

**SAFETY PROBLEMS CAUSED BY HYDRATE FORMATION IN DEEPWATER  
PRODUCTION OPERATION**

A Thesis

by

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Submitted to the Office of Graduate and Professional Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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August 2017

Major Subject: Safety Engineering

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## **ABSTRACT**

Although hydrate formation phenomenon has been identified for many years, this is still one of the most challenging problems in oil & gas industry as they are associated with flow assurance problems and safety issues. Although, many studies have focused on developing thermodynamic and kinetic models to understand and predict hydrate formation, this phenomenon is not fully understood and there is not a general methodology for the quantification of the risk that considers the uncertainty associated with key input parameters. Therefore, there is a need for developing risk assessment methodologies, which considers, not only the models for predicting hydrates, but also the organizational factors associated with the hydrate management system.

In this work, a comprehensive framework was developed for estimating the risk of hydrate formation in a subsea production operation taking into consideration the effectiveness of the entire hydrate management system. The proposed framework was divided in three areas: 1) definition of causal and consequence models; 2) application of Bayesian Networks; and 3) sensitivity analysis of the thermodynamic or kinetic models.

In order to probe the concept and illustrate the application of the proposed framework, a hypothetical case study was created based on literature data and inputs provided by flow assurance experts from academia and industry. Causal and consequence models were developed, including a visual representation of the preventive and mitigative measures. The hydrate equilibrium curves were generated using PVTsim Nova software, and the uncertainty analysis was done with Latin Hypercube Method and statistical

calculations. the Bayesian Networks method was used to understand the complexities associated with the Hydrate Management System. This model solved with AgenaRisk software using discrete and continuous distributions.

The results of this work include the visual representation of the probabilistic relationship between certain components and variables of a typical hydrate management system, which can affect the reliability of the control and preventive measures for hydrate control. The probability values calculated in this case study were in agreement with likelihood values typically used in a risk matrix, which probes that the proposed approach is a good starting point for future improvements to the proposed framework.

## **DEDICATION**

To my parents who encouraged me to fly towards my dreams. Thank you mom and dad for teaching me that failure is does not mean the end of the road, but the beginning of a wonderful learning experience!

## **ACKNOWLEDGEMENTS**

I gratefully acknowledge my advisor, Dr. Sam Mannan, for all his support, advice and encouragement. I am deeply grateful to him for giving me the opportunity to join his research group. I feel great pride in being part of this group that has helped me to grow not only as a professional but also as a person. Likewise, I thank him for his continue guidance during my research work. Furthermore, I thank him for his inspiration, encouragement, guardianship, and patience throughout this process.

I would also like to express my sincere appreciation to my committee members, Dr. Rashid Hasan and Dr. Maria Barrufet, for their time and advice for successful completion of this research.

I would also like to thank my team leader, Dr. Yogesh Koirala, for his constant help during all the stages of this research. Thanks are also extended to all the staff, especially Ms. Valerie Green, for her constant guidance in my professional career and life and for always looking after me.

Thanks also to my friends and professional mentors for their moral support and for continuously motivating me to accomplish this goal. This unforgettable journey was more enjoyable thanks to their presence. This great experience would not be the same without all of them.

Last but not the least, I would like to thank my wonderful family back home in Colombia for their support, motivation, and inspiration during these two years, because

without them I would not have achieved this dream. Special thanks to my father for reminding me that hard work and persistence can take me anywhere. I want also to thank my boyfriend for his support and for believing in me even when I questioned myself.

## **CONTRIBUTORS AND FUNDING SOURCES**

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### **Founding Sources**

Graduate study was supported by the “Harry West Memorial Scholarship” from the Mary Kay O’Connor Process Safety Center.

## NOMENCLATURE

AAs	Anti-agglomerates
BOP	Blowout Preventer
BWPD	Barrels of Water Per Day
CSMGem	Colorado School of Mines Gem
CSMHyK	Colorado School of Mines Hydrate Kinetics
DEH	Direct Electrical Heating
ETH	Electrical Trace Heating
FLET	Flowline End Termination
FPSO	Floating Production Storage and Offloading
HH	High-High
HMS	Hydrate Management System
KHI	Kinetic Hydrate Inhibitors
LDHI	Low Dosage Hydrate Inhibitors
LHS	Latin Hypercube Sampling
LL	Low-Low
MEG	Mono-Ethylene Glycol
MeOH	Methanol
THI	Thermodynamic Hydrate Inhibitors
UTA	Umbilical Termination Assembly



