

PREVENTION OF HYDRATES IN PIPELINES USING HYBRID THERMODYNAMIC INHIBITORS

A

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ABSTRACT

Chemical method is the most efficient and flexible method of hydrate control in offshore operations. In recent times, polymers and surfactants have been used to influence the kinetics of hydrate growth and coagulation. However, the traditional polar solvents are still relevant because of their ability to melt hydrates. Due to the large volume of polar thermodynamic inhibitors usually required in the field, this work examines the effect of hybrid hydrate inhibitors (HHI) comprising both polar and ionic thermodynamic hydrate inhibitors.

In this study, a Microsoft Excel-based program was developed for evaluating the effectiveness of various polar thermodynamic hydrate inhibitors and hybrid thermodynamic hydrate inhibitors in preventing hydrate deposition. Katz plot was used in obtaining the hydrate formation temperature, when the fluid composition and operating pressure were supplied. Østergaard, Hammerschmidt and Nielsen Bucklin equation gave the temperature depression and quantity of inhibitor required to prevent hydrate depression in the pipes. Two pipes, Branch 4 & Branch 9, in a fictitious offshore field were used as case study.

It was discovered that the quantity of Methanol (MeOH) required in Branch 4 and Branch 9 decreased by 44.5% when Methanol-hybrid Thermodynamic Hydrate Inhibitor (consisting of methanol and salt) was used. The required Mono Ethylene Glycol (MEG) and Di Ethylene Glycol (DEG) also decreased by 33.6% and 35.9% respectively when combined with salt. It was concluded that the most effective hybrid inhibitor is Methanol-Sodium Chloride hybrid because it saved 44.5% of Methanol when used in Branch 4 and 45% Methanol when used in Branch 9.

This work enables a flow assurance engineer to calculate the quantity of inhibitor required on the field to prevent hydrate formation on a salt free basis and when the produced water contains salt.

DEDICATION

To God Almighty for His goodness towards me.

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CHAPTER ONE

INTRODUCTION

1.1 GENERAL

As the potential for onshore oil and gas discoveries diminishes, oil operators and governments are moving offshore. Many countries with shorelines have already granted exploratory permits, and a large number of these have drilling and production concessions. The first offshore oil in the world was produced in the late 1940's. By 1973, production data show that 18.9% of the world's oil supply was produced from offshore. It has been said that while onshore reserves will ultimately double, offshore reserves will increase by a factor of four (ETA Offshore Seminars, 1976).

The Nigerian economy is highly dependent on petroleum. Currently, Nigeria has produced oil for over 50 years but the impact of our rapidly expanding demand for crude oil will require exploration of more petroleum prospects. Therefore, there has been an increasing interest in offshore production in Nigeria in the past few years. Some offshore fields in Nigeria include: Bonga, Akpo, Erha Field, Agbami, Abana, Amenam-kpono oil and gas field, Ekpe phase II, Exxon East area NGL II, Usan field and Yoho oil field.

Due to extreme water depths and harsh marine environment (extremely high pressures in the cold and dark recesses of the ocean bottom), production in deep water presents challenges far beyond those experienced in shallow waters or onshore. Production risers, the pipes which connect the producing wells to the Floating Production Storage and Off-loading vessel (FPSO), are exposed over considerable length to the straining pressures and temperature of multiple ocean currents which cause a lot of operational problems like hydrate formation, scale formation, asphaltenes, corrosion, slugging etc. To optimize production, flow assurance studies must be carried out to minimize these challenges and to determine the best operating practices required.

1.2 FLOW ASSURANCE

Flow assurance is a term originally coined by Petrobras in the early 1990's. The term in Portuguese was "Garantia de Fluxo", which translates literally to "Guarantee the Flow". Flow assurance is a study of the successful flow of hydrocarbon from reservoir to point of sale. It considers the interaction of fluid in the reservoir, well bore, surface facilities and pipelines, proffering techniques to ensure uninterrupted, optimum productivity in oil and gas streams. Flow assurance ensures that any development plan from exploration through abandonment is technically viable and designed for optimal operations throughout the field's life.

Flow assurance covers all aspects of the production system and incorporates topics such as: production surveillance, operational well remediation, pipeline remediation, PVT and Rheology analysis, Thermo-hydraulic analysis, Mechanical integrity, techniques to prevent and mitigate factors that can negatively affect optimized fluid flow, transient multiphase simulation and effectively handling many solid deposits, such as, gas hydrates, asphaltene, wax, scale and naphthalenes. Incorporation of flow assurance issues during completion design can have great impact in reducing incidence of hydrates and paraffin wax deposits.

Understanding reservoir fluid properties and their potential effects on the production system is a key prerequisite to any flow assurance study. Some challenges in Flow Assurance include: Organic Scales (Paraffin, Asphaltenes), Hydrates, Emulsions, Foaming, Mineral Scales, Sand deposition, Erosion, slugging, Corrosion and Multiphase Flow Instabilities.

Hydrocarbon solids have the potential to deposit anywhere from the near wellbore and perforations to the wellbore, surface facilities and pipelines (Jamaluddin *et al*, 2001). When the solid precipitation occurs in the wellbore, well tubing and transfer pipeline, it results in plugging the fluid channel, increasing the fluid pressure gradient and decreasing well productivity. Paraffin wax deposition and hydrate formation are primary examples of such problems that cost the industry millions of dollars in lost production and cleaning operations. Deposition of organic scales and hydrates is caused by the complex depositional relationship between the crude oil composition, Gas Oil Ratio, Cooling, Thermodynamic Equilibrium, pressure and temperature contrast. Therefore, monitoring production variables, such as temperature pressure and flow rates, is vital in flowing systems.

Commercial software used in handling of flow assurance issues include: PROCAP-2000, Olga, Hysys, etc.

1.3 GAS HYDRATE

The discovery of hydrates is credited to the famous English chemist, Sir Humphrey Davy in the 19th century when he reported chlorine hydrate. However, it remained a scientific curiosity until 1934 Hammerschmidt reported that they could form in natural gas pipelines and reduce gas flow.

Gas hydrates are non stoichiometric crystalline compounds that belong to a general class of inclusion compounds commonly known as clathrates. They occur when water molecules attach themselves together through hydrogen bonding and form cavities which can be occupied by a small molecule ($<7 \text{ \AA}$) of gas or volatile liquid at low temperature and high pressure.

At standard pressure and temperature, a methane hydrate molecule contains approximately 160 volumes of methane for each volume of water. The amount of organic carbon contained in

natural gas hydrate reserves around the globe is estimated to be twice the amount contained in all fossil fuels (coal, oil and conventional natural gas reserves) on earth. Naturally occurring hydrates are being looked upon as a future energy source and a potential global climate hazard.

Naturally occurring hydrates exist in vast quantities within and below the permafrost zone and in subsea sediments. If global warming occurs, the temperature will rise and decompose some of these naturally occurring hydrates. This will cause the release of methane and carbon dioxide. Methane is one of the most harmful green house gases and its effect could be potentially threatening. Methane is 21 times more efficient and effective a greenhouse gas than carbon dioxide. It may also lead to acceleration of global rise of the earth's temperature by 10 to 100 times, which would lead to future decomposition of hydrates and subsequent release of methane and carbon dioxide.

Use of natural gas hydrates for storing and transporting natural gas poses a serious alternative to the LNG technology (Gbaruko *et al.*, 2005). In this method, natural gas hydrates are refrigerated to stable conditions, enabling transport of natural gas in an insulated bulk carrier to distant gas markets. This method has been found to be simple and inexpensive.

Gas hydrates have practical implications for flow assurance and the safety thereof. Natural gas hydrates can pose a threat to any oil or gas production system that encounters low temperatures and high pressures. Hydrates can plug off a flow line during normal production operations. More vulnerable are the transient operations such as shut-in and start-up, where temperature tend to be lower, pressures can be higher, and water has time to accumulate in low spots. Carbon dioxide like methane is a component of natural gas and may form hydrates in all reservoirs during enhanced oil recovery thereby causing complications (Gbaruko, 2004). Hydrates formation in wells is an abnormal occurrence arising during drilling of the well (especially when a water based mud is used) or shut in/start up of the well. The presence of hydrates can have serious implication for drilling operations. At the conditions which prevail during drilling, hydrates can form in drilling risers, chokes, kill and blow out preventers (Edmonds *et al.*, 2001). In addition, the existence of naturally occurring hydrates close to the surface can also present serious hazard during drilling by releasing gas into the wellbore leading to well control difficulties and potential blow outs.

Hydrates problems are very severe in offshore environment where it is difficult to pressurize the system at immediate points due to distance and accessibility. The presence of hydrates should therefore be assessed and understood up time to prevent and neutralize these threats to the entire system after construction. Understanding the nature of the hydrate formation is critical to making the choices of design modification, initial prevention or neutralization operations.

1.3.1 Hydrate Formation

Water forms hydrates due to its hydrogen bond. The hydrogen bond causes the water molecules (host molecules) to align in regular orientations. The presence of certain compounds (guest/formers) causes the aligned molecules to stabilize the water lattice and form a hydrate. 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.

Hydrates are best described as a solid solution because there is no bonding between the guest (hydrocarbon) and host (water) molecules and the hydrocarbon molecules are free to rotate inside the cages built up from the host molecules. When all of the water cavities in hydrates are occupied, all common hydrate structures contain approximately 15 mol% hydrocarbons as guests, and 85 mol% water as hosts (Sloan *et al.*, 2009). Molecules with diameters less than about 3.8 Å (e.g. hydrogen and helium) or diameter larger than 7 Å (eg pentane, hexane and larger paraffin hydrocarbons) do not form hydrate.

The formation of a hydrate requires three basic conditions: the presence of a hydrate former, effect of temperature and pressure and sufficient amount of water.

1.3.1.1 The presence of a hydrate former

Hydrate formers are the molecules that combine with water at relatively high pressure and low temperature to form hydrates. They include methane, ethane, propane, iso-butane, hydrogen sulphide and carbon dioxide. The Physical and chemical properties of a former include:

a. Size

A guest molecule must be sufficiently small. Its size must be between 3.8 Å and 7 Å. If it is larger than 7 Å, it may be too large to enter the cage formed by the water molecules.

b. Solubility

A molecule may be sufficiently small but it may not form a hydrate if the molecule is soluble in water. However, carbon dioxide, hydrogen sulphide and sulphur oxide, which are quite soluble in water are hydrate formers. As a rule of thumb, gases more soluble than SO₂ (e.g. ammonia and hydrogen chloride) do not form hydrates.

c. Hydrogen bond

If the molecule interferes with the hydrogen bonding, a hydrate will not form. For instance, methanol does not form a hydrate because it is hydrogen-bonded and hence interferes with the hydrogen bonding among the water molecules.

1.3.1.2 Effect of temperature and pressure.

Hydrate formation is favoured by low temperature and relatively high pressure. The exact temperature and pressure depends on the composition of the former. However, hydrates form at temperatures greater than 0°C (32°F). For instance, methane hydrate formation in natural gas systems requires the presence of free water, temperatures lower than 40 °F and pressure greater than 166 psig or temperature greater than 70 °F and pressure higher than 2900 psig . (Gbaruko, 2005)

1.3.1.3 Sufficient amount of water.

Water is essential for hydrate formation. Water has several unusual properties which can be attributed to the shape of the water molecule and the interactions that result from its shape. The water molecule consists of a single atom of oxygen bonded to two hydrogen atoms. In the water molecule, the bond between the oxygen and hydrogen atoms is a covalent bond (i.e. a shared pair of electrons). There are two pairs of unbounded electrons on the “back” of the oxygen molecule.

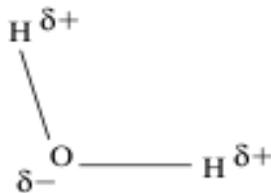


Figure 1.1 Shape of the water molecule

These electrons induce negative charges (δ^-) on the oxygen molecule and a small positive charge (δ^+) on the hydrogen atoms (Figure 1.1). Therefore, the water molecules will tend to align with a hydrogen molecule lining up with oxygen forming a “hydrogen bond.” The hydrogen bond is essentially an electrostatic attraction between the molecules. Each water molecule has two pair of unbound electrons and thus has two hydrogen bonds—two water molecules “stick” to each water molecule. When the water molecules line up, they form a hexagonal pattern (Figure 1.2). The hexagonal pattern of the water molecules is not planar and has an angle of 105°.

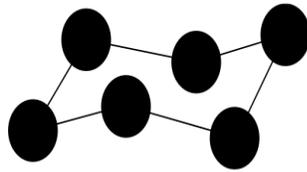


Figure 1.2: Three-dimensional hexagonal arrangement of water molecules in ice crystals

Heavy water can also form hydrates because heavy water still exhibits hydrogen bonding. However, with heavy water, a slightly higher pressure will be required to form hydrates than in regular water.

Other factors that can enhance hydrate formation include:

1.3.1.4 Turbulence:

Hydrate formation is favoured in regions where the fluid velocity is high. Regions with agitation, mixing in a pipeline, process vessel enhance hydrate.

1.3.1.5 Nucleation Sites:

A nucleation site is a point where a phase transition is favoured. Good nucleation sites for hydrate formation include an imperfection in the pipeline, a weld spot, or a pipeline fitting (elbow, tee, valve, etc.), Silt, scale, dirt and sand

1.3.2 Hydrate Types

Hydrates are classified based on their crystal structure. The two types of hydrates commonly encountered in the petroleum industry include: Type I (or structure I) and Type II (or structure II). A third type of hydrate that also may be encountered is Type H (also known as Structure H), but it is much less common. Hydrates are non-stoichiometric, that is, a stable hydrate can form without a guest molecule occupying all of the cages therefore, the compositions of the actual hydrates differ from the theoretical values.

1.3.2.1 Type I hydrates

The simplest of the hydrate structures is the Type I. It is made from two types of cages a Dodecahedron (small cage) and a Tetrakaidecahedron (large cage). A Dodecahedron is a twelve-sided polyhedron where each face is a regular pentagon, and a Tetrakaidecahedron is a fourteen-sided polyhedron with twelve pentagonal faces and two hexagonal faces.

Type I hydrates consist of 46 water molecules. If a guest molecule occupies each of the cages, the theoretical formula for the hydrate is $X \cdot 5 \frac{3}{4} \text{H}_2\text{O}$, where X is the hydrate former.

Some of the common Type I hydrate formers include methane, ethane, carbon dioxide, and hydrogen sulphide. In the hydrates of methane, carbon di oxide and hydrogen sulphide, the guest molecules can occupy both the small and the large cages. On the other hand, the ethane molecule occupies only the large cages.

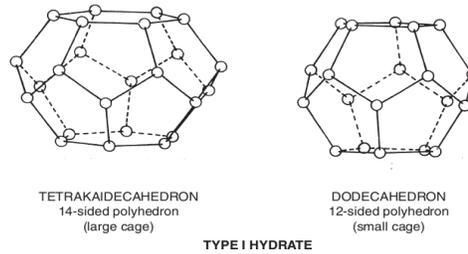


Figure 1.3: Type 1 hydrate

1.3.2.2 Type II hydrates

The structure of the Type II hydrates is more complicated than that of the Type I hydrate though they are also constructed from two types of cages. The unit structures of a Type II hydrate are Dodecahedron and Hexakaidecahedron. The dodecahedral cages are smaller than the hexakaidecahedron cages. Dodecahedron is a twelve-sided polyhedron where each face is a regular pentagon while Hexakaidecahedron, a sixteen-sided polyhedron with twelve pentagonal faces and four hexagonal faces. The Type II hydrate consists of 136 molecules of water.

If a guest molecule occupies all of the cages, the theoretical composition is $X \cdot 5 \frac{2}{3} \text{H}_2\text{O}$, where X is the hydrate former. However, if the guest occupies only the large cages, the theoretical composition is $X \cdot 17 \text{H}_2\text{O}$. Common Type II formers in natural gas are nitrogen, propane, and isobutane. Nitrogen occupies both the large and small cages of the Type II hydrate. On the other hand, propane and isobutane only occupy the large cages.

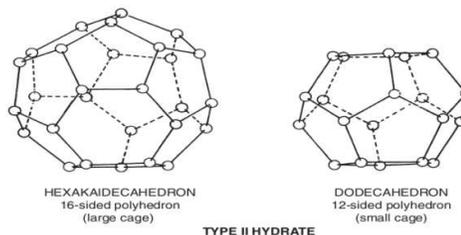


Figure 1.4: Type II hydrate

1.3.2.3 Type H Hydrates

Type H hydrates are much less common than Type I or II. To form this type of hydrate requires a small molecule, such as methane, and a Type H former. The Type H hydrates are constructed from three types of cages: (1) Dodecahedron, a twelve-sided polyhedron where each face is a regular pentagon, (2) An irregular dodecahedron with three square faces, six pentagonal faces, and three hexagonal faces, and (3) An irregular icosahedron, a twenty-sided polyhedron, with twelve pentagonal faces and eight hexagonal faces.

It is difficult to give the theoretical formula for a type H hydrate since two formers are required to form a type H hydrate. These formers are: a small molecule such as methane and a larger Type H forming molecule such as: 2-methylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, 2,2-dimethyl-pentane, 3,3-dimethylpentane, methylcyclopentane, ethylcyclopentane, methyl-cyclohexane, cycloheptane, and cyclooctane. The small guest molecules, such as methane, occupy the small and medium cages of the structure while a larger molecule occupies the large cage.

From a practical viewpoint, the structure type does not affect the appearance, properties, or problems caused by the hydrate. It does, however, have a significant effect on the pressure and temperature at which hydrates form. Structure II hydrates are more stable than Structure I. This is why gases containing propane (C_3H_8) and iso-butane ($i-C_4H_{10}$) will form hydrates at higher temperatures than similar gas mixtures which do not contain these components.

Usually in industrial practice we must deal with mixtures and not pure formers. If the gas mixture contains hydrate formers of only one type, the hydrate formed will be of that type. For example, a mixture of methane, hydrogen sulphide, and carbon dioxide, will form a Type I hydrate. However, if the mixture contains a Type I former and a Type II former the type of hydrate formed must be thermodynamically stable.

In most industrial cases, the mixture can contain non-formers which tend to be heavy hydrocarbons, and this will tend to liquefy at conditions where a hydrate might be encountered. For instance, the hydrate formation conditions in a mixture of methane and pentane (a non-former) are governed by the potential of the mixture to liquefy.

1.3.3 Hydrates and flow assurance.

Hydrates can pose a threat to any oil or gas production system that encounters low temperatures and relatively high pressures. Hydrates can plug off a flow line during normal production operations. More vulnerable are the transient operations such as shut-in and start-up,

where temperature tend to be lower, pressures can be higher, and water has time to accumulate in low spots. Therefore, the presence of hydrates should be assessed and understood upfront to prevent and neutralize these threats to the entire system after construction. Hydrate stability can be affected by the compositions of the fluid (gas, oil and water phases), operational conditions (flow rate, well head temperature, flow pattern), subsea layout (line length, flow lines layout, environmental conditions) and transient operations such as shut-in and start-up. In gas condensate systems, hydrates tend to form in the abundant gas- water interfaces, whereas, in low GOR gas-oil-water systems, they tend to form at the oil interfaces.

It is noted that crossing the thermodynamic conditions for the formation of hydrocarbon solids does not necessarily imply that a flow assurance problem will be encountered. In other words, if hydrocarbon solids form but do not deposit, they are not a problem. (Jamaluddin *et al.*, 2001). Hydrate does not necessarily agglomerate in the same location as it is formed. In a pipeline, the hydrate can flow with the fluid phase, especially the liquid. It would tend to accumulate in the same location as the liquid does. Usually, the accumulations of the hydrates cause the problems in pipelines, blocking the line and damaging equipment.

Methane hydrate is a serious problem for producers moving gas from offshore wells to onshore processing facilities; it is also found in gas storage facilities and transmission pipelines. Water is often associated with natural gas. In the reservoir, water is always present. Thus, produced natural gas is always saturated with water. In addition, formation water is occasionally produced along with the gas. As the temperature and pressure change during the production of the gas, water can condense out. This association of water and natural gas means that hydrates will be encountered in all aspects of the production and processing of natural gas.

Hydrocarbon solid deposition will have considerable impact on all aspects of a field. Some of the problems caused by hydrate deposition include: reduction of the internal diameter of tubular restricting and ultimately blocking flow, increased surface roughness on the pipe wall causing increased pumping pressure and reduced throughput, accumulations that fill process vessels and storage tanks, operational and safety problems due to interference with valve operation and instrumentation, reduced productivity of a well due to accumulation of hydrate deposits on the sand face and perforations, plugged surface flow lines, plugged tubing, production downtime, wear and tear of production tubing (during mechanical handling). All of these problems may result in production shut downs and hazardous conditions and will require extensive work-overs, production losses, and possible irreparable damage requiring equipment abandonment and replacement.

Therefore, it expedient to prevent hydrates from forming.

1.4 METHODS OF MANAGING GAS HYDRATE FORMATION IN PIPES.

A common practise among production experts is to approach the hydrate control in two ways: the preventive way, which means avoiding the deposition of hydrates thus preventing downtime and the corrective method which involves removing hydrate deposits periodically. Corrective method increases down time and production cost. Deep water production requires acknowledgement of hydrate deposition and its solution may require not just a special technique but the combination of techniques leads to better results. (Gomes *et al.*, 1996). Hydrate risks can be reduced by removal of water from the system, keeping the operating temperature above the hydrate formation threshold (using insulation, hot oil, hot water circulation and electrical heating) and setting the operating pressure below the hydrate formation threshold. Methods of managing hydrates include:

1.4.1 Pressure control:

Design and operate system with pressures low enough to maintain the fluids outside the hydrate envelope. This approach is often impractical for normal operation since the pressure required for transportation of production fluid will usually exceed the hydrate formation pressure at the ambient temperature. However, for the removal of hydrates, following unplanned shut down, depressurisation outside the hydrate envelope is normal practice.

1.4.2 Mechanical method (pigging):

Pigging is the process of inserting Rod scrapers (called a “pig”) into the line. Modern pigs have many functions, but the main one remains pipeline cleaning. The pig fits tightly into the line and scrapes the inside of the pipe. It is transported along the line with the flow of the fluid, and by doing so removes any solids (hydrate, wax, dirt, etc.) from inside the line. The pigging can also be used to remove accumulations of liquids. Another benefit of pigging is the removal of salt, scale, etc, which is important for the proper operation of a pipeline. It also means that potential nucleation sites for hydrate formation are removed. Continuous scraping can help maintain production level however, it may cause damage to equipment and necessitate replacement, pigging is time consuming and will increase labour hour and production down time. Also, the metal to metal contact roughens the pipe wall thereby encouraging more deposition.

Pigging of production flow-line is a common procedure for many oil fields, on land and

shallow waters. However, it is a big challenge to the deep offshore fields due to accessibility problems and the complexity of sub-sea operations. It is necessary to determine the best pigging periodicity to decrease operational risks. The application of this technique requires the following facilities: Pig launchers and receivers, sub-sea equipment prepared for pigging, facilities to drive the pig, pressure transducers and pig signallers on subsea equipment.

1.4.3 Thermal Insulation

One of the effective hydrate prevention, method is reservoir heat retention. Fluids at the well head are typically at temperature from 175°F to 212°F. When the reservoir fluids flows through a deep ocean pipeline with an outer temperature at 40°F, the temperature can quickly cool into the hydrate region as determined by the heat transfer coefficient (U) between pipe and ocean

Thermal insulation is an attractive measure for preventing hydrate and wax deposition. Thermal insulation works by keeping the flowing fluids above the hydrate formation temperature throughout the length of the production conduit. This typically involves filling the annulus completely or partially with a low thermal conductivity material (insulator) in order to prevent heat loss. This technique is always desirable because it collaborates in maintaining the oil temperature. Thermal insulation is a cost effective, preventive measure for minimizing solids deposition by altering the fluid flow characteristics in the wellbore. However, optimal use of this technique involves intelligent application of insulating materials, flow rate variation and completion design (Owodunni and Ajiienka, 2007). Hydrate dissociation is more difficult in insulated pipes. If hydrates form in an insulated pipeline, the pipeline may be depressurized to achieve a hydrate equilibrium temperature just above 32°F, so that heat will flow into the hydrate from the ocean which has a temperature around 40°F. However, the insulation acts as a hindrance or barrier which prevents heat flow from the ocean, making hydrate dissociation more difficult.

1.4.4 Heat Treatment

This involves the use of hot oil treatments, heat treated vessels/flow lines, hot water/steam or di-electrical heating (DEH) of steel pipes. It gives immediate results however, it is a short term solution because the temperature cools down at some stage in the system. Also, the crude will lose many light ends and this may encourage further hydrate formation. It is an expensive process because of the cost of fuel required to heat the vessels/flow lines and high power requirement in DEH. Also, there is risk of oil loss during hot oiling as well as potential formation damage. Excessive heating may shorten the life span of the pipe. There is also uneven heating in DEH which is a safety concern for hydrates. For offshore fields, the electrical heating of steel pipes has been

proposed recently by some manufacturers, but for flexible lines this technique is not available yet.

1.4.5 Remove the hydrate formers:

Prevent the formation of hydrate by removing the supply of hydrate forming molecules perhaps by gas-liquid separation. This approach has been proposed for subsea operations where gas and liquid are separated subsea and are transported to the processing facilities in separate pipelines. The gas pipeline still requires hydrate inhibition (through chemical inhibition) but the liquid 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 a system such as this has been installed and operated in this way.

1.4.6 Chemical Method

This involves the use of inhibitors. It is a dynamic field, changing rapidly with substantial research and development. Chemical inhibitors can be broadly classified into Low Dosage Hydrate Inhibitors (LDHI) and Thermodynamic Hydrate Inhibitors. The purpose of thermodynamic inhibitor is to depress the freezing point by shifting the equilibrium to lower temperature, thus reducing the region where hydrates can exist. Whereas, the purpose of LDHI is to impede the growth of hydrate crystals and prevent hydrates from coagulating.

