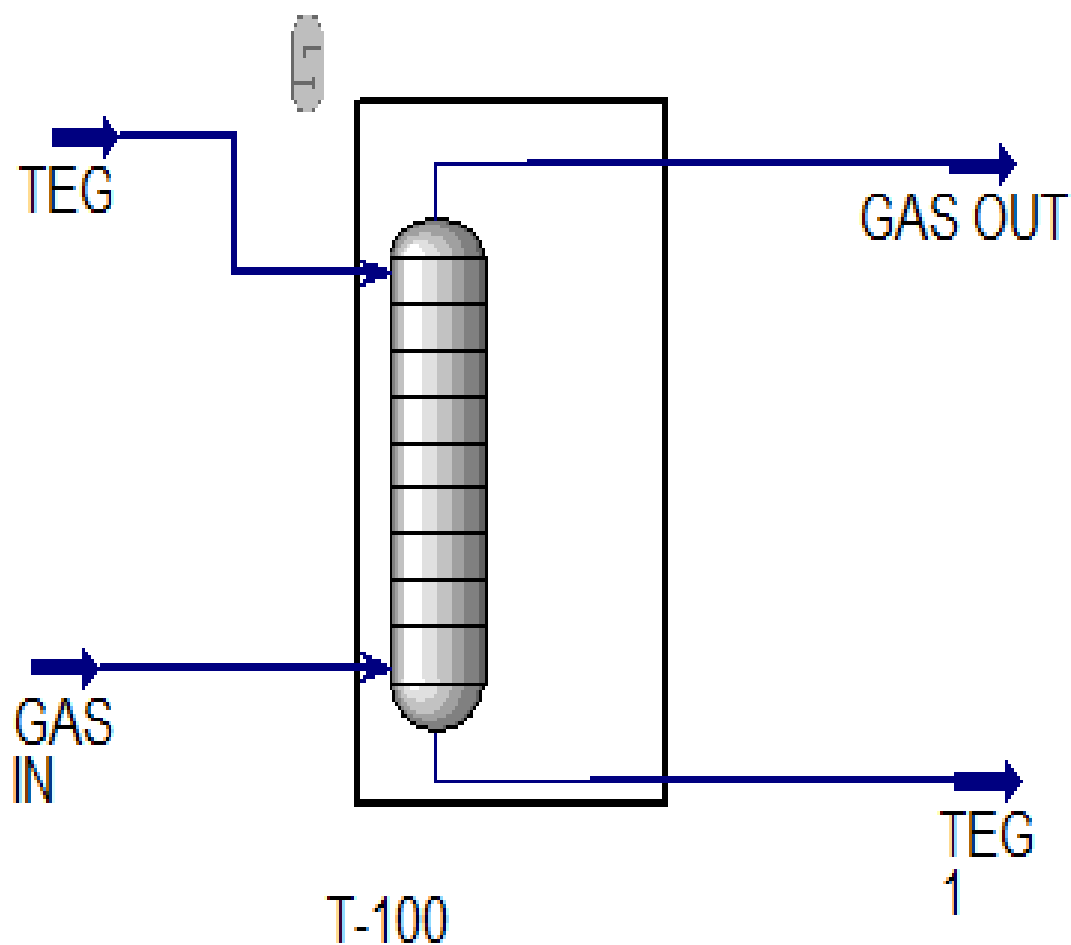
Figure III. 1: Model for absorber inputs and outputs