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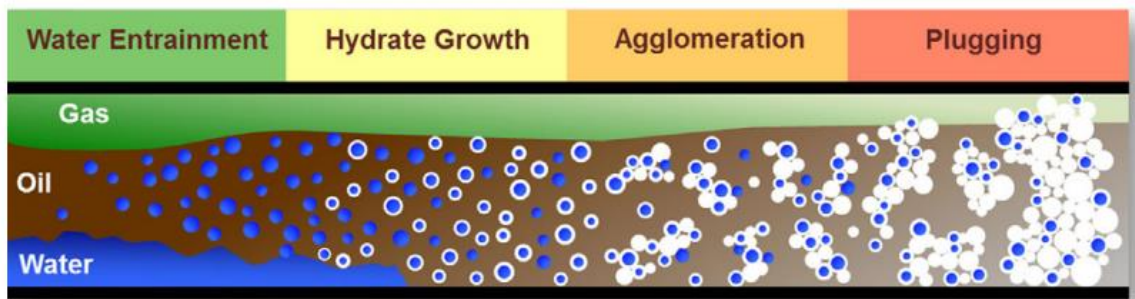
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# 1 INTRODUCTION

## 1.1 Background and Motivation

Gas molecules (methane, ethane, propane and others) can become trapped inside a crystal water structure, (comprised of water cages connected in a three-dimensional lattice) resulting in solid-ice like formations known as “hydrates.” The required conditions for hydrates to form are the presence of water (small percentage), an oil/gas composition (light gas molecules), a high pressure, and a low temperature. Hydrate crystals can grow by an agglomeration process that can result in a plug (Figure 1) reprinted with permission from (Joshi et al., 2013), becoming a serious hazard at normal conditions in common subsea operations. There are other conditions that can influence hydrate formation and growth, including liquid loading, mixture velocity, salt content, presence of surfactants, water droplet diameter (water surface area), pipeline length, location, water depth, flow line geometry (*i.e.*, presence of low spots) and inhibitor concentration (Chaudhari, 2016).



**Figure 1. Schematic of hydrate formation and plugging mechanism in low water cut systems, "water emulsified oil." Reprinted with permission from (Joshi et al., 2013).**

Hydrate formation is a challenging and a potentially dangerous problem as there is no complete understanding of hydrate formation phenomena. Hydrates can cause flow assurance problems (Gudmundsson, 2002), including blockages in wells, risers, flow-lines, and manifolds, which could result in kicks, ruptures, leakages or even blowouts (Sloan, Koh, & Sum, 2010); thereby, causing significant process safety issues and severe environmental impacts.

Although hydrates have been identified as a potential hazard in offshore drilling and production operations, the number of documented incidents is small. Unfortunately, it has been difficult to find conclusive evidence to link hydrate formation as a root cause to those incidents, because the evidence disappears easily. However, some incidents in which hydrate formation was suspected to be a contributing factor are shown in Table 1.

**Table 1. List of Incidents Due to Problems Related to Hydrate Formation**

<b>Name of incident or company</b>	<b>Year</b>	<b>Problems related to hydrate Formation</b>	<b>Consequences</b>
Piper Alpha (Johnsen, 1990)	1998	An incident investigation concluded that hydrate slurry arriving at the condensate injection pump could have blocked the pump discharge valve and the downstream process lines. It is possible that this blockage was the cause for tripping the injection pump, which started the chain of events that led to the Piper Alpha disaster.	Process Safety and Environmental
Energy Company in Alberta (Sloan Jr & Koh, 2007)	1991	A supervisor died due to the impact of a hydrate projectile arising during a wrong implementation of a depressurization process.	Process Safety

Table 1 Continued

Name of incident or company	Year	Problems related to hydrate Formation	Consequences
Macondo Well Explosion and Fire (Giavarini & Hester, 2011)	2010	BP faced hydrate formation issues during the utilization of the cofferdam, which was part of the Deepwater Horizon Oil Spill Response.	Process safety, environmental, asset damage, production losses, and reputational impact

Even with such incidents related to hydrate formation, there is a lack of fundamental understanding of the phenomena, especially it has been difficult to estimate incident probability and understand the formation conditions. In addition, the probability of blockage, associated consequences, and systematic risks are not properly understood. Therefore, further research is required to find a solution to this problem. This is particularly important considering that the oil and gas industry is moving towards deep-water environments (higher pressures & lower temperatures) where hydrates can form and potentially lead to environmental or process safety incidents. The focus of these research should be aimed to understand the hydrate formation phenomena and be able to estimate the associated risk of the Hydrate Management System (HMS).