1.4.6.1 Low Dosage Hydrate Inhibitors (LDHI)

LDHI are so called because they are used in lower concentration than thermodynamic inhibitors (typically less than 1wt% -3wt% in the aqueous phase). They can be classified into two:

1. Kinetic Hydrate Inhibitors (KHI)
2. Anti Agglomerant (AA)

Substantial advantages claimed for the use of LDHI include:

- Lower inhibitor loss caused by evaporation,
- Reduced capital expenses through decreased chemical storage and injection rate requirements; and no need for regeneration because the chemicals are not currently recovered.
- Easy offshore application where weight and space are critical to costs.
- Reduced operating expenses in many cases through decreased chemical consumption and delivery frequency

LDHI however cannot dissolve hydrate plugs, hence, their use has been limited to those applications that are not critical.

i) Kinetic Hydrate Inhibitors (KHI)

Kinetic inhibitors prevent hydrate crystal nucleation and growth to a critical radius by modifying the kinetics of hydrate formation. It slows the process in which hydrates crystallises. The objective of kinetic inhibition is to maintain the operating condition of a pipeline as far as possible to the left of the hydrate formation line without formation of hydrate plugs during the residence time of the fluids in the flow line. However, given sufficient time, hydrates will form in the presence of KHI. Kinetic inhibitors are commonly water soluble polymers. One of the first kinetic inhibitor developed was polyvinyl pyrrolidone (PVP)

There is no established method for predicting the effect of kinetic hydrate inhibitors on the onset of hydrate formation. It seems unlikely that such models will be available in future because the fundamental interactions between hydrates and kinetic inhibitors are poorly understood. At this time, the only practical way to confirm the effectiveness of a particular inhibitor is to test the chemical with representative fluid sample.

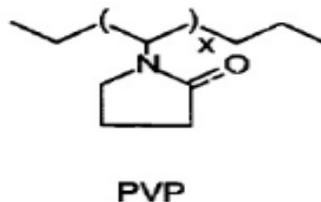


Figure 1.5 Poly vinyl pyrrolidone (PVP)

KHIs are applicable under most producing conditions however, at water salinity greater than 17%, the polymer may come out of solution, reducing the effectiveness of the KHI. Also, a solution of KHI in water does not provide protection from freezing or icing conditions in the line being treated. Therefore, if ambient temperatures are expected to fall below freezing, the KHI storage volume must be freeze-protected through the use of insulation on the container and piping or addition of antifreeze (typically ethylene glycol) to the KHI solution.

The KHI delivery system must be capable of providing sufficient dosage to achieve a hold time (i.e., period of effectiveness) greater than the water residence time in the piping since the KHI cannot be used for deplugging the system. The KHI polymer may suffer degradation effects at temperatures above 249°C.

ii) Anti Agglomerants/ Anticoagulant (AA)

Chemical method can involve adding anti-agglomerates that prevent the aggregation of hydrate crystals by dispersing the free water as droplets suspended within entrained oil or condensate. AA are surface active chemicals (surfactants) which adhered to hydrate crystals helping to stabilize the crystal in a continuous oil phase. The hydrate stays in slurry that can be transported and will not plug the line. Anti agglomerant inhibitors are particularly effective in preventing hydrate plugs or flow stoppages such as shut-ins, with subsequent cooling and restarting. This method holds great promise especially for deep, highly sub cooled systems and shut down with cold restart situation. Even though hydrates are formed, their suspension may provide acceptable flow properties such as low pressure drops.

As surfactant molecules, anti agglomerants have one water attractive end while the other end attracts oil, causing a lower surface tension between oil and water. Their unique chemical structure significantly reduces the rate of nucleation and hydrate growth during conditions thermodynamically favorable for hydrate formation, without altering the thermodynamic hydrate formation conditions (i.e., temperature and pressure).



Figure 1.6 Pipeline without Anti Agglomerants

The difference in plugging behaviour is attributed to the type and amount of natural surfactant present in the oil or condensate. In general, oils with little tendency to form stable emulsion have been observed to form hydrate plugs more easily than oils more prone to form stable emulsion (Slaon, 1998)

The effectiveness of AA is dependent on the type of oil/condensate, the salinity of the formation water and the water cut. Their main limitation is that they require a continuous oil phase and are therefore applicable for low water cut. The maximum water to oil ratio (volume basis) for the use of an anti agglomerant is 40:60 ppm a volume basis. Higher water cuts can invert the emulsion (i.e., change the continuous liquid phase from liquid hydrocarbon to water) and make the AA ineffective. Examples of AA include alkyl aromatic sulphonates or Alkylphenylethoxylates.

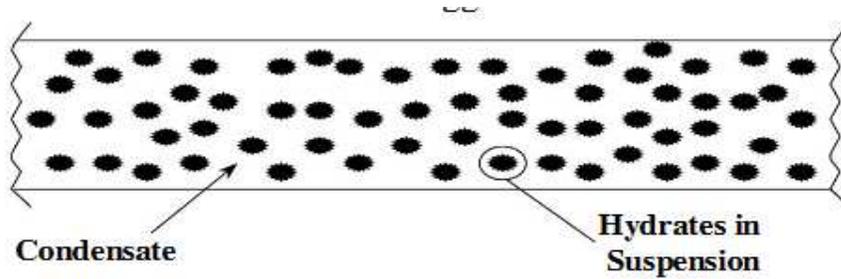


Figure 1.7 Pipeline with Anti Agglomerants

Economics of anti agglomerants should include surfactant cost, emulsion breaking & recovery and environmental considerations. Anti agglomerant chemicals are proprietary and chemical structures, properties and performance are not in the open literature. Specific surfactants must be formulated and tested as emulsifying agents for each composition of condensate. Weakness of the method includes toxicity concerns, the need to break emulsion and the need to recover the expensive dispersant additive.

Some AAs have a maximum salinity criterion that is normally not exceeded with produced water. Since AAs are based on dispersing polar hydrate crystals in a nonpolar oil or condensate phase, they may sometimes require a de-emulsifier for oil and water separation. Further, the addition of a heater upstream or heat coil inside a separator may be required to melt the hydrate crystals. AAs form crystals that are then dispersed in the liquid hydrocarbon phase, hence, careful consideration of the potential impact on viscosity should be considered including steady state flow, shut-in flow and restart conditions.

1.4.6.2 Thermodynamic Inhibitors

These chemicals work by altering the chemical potential of the aqueous phase such that the equilibrium dissociation curve is displaced to lower temperatures and higher pressures. They are added at relatively high concentrations (10%-60%) in the aqueous phase. They are time independent method for preventing hydrate plug formation. The main benefits of the traditional thermodynamic hydrate inhibitor are their effectiveness and reliability provided sufficient quantities are injected. Continuous application of this method involves minimum labour and may lessen or eliminate mechanical or thermal applications. However, the amount of chemical required for an effective chemical treatment may be cost prohibitive. Chemical misapplication may result in production downtime and lost revenues. Hydrate inhibition using thermodynamic inhibitors will increase the

quantity of chemical products to be handled on the platform. Thermodynamic inhibitors can be used to remove hydrate plugs. The choice of chemical to use depends on the plug location, fluid effects and properties of the plug in question.

Thermodynamic inhibitors can be polar or ionic. The polar thermodynamic inhibitors include alcohols and glycols while the ionic thermodynamic inhibitors are the salts.

i) Polar thermodynamic inhibitors

Alcohols and glycols are usually used as polar thermodynamic inhibitors and they are usually injected when the oil temperature is higher than the hydrate formation temperature. They exhibit hydrogen bonding so they can interfere with hydrogen bond of water so that much of the free water is hydrogen bonded to the inhibitor. This reduces the water activity so that lower temperatures and higher pressures are required to form hydrates. Examples of polar thermodynamic inhibitors include methanol, mono ethylene glycol, tri ethylene glycol, etc.

Methanol is a chemical with formula CH_3OH (often abbreviated MeOH). It is the simplest alcohol, and is a light, volatile, colourless, flammable, liquid with a distinctive odour that is very similar to but slightly sweeter than ethanol (drinking alcohol). At room temperature it is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol. Methanol is useful for combating hydrates in pipelines and topside on platforms. Methanol is regularly used for system restarts. It is injected until the fluids have warmed above hydrate conditions. Methanol is also used to treat and/or displace fluids in wellbores, trees, jumpers, and manifolds during shutdowns. Methanol however has its adverse effect on subsequent processing of the hydrocarbon stream; methanol-hydrocarbon systems are difficult to model accurately hence problematic for design engineers also, methanol will increase the chances of pipe corrosion by dissolving the alcohol based corrosion inhibitor and also increase corrosion due to the presence of dissolved air in the methanol. Methanol loss can be substantial when total fraction of either the vapour or the oil/condensate phase is very large relative to the water phase. Methanol recovery is possible from vapour phase using a cryogenic recovery process but this is seldom used due to the cost involved.

Mono ethylene glycol (MEG) also known as ethane-1,2-diol with formula $\text{HOCH}_2\text{CH}_2\text{OH}$ is an organic compound widely used as an antifreeze and a precursor to polymers. In its pure form, it is an odourless, colorless, syrupy, sweet-tasting toxic liquid. Due to its low freezing point and tendency to form glasses, ethylene glycol resists freezing. A mixture of 60% MEG and 40% water does not freeze until temperatures below $-45\text{ }^\circ\text{C}$. (MEG disrupts hydrogen bonding when dissolved in water therefore the freezing point of the mixture is depressed significantly. MEG is a useful desiccant. It is widely used to inhibit the formation of natural gas clathrates (hydrates) by

depressing the temperature at which hydrates form in long multiphase pipelines that convey natural gas from remote gas fields to an onshore processing facility.

MEG has a higher molecular weight and lower volatility than methanol and may be recovered and recycled more easily on the platforms however, this is usually not done because MEG is usually recovered with 60%-80% produced water which contains salt which is concentrated during recovery. The salt limit in MEG is frequently exceeded, resulting in salt precipitation and fouling of columns, trays, exchangers and other equipment. MEG losses to the vapour and condensate are very small relative to methanol. MEG is most applicable for small water fractions when gas and oil/condensate fractions are very high. MEG injection is used when the required methanol injection rate exceeds 30gal/hr (Sloan, 1998). MEG low vapour pressure requires that it be atomized into a pipeline. After injection, MEG is retained with the water phase and provides no hydrate protection above the water level. Due to its high viscosity and density, MEG is seldom used to dissociate a hydrate plug unless the injection point is vertically above a hydrate plug (as in a riser or well)

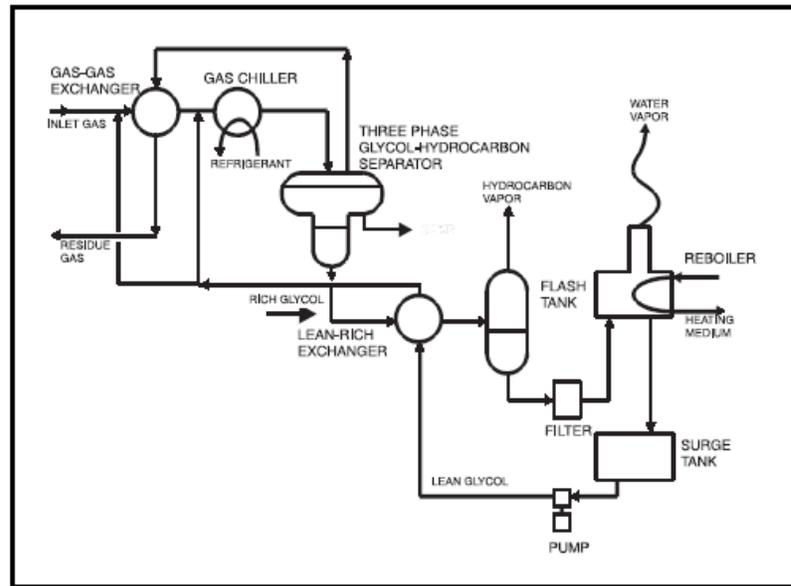


Figure 1.8: Glycol injection system

Other glycol such as di-ethylene glycol, tri-ethylene glycol can be used in inhibition hydrates. The glycol chosen must be hygroscopic, non corrosive, non-volatile, easily regenerated to high concentrations, insoluble in liquid hydrocarbons and non-reactive with hydrocarbon, CO₂ and sulfur compounds.

Diethylene glycol (DEG) is an organic compound with the formula (HOCH₂CH₂)₂O. It is a colorless, practically odorless, poisonous, viscous, and hygroscopic liquid with a sweetish taste. It is

miscible in water, alcohol, ether, acetone and ethylene glycol. A dilute solution of diethylene glycol can also be used as a coolant. DEG can also be used to inhibit hydrates. Triethylene glycol, TEG, or triglycol is a colorless odorless viscous liquid with molecular formula $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$. TEG's lower vapor pressure made it a very effective desiccant since vaporization losses at the absorber are insignificant and the TEG could be easily regenerated to the high concentrations needed to meet pipeline water dew point specifications. TEG is the primary gas dehydration process used to meet pipeline specifications.

ii) **Ionic Inhibitors.**

Ionic compounds may also inhibit formation of hydrates due to ionic bonding. Sodium chloride can be used to inhibit hydrate formation. It is often used as a cheap and safe desiccant because it has some hygroscopic properties. Sodium chloride salts can be used in snow removal. NaCl does not release heat upon solution; however, it does lower the freezing point. NaCl is also more readily available and does not have any special handling or storage requirements.

Calcium chloride is preferred over sodium chloride in de icing roads because CaCl_2 releases energy upon forming a solution with water, heating any ice or snow it is in contact with. It also lowers the freezing point, depending on the concentration. Calcium chloride is thought to be more environmentally friendly than sodium chloride, however a drawback is that it tends to promote corrosion also it has to be kept in tightly sealed air tight containers because of its hygroscopic nature. Calcium chloride is more effective at lower temperatures than sodium chloride. Solutions of calcium chloride can prevent freezing at temperature as low as $-52\text{ }^\circ\text{C}$ ($-62\text{ }^\circ\text{F}$).

The chemical compound Potassium Chloride (KCl) is a metal halide salt composed of potassium and chlorine. In its pure state it is odourless. It has a white or colourless vitreous crystal, with a crystal structure that cleaves easily in three directions. Potassium chloride crystals are face-centred cubic. Potassium chloride can lower the depression temperature and inhibit hydrate formation.

1.5 STATEMENT OF THE PROBLEM

Hydrate plugs form so rapidly and without warning due to low temperatures and relatively high pressures in marine environment. Kinetic Hydrate Inhibitors and Anti Agglomerate have been used to control the kinetics of hydrate formation and agglomeration. They however are expensive and do not melt hydrate plugs. Polar Thermodynamic Inhibitors on the other hand are highly effective in melting hydrate plugs and preventing hydrate formation in pipelines but they are required in large volume and are rarely regenerated because of high cost of regeneration. Hence, it

is necessary develop hybrid inhibitors in order to reduce the quantity of polar thermodynamic inhibitors required in the field.

1.6 OBJECTIVES

1. Determination of hydrate formation conditions for a particular fluid.
2. Design a spread sheet for determining the quantity of inhibitor required in a flow line to prevent hydrate formation
3. Evaluation of the effect of Methanol, Mono-Ethylene Glycol and Di-Ethylene Glycol on hydrate formation.
4. Determination of the quantity of hybrid inhibitor, consisting of an ionic and a polar thermodynamic inhibitor required to inhibit hydrate.

1.7 SCOPE OF WORK

Asphaltenes, waxes and hydrates are the three major solids that cause flow assurance challenges. However, this work focuses on hydrate inhibition. Hydrates can be formed in the reservoir, while drilling, in the tubing, in flow lines, etc. This work is limited to hydrate prevention in flow lines. Several methods of hydrates have been discussed in this work but the method used in carrying out this research is the chemical method. The chemicals used in this work are restricted to thermodynamic hydrate inhibitors.

CHAPTER TWO

LITERATURE REVIEW

A successful flow rate is crucial to increasing production and avoiding pipeline maintenance and repair. With so many factors around that can cause flow to be disrupted, it is essential to understand the different options available to increase flow and minimize blockages. (Dorrian, 2010). The precipitation and deposition of hydrates occur along flowlines when multiphase flow experiences pressure and temperature decline as the oil or gas is being transported. Hydrates have specific pressure-temperature equilibria and/or combination of parameters that would promote precipitation. Hence, most techniques for addressing hydrate deposition issues are based on avoiding the specific pressure-temperature equilibria that would promote precipitation.

2.1 HYDRATE INHIBITION, PAST, PRESENT AND FUTURE.

Over the years, chemical inhibitors have been used to suppress the hydrate formation temperature. Becke *et al.* (1992) investigated the effect of adding an oil phase to a gas on hydrate formation. Experimental investigations on hydrate equilibrium conditions in multiphase mixtures incorporating a gas phase, a liquid hydrocarbon phase and an excess water phase were performed. Measurements were conducted in a stirred autoclave at pressures up to 12 MPa and a temperature range of 275 to 295 K. The gas phase consisted of both pure hydrocarbon gases (methane, ethane and propane) and their mixtures. The Liquid hydrocarbon phase consisted of pure alkanes, cyclo-alkanes, aromatics, their mixtures, and crude oils. They observed that the addition of oil produced a beneficial reduction in the hydrate formation temperature in gas mixtures but not with pure methane. This was due to selective solubility of the preferred hydrate former (e.g. propane) in the liquid hydrocarbon phase and the reduction in the molecular weight of the gas. The presence of liquid hydrocarbons in a gas-water mixture leads to a constant hydrate equilibrium temperature depression. The temperature depression is about 20 times less than that of inhibitors.

Steven Cochran (2003) discussed hydrate inhibition by the use of cold slurry transport. Cold slurry transport is a technique still in the research and development stage. In this technique an apparatus cools the production stream to ambient temperatures, and in doing so, forms small hydrate crystals that will stay in the flow stream as slurry. The apparatus would do the same for the wax. Such an apparatus has yet to be fully developed and tested, and thus it may be several years before this technique is ready for the field. The advantages of such a technique are that it can reduce CAPEX by using a single flowline rather than dual flowlines and by eliminating insulation.

Operations can potentially be simplified. The technique may need to be combined with water separation and disposal.

Dana, *et al* (2004) carried out laboratory work to explore possible synergistic effects between methanol and LDHI. A strong synergistic effect was discovered at a certain ratio of methanol and low molecular weight oligomer type hydrate inhibitor. These observations allowed a formulation of a superior hydrate inhibitor known as Ice-Chek which is a combination of LDHI and methanol. Due to this novel approach to hydrate problems, the operator experienced more trouble-free field operation and increased gas production, improved economics with less down time and lower total cost of chemicals and delivery. After analyzing the work results, it was noticed that some LDHI dilutions performed better than expected. It was also noticed that hydrate forms slowly in the presence of the LDHI/MeOH mixture. The combination product is commercially viable for protecting production gas wells against hydrate blockages. Ice-Chek's unique ability to slow hydrate progress even after the system starts producing hydrates makes it a safer product for field operators.

Szymczak *et al.* (2005) carried out a study on Hybrid Hydrate Inhibitor (HHI) which is the combination of thermodynamic inhibitors and LDHI on a well in the Gulf of Mexico that had a subsea completion with a 4½" flow line to the treating facility. The operator selected a hybrid hydrate inhibition (HHI) technology that provided thermodynamic, kinetic and anti-agglomerate solutions to hydrate formation. The effective concentration of a HHI is in a range of 2-5%. When HHI was used in this particular GOM subsea shelf application it fulfilled the operator's expectations. Costs were reduced, performance was increased and secondary costs, i.e. transportation, footprint, crane lifts, pump costs and corrosion, were reduced. The operator realized better performance at a reduced cost

Swanson & Petrie (2005) discussed the use of Kinetic Hydrate Inhibitor with the addition of paraffin control additives in the Gulf of Mexico. This field application was conducted on a pipeline for a newly re-completed well which was predicted to have water cuts in the 20% range. A kinetic hydrate inhibitor (KHI) was injected after the production rates had stabilized. The kinetic hydrate inhibitor was chosen based on data from lab testing and computer modelling. The KHI provided lower operating costs plus better environmental conditions than methanol, which had been used before the well was re-completed. It was seen that with KHI, there was no undesirable methanol in the crude and no oil/water quality issue. LDHI worked well in this deepwater pipeline in the Gulf of Mexico for several months (more than half a year) and replaced the larger amounts of methanol use previously. It was discovered that LDHI works well with the paraffin control additives and there were no incompatibilities.

However, the KHI works at lower amounts of subcooling such as up to 18 °F -22 °F (10 °C -12 °C) under a standard 48 hour residence period, while AAs can operate at higher subcooling levels (27 °F to 36 °F or 15 °C -20 °C).

Carroll (2009) suggested Ammonia as an inhibitor for hydrate formation. Based on the Hammerschmidt equation, a 10°C depression in the hydrate formation temperature requires an 11.6 wt% ammonia solution vs. a 19.8 wt% methanol solution. Ammonia may be more useful in thawing hydrate plugs in pipelines. Unlike liquid inhibitors, which require pressure drop in order to flow to reach a plug, ammonia can diffuse through the gas phase to reach the hydrate plug due to its volatility. However, ammonia is toxic, it reacts with carbon dioxide and hydrogen sulfide in the aqueous phase and maybe difficult to handle in oil field applications also, its high volatility translates into larger losses to the vapour. Therefore, ammonia is hardly used as hydrate inhibitor because the disadvantage outweighs any possible advantage.

Azarinezhad, *et al* (2010) developed HYDRAFLOW a new, patented cold-flow-assurance technology at the Centre for Gas Hydrate Research, Heriot-Watt University, Edinburgh. This technique is a risk-management tool for preventing hydrate blockage. HYDRAFLOW concept is to allow/encourage gas-hydrate formation, but prevent agglomeration in the pipeline and thus avoid blockage. The idea is to convert most of the gas phase into hydrates and transfer it in the form of hydrate-slurry in the pipeline. Where produced water is insufficient for maximum hydrate formation, excess water can be added from other sources such as seawater (hence wet cold flow). It is also possible to adjust the hydrate-slurry viscosity by adjusting the amount of water. Anti Agglomerants (AAs) and other additives may be necessary to control the hydrate-crystal size and prevent solid blockage in these systems. This concept can also potentially reduce wax-deposition problems by maintaining the fluid temperature for a longer time through exothermic hydrate-formation reaction, providing solid seeds for wax nucleation in the flowing liquid phase rather than on pipeline walls. Also, this wet cold flow concept could eliminate the need for a hydrate reactor and/or the need for multiphase subsea/remote pumps for circulating hydrate seed nuclei.

2.2 POINT OF DEPARTURE

Thermodynamic inhibitors have proven track record of efficiently inhibiting hydrate formation and unplugging hydrate plugs. However, they are required in large quantities on the field and are not usually regenerated because of the high cost of regeneration. Several hybrid inhibitor consisting of LDHI and polar THI have been proposed. These have been effective in a way but the usage of such hybrid has been limited to the specific field which the LDHI was designed for. It is expedient to design hybrid that will reduce cost and work on all fields. Hence, this research studies

the synergy between ionic and polar thermodynamic inhibitor and their effect in hydrate inhibition.

CHAPTER THREE

METHODOLOGY

In this study, the following polar thermodynamic inhibitors were used: Methanol (MeOH), Mono Ethylene Glycol (MEG or EG), Di Ethylene Glycol (DEG). The ionic thermodynamic inhibitors used are: Sodium chloride, Potassium chloride and Calcium chloride.

3.1 HYDRATE PREDICTION

Hydrate Prediction was carried out in the absence of an inhibitor using the Gas gravity method. This method predicts the worst-case hydrate forming conditions. It is assumed that sufficient water is present to form a hydrate. Thus, the mole fractions in this calculation are on a water-free basis.

The specific gravity (SG) of the gas was calculated using this expression

$$SG = \frac{\sum_{i=1}^n (y_i * MW_i)}{MW_{air}}$$

(3.1)

Katz correlation gives accurate results for pipeline quality gases.

Katz plot curve fit equations (Owodunni & Ajeinka, 2007):

$$T = 15.781 * Ln(P) - 60.679$$

(3.2)

For gas specific gravity of 0.554

$$T = 13.055 * Ln(P) - 31.29$$

(3.3)

For gas specific gravity of 0.6

$$T = 12.116 * Ln(P) - 20.818$$

(3.4)

For gas specific gravity of 0.7

$$T = 11.748 * Ln(P) - 16.493$$

(3.5)

For gas specific gravity of 0.8

$$T = 11.39 * \ln(P) - 12.7999$$

(3.6)

For gas specific gravity 0.9

$$T = 10.72 * \ln(P) - 7.0929$$

(3.7)

For specific gas gravity of 1.0

3.2 TEMPERATURE DEPRESSION

The temperature depression for Methanol, Mono Ethylene Glycol and Di Ethylene Glycol was calculated using Hammerschmidt equation. However, for methanol weight greater than 25% by weight, the Nielsen Bucklin equation was used. The temperature depression for salts used was evaluated using the correlation (Østergaard *et al*, 2005)

3.2.1 Hammerschmidt equation:

$$\Delta T_{polar} = \frac{CW}{M(100 - W)}$$

(3.8)

Assumptions made in Hammerschmidt equation include:

- The inhibition effect of the inhibitor is independent of the pressure.
- The temperature depression is independent of both the nature of the hydrate former present and the type of hydrate formed.