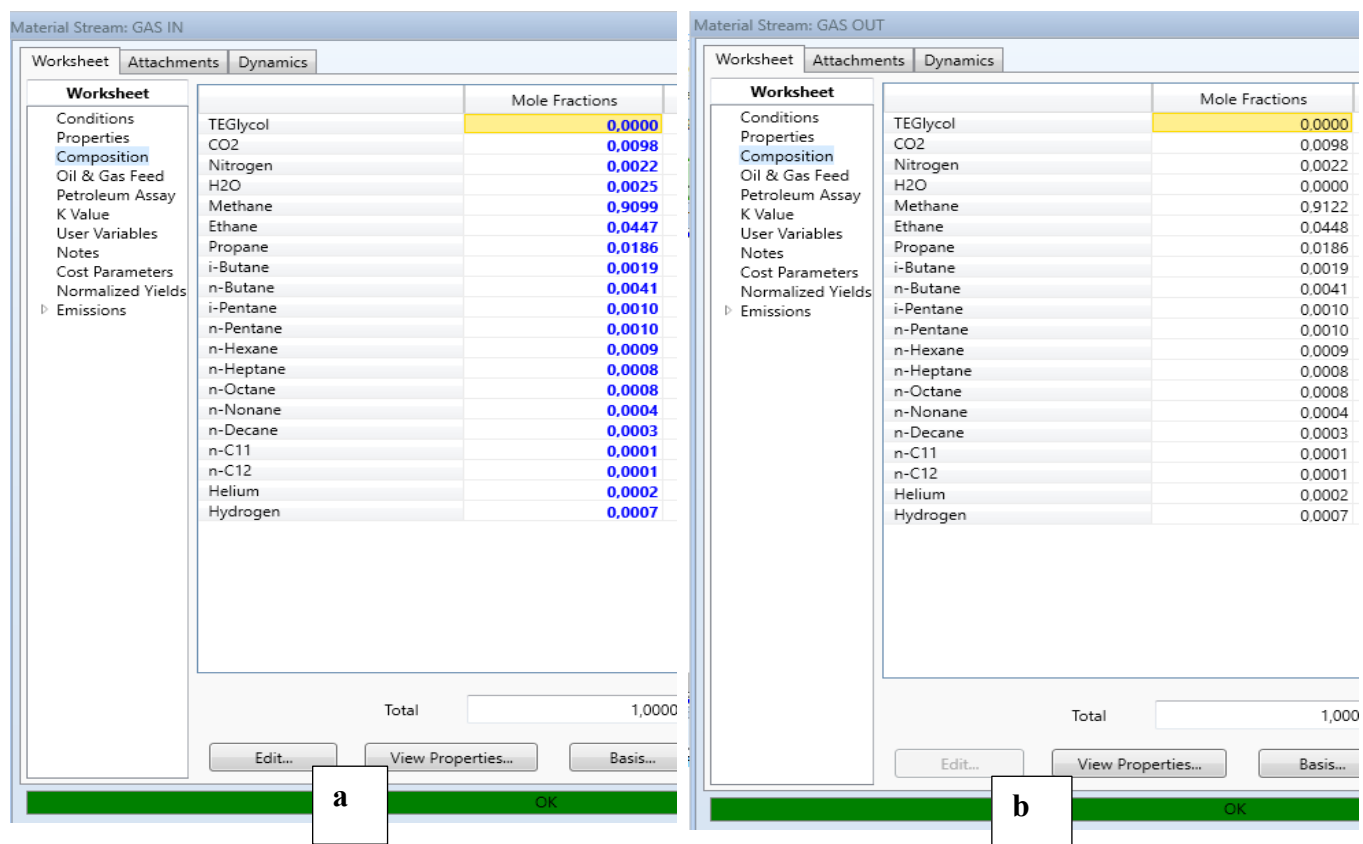## III.4.3 Simulation Result:

Figure III. 2: Comparison of gas composition. **a:** gas in **b:**after TEG absorption

Table III. 5: Water content on different TEG concentration

H2O%	TEG%	H2O in TEG
0.0004	0.8	0.2
0.0003	0.85	0.15
0.0002	0.89	0.11
0.0001	0.95	0.05
0	0.9862	0.0138
0	0.99	0.01
0	0.995	0.005
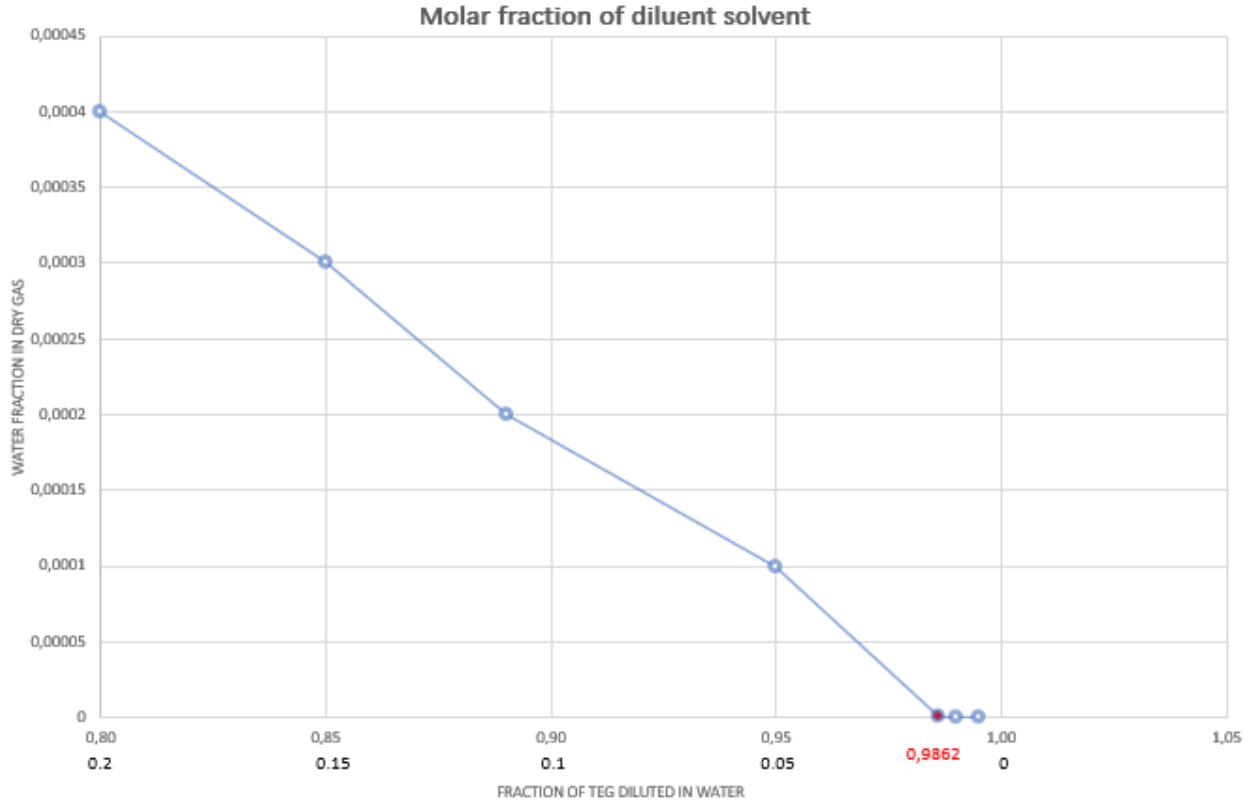
Figure III. 3: curve showing water content in function of TEG concentration