Over the past few years, considerable research efforts have focused on developing thermodynamic and kinetic models to understand hydrate formation. One of the challenges faced in this journey is that the hydrate formation phenomenon involves multiphase flow and multi-component environments, which makes it difficult to develop accurate



prediction models. Although the hydrate formation mechanism is not completely understood, and therefore it is difficult to accurately predict their formation, the industry have been using different techniques to prevent hydrate formation including: use of Thermodynamic Hydrate Inhibitors (THI) (Brustad, Løken, & Waalmann; Frostman, Thieu, Crosby, & Downs, 2003); Low Dosage Hydrate Inhibitors (LDHI) (Chua, Kelland, Hirano, & Yamamoto, 2012; Daraboina, Malmos, & von Solms, 2013; Lou *et al.*, 2012; Webber & Nagappayya, 2016), which are divided into Kinetic Hydrate Inhibitors (KHI) and Anti-Agglomerates (AAs); Direct Electrical Heating (DEH) (Bollavaram and Sloan Jr 2003); Electrical Trace Heating (ETH) (Tzotzi *et al.*, 2014); and Depressurization methods (Bollavaram & Sloan Jr, 2003; Sloan *et al.*, 2010). The selection of a particular preventive, and mitigation strategy depends on the operational conditions, the inherent risk associated with the operations, environmental regulations, and economics.

The use of inhibitors (J. Kim, Noh, Chang, & Chang, 2016) is the most common technique to control hydrate formation. The so called THI, like methanol (MeOH) or mono-ethylene glycol (MEG), shift the hydrate equilibrium towards higher pressures and lower temperatures. Kinetic hydrate inhibitors (KHI) delay hydrate nucleation and crystal growth. Anti-agglomerates (AAs) do not prevent the formation of hydrates, but they prevent hydrate particles from agglomerating and forming a plug. Although these types of inhibitors have demonstrated to be effective, the oil & gas industry is conducting exploration activities in deeper and colder waters, which requires an incremental increase in inhibitor injection rates; therefore, increasing the overall production costs (J. Kim, Noh, Ryu, Seo, & Chang, 2016). Although, low dosage hydrate inhibitors could overcome part

of this problem, it is necessary to develop a special monitoring system to monitor the operations effectively (Clark & Anderson, 2007; Patel, 2015; Tian, Bailey, Fontenot, & Nicholson, 2011). According to the literature, an insufficient supply of AAs were responsible for hydrate blockage formation in the Longhorn gas-condensate field operation (Patel, Dibello, Fontenot, Guillory, & Hesketh-Prichard, 2011). Also, during the depressurization process as part of the remediation method, the main concern is the hydrate's velocity when it breaks free to dissociate the plug, especially for one-sided depressurization (Xiao, Shoup, Hatton, & Kruka, 1998). As depicted by these cases, all the existing techniques have notorious and uncontrollable drawbacks, which somehow affect the solution to stop and/or control hydrate formation as part of flow assurance issues.

Earlier approaches to hydrate control have focused on the avoidance of hydrate formation by using preventive methods like THI's. Nowadays, hydrate prevention is moving towards a risk-based approach (Sloan, 2005). This new approach allows for a controlled hydrate formation inside pipelines to prevent blockage (J. Kim, Noh, Chang, *et al.*, 2016), and recommends implementing AAs inhibitors that must be closely monitored (Patel, 2015). Still, an estimation of the risk associated with this approach is in question, as uncertainties coming from human interface, equipment reliability and software used to predict hydrate formation are not well defined.

Different types of software packages, such as CSMGem (Ballard & Sloan Jr, 2004), DBR Hydrate (Schlumberger, 2017), Multiflash (KBC, 2016), PVTsim (Calsep, 2015), HydraFlash (Mazloum, Chapoy, Yang, & Tohidi, 2011), and OLGA (Boxall, Davies, Koh, & Sloan, 2009), include models to obtain thermodynamic and kinetics

information, which is useful for estimating hydrate formation risk. However, none of them seems to include a probabilistic relationship that takes into consideration all the operational variables and the conditions that contribute to hydrate formation. Knowing this relationship information is fundamental to understand the behavior of the system under different operational scenarios (drilling, normal operations, shutdown, and start up) and the complex procedures that require human intervention.