TABLE 3.1: Physical constants of inhibitors (Yong and Qiang, 2005)

Component	Molecular weight	C (K value)
Methanol	32	2335
Mone ethylene glycol (MEG)	62.07	2700
Di ethylene glycol (DEG)	106.12	4000

3.2.2 Nielsen Bucklin equation:

$$\Delta T_{polar} = -72 * \ln(1 - X_m)$$

(3.9)

The relationship between the mole fraction and the weight percent is given below:

$$W = \frac{X_m}{18.015 + X_m(M - 18.015)}$$

(3.10)

3.2.3 Østergaard *et al.* (2005)

a) Sodium Chloride

$$\Delta T_{ionic} = (0.3534W + 1.375 \times 10^{-3}W^2 + 2.433 \times 10^{-4}W^3)(4.056 \times 10^{-2} \ln P + 0.7994)(2.5 \times 10^{-5}(P_0 - 1000) + 1)$$

(3.11)

b) Calcium Chloride

$$\Delta T_{ionic} = (0.194W + 7.58 \times 10^{-3}W^2 + 1.953 \times 10^{-4}W^3)(4.253 \times 10^{-2} \ln P + 1.023)(2.8 \times 10^{-5}(P_0 - 1000) + 1)$$

(3.12)

c) Potassium Chloride

$$\Delta T_{ionic} = (0.305W + 6.77 \times 10^{-4}W^2 + 8.089 \times 10^{-5}W^3)(3.858 \times 10^{-2} \ln P + 0.714)(2.2 \times 10^{-5}(P_0 - 1000) + 1)$$

(3.13)

3.2.4 Combined Thermodynamic Hydrate Inhibitors

To estimate the hydrate formation temperature in the presence of mixed thermodynamic inhibitors, the depression temperature due to each individual inhibitor is added up. (See Appendix A)

$$\Delta T = \Delta T_{ionic} + \Delta T_{polar}$$

(3.14)

3.3 ESTIMATION OF HYDRATE INHIBITORS NEEDED IN FLOWLINE.

Three considerations must be analysed before injecting inhibitors to pipelines

1. Amount of inhibitors in free water phase
2. Amount of inhibitor lost to gas phase
3. Amount of inhibitor lost to condensate phase

The mass of inhibitor required in the free water phase is estimated using the following expression:

$$M_{inhibitor} = \frac{Wt\%_{inhibitor} \times M_{total_water}}{100 - Wt\%_{inhibitor}}$$

(3.15)

For the purpose of this work, it is assumed that 15% of methanol required in the free water phase will be lost to gas and condensate phase. It is also assumed that 0.001% of the required glycols will be lost to the gas and condensate phase.

3.4 SPREAD SHEET DEVELOPMENT

A Spread sheet was developed to calculate the hydrate formation temperature at certain pressures with varying concentrations of inhibitors. The spread sheet combines the Katz equation, Hammerschdmitt equation, Nielsen Bucklin and Østergaard equation to calculate these parameters.

Inhibitors used in this spread sheet include: MEOH, MEG, DEG, MeOH-NaCl hybrid inhibitor, MeOH-CaCl₂ hybrid inhibitor, MeOH-KCl hybrid inhibitor, MEG-NaCl hybrid inhibitor, MEG-CaCl₂ hybrid inhibitor, MEG-KCl hybrid inhibitor, DEG-NaCl hybrid inhibitor, DEG-CaCl₂ hybrid inhibitor and DEG-KCl hybrid inhibitor.

The input data into the spread sheet include the composition of the stream, the physical constants of the inhibitors used, the ambient temperature of the environment and the highest operational pressure expected in the pipe being considered. The spread sheet calculates the specific gravity of the fluid. With the specific gravity of the fluid, the hydrate formation temperatures at specific pressures are calculated. When an inhibitor is added, Hammerschdmitt, Nielsen Bucklin and Ostegaard equations calculate the temperature depression for the inhibitor. The temperature depression is subtracted from the hydrate formation temperature at specific pressures to give the current hydrate formation temperature with inhibition. Curves are generated for the hydrate formation curve with depressed temperature at different concentration of methanol, mono-ethylene glycol, di-ethylene glycol and a combination of the polar thermodynamic inhibitors and ionic thermodynamic inhibitors. These curves are superimposed on the temperature pressure profile of the pipe gotten from Hysys.

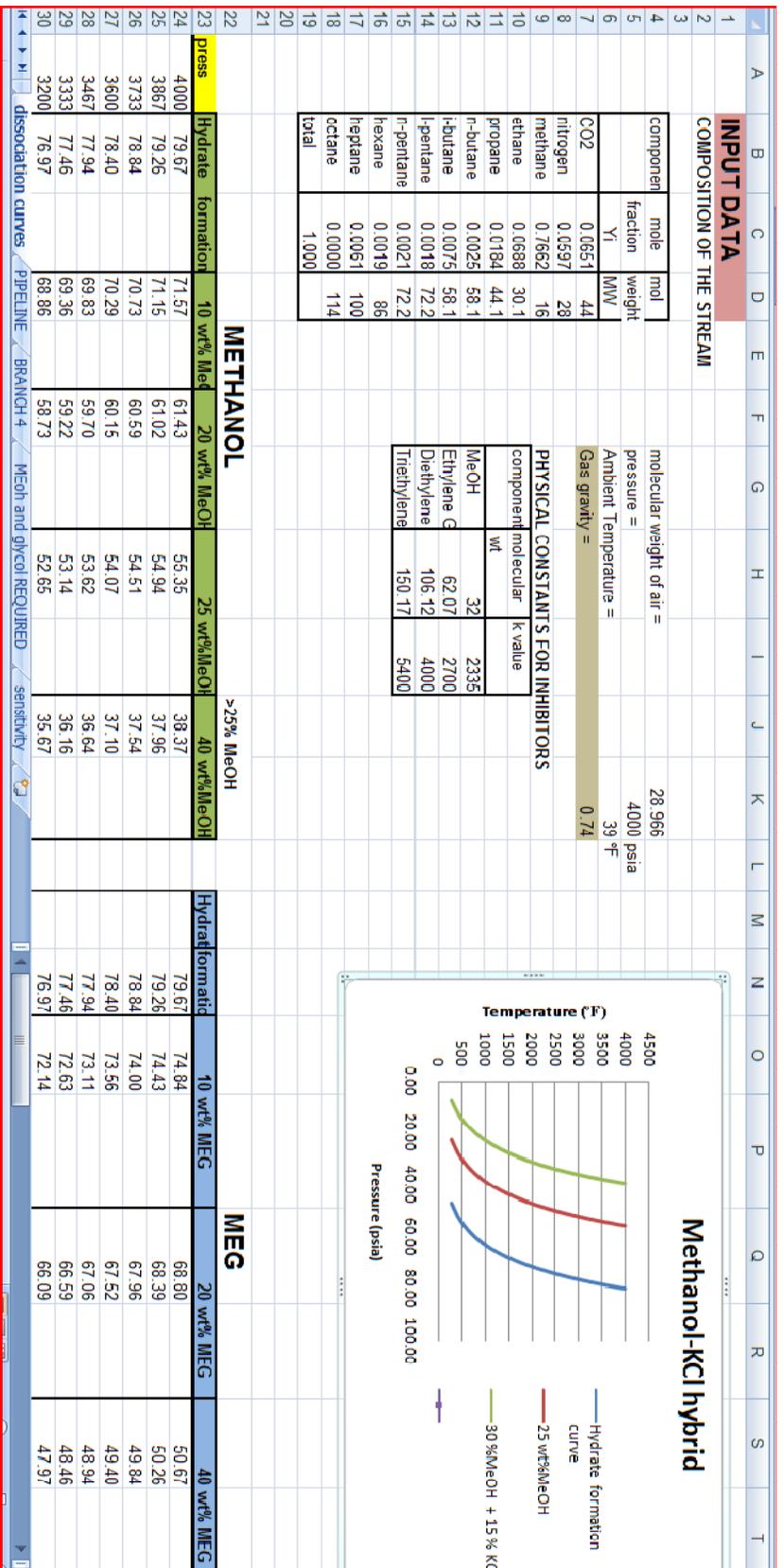


Figure 3.1 Spread sheet

3.5 CASE STUDY

An offshore field consisting of two oil wells (well A and well B) and two gas wells (well C and well D) was modelled using Hysys. The beggs and brills correlation was used for all pipes used. Fluid from Well A flows through Branch 1 to Branch 5 where it is mixed with fluids coming from Well B. Fluid in Branch 5 is combined with fluid coming from gas well C (Figure 3.1). Fluid in Branch 5 mixes up with fluid from Branch 4. The mixture of the various streams passes through a riser, Branch 7, to the production platform. On the production platform, the fluid passes through a 3 phase separator and it is separated into the gas, liquid and aqueous phase. The fictitious offshore field data can be found in Appendix D.

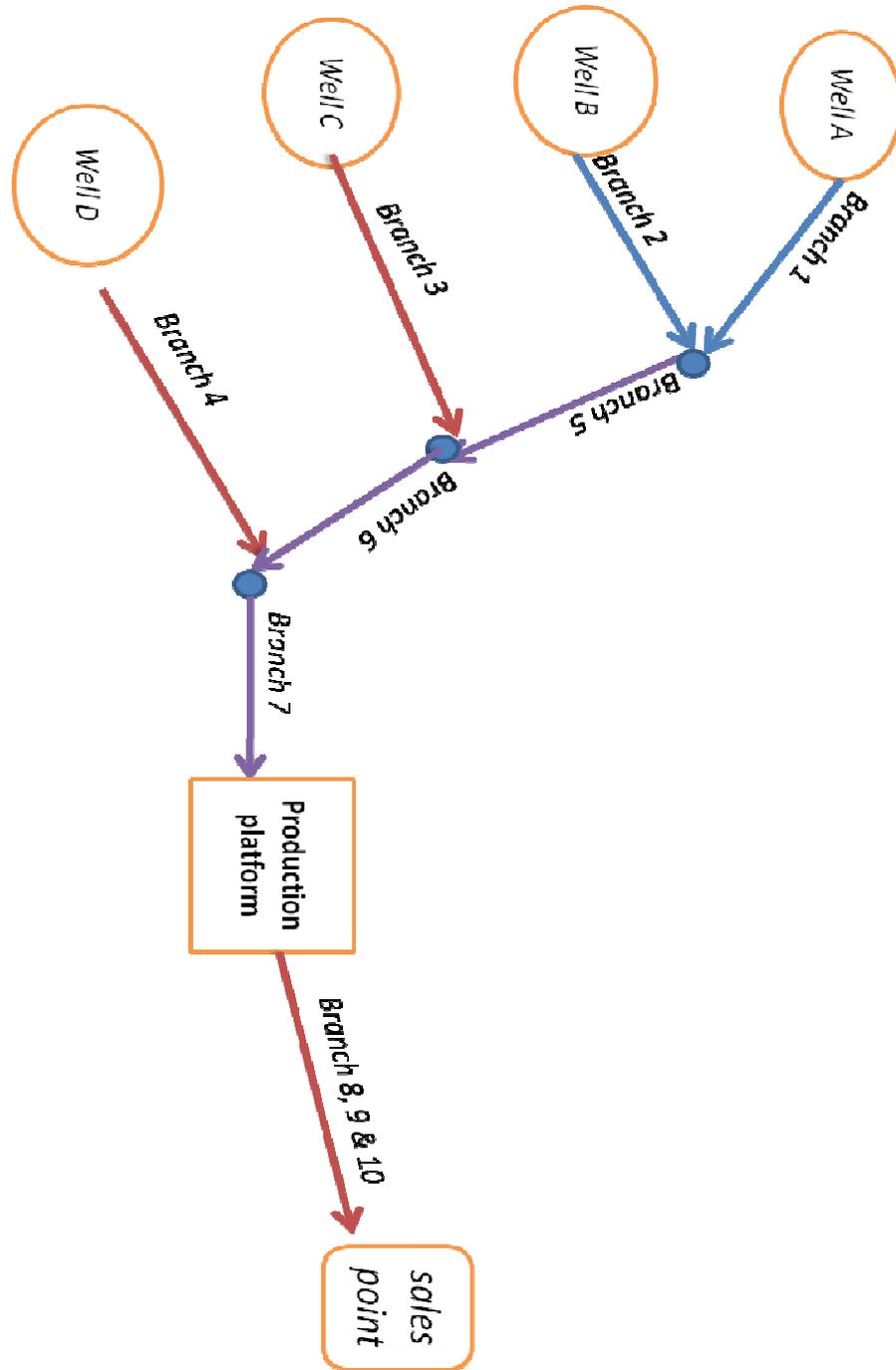


Figure 3.2: Schematics of the fictitious offshore field

CHAPTER FOUR

RESULTS & DISCUSSION

4.1 RESULTS

Table 4.1 shows the rate at which fluid flows through the various branches. It also has the inlet and outlet conditions of the various pipes in the field and the water content of the streams. In Table 4.2, the quantity of THI required to prevent hydrate formation in Branch 4 and Branch 9 are given. Table 4.3 gives the amount of polar THI saved by addition of ionic THI (salt) while, Table 4.4 shows the effect of polar THI on hydrate formation temperature at specific pressures. Table 4.5 shows the effect of hybrid THI on the hydrate formation temperature at specific pressures while Table 4.6 gives the effect of polar THI and hybrid THI on temperature depression. Table 4.7 shows the subcooling temperature and the operating pressure of Branch 4 and 9

Table 4.1: Pipe condition

	Flow rate (MMScf)	Inlet conditions		Outlet conditions		Water (bbl/day)
		Temperature (°F)	Pressure (psia)	Temperature (°F)	Pressure (psia)	
Branch 1	96.20	124.10	3185	39.00	3009	3500.00
Branch 2	92.70	113.40	4400	53.91	4368	2508.57
Branch 3	57.37	119.20	5303	39.09	5288	0.00
Branch 4	150.00	125.00	5493	40.30	5088	998.63
Branch 5	188.70	49.08	3009	41.82	2826	5991.78
Branch 6	246.10	41.28	2826	40.96	2783	5991.78
Branch 7	396.10	51.41	2783	33.44	1912	6990.60
Branch 8	155.30	33.44	1916	32.27	1873	2.79
Branch 9	154.50	84.50	3450	34.93	2023	2.68
Branch 10	154.50	56.00	3450	32.17	2135	2.68

Table 4.2: Quantity polar THI required

	MeOH		MEG		DEG	
	wt%	bbl/day	wt%	bbl/day	wt%	bbl/day
BRANCH 4						
Without salt	40.0	3763.2	48.0	4531.0	52.0	5317.6
With 15% NaCl	27.0	2087.8	38.0	3008.5	41.0	3411.0
With 15% CaCl ₂	27.0	2087.8	38.0	3008.5	42.5	3628.1
With 15% KCl	30.0	2419.2	42.0	3554.5	44.5	3935.7
BRANCH 9						
Without salt	39.0	9.8	47.7	12.2	51.4	14.2
With 15% NaCl	26.0	5.4	37.0	7.9	40.5	9.1
With 15% CaCl ₂	26.5	5.6	37.5	8.0	41.5	9.5
With 15% KCl	29.0	6.3	37.0	7.9	44.5	10.7

Table 4.3: Quantity of polar THI inhibitor saved by addition of salts

	MeOH			MEG			DEG		
	Required bbl/day	Saved		Required bbl/day	Saved		Required bbl/day	Saved	
		bbl/day	%		bbl/day	%		bbl/day	%
BRANCH 4									
Without salt	3763.2	0	0	4531.0	0.0	0.0	5317.6	0.0	0
With 15% NaCl	2087.8	1675.4	44.5	3008.5	1522.5	33.6	3411.0	1906.6	35.9
With 15% CaCl ₂	2087.8	1675.4	44.5	3008.5	1522.5	33.6	3628.1	1689.5	31.8
With 15% KCl	2419.2	1344.0	35.7	3554.5	976.5	21.6	3935.7	1381.9	26.0
BRANCH 9									
Without salt	9.8	0.0	0.0	12.2	0.0	0.0	14.2	0.0	0.0
With 15% NaCl	5.4	4.4	45.0	7.9	4.4	35.6	9.1	5.0	35.6
With 15% CaCl ₂	5.6	4.3	43.6	8.0	4.2	34.2	9.5	4.7	32.9
With 15% KCl	6.3	3.6	36.1	7.9	4.4	35.6	10.7	3.4	24.2

Table 4.4 Effect of Polar THI on hydrate formation temperature

Pressure (psia)	Temperature (°F)									
	BRANCH 4									
	no inhibition	10% inhibitor			20% inhibitor			40% inhibitor		
	MeOH	MEG	DEG	MeOH	MEG	DEG	MeOH	MEG	DEG	
7000	87.5	79.4	82.7	83.3	69.3	76.6	78.1	46.2	58.5	62.4
6000	85.7	77.6	80.9	81.5	67.5	74.8	76.3	44.0	56.7	60.6
5000	83.6	75.5	78.7	79.4	65.3	72.7	74.1	42.3	54.6	58.4
4000	81.0	72.8	76.1	76.8	62.7	70.1	71.5	39.6	51.9	55.8
3000	77.6	69.5	72.7	73.4	59.3	66.7	68.1	36.3	48.6	52.4
2000	72.8	64.7	68.0	68.6	54.6	61.9	63.4	31.5	43.8	47.7
1000	64.7	56.6	59.8	60.5	46.4	53.8	55.2	23.4	35.7	39.5
	BRANCH 9									
	no inhibition	10% inhibitor			20% inhibitor			40% inhibitor		
	MeOH	MEG	DEG	MeOH	MEG	DEG	MeOH	MEG	DEG	
4000	79.7	71.6	74.8	75.5	61.4	68.8	70.3	38.4	50.7	54.5
3500	78.1	69.9	73.2	73.9	59.8	67.2	68.6	36.8	49.1	52.9
3000	76.2	68.1	71.4	72.0	57.9	65.3	66.8	34.9	47.2	51.1
2500	74.0	65.9	69.1	69.8	55.7	63.1	64.6	32.7	45.0	48.8
2000	71.3	63.2	66.4	67.1	53.0	60.4	61.9	30.0	42.3	46.1
1500	67.8	59.7	63.0	63.6	49.5	59.4	63.4	26.5	42.7	47.7
1000	62.8	54.8	58.0	58.7	44.6	52.0	54.5	21.6	33.9	37.7

Table 4.5: Effect of hybrid inhibitor on hydrate formation Temperature

Pressure (psia)	Temperature (°F)									
	without inhibitor	27 wt% MeOH + 15wt%			27 wt% MEG+ 15wt%			27 wt% DEG + 15wt%		
		NaCl	CaCl2	KCL	NaCl	CaCl2	KCL	NaCl	CaCl2	KCL
BRANCH 4										
7000	87.5	46.5	46.9	51.1	57.4	57.8	62.0	59.6	60.7	64.2
6000	85.7	44.8	45.1	49.3	55.7	56.0	60.2	57.8	58.9	62.4
5000	83.6	42.7	43.0	47.3	53.6	53.9	58.2	55.8	56.8	60.3
4000	81.0	40.2	40.5	44.7	51.1	51.4	55.6	53.3	54.3	57.8
3000	77.6	37.0	37.2	41.4	47.9	48.1	52.3	50.0	51.0	54.5
2000	72.8	32.4	32.6	36.8	43.3	43.5	47.7	45.4	46.4	49.8
1000	64.7	24.6	24.8	28.9	35.5	35.7	39.8	37.6	38.6	41.9
BRANCH 9										
4000.0	79.7	38.9	39.2	43.4	49.8	50.1	54.4	52.0	53.0	56.5
3500.0	78.1	37.4	37.7	41.9	48.3	48.6	52.8	50.4	51.5	54.9
3000.0	76.2	35.6	35.9	40.0	46.5	46.8	51.0	48.6	49.7	53.1
2500.0	74.0	33.5	33.7	37.9	44.4	44.6	48.8	46.5	47.5	50.9
2000.0	71.3	30.9	31.1	35.3	41.8	42.0	46.2	43.9	44.9	48.3
1500.0	67.8	27.5	27.7	31.9	38.4	38.6	42.8	40.6	41.5	44.9
1000.0	62.9	22.8	23.0	27.1	33.7	33.9	38.0	35.8	36.8	40.1

Table 4.6: Temperature depression

Inhibitor	10wt%	20wt%	30wt%	40wt%
MeOH	8.1	18.2	28.0	41.3
MEG	4.8	10.9	18.6	29.0
DEG	4.2	9.4	16.2	25.1
15%NaCl+MeOH	22.0	32.2	45.2	62.6
15% CaCl2+MeOH	21.7	31.9	44.9	62.3
15%KCl+MeOH	17.5	27.6	40.6	58.0
15%NaCl+MEG	18.8	24.8	32.6	42.9
15% CaCl2+MEG	18.4	24.5	32.3	42.6
15%KCl+MEG	14.2	20.2	28.0	38.4
15%NaCl+DEG	18.1	23.3	30.1	39.1
15% CaCl2+DEG	17.0	22.3	29.0	38.0
15%KCl+DEG	13.6	18.8	25.5	34.5

Table 4.7: Subcooling Temperature

BRANCH 4				BRANCH 9			
pressure psia	operating temp (°F)	hydrate formation temperature(°F)	sub cooling (°F)	pressure psia	operating temp (°F)	hydrate formation temperature(°F)	sub cooling (°F)
5493	125	85	40	3450	56	78	-22
5316	105	84	21	3591	42	78	-37
5135	89	84	5	3666	41	79	-38
4950	77	83	-7	3822	41	79	-39
4764	66	83	-17	3609	39	78	-40
4577	58	83	-24	3162	39	77	-38
4452	54	82	-29	2924	39	76	-37
4328	50	82	-32	2673	38	75	-36
4204	46	82	-36	2544	36	74	-38
4080	43	82	-39	2290	36	73	-37
3957	40	82	-42	2043	35	72	-37

4.1.1 BRANCH 4

Figure 4.1 is the temperature profile of Branch 1 while Figure 4.2 is the pressure profile of Branch 4. Figure 4.3 shows the hydrate formation curve of fluid in Branch 4 and temperature-pressure profile of Branch 4. It indicates the onset of hydrate formation in Branch 4. The effect of MeOH on fluid in Branch 4 is shown in Figure 4.5. Figure 4.6, Figure 4.7 and Figure 4.8 show the effect of MeOH hybrid inhibitors on fluid in Branch 4.