III.4.4 Result interpretation

On the basis of the data studied in the preceding figure, we find the most effective in diluting the solvent and giving satisfactory results which is at a fraction molar of 0.9862 TEG and 0.0138 H_2O. Which gives us a great effect on the drying of the gas and achieve an ideal result by removing the fraction of water molecules in the gas dried, the molar fraction of the water present in the dried gas has been estimated at 0.000.

III.5 . Methanol injection mechanism for hydrate prevention:

III.5.1 Methanol theoretical mechanism:

The addition of methanol will reduce the chemical potential of water through both dilution and methanol dipole moments (and methyl groups) disrupting water hydrogen bonding network. From a classical thermodynamic point of view, this effect is typically described in terms of water

as function of the mole fraction of methanol. Since water and methanol are mutually soluble, a uniform distribution may be assumed.[16]

III.5.2 Hysys simulation for methanol mechanism illustration:

III.5.2.1 Gas field and methanol conditions:

Table III. 6: Gas field composition used in the mixer

Composition	Chemical formula	Mole fraction
Methane	CH4	0.8391
Ethane	C2H6	0.741
Propane	C3H8	0.356
I-Butane	C4H10	0.0056
n-Butane	C5H12	0.0098
I-Pentane	C5H12	0.0043
n-Pentane	C5H12	0.0033
n-Hexane	C6H14	0,0037
n- Heptane	C7H16	0,0045
Hydrogen sulfide	H2S	0.0001
Carbone dioxide	CO2	0.168
Water	H2O	0.0031

The input gas constituents in the mixer are taken from a gas treatment unit of Tiguentourin are given above.

we took the same operating conditions of gas and for methanol pressure as a standard practice in petroleum industry it has to be 100-200 psi above gas pressure also for the temperature it should be around gas temperature.

Table III. 7: Gas and methanol input conditions

	Methanol	Gas input
T (°C)	20	12.5
P (kpa)	7239	6550
Q(kgmole/h)	/	16480

III.5.2.1 Simulation steps:

- Enter gas composition and solvent component (Methanol)
- Choose fluid package (Peng-Robinson)
- Enter gas and methanol conditions
- Enter gas and methanol composition
- Open simulation box and choose mixer
- Choose in the inlet streams in the mixer
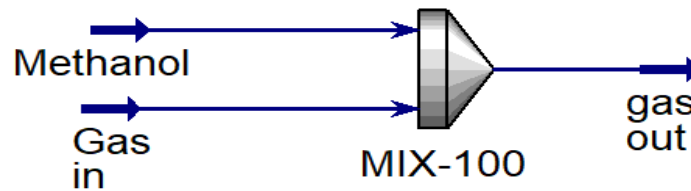
III.5.2.2 Simulation Diagram

Figure III. 4: Methanol simulation model diagram.