Although the Bayesian Networks method has not been fully applied to offshore quantitative risk assessments, Bayesian Networks (BN) can be used to represent the probabilistic relationships among operational variables and the conditions that contribute to hydrate formation, as this method is effective in representing probabilistic relationship among a large number of random variables (Bhandari, Abbassi, Garaniya, & Khan, 2015). Therefore, this method provides a promising opportunity to improve the analysis of hydrate formation by integrating updated mechanisms, as mentioned by Herath (Herath, Khan, Rathnayaka, & Rahman, 2015). After an extensive literature review into the application of BNs to analyze the existing hydrate formation issue in subsea operations, this was found to be extremely limited. This presents a unique opportunity to apply the Bayesian probabilistic models to improve prediction and evaluation of equipment failure due to or related to hydrate formation and assess the actual risk. It is expected that by employing this approach it will be possible to expand the operational windows, without compromising safety or costs, and assist in proactive measures against hydrate formation leading to safer, continuous, and economical production.

## 1.2 Problem Statement and Objectives

Although there are several studies aimed at understanding the hydrate formation mechanisms, there is not a complete understanding of this phenomenon yet. Consequently, there is no ultimate solution for estimating the actual risk posed by hydrates to subsea production operations. Therefore, research is required to develop new approaches. In recent years, the industry has moved towards the use of risk-based approaches for assessing hydrate formation. However, the development of a true more comprehensive approach is required for assessing the hydrate formation problem. The proposed work is a step in that direction.

The aim of this research is to review existing deterministic approaches for hydrate formation prediction and develop a framework for estimating the risk using probabilistic methods. Specific objectives of the present work are summarized as:

- Analyze common subsea production systems and identify the different scenarios in which hydrate formations could occur and potentially impact process safety and environmental concerns.
- Review and evaluate deterministic and probabilistic methods for the prediction of hydrate formation and identify opportunities for optimization of these methods (*i.e.*, apply Bayesian probability theory).
- The aim of this research is to propose a framework for quantifying the risk of hydrate formation and recommend strategies for managing this risk in deepwater subsea operations.

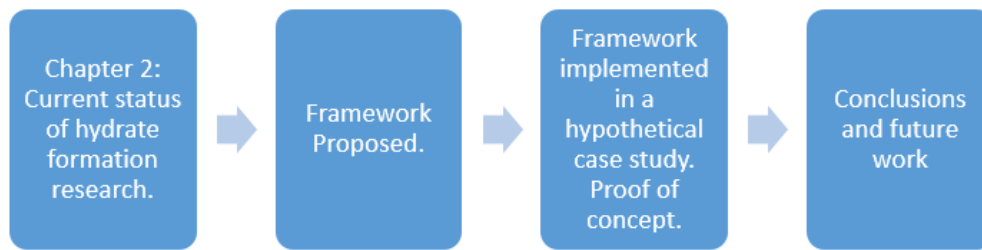
### **1.3 Thesis Structure**

First, an extensive literature review was conducted to understand the process safety problems that could be caused by hydrate formation in deepwater production operations. The second part of the literature review was focused on answering four main questions: 1) What has academia and the industry been doing to prevent and/or mitigate those problems? 2) How has the hydrate management system been applied in different companies? 3) Does the hydrate management system rely on different components, for instance, “human interface or equipment reliability?” 4) What are the general knowledge gaps in academia and industry?

Therefore, after having identified different knowledge gaps, including the limited availability of probabilistic approaches of hydrate formation, Section 3 describes the comprehensive framework proposed for modeling the operational risk of hydrate management systems using Bayesian Networks, which includes a probabilistic analysis.

Section 4 shows the applicability of the proposed framework by developing a hypothetical case study of a natural gas flow line. This exercise was developed to probe the concept with limited information and some experts’ inputs, but with the purpose of looking for opportunities to improve the proposed framework.

Finally, Section 5 summarizes the conclusions and recommendations for future work on this topic and includes some more ideas to improve the framework. Figure 2 shows a summary of the thesis structure.