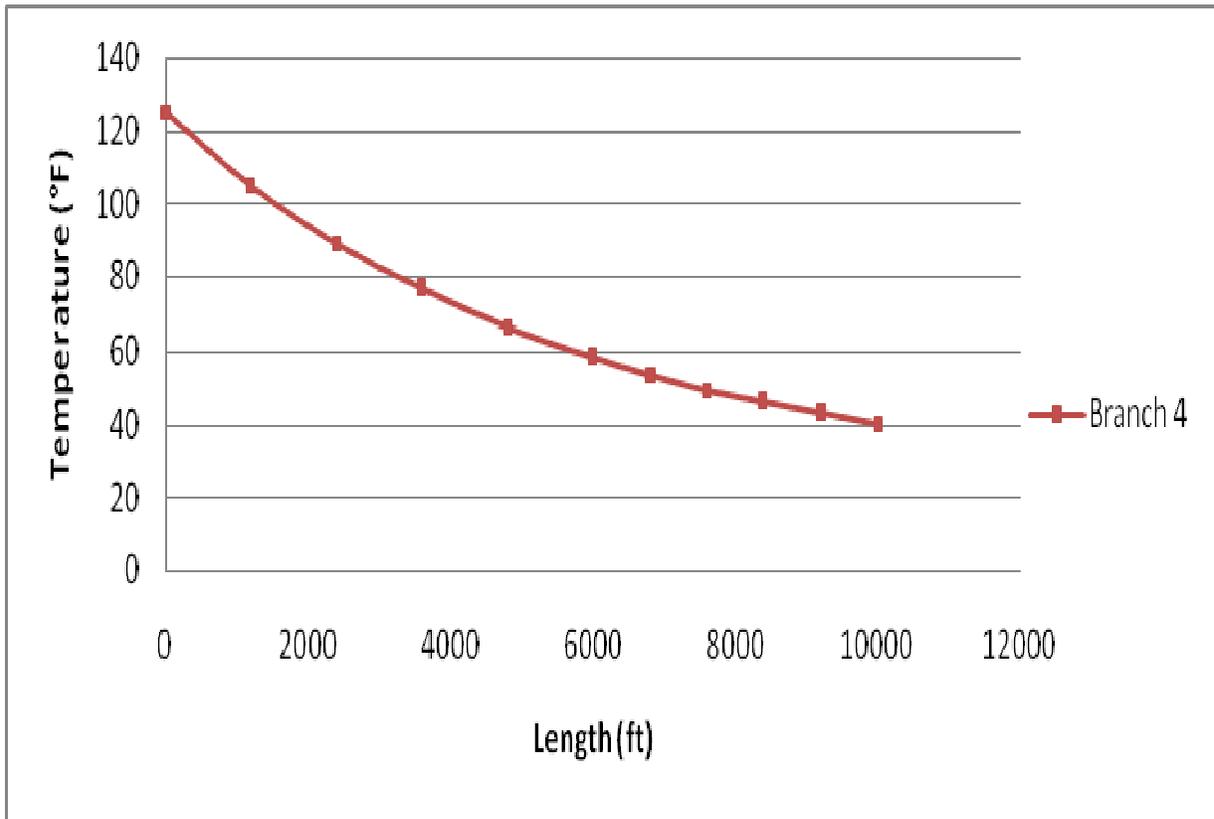


Figure 4.1: Temperature Profile of Branch 4

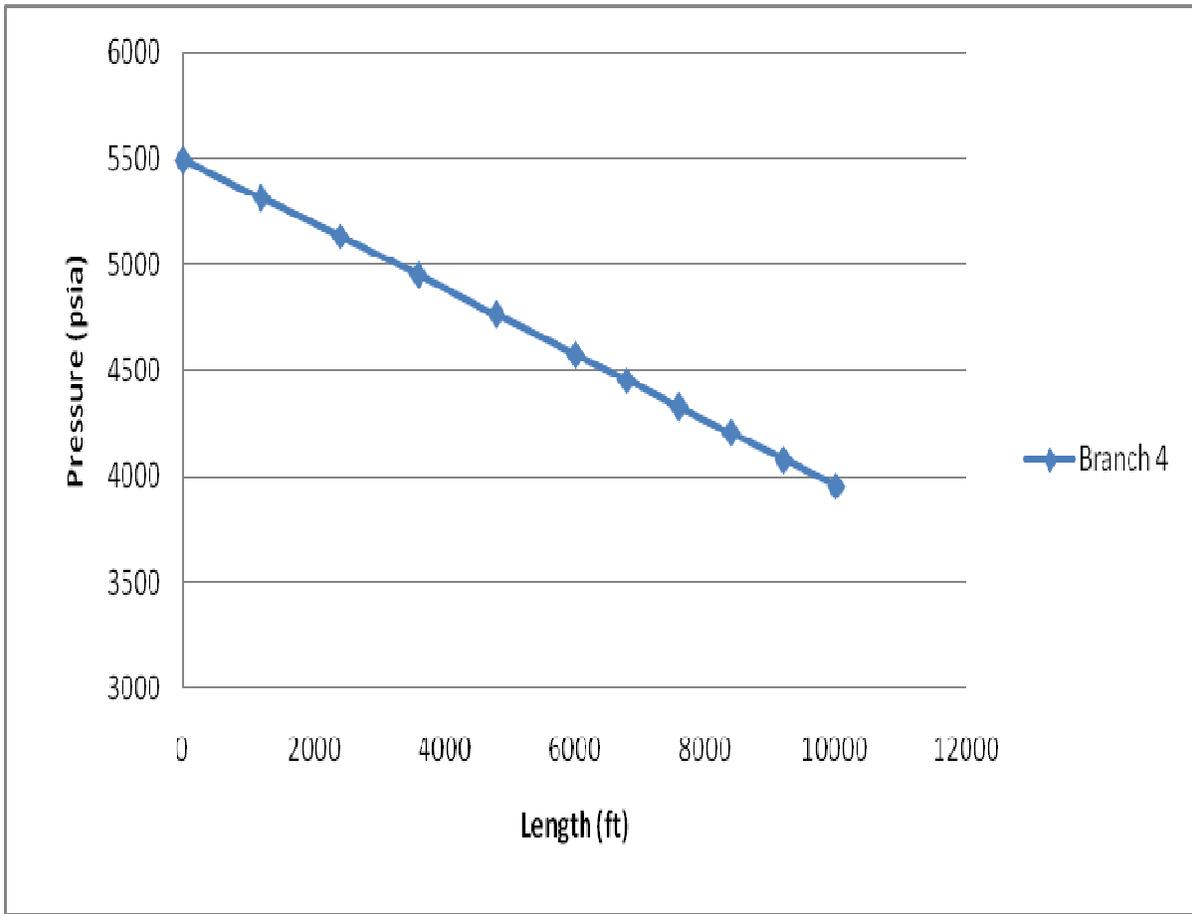


Figure 4.2: Pressure Profile of Branch 4

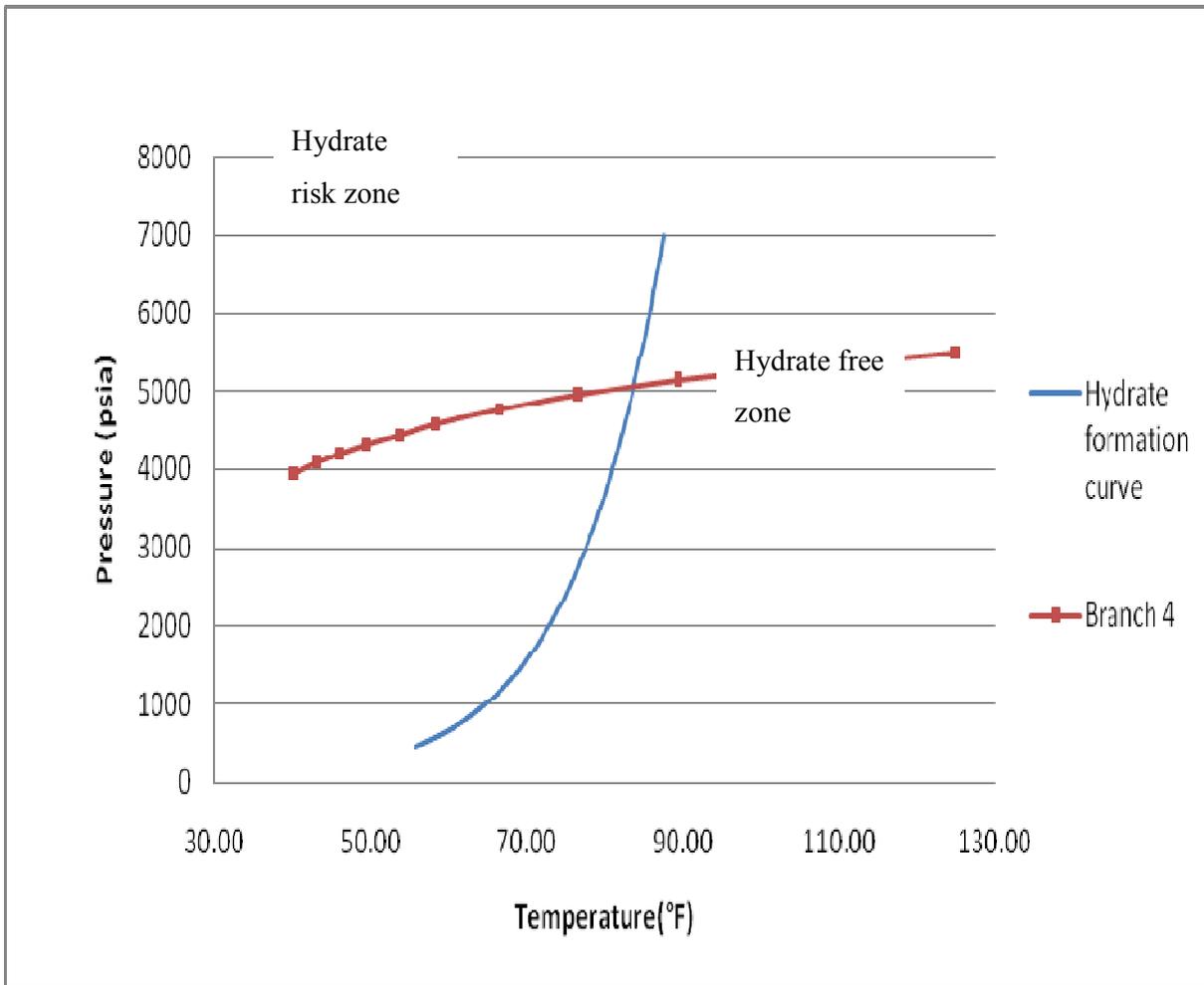


Figure 4.3: Hydrate formation curve and Temperature-Pressure profile of Branch 4

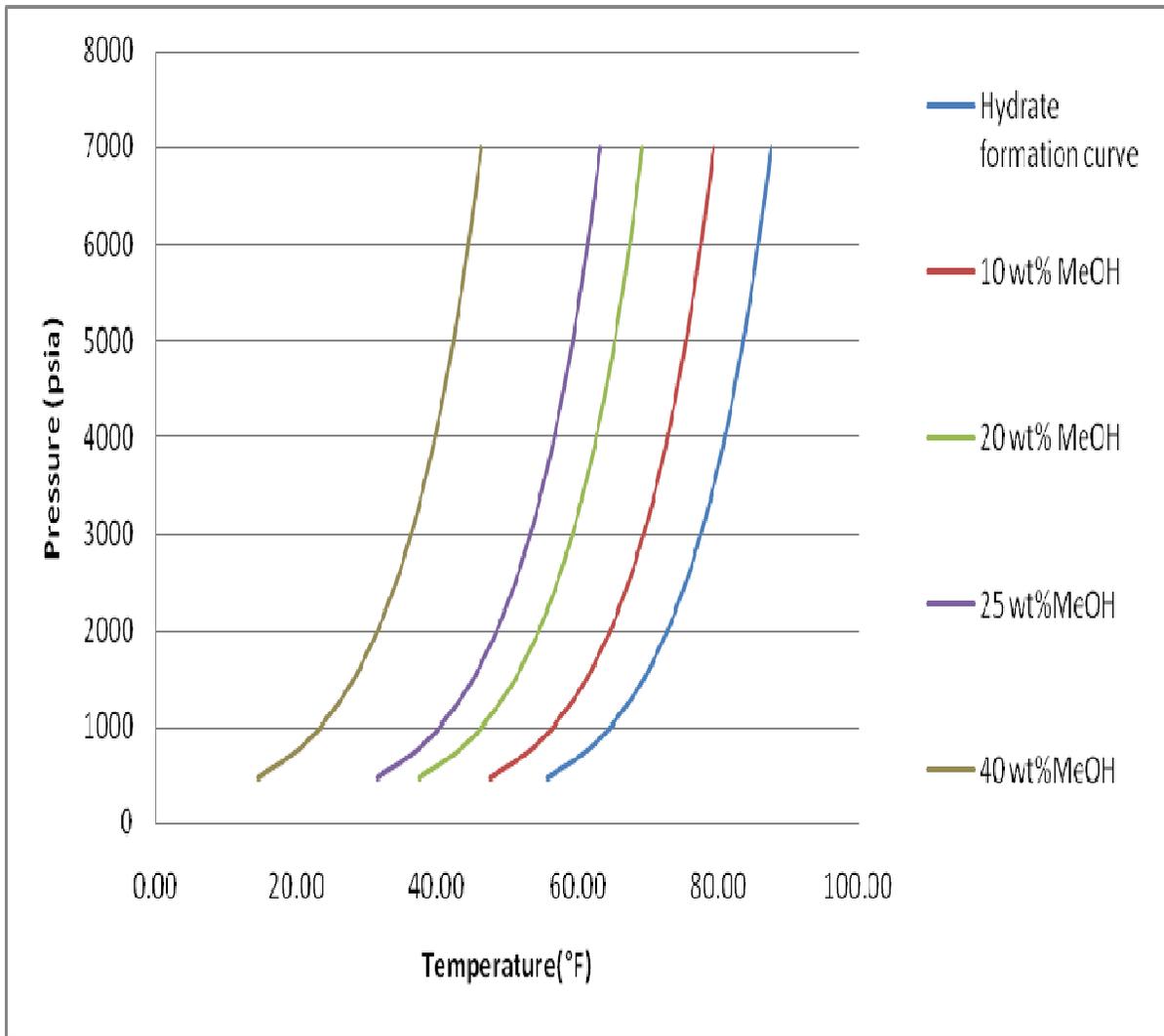


Figure 4.4 Hydrate formation curve with varying methanol concentration

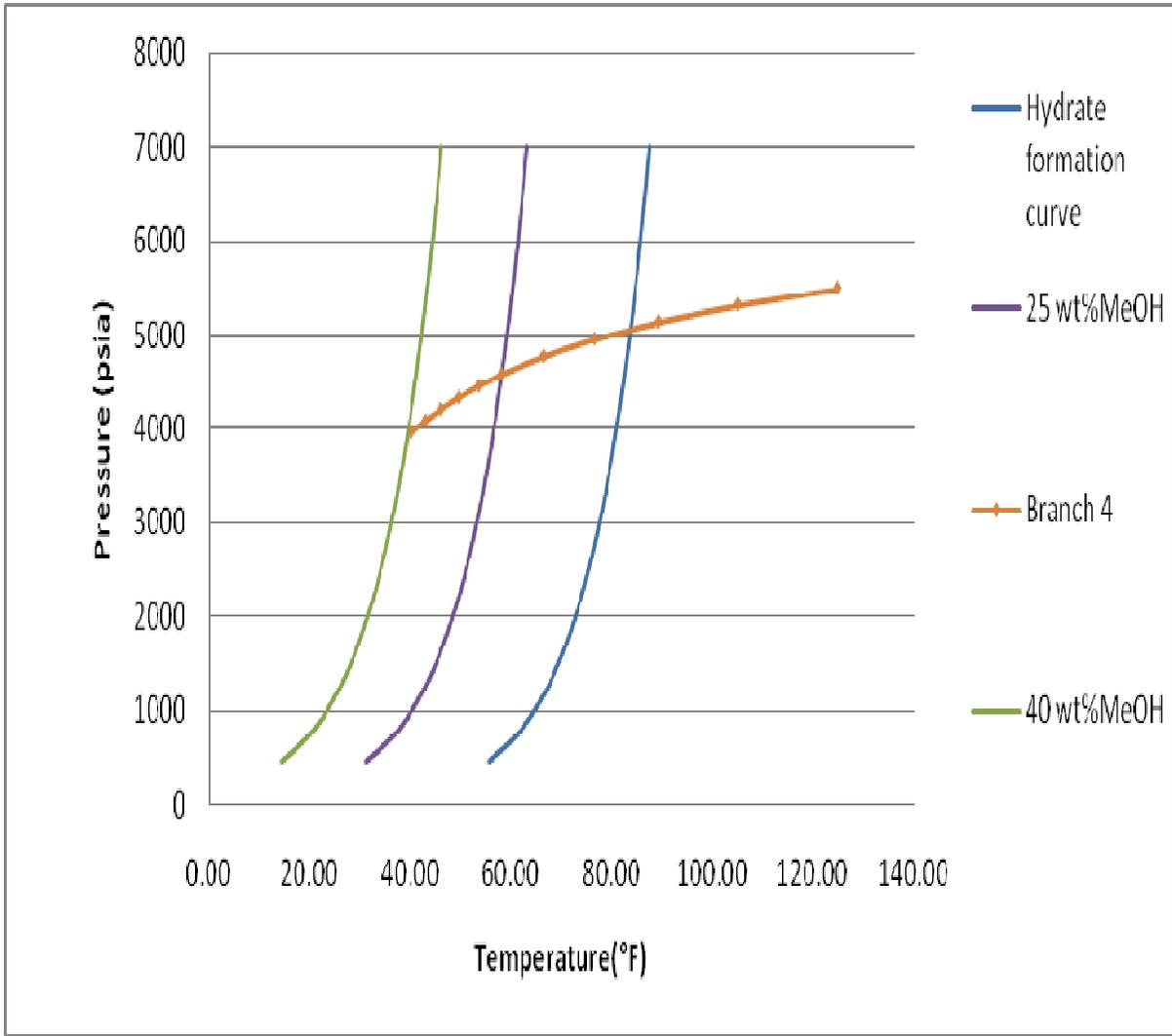


Figure 4.5: Effect of MeOH on fluids in Branch 4.

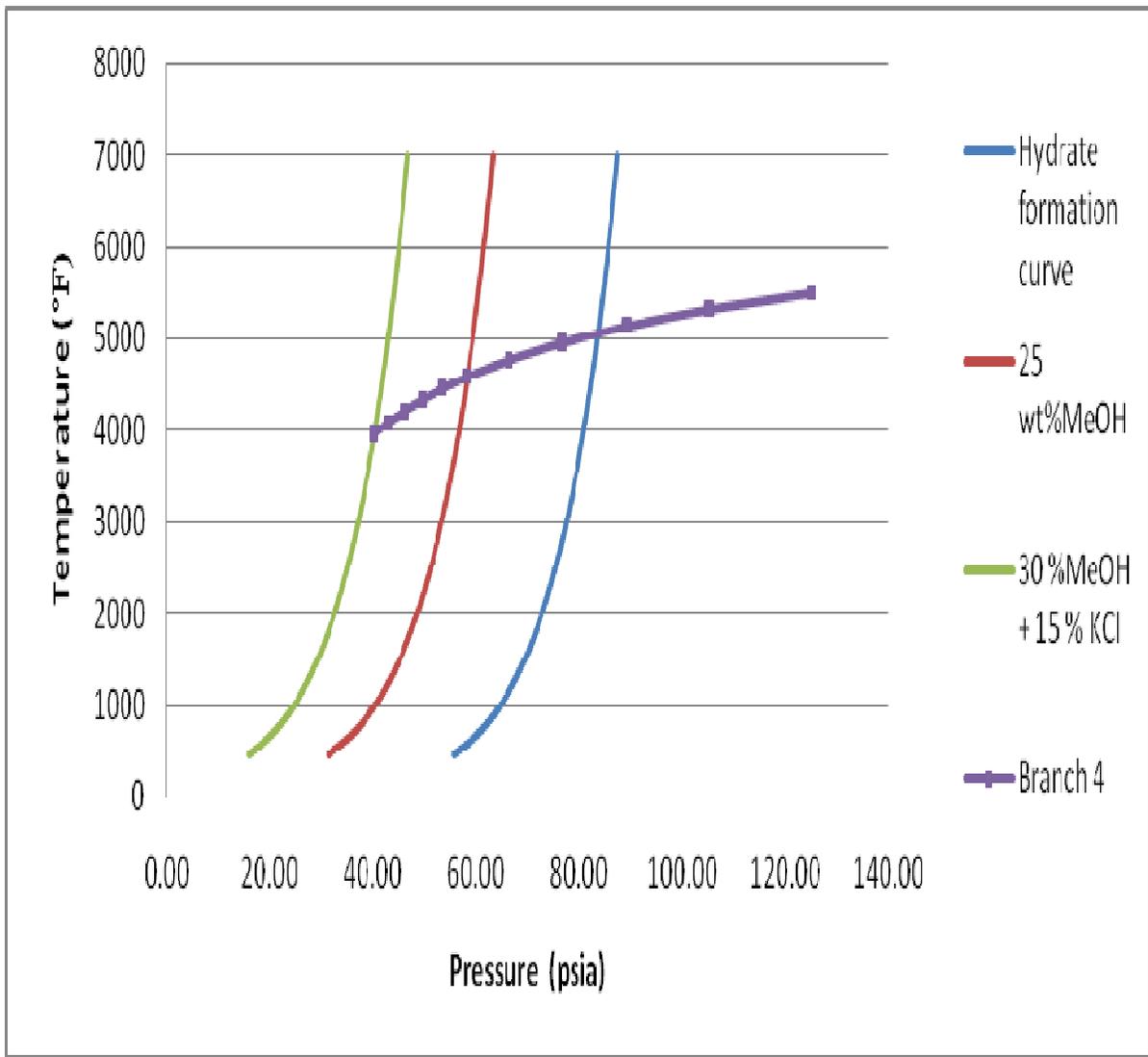


Figure 4.6: Effect of MeOH – KCl hybrid inhibitor on Branch 4.

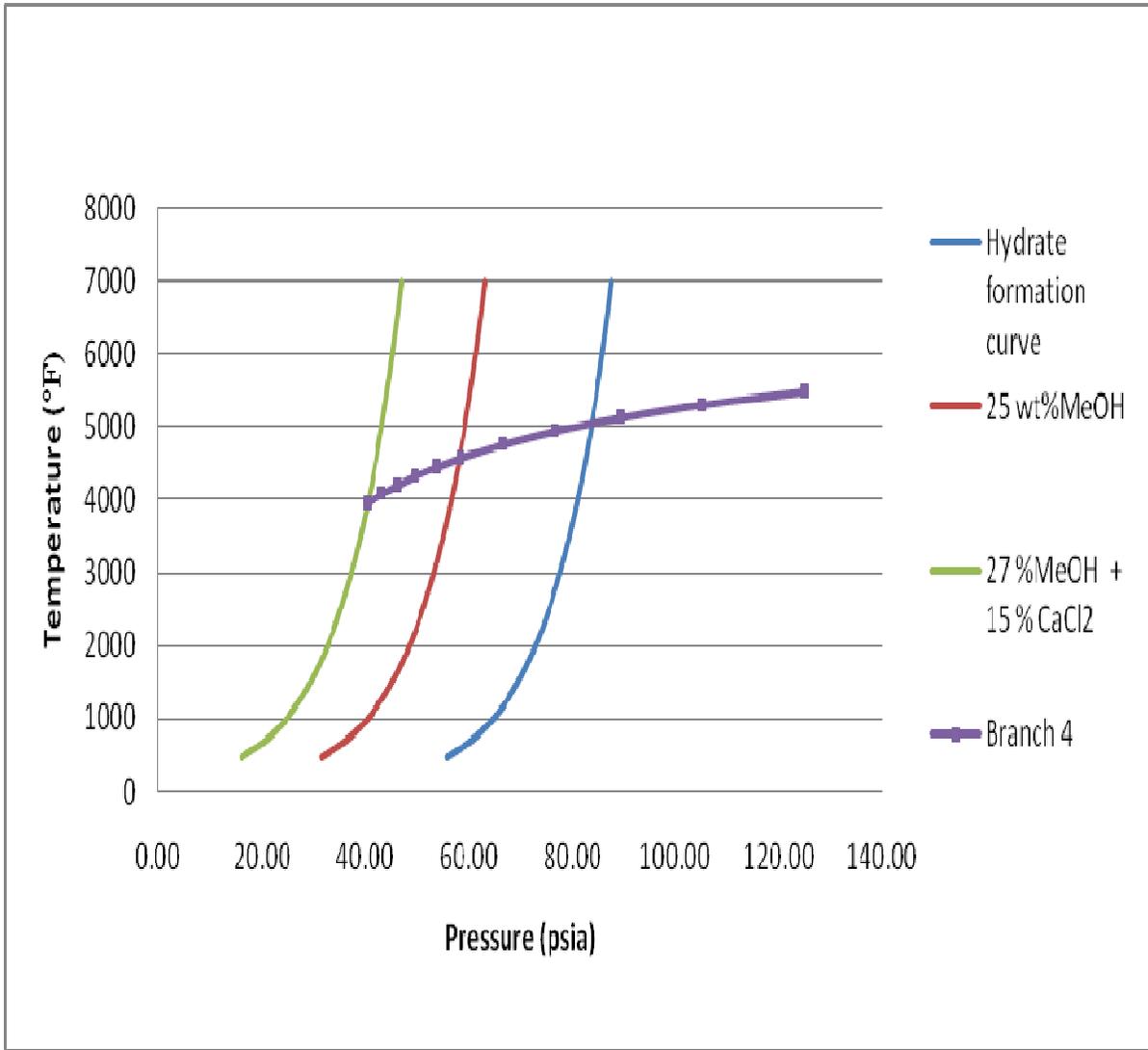


Figure 4.7: Effect of MeOH - CaCl₂ hybrid inhibitor on fluids in Branch 4.

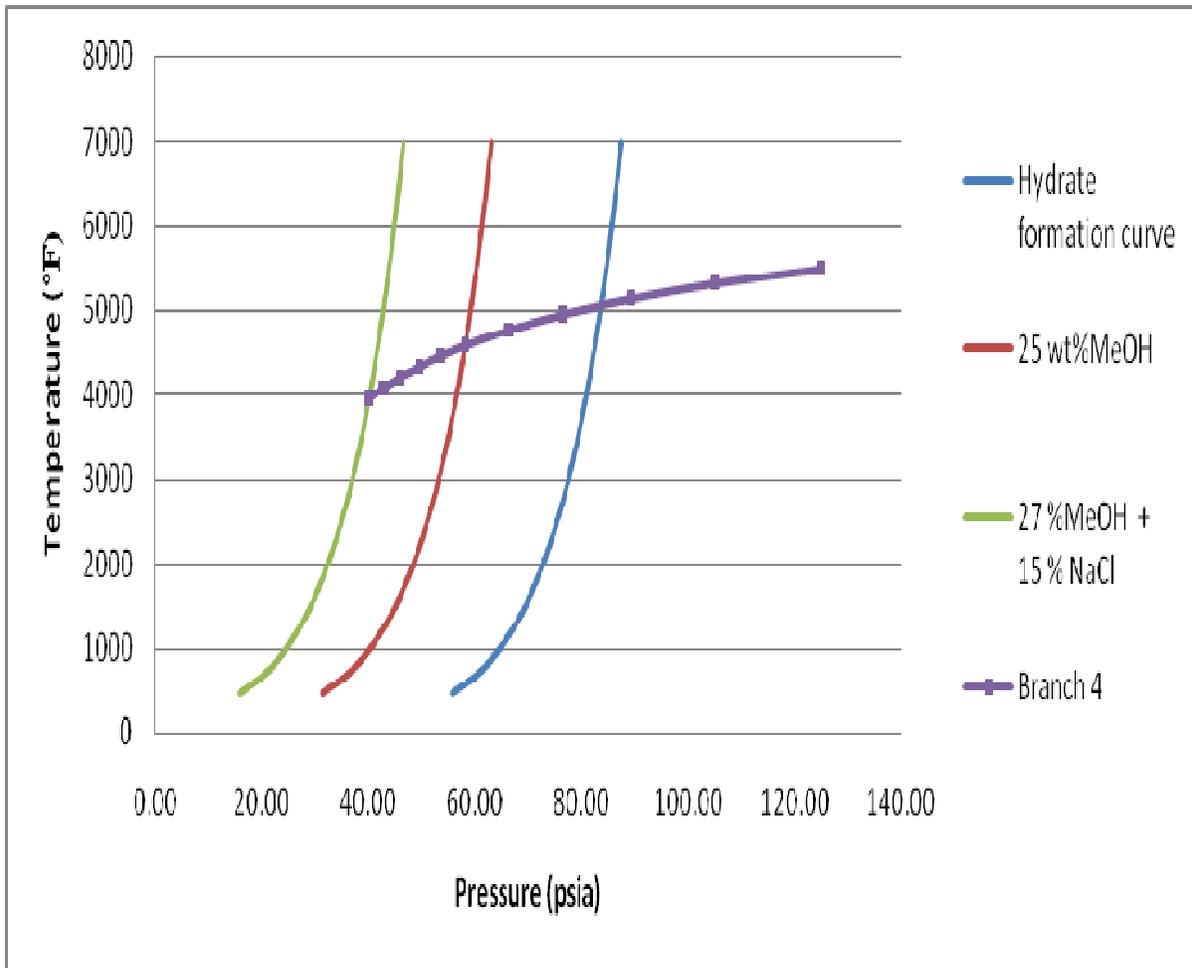


Figure 4.8: Effect of MeOH - NaCl hybrid inhibitor on fluids in Branch 4

4.1.2 BRANCH 9

Figure 4.9 is the pressure profile of Branch 9 while Figure 4.10 is the temperature profile of Branch 9. Figure 4.11 shows how the temperature of the fluid in Branch 9 varies with the pressure as the fluid flows through Branch 9. The hydrate formation curve of fluid in Branch 9 is given in Figure 4.12. Figure 4.13 shows the hydrate formation curve and the temperature-pressure profile of Branch 9. It indicates that Branch 9 is operating in the hydrate risk zone. Figure 4.14, Figure 4.15, Figure 4.16 and Figure 4.17 show effect of MeOH and MeOH hybrid inhibitors on hydrate formation conditions of Branch 9 fluid. Figure 4.18 is the process flow diagram of the field considered.