III.5.3 Simulation Result:

After many tests on the simulation model, it turns out that the minimum optimized solution to stay out of the hydrate formation zone is as follows:
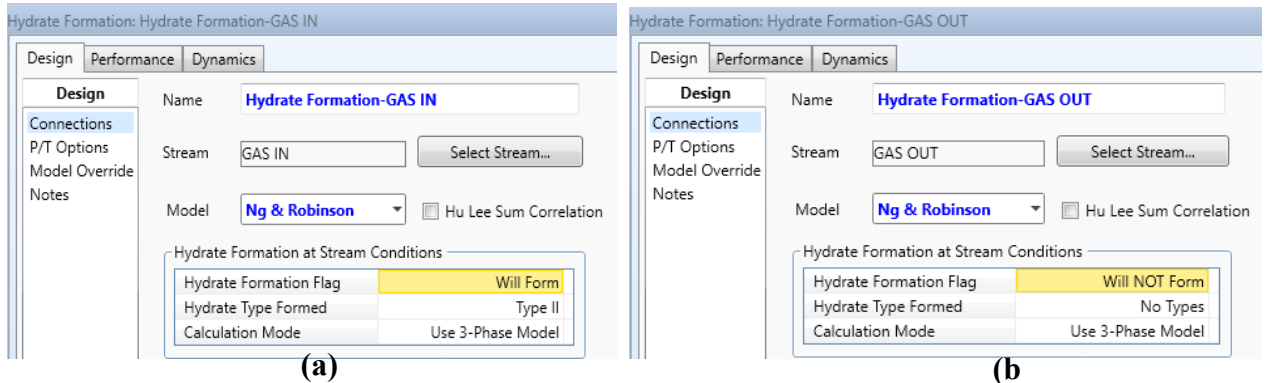

Figure III. 5: Hydrate formation flag. **a:** before methanol **b:** after methanol

And for the molar flow 30 kgmole/h will be sufficient to lower the HFT below the gas temperature.

Composition	Chemical formula	Mole fraction
Water	H2O	0.7
Methanol	CH3OH	0.3

As figure III.5 shows that our solution had changed hydrate formation flag from will form to will not form after injecting 30% methanol into the gas stream with $3m^3/h$ injection rate.
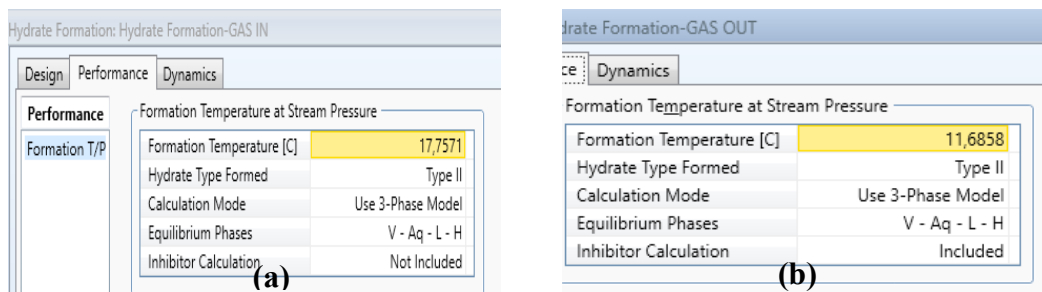
Figure III. 6: Gas hydrate formation temperature. **a**: before methanol **b**: after 30% methanol

In figure III.6 we observe that HFT had changed before and after injecting methanol with 30% concentration at $3m^3/h$ from 17.7571 C° to 11.6858 C°, which is below our gas temperature.

III.5.4 Result interpretation:

On the basis of the data studied in the preceding tables, we find that methanol prevents hydrates formation, Methanol reduces the temperature of hydrate formation primarily through its ability to lower the freezing point of water. The process takes place by (Freezing Point Depression and Thermodynamic Effects). By lowering the freezing point of water and altering the thermodynamic properties of the system, methanol effectively reduces the temperature from 17.7571(C°) to 11.6858(C°) at which hydrate formation can occur. This is crucial in preventing hydrate blockages in pipelines and equipment where low temperatures and high pressures are present

III.6 Comparison between TEG and Methanol in preventing hydrate formation:

III.6.1 Comparison justification:

The most common inhibitors are methanol, ethylene glycol (EG), and TEG. Since glycol's viscosity makes effective separation difficult at cryogenic conditions, methanol is usually preferred under these circumstances. For continuous injection in non-cryogenic conditions, one of the glycols generally offers an economic advantage. Typically, methanol is used in a non-regenerable system while EG and TEG are used in regenerable processes. The regenerable process purifies the glycol in a regenerator and recycles it to the injection site

III.6.2 TEG and Methanol mechanism comparison:

The water content in natural gas can cause problems downstream, including freezing in piping or forming hydrates.

On this, as we discussed before TEG dehydration units used to depress the hydrate formation point by removing water from the gas.

As for Methanol inhibits hydrate formation by disrupting the hydrogen bonding network that forms the solid hydrate lattice. When methanol is present in the gas stream or in the liquid phase, it interferes with the water molecules' ability to arrange themselves into the crystalline structure necessary for hydrate formation.