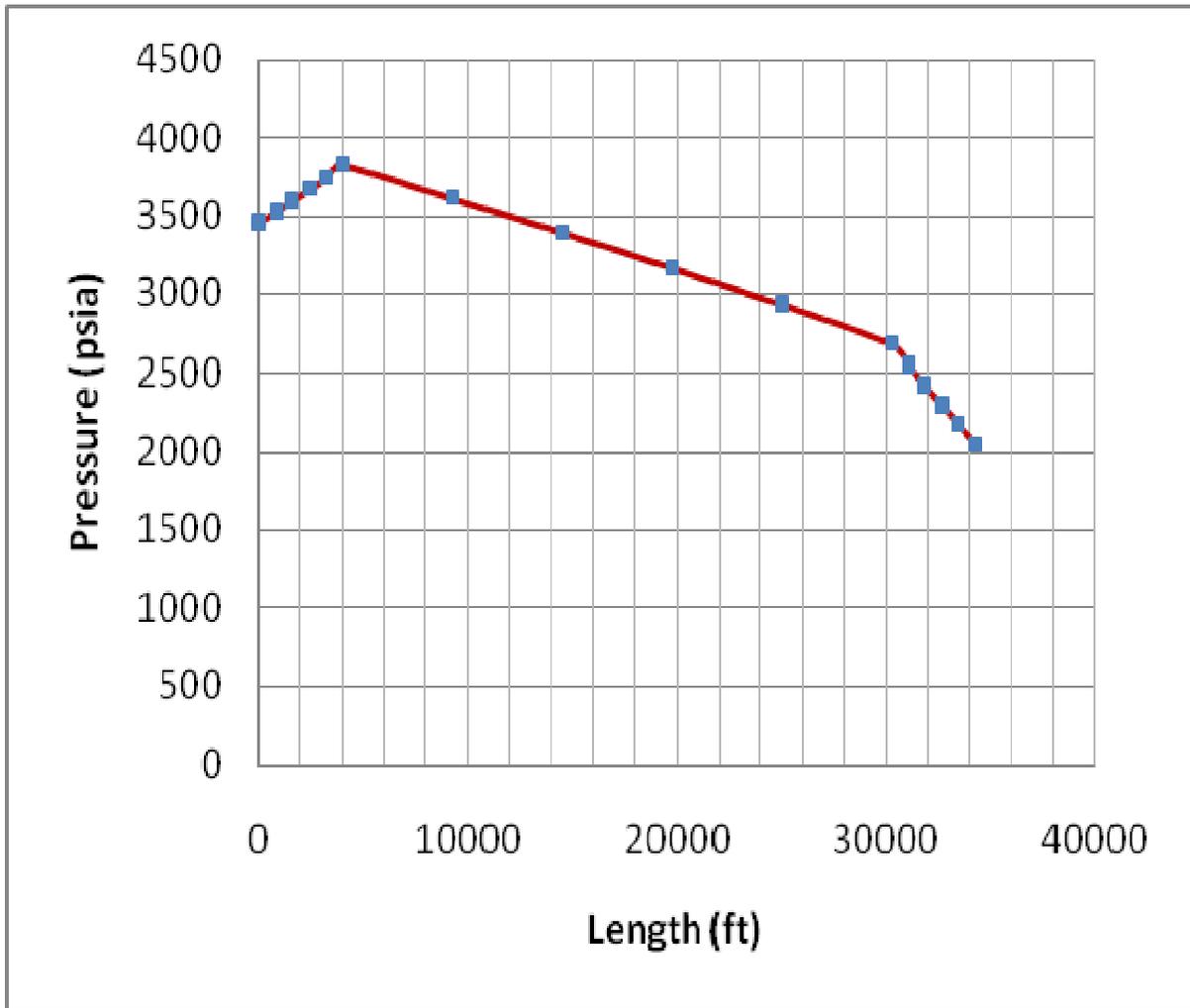


Figure 4.9 Pressure profile of Branch 9.

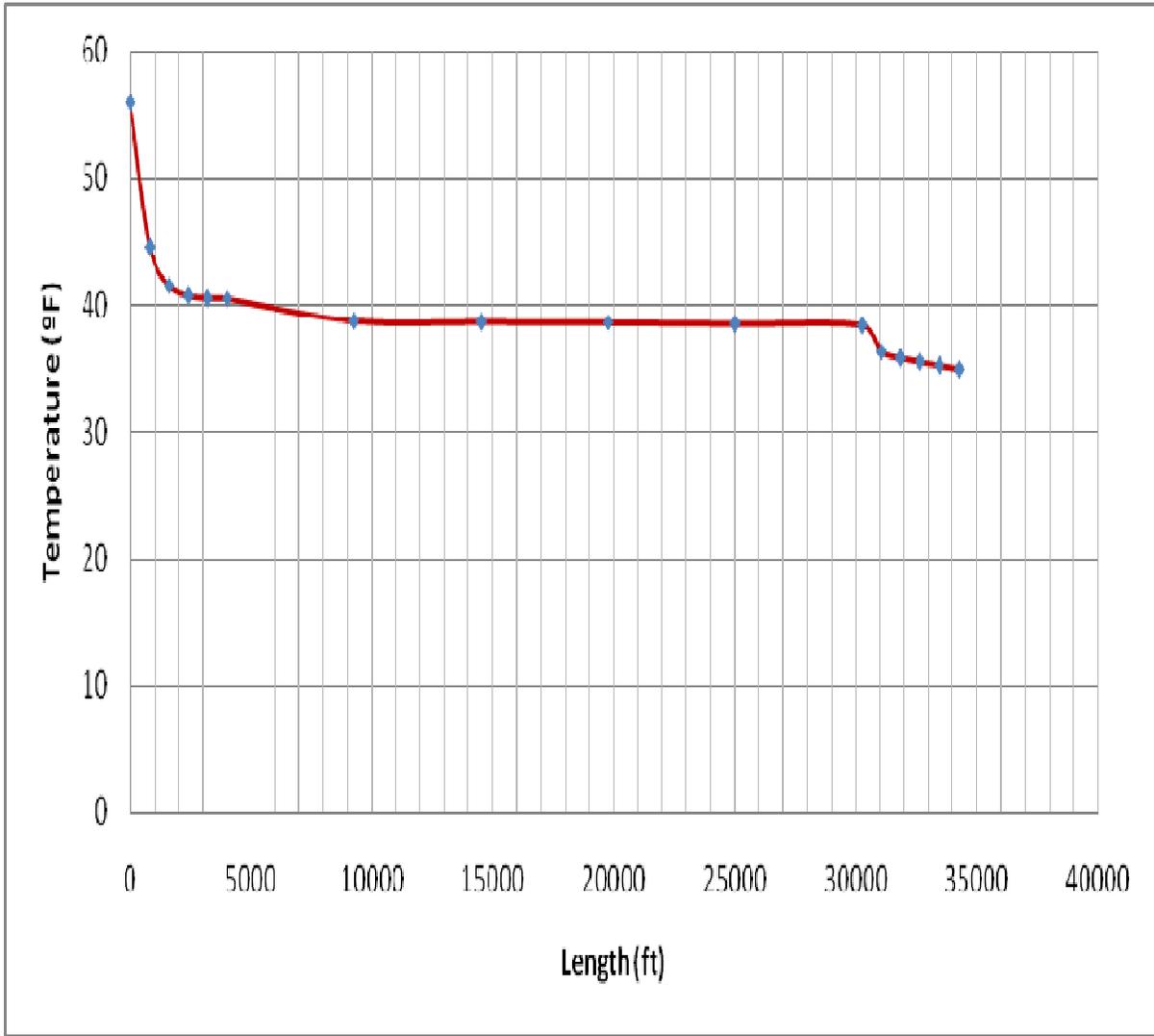


Figure 4.10 Temperature profile of Branch 9

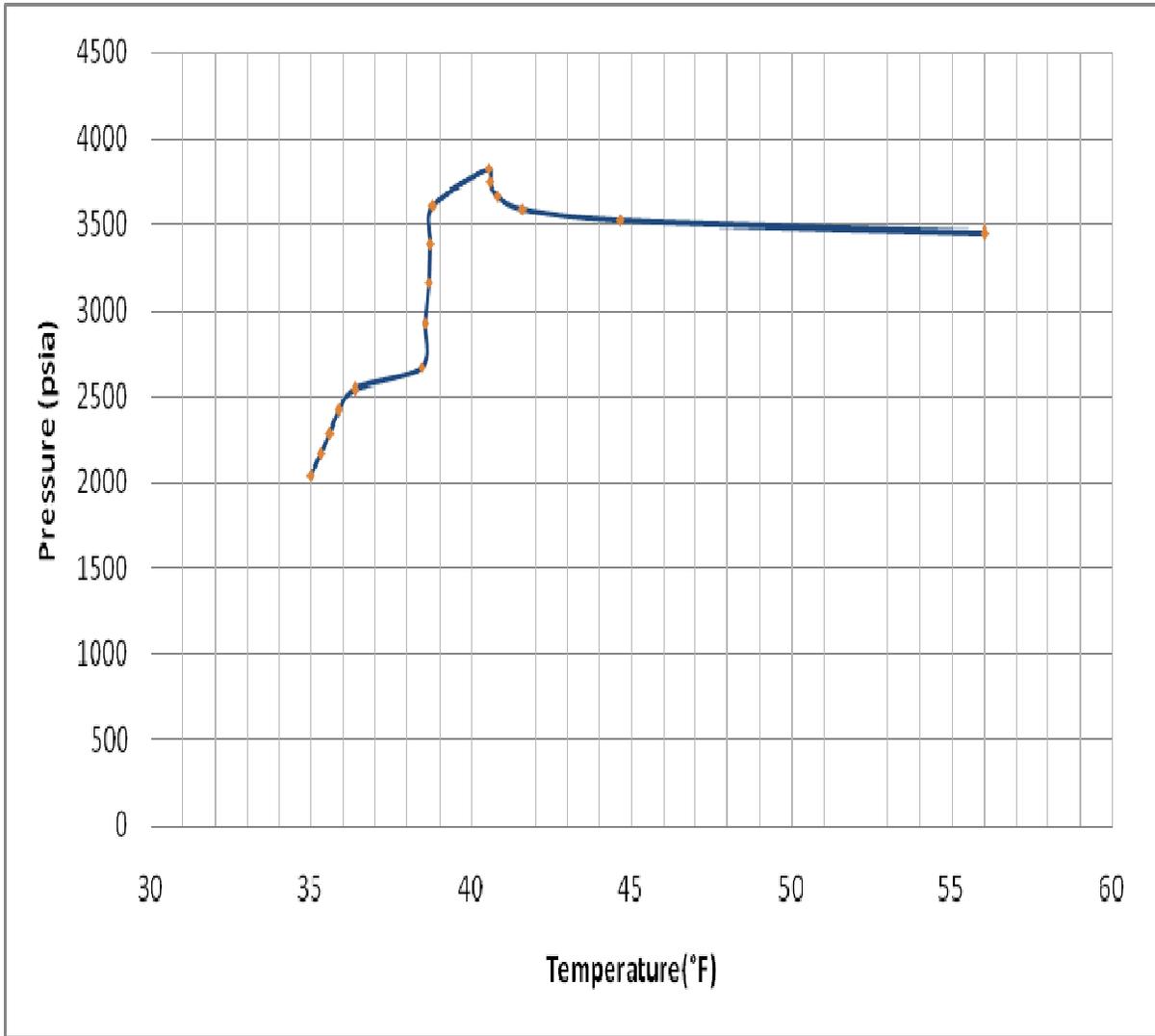


Figure 4.11 Temperature-Pressure Profile Branch 9.

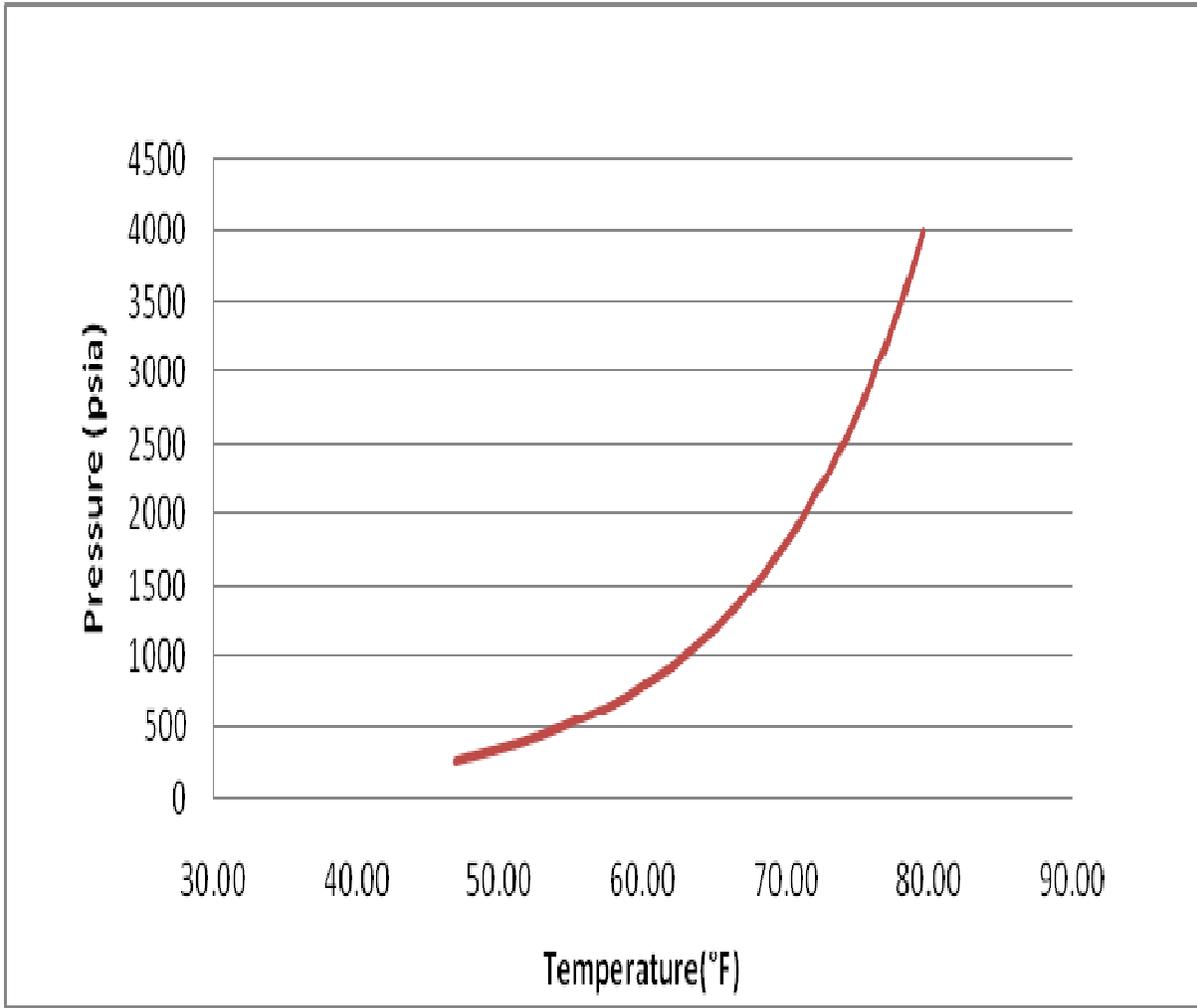


Figure 4.12: Hydrate formation curve of fluid in Branch 9

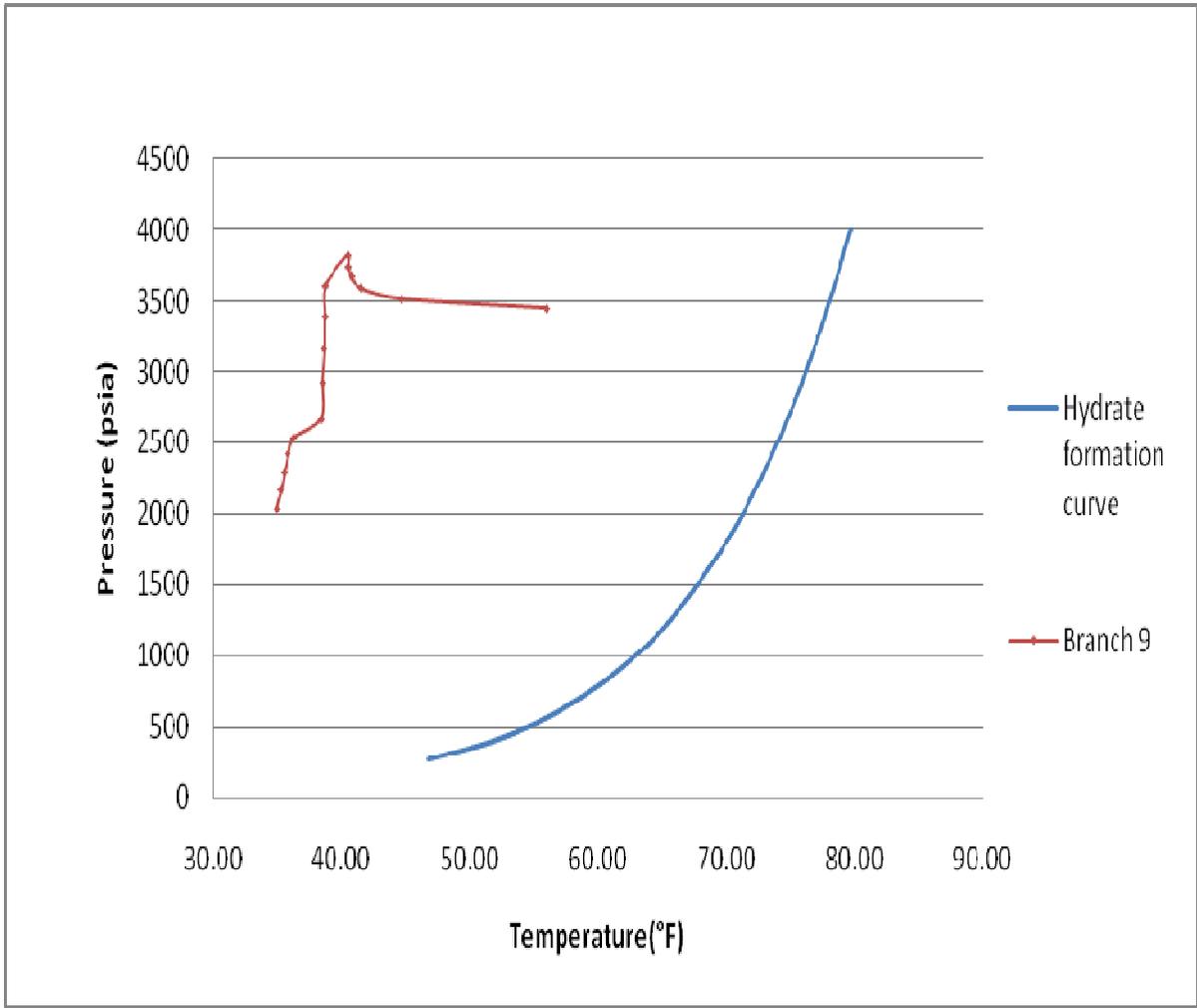


Figure 4.13 Hydrate formation curve and temperature- pressure profile of Branch 9.

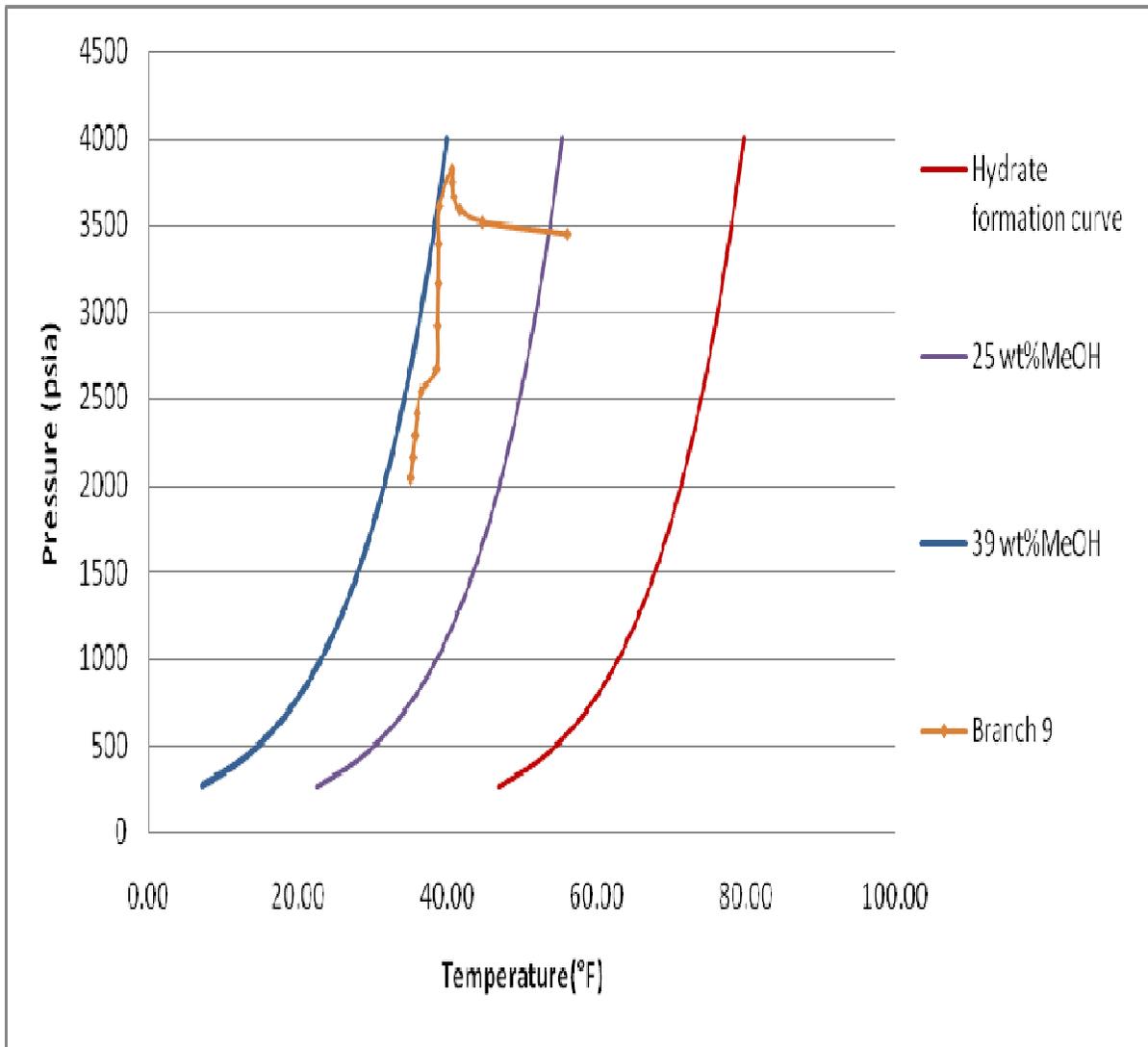


Figure 4.14: Effect of MeOH on fluids in Branch 9

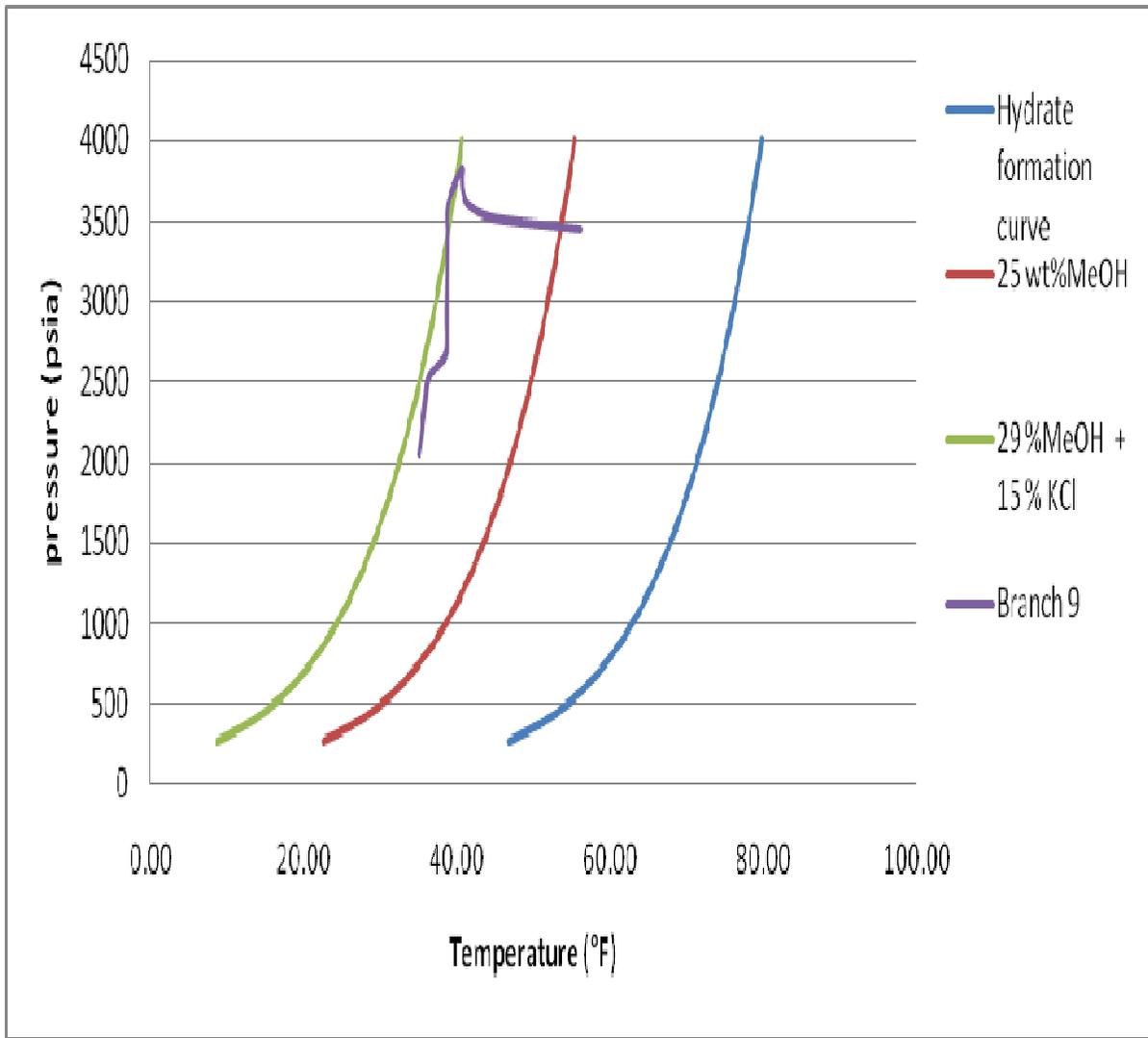


Figure 4.15: Effect of MeOH-KCl hybrid on Branch 9

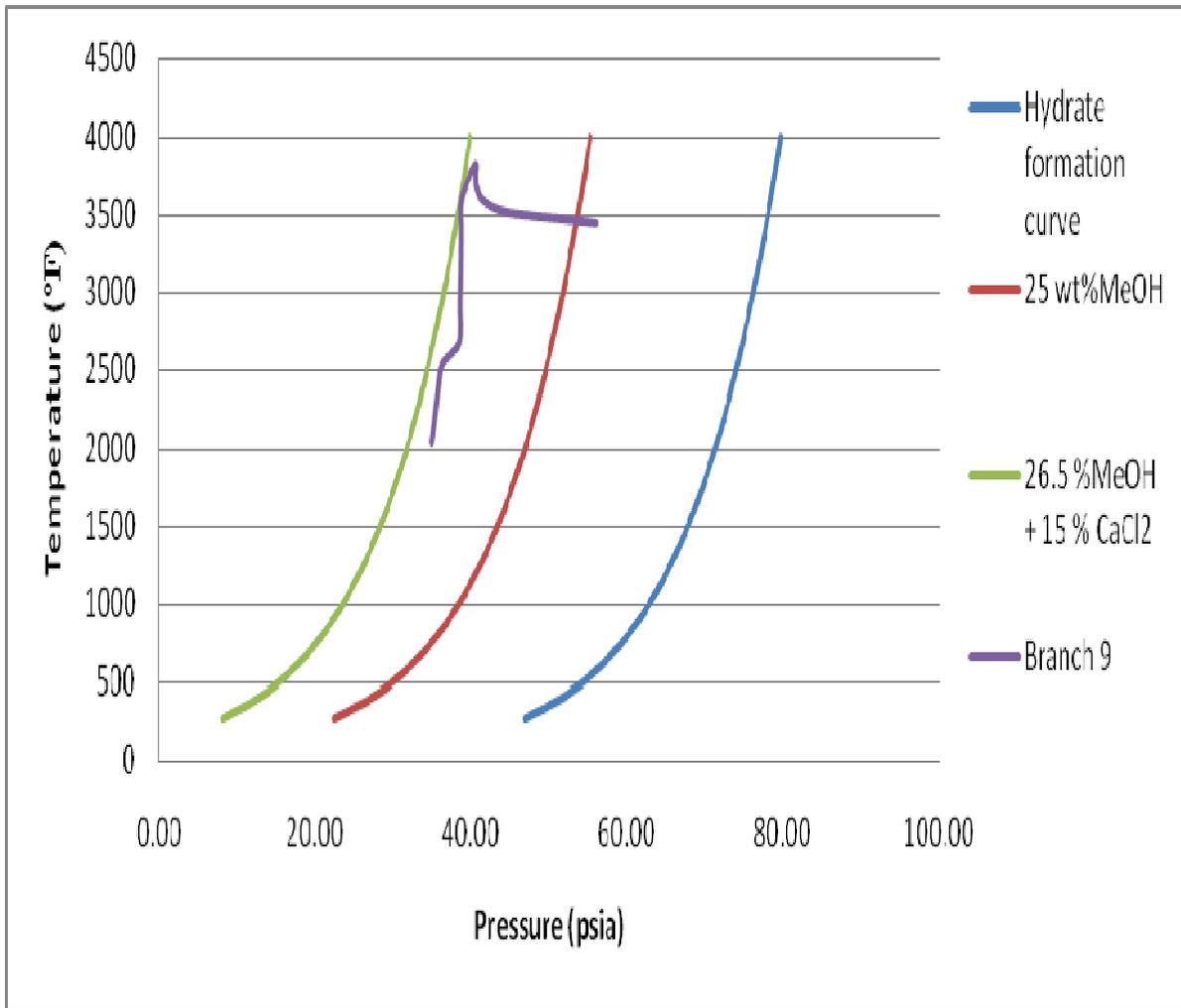


Figure 4.16: Effect of MeOH-CaCl₂ Hybrid on Branch 9

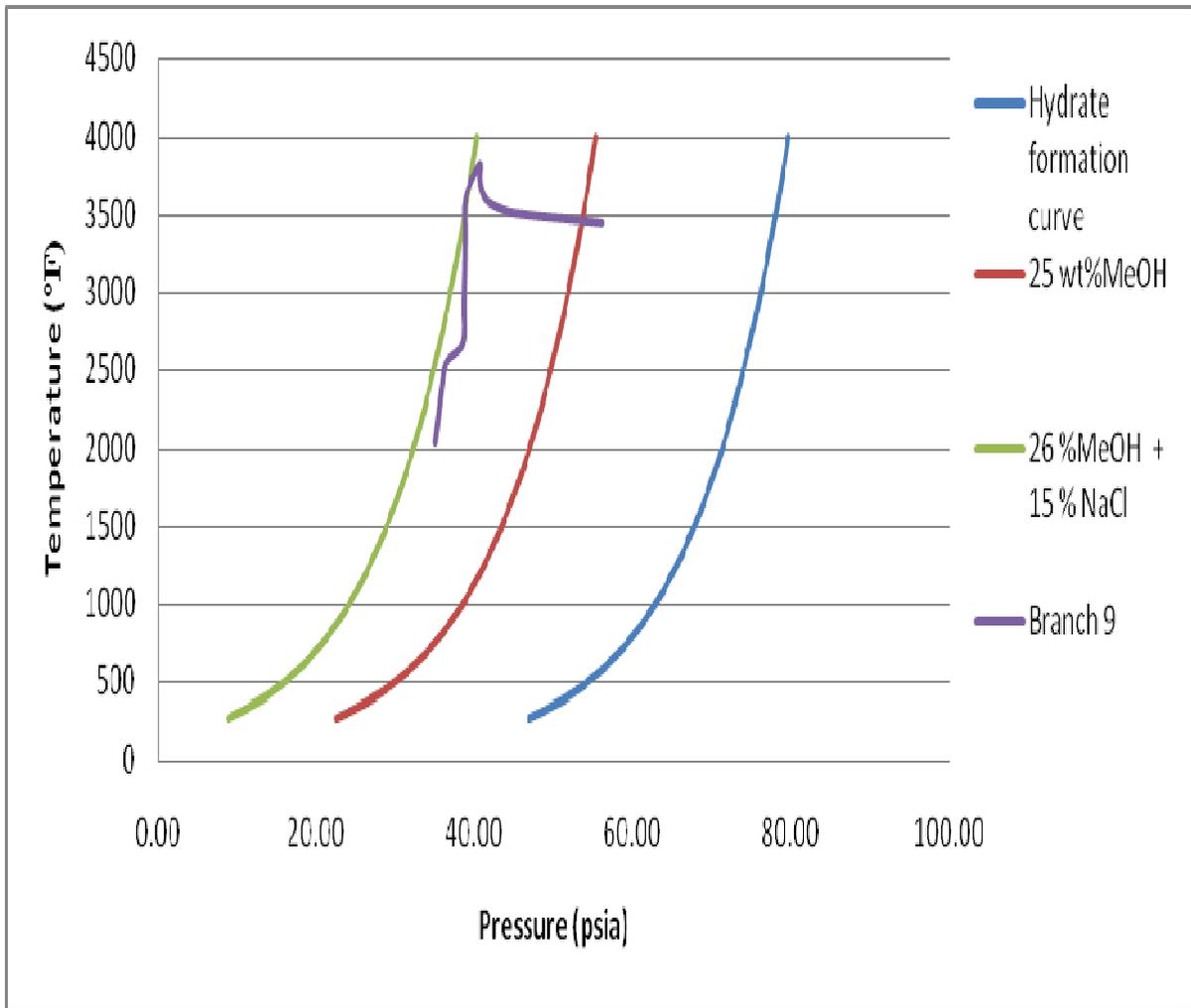


Figure 4.17: Effect of MeOH-NaCl hybrid on Branch 9

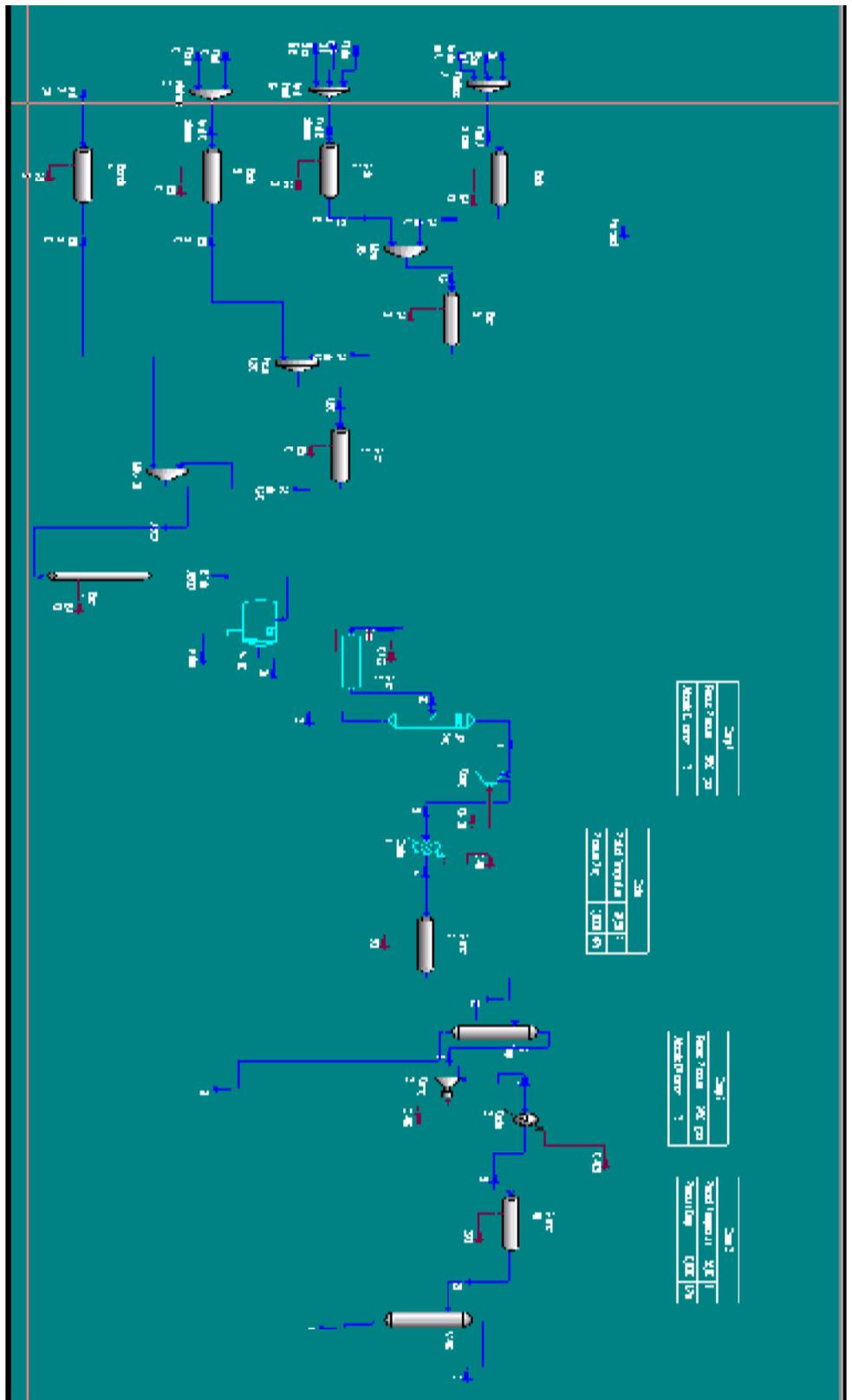


Figure 4.18: Process Flow Diagram of fictitious offshore field modelled with Hysys

4.2 DISCUSSION

The field considered is a fictitious offshore field which delivers 147 MMScf/day of gas to a sales point 16 km away from the production platform. This field, with water depth of 4000ft, has two gas wells, (Well C and Well D) and two oil wells (Well A and Well B). Oil Well A flows into Branch 1 at a temperature of 124.1 °F and a pressure of 3185 psia, while oil from Well B flows into Branch 2 at a temperature of 113.4 °F and a pressure of 4000 psia. The two oil streams mix up and pass through Branch 5 at a pressure of 3000 psia and a temperature of about 49 °F. Gas well C flows into Branch 3 at a pressure of 5303 psia and a temperature of 120 °F. This stream is mixed with oil coming from Branch 5 and gas from Well D, flowing through Branch 4 at a pressure of 5493 psia. The mixture of oil and gas streams flows through the production riser (Branch 7) to the production platform 4000 ft above the sea bed, where separation takes place.

After separation into three phases (oil, gas and water), the outlet gas stream from the separator has a pressure of 1873 psia (Table 4.1) which is insufficient to transport the gas from the production platform to the sales point 16 km away. Hence, the pressure of the gas is boosted by passing it through a compression station. Notice that the gas stream is passed through a vertical separator where 0.11 bbl/day of water is knocked out before it is sent to the compressor where the gas pressure is increased to 3450 psia (Figure 4.18). This pressure will enable the gas travel 8km from the production platform to land (through Branch 9) where another compression station boosts the pressure to 3450 psia so that the gas finally travels through Branch 10 to the sales point which is 8km away from the shore.

The ocean floor temperature, which is uniform at about 39 °F, provides an infinite cooling medium for the warm fluids flowing through the pipes. This causes the temperature of the fluid in the pipes to drop. There is also pressure loss as the mass of fluid traverses the pipes due to friction. Gas from Well C enters Branch 3 at a temperature of 119.2 °F, but leaves at a temperature of 39.1 °F and experiences a pressure drop of 15 psia. Gas from Well D enters Branch 4 at a temperature of 123.1 °F but leaves at a temperature of 40.3 °F and a 567 psia pressure drop is experienced. Branch 4 (10000ft) experiences more pressure drop than Branch 3 (2460 ft long) due to the distance the fluid has to travel. Notice that Branch 7 which is 4000ft long experiences a pressure drop of about 871 psia which is greater than the pressure drop experienced by the 10000 ft pipe (Branch 4). This is because, unlike other pipes in this field, Branch 7 is a vertical pipe and will be affected by frictional and gravitational forces, whereas flow through other horizontal pipes will be affected by only frictional forces.

Due to high pressures experienced in this field, low marine temperature and water production during the late stage of the field, there is high risk of hydrates plugs forming in the

flowlines. Branch 4 and Branch 9 will be critically examined for hydrate problems the effect of the various inhibitors on hydrate formation conditions of fluids in these pipes (Branch 4 and Branch 9) are discussed.

4.2.1 Branch 4

Branch 4 is the 10000 ft long flow line that conveys gas from well D. Gas flows into Branch 4 at a temperature of 123 °F and a pressure of 5493 psia and leaves Branch 4 at a temperature of 40.3 °F and a pressure of 4926 psia.

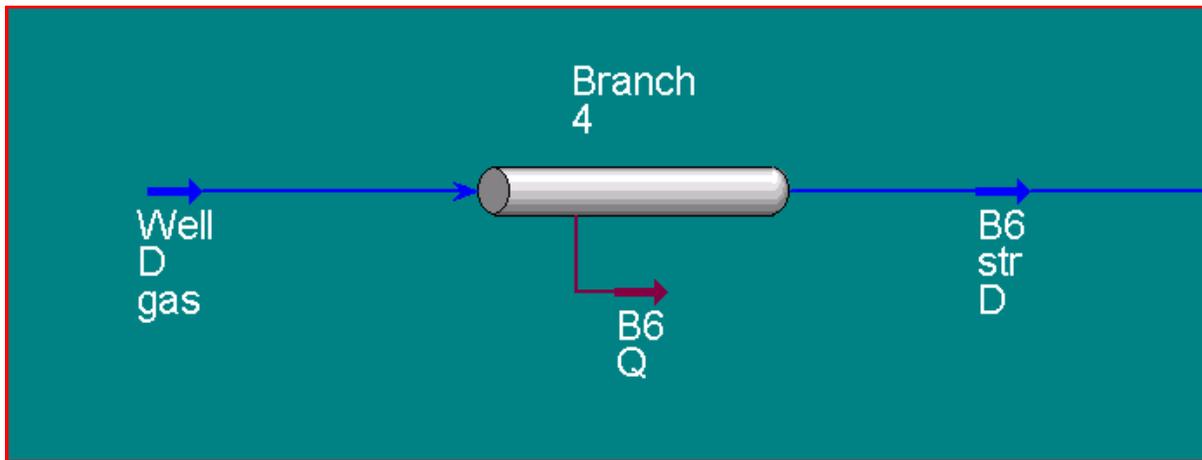


Figure 4.19: Hysys representation of Branch 4

The hydrate formation curve for Branch 4 fluid slopes downwards from right to left. At high pressures, hydrate formation temperature is relatively high and at low pressures, it is relatively low. At a pressure of 7000psia, the hydrate formation temperature for fluids in Branch 4 is 87.5 °F, at 5000 psia, the hydrate formation temperature is 83.6 °F, while, at 1000psia, the hydrate formation temperature is 64.7 °F.

The hydrate risk zone is the region by the left of the hydrate formation curve (Figure 4.3), while the region by the right of the curve is the hydrate free zone. The hydrate risk zone covers temperatures as high as 87 °F (at 7000 psia) to temperatures of 55°F (at 466 psia). Branch 4 operates at temperatures lower than 55°F (Figure 4.2) and experiences subcooling as high as 42 °F at 3957 psia (Table 4.7). Without inhibition, the risk of hydrate formation is high. At 84°F, fluids in Branch 4 will cross the hydrate formation curve from the hydrate free zone to the hydrate risk zone (Figure 4.3). This occurs at a length of 4000ft (Figure 4.1). Inhibitors will therefore be required to move

the gas though the 10000ft flowline without hydrate blockage.

Hydrate formation curves with varying concentration of MeOH, MEG and DEG were obtained using Katz, Nielsen Bucklin and Hammerschmidt equations. With increasing weight of methanol, the hydrate formation curve shifts towards the left, increasing the hydrate free zone (Figure 4.4). For a pressure of 7000 psia and a methanol concentration of 20wt%, the hydrate formation temperature of fluid in Branch 4 reduces to about 69.3 °F from the initial 87.5 °F (Table 4.4). The addition of MEG and DEG display a similar trend, shifting the hydrate formation curve to the right with increasing concentration of DEG and MEG (Appendix B)

MeOH gives a higher temperature depression than the DEG and MEG at specific concentration. 10% by weight of MeOH causes a temperature depression of 8.1°F (Table 4.6) which reduces the hydrate formation temperature of fluid in Branch 4 to 79.4 °F at a pressure of 7000 psia (Table 4.4). The temperature depression when 10% by weight of MEG and 10% by weight of DEG were considered was 4.8°F and 4.2°F respectively. In like manner, this reduced the hydrate formation temperature at 7000 psia to 82.7 °F when MEG is used and 83.3 °F when DEG is used.

Increasing the quantity of inhibitor used increases the temperature depression and reduces the hydrate formation temperature at a particular pressure. When 20% by weight of MeOH was used, the temperature depression increased to 18.2 °F (Table 4.6) and the hydrate formation temperature was given as 65.3 °F at 5000 psia (Table 4.4). At 40% by weight of MeOH, the temperature depression was 41.3°F decreasing the hydrate formation temperature of fluids in Branch 4 at 5000 psia to 42.3°F (Table 4.4). Temperature depression also increases in the presence of an ionic THI. The temperature depression observed when a 20wt% MeOH is used is 18.2 °F whereas, with a 10 wt% MeOH in the presence of 15wt% CaCl₂, the temperature depression is about 21.7 °F (Table 4.6). A similar trend is observed when Mono Ethylene Glycol and Di Ethylene Glycol are combined with the sodium chloride, calcium chloride and potassium chloride salts. Charts are given in Appendix B.

40% by weight of MeOH is required to prevent hydrates from forming in Branch 4 (Figure 4.5). The amount of methanol required to prevent hydrates from forming reduces drastically when MeOH is combined with salt. 30% by weight of MeOH when combined with 15% KCl salt will fully prevent fluid in Branch 4 from forming hydrates (Figure 4.6). This implies that 10% by weight of MeOH will be saved by the addition of 15% by weight of KCl salt. When the hybrid consists of MeOH and CaCl₂, about 27% by weight MeOH will be combined with 15% by weight of CaCl₂ to prevent hydrate formation (Figure 4.7). Similarly, 27% by weight of MeOH when combined with 15% by weight NaCl will effect a hydrate free operation in Branch 4 (Figure 4.8).

4.2.2 Branch 9

Branch 9 travels 8km from the production platform to land conveying gas leaving the separator. Gas from separator enters Branch 9 at 56 °F and 3450 psia and leaves Branch 9 at 35.53 °F and a pressure of 2179 psia.

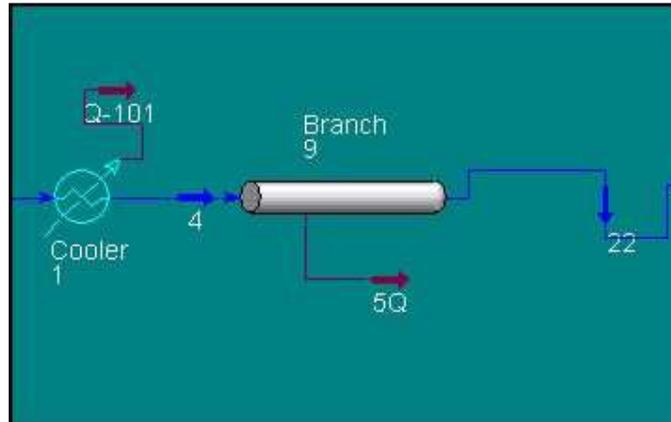


Figure 4.20: Hysys representation of Branch 9

The pressure of gas in Branch 9 increases from 3450 psia to 3821 psia (Figure 4.9) as Branch 9 approaches the sea bed from the production platform. This is followed by a gradual decrease in pressure from 3821 psia and a subsequent rapid decrease in pressure to 2043 psia. The temperature of gas in Branch 9 decreases from 54 °F to 34 °F (Figure 4.10). The shape of the pressure profile and Temperature profile of Branch 9 is due to the elevation profile of Branch 9 (Figure 4.21).

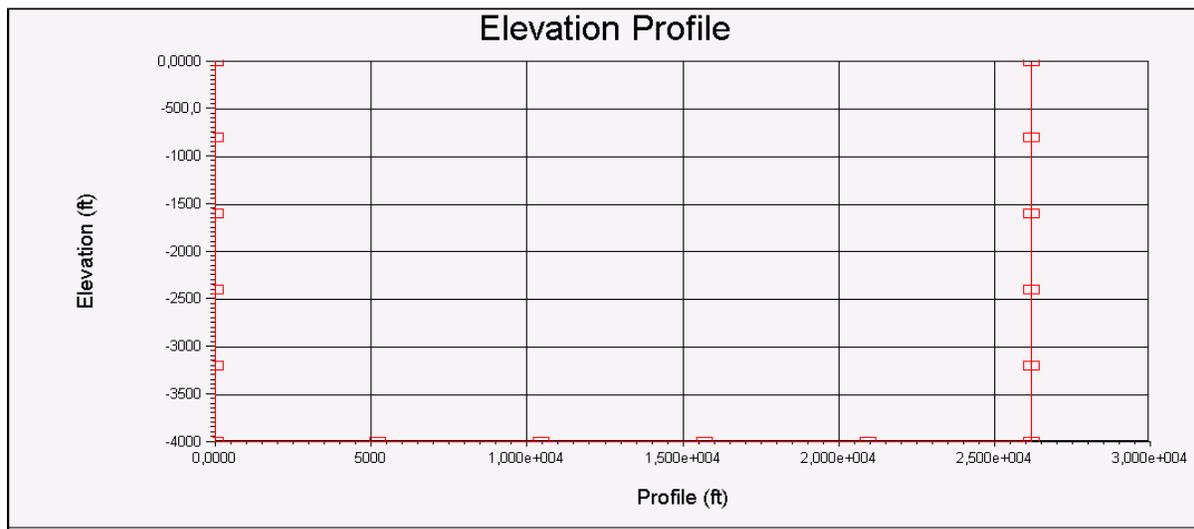


Figure 4.21: Elevation Profile of Branch 9

The hydrate formation curve of Branch 9 has a similar shape to that of Branch 4 (Figure 12). At pressure of 4000 psia, the hydrate formation temperature is 79.9 °F, at 3000 psia, the hydrate formation temperature is 76.2 °F and at 1000 psia, the hydrate formation temperature reduces to 62.9 °F. This implies that at higher pressures, the hydrate formation temperature is relatively high. The hydrate risk zone is the region by the left of the hydrate formation curve of Branch 9 while the hydrate free zone is the region by the right of the hydrate formation curve of Branch 9. Branch 9 operates at temperatures as low 35 °F as and experiences subcooling as high as 40 °F (Table 4.7). Figure 4.12 indicates that that Branch 9 operates in the hydrate risk zone. Therefore, there is high tendency of hydrate plugs forming in Branch 9. Inhibitor will therefore be required to effectively move the gas through Branch 9 without hydrate problems.

The effect of MeOH, MEG and DEG and their hybrid were evaluated. Increasing concentration of inhibitor causes an equivalent increase in temperature depression and a subsequent decrease in the hydrate formation temperature. This causes the hydrate formation curve to shift towards the left, increasing the hydrate free zone and decreasing the hydrate risk zone (Figure 4.14). The hydrate formation curve shifts to the left when 25% by weight of MeOH was used in Branch 9. However, hydrates problems will still be encountered since a larger portion of Branch 9 still operate in the hydrate risk region (Figure 4.14). As the concentration of MeOH inhibitor increases, the hydrate formation curve gradually shifts to the right until the MeOH concentration was increased to 39% by weight of MeOH. At this point, the temperature-pressure curve of Branch 9 completely crosses from the hydrate risk zone to the hydrate free zone. This implies that if 39% by weight of MeOH is added to Branch 9, there is no risk of hydrates plugging the line. A similar trend is obtained when MEG and DEG inhibitors are used. 47.7% by weight of MEG will be required to ensure Branch 9 operates in a hydrate free zone and 51.4% by weight of DEG ensures a hydrate free operation of Branch 9 (Table 4.2).

At 4000 psia, 40 % by weight of MeOH will be required to depress the hydrate formation temperature of fluids in Branch 9 to 38.4 °F (Table 4.4) whereas, in the presence of 15% CaCl₂ salt, only 27% by weight of MeOH, is required to achieve a hydrate formation temperature of 39.2 °F (Table 4.5).