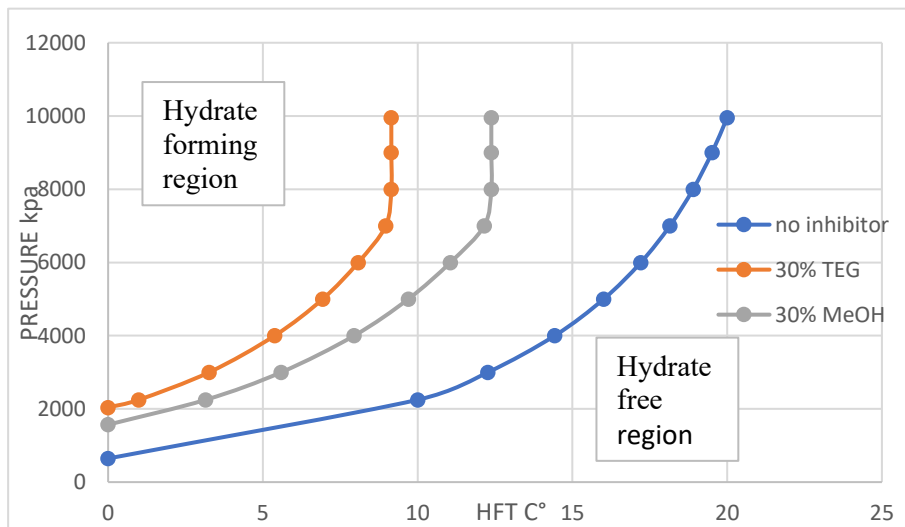### III.6.3 TEG and Methanol effectiveness comparison:

Figure III. 7: Curve showing hydrate forming and free regions. Cases: no inhibitor, 30% TEG and 30% MeOH

Figure III.7 showing hydrate forming and free regions, for the baseline scenario with no inhibitor we observe that as the pressure increases the HFT also increases. This is expected because higher pressure favors the formation of hydrates.

For the 30% TEG curve compared to the no inhibitor curve, the TEG is shifted to the right, indicating that TEG effectively lowers the HFT at a given pressure.

30% MeOH curve is similar to TEG, methanol also shifts the HFT to higher values compared to no inhibitor case. However, this indicates that TEG has more effectiveness than MeOH.

At lower pressures methanol seems to be more effective than TEG. However, at higher pressures on the contrary of methanol TEG continues to show a steady reduction in HFT.

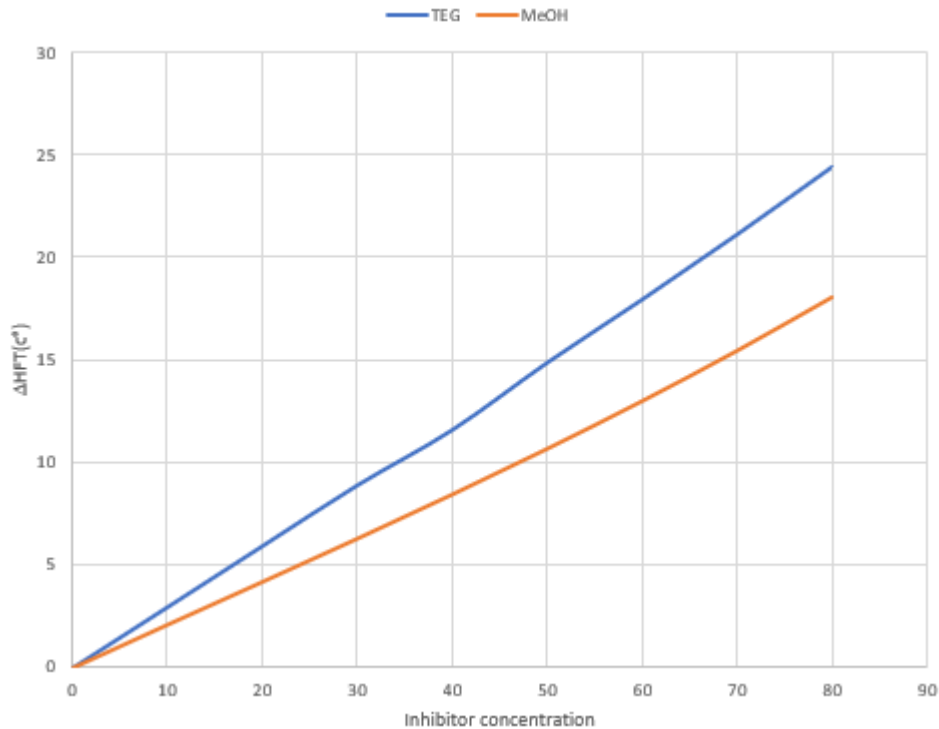### III.6.4 TEG and Methanol concentration comparison:

Figure III. 8: TEG and MeOH concentration effect on delta HFT

Figure III.8 shows the effect of inhibitors concentration on ΔHFT, higher ΔHFT indicates a more effective inhibitor.