The temperature depression when 10wt% MeOH was used is 8.1 °F this increases to 41.3 °F when a 40wt% MeOH was used, decreasing the hydrate formation temperature of fluids in Branch 4 at 4000 psia, from 79.7 °F (without inhibition) to 38.4 °F when 40% by weight of MeOH is used. When hybrid inhibitors were considered, the temperature depression greatly increased. In the presence of 15% CaCl₂ salt and 20% by weight of MeOH the temperature depression increased to 31.9 °F (Table 4.6), decreasing the hydrate formation temperature to 47.8 °F at 4000 psia. The

temperature depression when a 20% by weight MeOH in the presence of 15% by weight KCl salt was used is 27.6 °F and the hydrate formation temperature is 52.1 °F at 4000psia. When a MeOH NaCl hybrid is used, the hydrate formation temperature at 20 wt% MeOH and 15 wt% NaCl is 47.5 °F and the temperature depression is 32.2 °F. The same trend is observed when MEG-KCl, MEG-CaCl₂, MEG-NaCl, DEG-KCl, DEG-CaCl₂ and DEG-NaCl, are used in Branch 9 (Appendix C).

The quantity of inhibitor required in each pipe is a function of design temperature and pressure, fluid composition and water available for hydrate formation. The inhibitors added interfere with the hydrogen bond of water in the stream to prevent hydrate formation. Branch 4 has 998.63 bbl/day of water while Branch 9 has 2.678 bbl/day of water in the stream (Table 4.1). Branch 4 will therefore require a larger volume of inhibitor than Branch 9.

The quantity of MeOH required in each case is always less than the quantity of MEG or DEG required. For instance, the quantity of MeOH required in Branch 4 when no inhibitor was used is 3763 bbl/day while the MEG required is 4531 bbl/day and the DEG required is 5317bbl/day (Table 4.2). Similarly, the quantity of MeOH required to completely prevent hydrate formation in Branch 4 in the presence of NaCl is 2087 bbl/day the MEG is 3008.5 bbl/ day and the required DEG is 3411 bbl/day. 44.5% of MeOH will be saved when MeOH-NaCl and MeOH CaCl₂ hybrid is used in Branch 4. Similarly, 45% of MeOH will be saved when MeOH-NaCl hybrid is used in Branch 9 (Table 4.3).

When equal volumes of Methanol and salt are used at specific pressures, the hydrate formation temperature in the presence of NaCl is always less than the hydrate formation temperature in the presence of other salts. The hydrate formation temperature of fluid in Branch 4 at 5000 psia in the presence of 27 wt% MeOH and 15 wt% CaCl₂ is 43.0°F, the hydrate formation temperature at same pressure when MeOH-NaCl hybrid is used is 42.7°F while the hydrate formation temperature when MeOH-KCl hybrid is used at 5000 psia in branch 4 is 47.3°F (Table 4.5). This trend was observed when equal concentration of salt (15% by weight) was combined with 27% by weight of MEG and 27% by weight of DEG in Branch 4 and Branch 5 (Table 4.5). This implies that NaCl is more effective at depressing the hydrate formation temperature when compared to KCl and CaCl₂.

Due to the composition of the gases (Appendix D), both Type I and Type II hydrates will form in Branch 4 and Branch 9. However, the hydrate formation temperature of fluids in Branch 4 is always higher than the hydrate formation temperature of fluids in Branch 9 at a particular pressure. At a pressure of 4000psia, the hydrate formation temperature of fluids in Branch 4 is 81 °F while, that of fluids in Branch 9 is 79.7 °F. Also, at 1000 psia, the hydrate formation temperature of

Branch 4 fluids is 64.7 °F whereas the hydrate formation temperature for Branch 9 fluids at 1000 psia is 62.8 °F. The difference in hydrate formation temperatures is due to the presence of non formers, such as pentane, hexane and heptanes in Branch 9. These non formers have the tendency to lower the hydrate formation temperature of the fluid.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

From the results and discussion, the following can be concluded:

- Methanol is a more effective inhibitor because it is required in smaller quantity than other polar solvents used. When only MeOH was used, 3763 bbl/day was required in Branch 4 and 9.8 bbl/day of MeOH was required in Branch 4.
- Increasing the concentration of inhibitor will increase the temperature depression and decrease the hydrate formation temperature at a particular pressure.
- Hybrid inhibitors will reduce the quantity of polar thermodynamic inhibitor required on the field by an average of 30%, thereby, reducing operational cost and cost of storing polar thermodynamic inhibitors.
- MeOH-NaCl hybrid inhibitors performed best on Branch 4 and Branch 9 because it saved about 44.5% of the required MeOH in Branch 4 and 45% of the required MeOH in Branch 9.

5.2 RECOMMENDATION

The following recommendations are suggested.

- A critical study of the effect of hybrid inhibitors on all pipes in field should be considered.
- Other hybrid inhibitors should be formulated from THI and AAs. This will have a combined effect of depressing the hydrate formation temperature and avoiding coagulation of formed hydrates.
- Other hydrate control methods, such as heating the gas at the well head or using a better insulator, should be considered.

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NOMENCLATURE

Y_i = Mole fraction of component i

MW_i = Molecular weight of component i

MW_{air} = Molecular weight of air

ΔT = Temperature of depression given by $(T - T_{environment})$

M = Molar Mass

C = Physical constant of inhibitor

P = Pressure

T = Temperature

X_m = Mole fraction

W = Concentration of inhibitor in weight percent in the aqueous phase

P_0 = Dissociation pressure of hydrocarbon fluid in pure water at 0°C, Kpa

MEG = Mono Ethylene Glycol

MeOH = Methanol

DEG = Di Ethylene Glycol

THI = Thermodynamic Hydrate Inhibitor

AA = Anti Agglomerant

APPENDIX A
COMBINED THERMODYNAMIC HYDRATE INHIBITORS

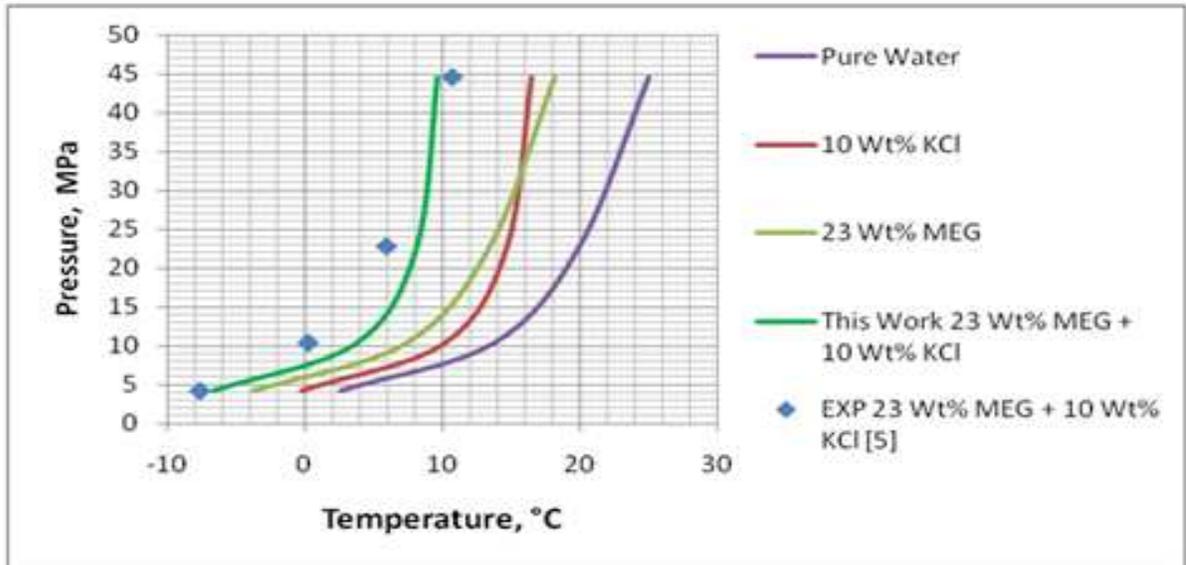


Figure A1: Contribution of MEG and KCl to the hydrate formation temperature of methane.
From www.jmcampbell.com/june-2010.php

Jmcampbell.com proposed a simple procedure for estimation of the hydrate formation temperature in the presence of mixed THIs such as MEG plus a salt solution by adding the depression temperature of MEG and KHI. This was compared to the outcome from experimental (Figure A1). This procedure can be used for a mixture of glycol and electrolyte solutions. The procedure is relatively simple and its accuracy is good enough for facility calculations.

**APPENDIX B:
HYDRATE FORMATION CURVES OF FLUID IN BRANCH 4**

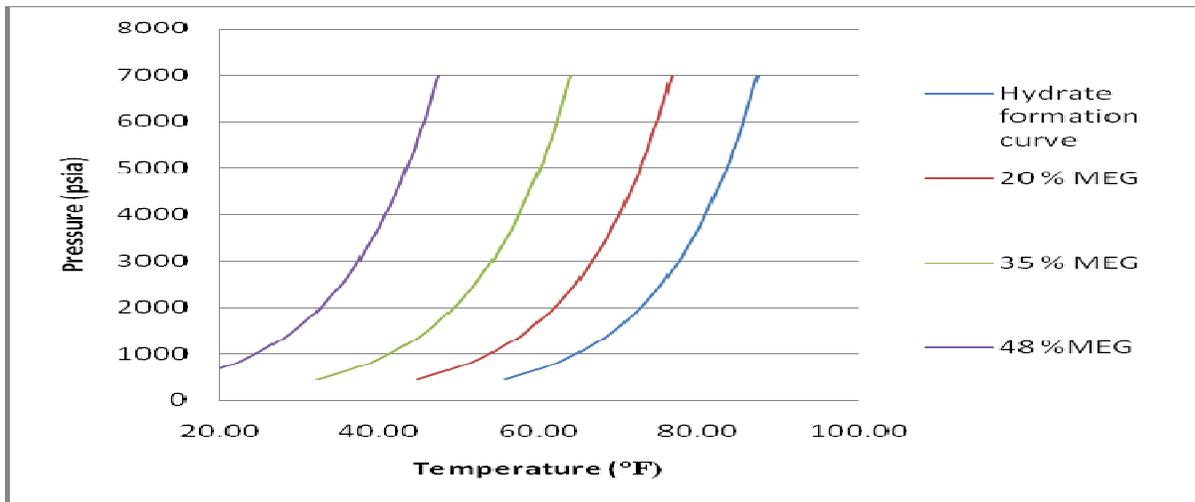


Figure B1: Hydrate formation curve with varying concentration of Mono Ethylene Glycol

Figure B1 shows the effect of MEG on hydrate formation conditions. The hydrate formation curve gradually shifts to the left as the concentration of MEG increases, increasing the hydrate free zone and decreasing the hydrate risk region

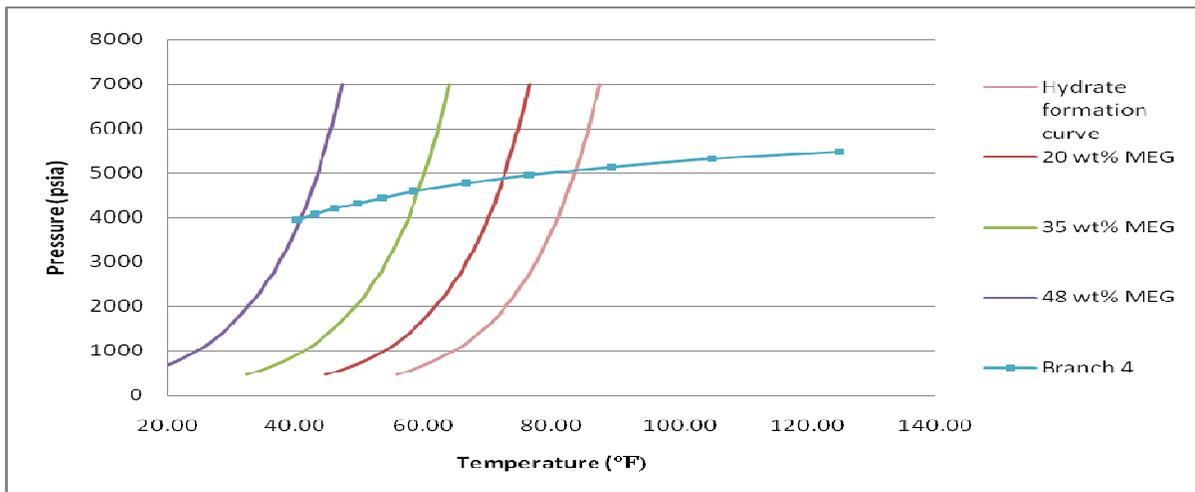


Figure B2: Effect of MEG on Branch 4

Figure B2 shows that 48wt% of MEG will be required to prevent hydrates from forming in Branch 4.

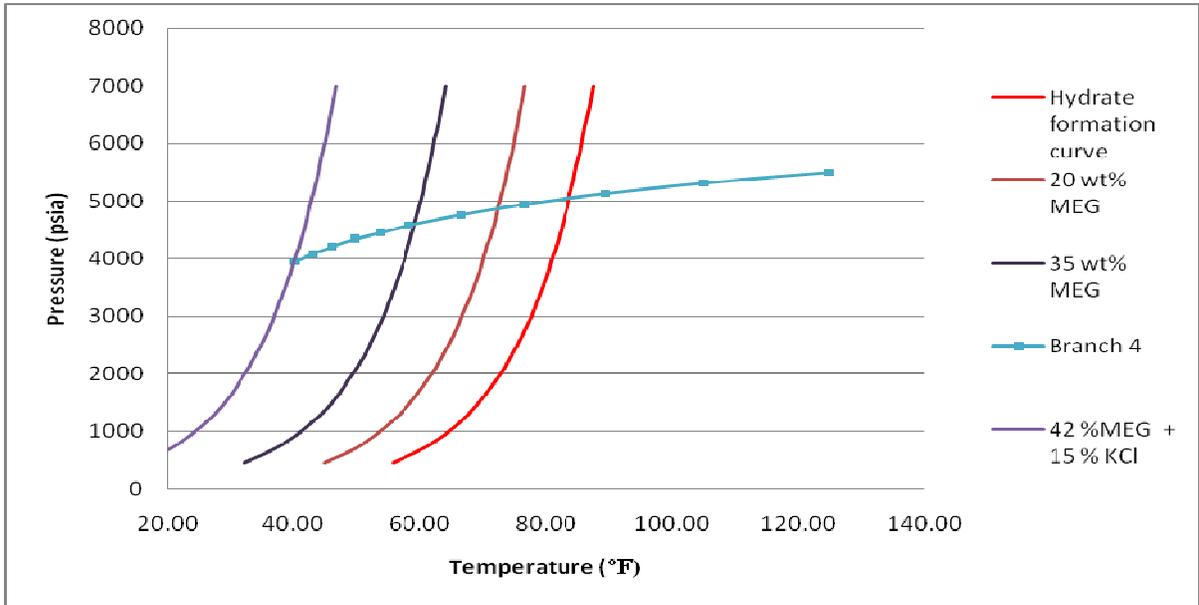


Figure B3: Effect of hybrid inhibitor (MEG + KCl) on the insulated flow line

When MEG-KCl hybrid was considered, the amount of MEG required to prevent hydrate formation in Branch 4 reduced to 42% by weight of MEG in the presence of 15% by weight of KCl.

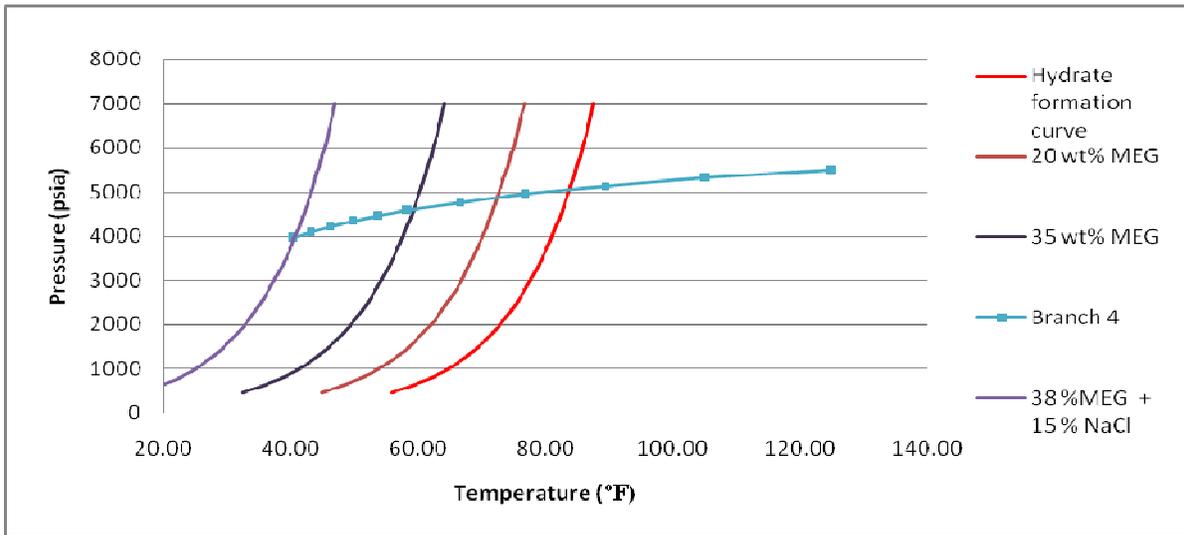


Figure B4: Effect of hybrid inhibitor (MEG + NaCl) on the insulated flow line

With MEG-NaCl hybrid, the required polar THI is 38% by weight of MEG in the absence of 15% by weight of NaCl salt.

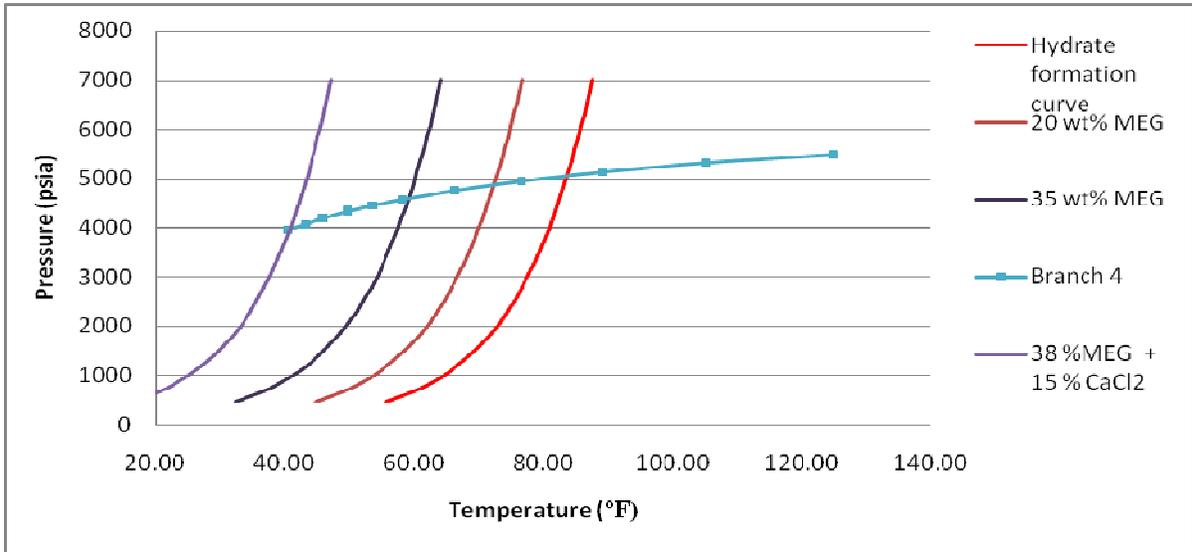


Figure B5: Effect of MEG-CaCl₂ hybrid inhibitor on the insulated flow line

The MEG-CaCl₂ required only about 38% by weight of MEG in the presence of 15% by weight of CaCl₂ salt to prevent hydrates from forming in Branch 4.

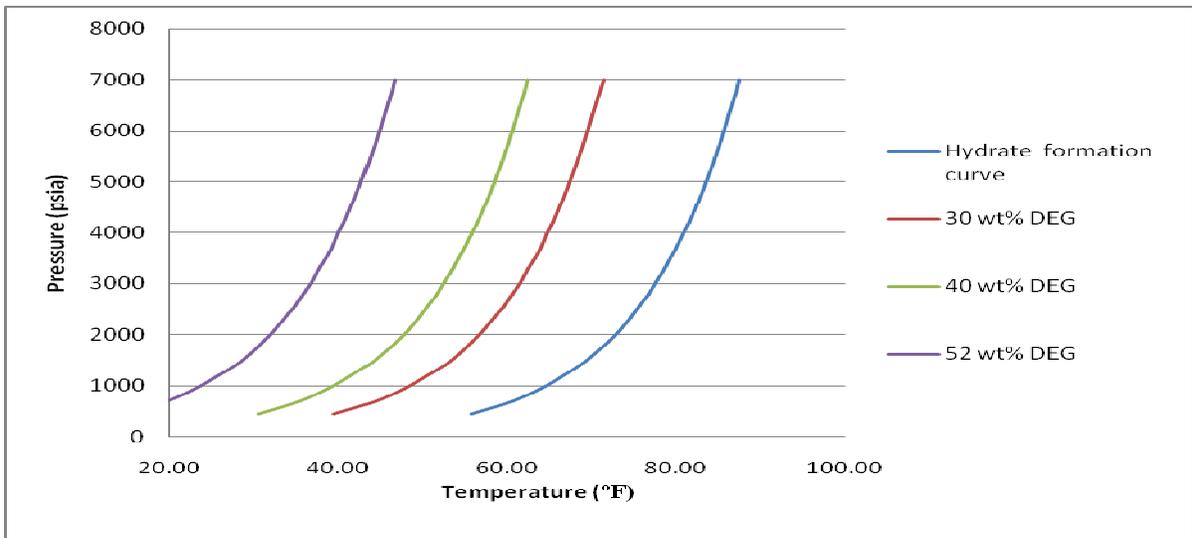


Figure B6: Hydrate formation curve with varying Di Ethylene Glycol concentration

Figure B6 shows the effect of DEG on hydrate formation conditions of fluids in Branch 4. Increasing concentration of DEG reduces the hydrate risk zone and increases the hydrate free zone.

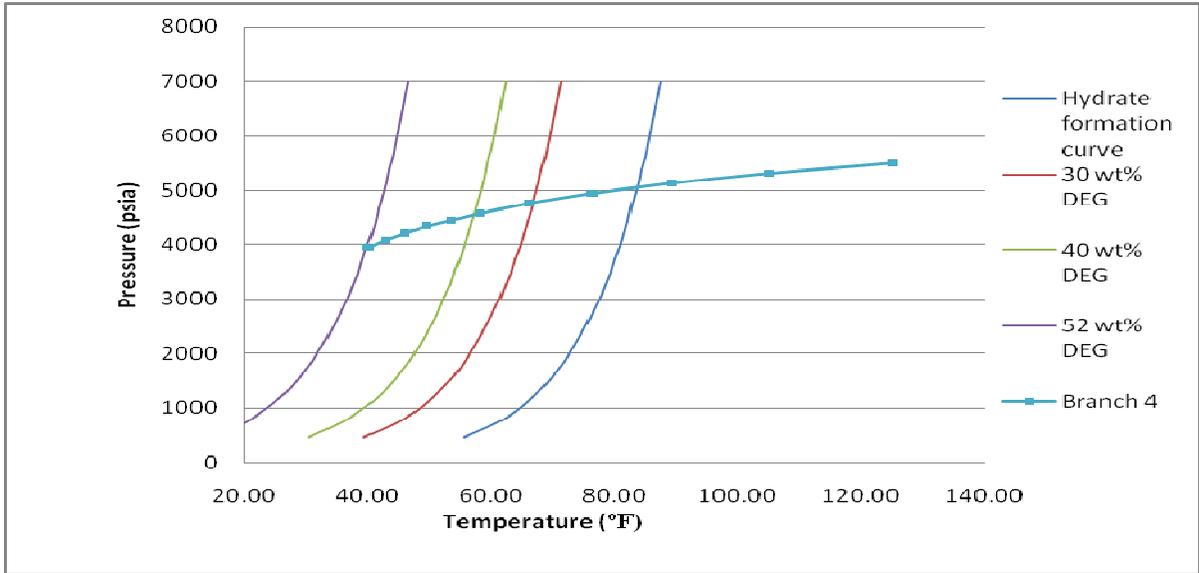


Figure B7: Effect of DEG on insulated Branch 4

Figure B7 shows that 52% by weight of MEG will be required to stop hydrate formation in Branch 4.

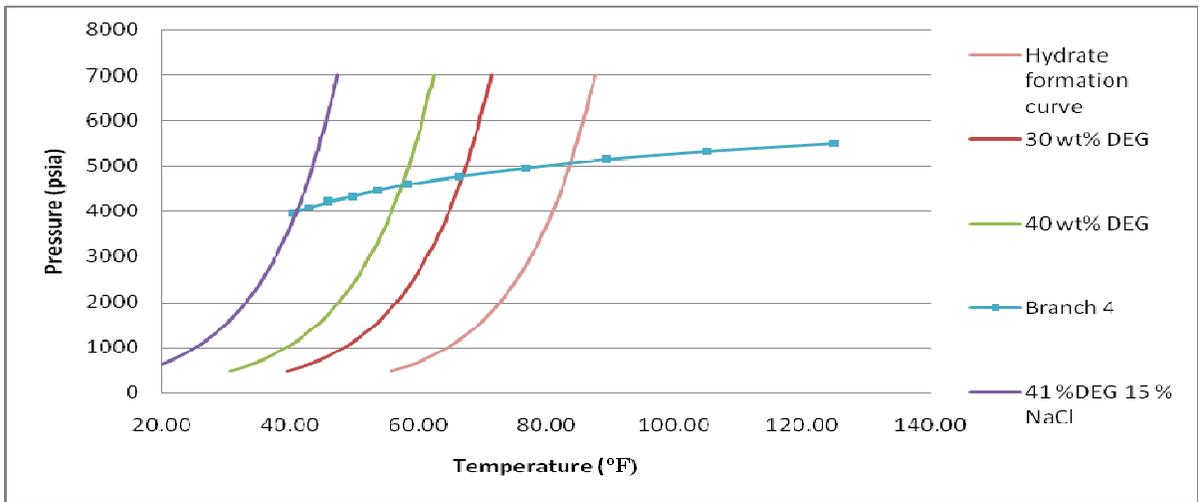


Figure B8: Effect of DEG-NaCl hybrid inhibitor on Branch 4

When DEG-NaCl hybrid inhibitor was used, the required DEG reduced from 52% by weight DEG to 41% by weight DEG in the presence of 15% by weight NaCl.

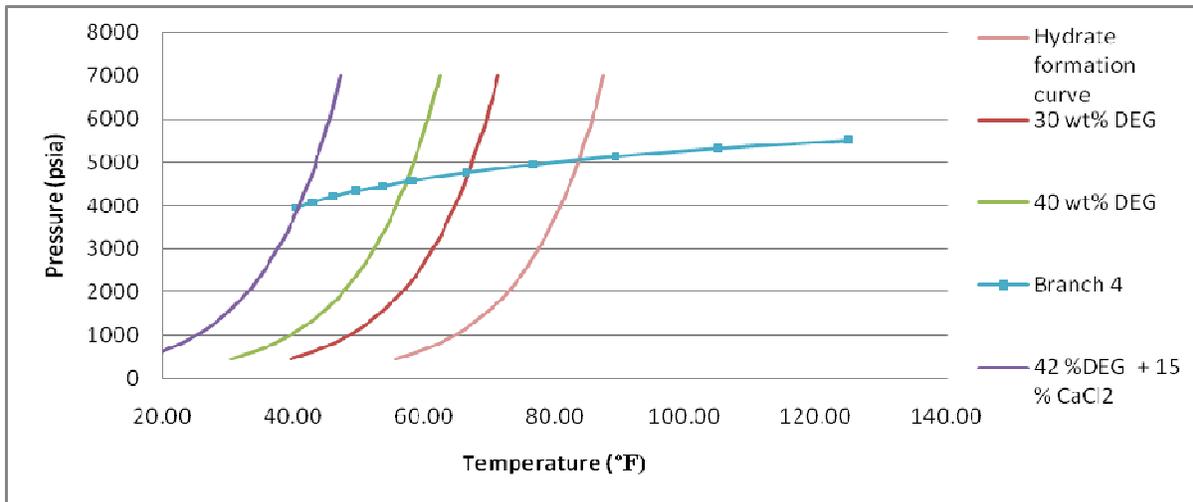


Figure B9: Effect of DEG -CaCl₂ hybrid inhibitor on Branch 4

The DEG-CaCl₂ requires 42% by weight of DEG in the presence of 15% by weight of CaCl₂ to completely inhibit hydrate formation in Branch 4.

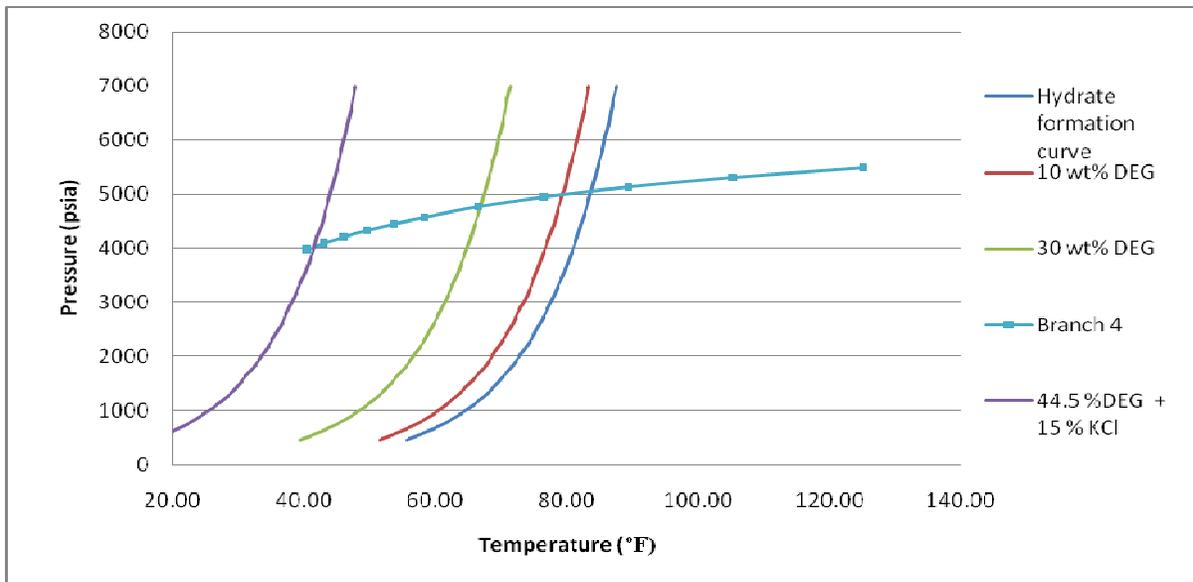


Figure B10: Effect of DEG-KCl hybrid inhibitor on Branch 4.

DEG-KCl hybrid inhibitor requires 44.5% by weight of DEG and 15% by weight of KCl to prevent hydrate formation in Branch 4.

APPENDIX C
HYDRATE FORMATION CURVES OF FLUID IN BRANCH 9

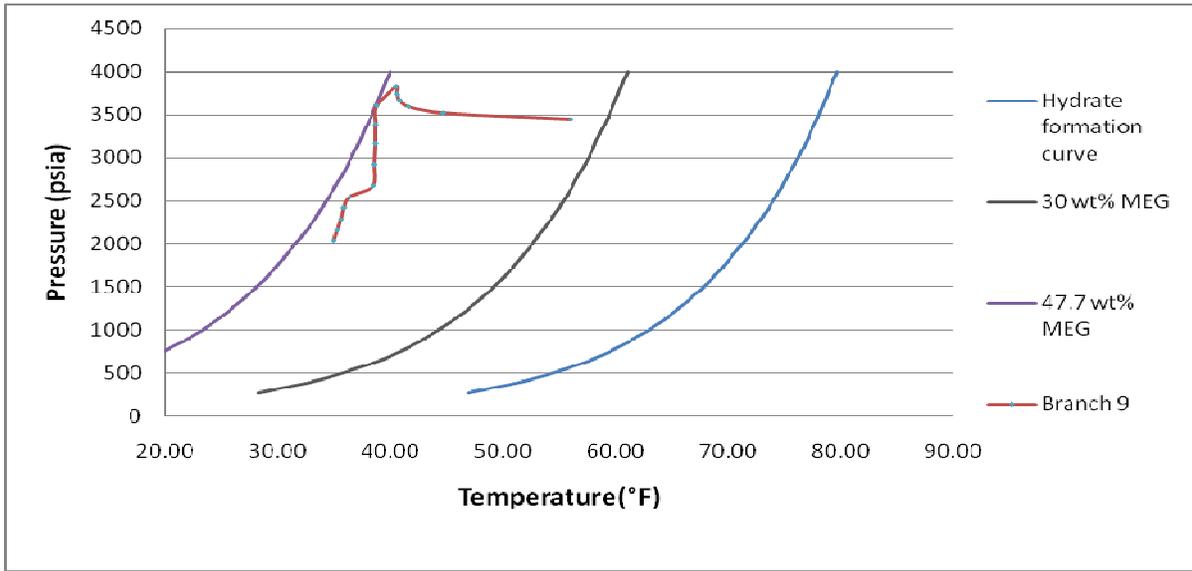


Figure C1: Effect of MEG on fluids in Branch 9.

Figure C1 shows the effect of MEG on Branch 9 fluid. 30wt% MEG wasn't sufficient to prevent hydrate formation but 47.7 wt% MEG will prevent hydrate formation in Branch 9.

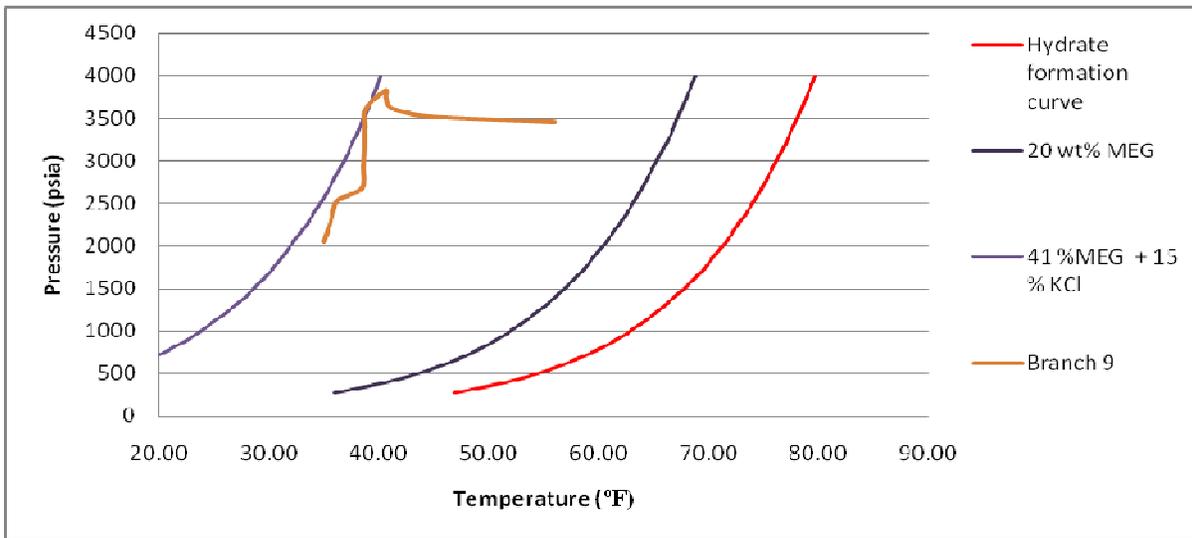


Figure C2: Effect of MEG-KCl hybrid on Branch 9.

41wt% MEG in the presence of 15wt% KCl will prevent hydrates from forming in Branch 9.

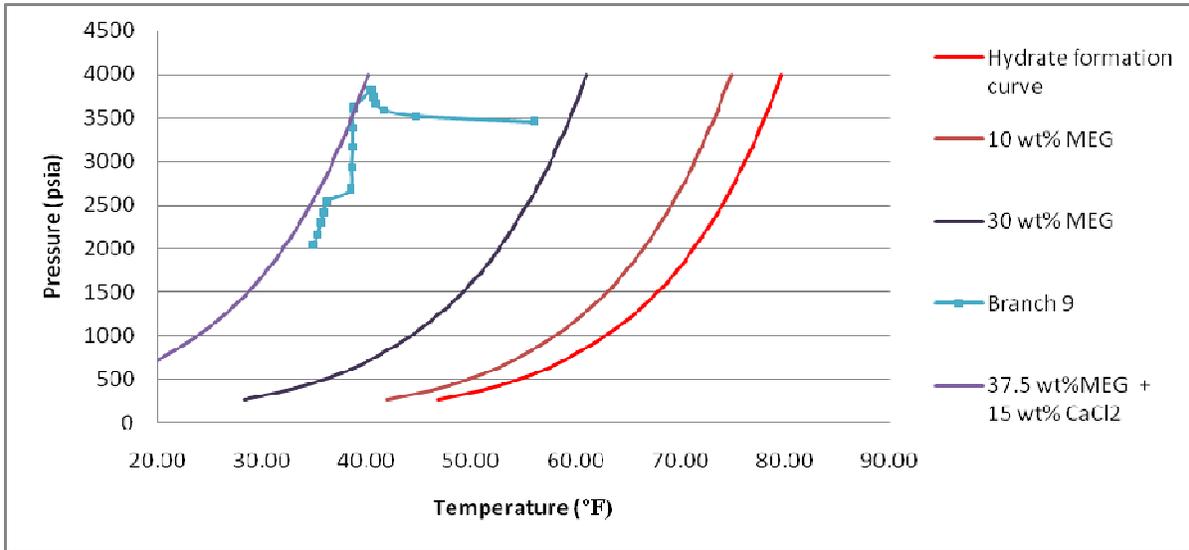


Figure C3: Effect of MEG- CaCl₂ hybrid on Branch 9

37.5wt% MEG in the presence of 15wt% CaCl₂ will prevent hydrates from forming in Branch 9.

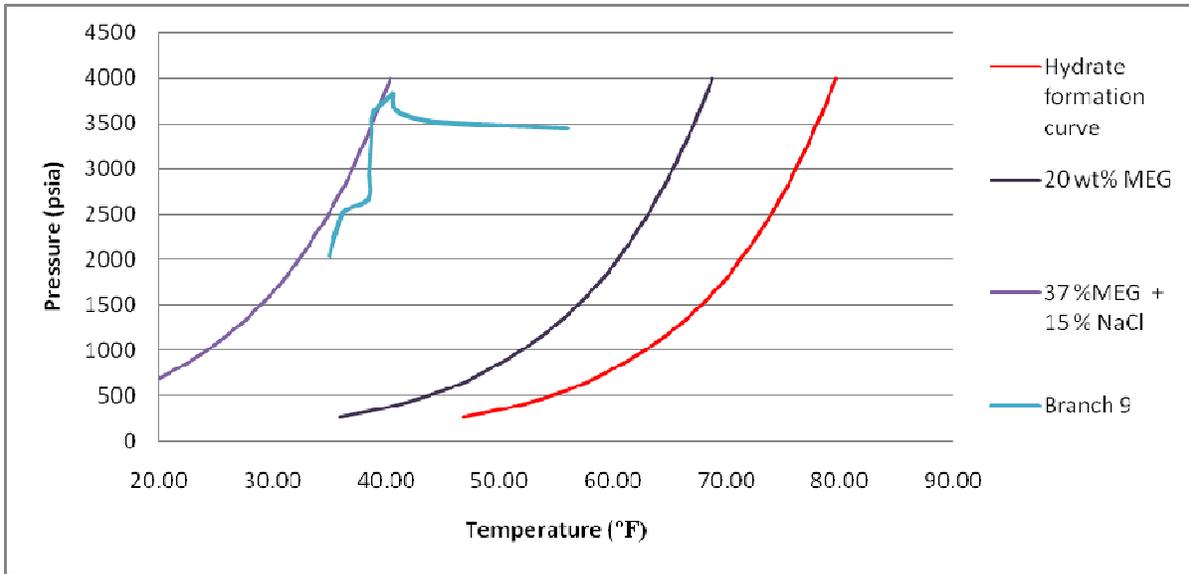


Figure C4: Effect of MEG-NaCl hybrid on Branch 9

When MEG-NaCl hybrid is used, 37.5wt% MEG was required in the presence of 15wt% MEG.

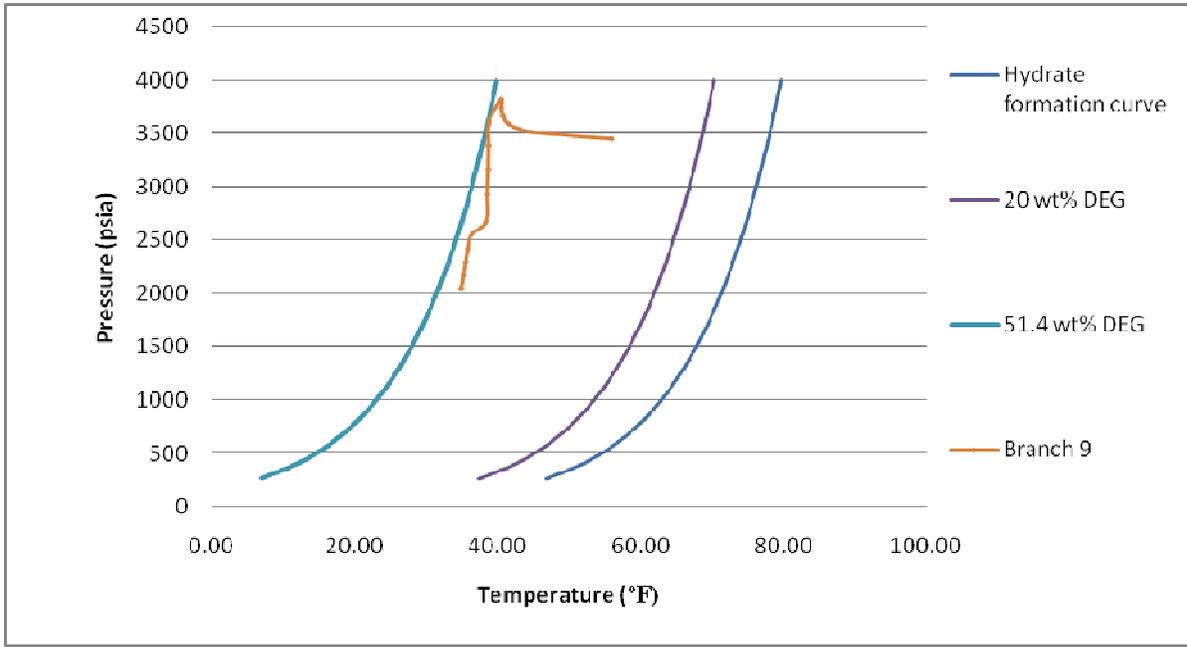


Figure C5: Effect of DEG on fluids in Branch 9.

51.4 wt% of DEG was required to prevent hydrate formation in Branch 9.

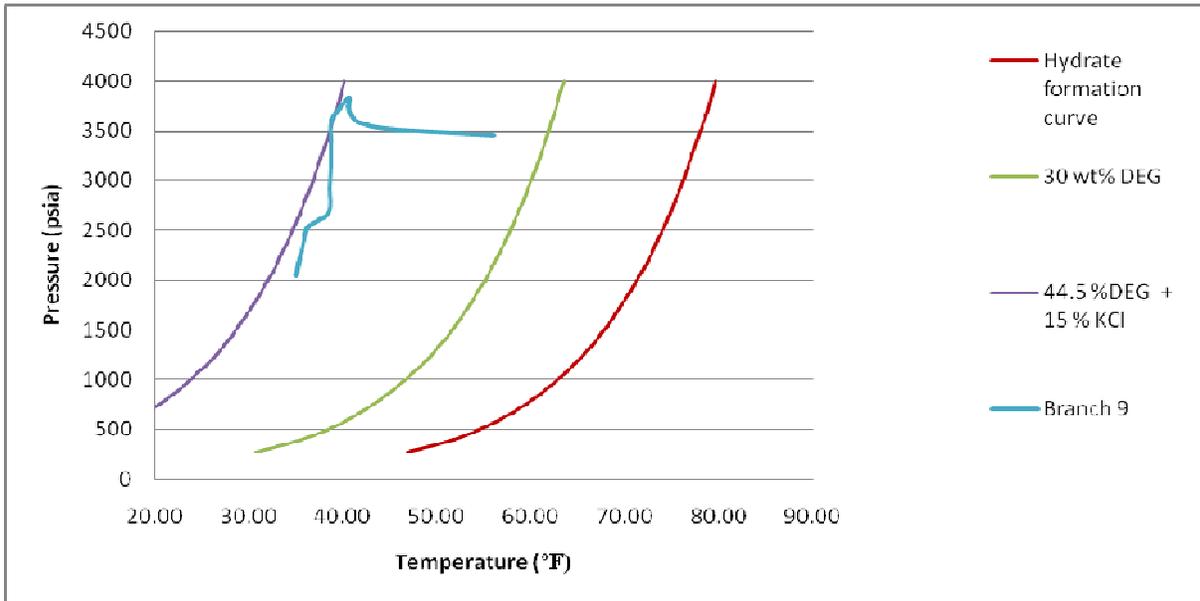


Figure C6: Effect of DEG-KCl hybrid on pipeline

44.5 wt% DEG combined with 15wt% KCl was sufficient to prevent hydrate formation in Branch 9

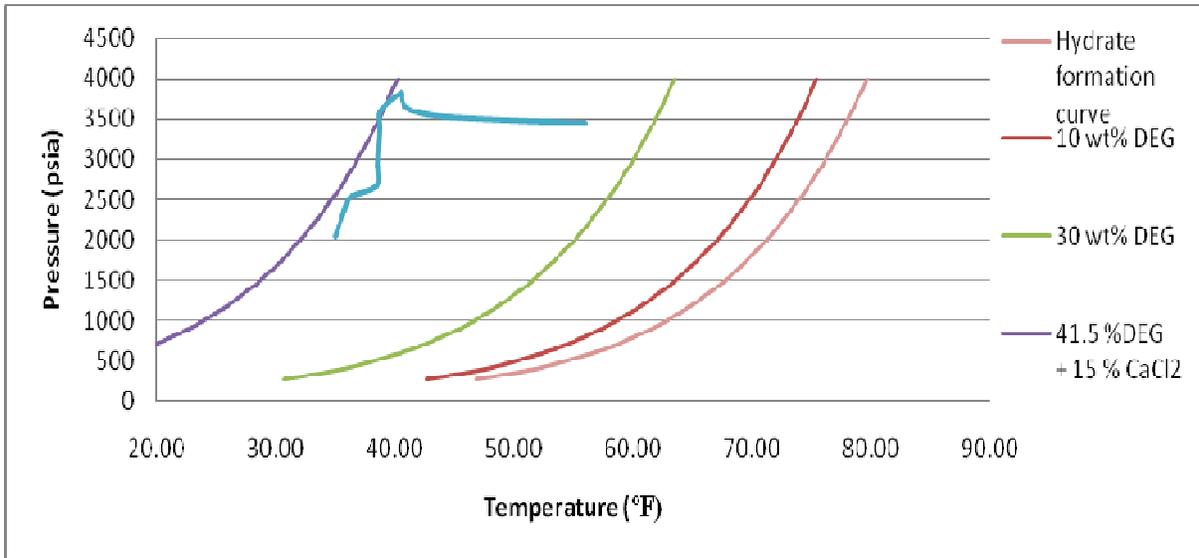


Figure C7: Effect of DEG-CaCl₂ hybrid on Branch 9

When DEG-CaCl₂ hybrid was considered, the amount of DEG required to prevent hydrate formation in Branch 9 reduced to 41.5wt% DEG in the presence of 15%wt CaCl₂.

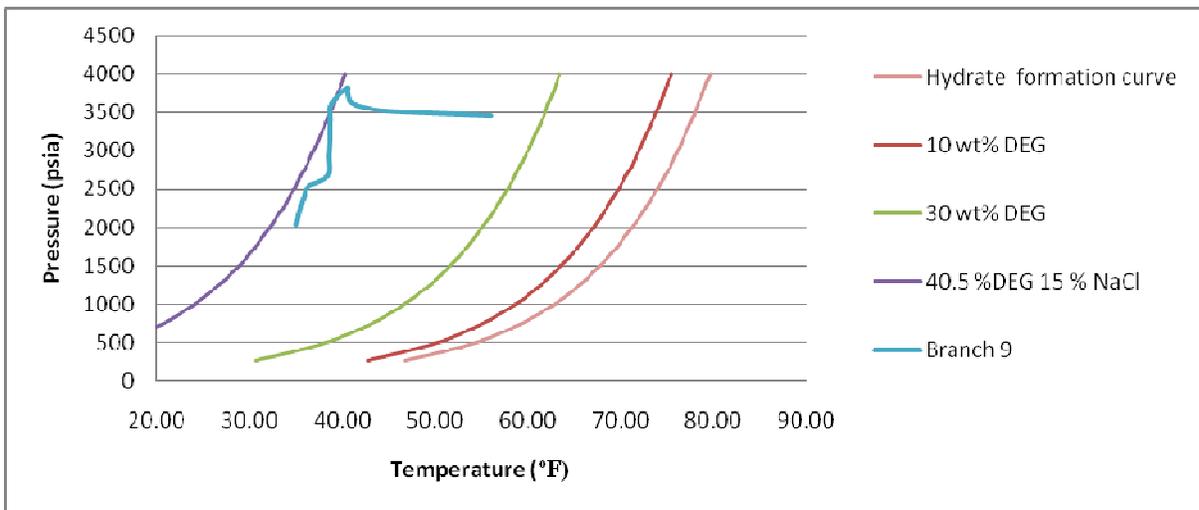


Figure C8: Effect of DEG-NaCl hybrid on Branch 9

When DEG-NaCl hybrid was used, the amount of DEG required to inhibit hydrate in Branch 9 reduced to 40.5 wt% DEG in the presence of 15wt% DEG.

APPENDIX D

FIELD DATA

The field data used for this study is given below:

Table D1: Pipe Diameter for the branches

Pipe branch	nominal diameter
Branch 1	8"
Branch 2	8"
Branch 3	8"
Branch 4	8"
Branch 5	8"
Branch 6	10"
Branch 7	12"

Table D2: Well head conditions

	Well A	Well B	Well C	Well D
Temperature (°F)	124	113	119	125
Pressure (psia)	3185	4400	5303	5493
Flow (lbmole/hr)	1054	1018	6299	1647

Table D3: Composition of stream

	Branch 4	Branch 9
CO ₂	0.1419	0.065052
Nitrogen	0.0596	0.059657
H ₂ S	0	0
Methane	0.716	0.76621
Ethane	0.0473	0.068811
Propane	0.0194	0.01839
i-butane	0.0079	0.007518
n-butane	0.0079	0.00251
i-pentane	0	0.001791
n-pentane	0	0.002052
n-hexane	0	0.001873
n-heptane	0	0.006136

Schedule 40 steel pipe is used throughout and all branches. All pipes are neoprene insulated.

Elevation data for each of the branches are provided in the following table. Branches that traverse undulating terrain have been subdivided into a number of segments with elevation points assigned at locations where there is a significant slope change.

Table D4: Pipe length and Segment

Branch	Segment	Length (feet)	Elevation (feet)
Branch 1			
	1	2297	20
	2	2297	12
	3	1312	25
Branch 2			
	1	820	0
	2	250	2
Branch 3			
	1	820	0
	2	820	12
	3	820	-5
Branch 4			
	1	6000	0
	2	4000	12
Branch 5			
	1	1640	-13
Branch 6			
	1	328	-52
Branch 7			
	1	4000	4000
Branch 8			
	1	820	0
	2	9843	0
Branch 9			
	1	4000	-4000
	2	26250	0
	3	4000	4000
Branch 10			
	1	13120	0
	2	13120	