As the concentration of TEG increases the ΔHFT also increases, indicating that higher concentrations of TEG are more effective at lowering the HFT.

Similarly, as the concentration of Methanol increases; ΔHFT increases, indicating improved inhibition of hydrate formation.

At low concentration range both TEG and methanol show a linear increase in ΔHFT with increasing concentration, but TEG exhibits a higher ΔHFT than methanol at the same concentration, indicating it is more effective at lower concentration.

At highest concentration (80), TEG achieves a ΔHFT of approximately 28°C, while MeOH achieves around 18°C. This indicates that TEG is significantly more effective at inhibiting hydrate formation than MeOH.

In conclusion, the graph clearly indicated that both TEG and MeOH are effective hydrate inhibitors, but TEG shows superior performance compared to MeOH across all concentrations.

General Conclusion

General conclusion

In this thesis, we evaluated various methods for preventing hydrate formation in natural gas pipelines and processing facilities using the process simulation software HYSYS. Our analysis focused on the use of heat exchangers and chemical inhibitors, specifically Triethylene Glycol (TEG) and Methanol. The key findings and conclusions drawn from this research are as follows:

1. Effectiveness of Heat Exchangers:

Our study case interpretations demonstrated that heat exchangers are highly effective in preventing hydrate formation, especially when the hot stream is significantly hotter. Maintaining the gas temperature well above the hydrate formation threshold ensures that hydrates do not form, thus preventing blockages and ensuring smooth gas flow.

The efficiency of heat exchangers increases with the temperature differential between the hot stream and the gas stream. This finding underscores the importance of optimizing heat exchanger design and operation to maximize the temperature gain in the gas stream.

2. Performance of Triethylene Glycol (TEG):

TEG was found to be a superior hydrate inhibitor compared to Methanol. TEG effectively absorbs water from the gas stream, which is crucial in lowering the hydrate formation temperature and preventing hydrate crystals from forming.

In terms of efficiency, TEG exhibited better performance than Methanol, requiring lower dosages to achieve the same level of hydrate suppression. This efficiency translates into significant operational advantages, including reduced chemical consumption and lower overall costs.

4. Environmental Considerations:

The environmental impact of using TEG versus Methanol was considered. TEG, being less volatile and less toxic, presents a lower environmental risk compared to Methanol. This aspect adds to the desirability of TEG as a hydrate inhibitor in natural gas processing.

- Recommendations

Based on the conclusions drawn from this research, the following recommendations are made:

- Optimize Heat Exchanger Design: Ensure that the heat exchangers used in gas processing are designed to maximize the temperature differential, thereby enhancing their efficiency in preventing hydrate formation.
- Prefer TEG over Methanol: Given its superior efficiency, cost-effectiveness, and lower environmental impact, TEG should be preferred over Methanol for hydrate inhibition in natural gas processing facilities.
- Continuous Monitoring and Adjustment: Regularly monitor the performance of hydrate prevention methods and make necessary adjustments based on operational conditions to maintain optimal performance and cost efficiency.

References:

[1]. BP Statistical Review of World Energy, Publication d'IFP, Edition Technip, Juin 2010.

[2] Gaz naturel, production, traitement et transport, revue SONATRACH, 2002.

[3] Yo Antoine Touali, Carbon Dioxide Corrosion studies in Oil and Gas Production, November 2013.

[4] Alsafran, M. and Brill J. Applied Multiphase Flow in Pipes and Flow Assurance. Society of Petroleum Engineers, 2017.

[4] GROUP SCOTEC INDUSTRIE SERPRO.S. N RECUPERATION ASSISTEE PAR 'GAS-LIFT';2011.

[5] John carol, Natural gas hydrates, A guide for engineer's 3rd edition, Gulf Professional Publishing, 2004

[6] S. Goshovskyi, O. Zurian, GAS HYDRATES – HISTORY OF DISCOVERY, Мінеральні ресурси України , 2019

[7] E.Dendy Sloan, Fundamental Principles and applications of Natural Gas Hydrate, centre for hydrat research, Colorado school of mines, Nature publishing group, vol426, Novembre 2003.

[8] Turner D. Clathrate hydrate formation in water-in-oil dispersions. Ph.D. Thesis. 2005 Colorado School of Mines. Golden, Colorado, USA.

[9] Paschal Ogadi Mokwenye, Evaluation of Gas Hydrate Gas Pipeline Transportation, University of North Dakota UND Scholarly Commons, 2020.

[10] Adam Daniel Effendi" Polysaccharides from Tamarindus indica L. as natural kinetic hydrates inhibitor at high subcooling environment",11 March 2022

[12] Maurice I, Hydrate Prediction and Prevention in Surface Production Operations (Third Edition), Volume 2, 2014.

[13] R. N. Abu, L. G. Amah, A. Dulu and Olalekan M. Adeloye , Chemical control of natural gas hydrate, European journal of engineering research and science, 2016.

[14] Zerrouk Rached, Manane Tahar "Optimization and Simulation of Glycol Losses at the Dehydration Section in the Unit (RGTE) at In Amenas by HYSYS" ,Master's thesis, Kasdi Merbah University, Ouargla, 2015.

[15] Octave Levenspiel '' Engineering Flow and Heat Exchange'' Third Edition 2014.

[16] Nikhil Deepak Kundnaney, Deepak Kumar Kushwaha« A Critical Review on Heat Exchangers used in Oil Refinery » Afro - Asian International Conference on Science, Engineering & Technology; AAICSET-2015.

[17] aspentech .(2023, May 22), Extrait de https://www.aspentech.com/en

APENDIX

Component	Type	Group
TEGlycol	Pure Component	
CO2	Pure Component	
Nitrogen	Pure Component	
H2O	Pure Component	
Methane	Pure Component	
Ethane	Pure Component	
Propane	Pure Component	
i-Butane	Pure Component	
n-Butane	Pure Component	
i-Pentane	Pure Component	
n-Pentane	Pure Component	
n-Hexane	Pure Component	

ANNEXE 1: Gas component selection

Property Package Selection

- Chien Null
- Clean Fuels Pkg
- CPA
- Esso Tabular
- Extended NRTL
- GCEOS
- General NRTL
- Glycol Package
- Grayson Streed
- IAPWS-IF97
- Kabadi-Danner
- Lee-Kesler-Plocker
- MBWR
- NBS Steam
- NRTL
- Peng-Robinson
- PR-Twu

Options

Enthalpy	**Property Package EOS**
Density	**Costald**
Modify Tc, Pc for H2, He	**Modify Tc, Pc for H2, He**
Viscosity Method	**HYSYS Viscosity**
Peng-Robinson Options	**HYSYS**
EOS Solution Methods	**Cubic EOS Analytical Method**
Phase Identification	**Default**
Surface Tension Method	**HYSYS Method**
Thermal Conductivity	**API 12A3.2-1 Method**

ANNEXE 2: Fluid package selection

Material Stream: GAS IN

Stream Name	GAS IN	Vapour Phase	Aqueous Phase
Vapour / Phase Fraction	1,0000	0,9998	0,0002
Temperature [C]	53,20	53,20	53,20
Pressure [kPa]	8361	8361	8361
Molar Flow [kgmole/h]	1,423e+004	1,423e+004	3,002
Mass Flow [kg/h]	2,585e+005	2,585e+005	54,09
Std Ideal Liq Vol Flow [m3/h]	799,6	799,5	5,420e-002
Molar Enthalpy [kJ/kgmole]	-8,056e+004	-8,051e+004	-2,839e+005
Molar Entropy [kJ/kgmole-C]	150,2	150,2	60,62
Heat Flow [kJ/h]	-1,146e+009	-1,145e+009	-8,522e+005
Liq Vol Flow @Std Cond [m3/h]	3,354e+005	3,353e+005	5,329e-002
Fluid Package	Basis-1		
Utility Type			

Material Stream: TEG

Stream Name	TEG	Liquid Phase
Vapour / Phase Fraction	0,0000	1,0000
Temperature [C]	59,07	59,07
Pressure [kPa]	8360	8360
Molar Flow [kgmole/h]	113,2	113,2
Mass Flow [kg/h]	1,679e+004	1,679e+004
Std Ideal Liq Vol Flow [m3/h]	14,88	14,88
Molar Enthalpy [kJ/kgmole]	-7,791e+005	-7,791e+005
Molar Entropy [kJ/kgmole-C]	176,7	176,7
Heat Flow [kJ/h]	-8,819e+007	-8,819e+007
Liq Vol Flow @Std Cond [m3/h]	14,90	14,90
Fluid Package	Basis-1	
Utility Type		

ANNEXE 3: Inlet gas and TEG properties

Material Stream: TEG

	Mole Fractions	Liquid Phase	
TEGlycol	0,9862	0,9862	
CO2	0,0000	0,0000	
Nitrogen	0,0000	0,0000	
H2O	0,0138	0,0138	
Methane	0,0000	0,0000	
Ethane	0,0000	0,0000	
Propane	0,0000	0,0000	
i-Butane	0,0000	0,0000	
n-Butane	0,0000	0,0000	
i-Pentane	0,0000	0,0000	
n-Pentane	0,0000	0,0000	
n-Hexane	0,0000	0,0000	
n-Heptane	0,0000	0,0000	
n-Octane	0,0000	0,0000	
n-Nonane	0,0000	0,0000	
n-Decane	0,0000	0,0000	
n-C11	0,0000	0,0000	
n-C12	0,0000	0,0000	
Helium	0,0000	0,0000	
Hydrogen	0,0000	0,0000	
Total		1,00000	

ANNEXE 4: TEG composition

ANNEXE 5: output gas composition
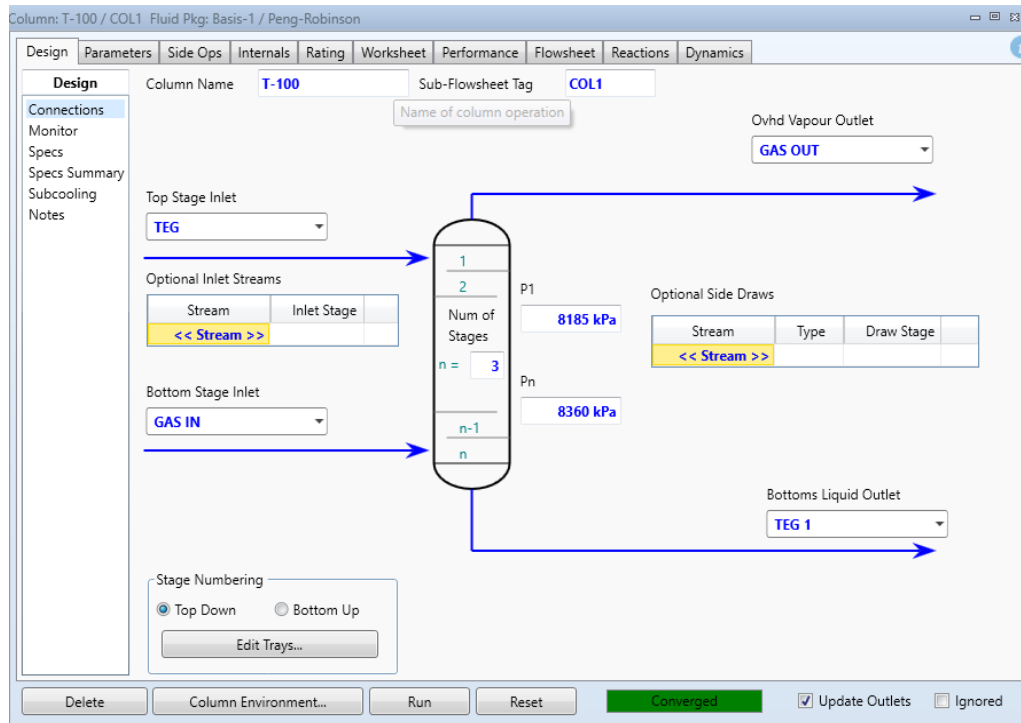
ANNEXE 6: Absorber caracteristics

Material Stream: Gas in					Stream: methanole			

Worksheet | Attachments | Dynamics

Worksheet	Stream Name	**Gas in**	Vapour Phase	Liquid Phase
Conditions	Vapour / Phase Fraction	**1,0000**	0,9951	0,0027
Properties	Temperature [C]	**17,68**	17,68	17,68
Composition	Pressure [kPa]	**8360**	8360	8360
Oil & Gas Feed	Molar Flow [kgmole/h]	**1,423e+004**	1,416e+004	39,02
Petroleum Assay	Mass Flow [kg/h]	2,585e+005	2,552e+005	2796
K Value	Std Ideal Liq Vol Flow [m3/h]	799,6	794,5	4,527
User Variables	Molar Enthalpy [kJ/kgmole]	-8,249e+004	-8,179e+004	-1,774e+005
Notes	Molar Entropy [kJ/kgmole-C]	144,0	144,2	137,3
Cost Parameters	Heat Flow [kJ/h]	-1,174e+009	-1,158e+009	-6,923e+006
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	3,354e+005	3,337e+005	4,423
Emissions	Fluid Package	*Basis-1*		
	Utility Type			

Worksheet | Attachments | Dynamics

Worksheet	Stream Name	**methanole**	Aqueous Phase
Conditions	Vapour / Phase Fraction	**0,0000**	1,0000
Properties	Temperature [C]	**20,00**	20,00
Composition	Pressure [kPa]	**8360**	8360
Oil & Gas Feed	Molar Flow [kgmole/h]	**113,2**	113,2
Petroleum Assay	Mass Flow [kg/h]	2261	2261
K Value	Std Ideal Liq Vol Flow [m3/h]	2,394	2,394
User Variables	Molar Enthalpy [kJ/kgmole]	-2,813e+005	-2,813e+005
Notes	Molar Entropy [kJ/kgmole-C]	48,13	48,13
Cost Parameters	Heat Flow [kJ/h]	-3,184e+007	-3,184e+007
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	2,356	2,356
Emissions	Fluid Package	*Basis-1*	
	Utility Type		

OK | OK

ANNEXE 7: inlet gas and methanol properties.