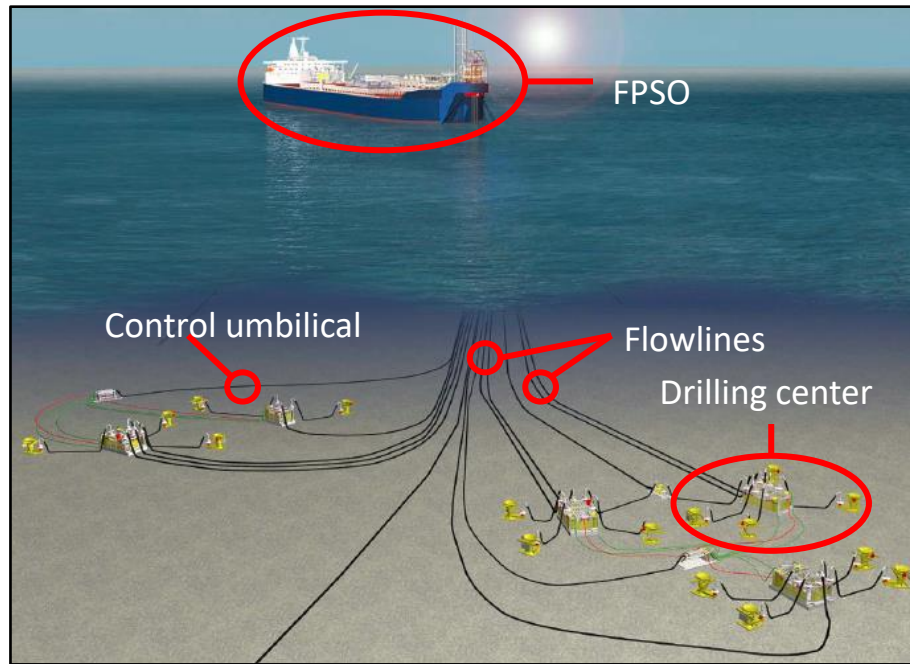


**Figure 2. Summary of the thesis structure.**

## 2 STATUS OF HYDRATE FORMATION RESEARCH

Increasing energy demand in the last decades has led to a need for more frequent exploration and development of deep and ultra-deep water production to satisfy oil and gas demand. Thereby the deep and ultra-deep production have been increasing the system's complexity and operational expenditures due to the harsh environments (high pressures, low temperatures, and high salinity), leading to many challenges, for instance: equipment integrity, operation complexity (difficulty of performing real-time monitoring), flow assurance issues (gas hydrates and wax), sinking wellheads, loss of circulation, and drilling geohazards (overpressured sands, irregular topography, sea floor erosion, gas hydrates) (Rocha, Junqueira, & Roque, 2003) among others.

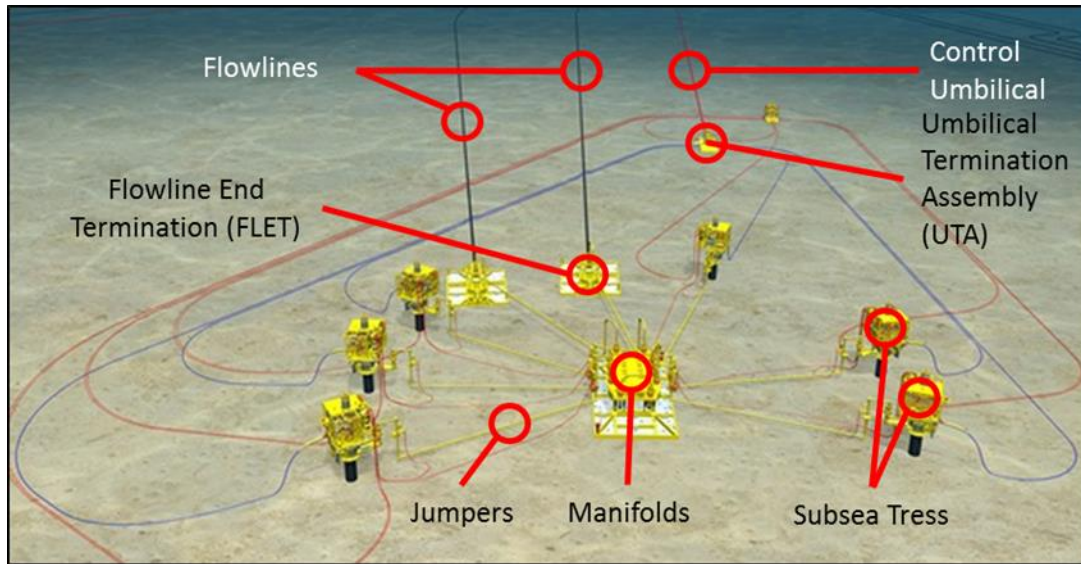
Recently, offshore oil reservoirs produced 30% of the total global oil production. Reaching about 9.3 million barrels per day in 2015, offshore oil and gas production occurs at different depths, roughly as follows: deepwater (410 to 4922 ft) and ultra-deepwater (more than 5,000 ft) (Manning, 2016). These systems can easily reach hydrostatic pressures that exceed 5,000 psi and temperatures lower than 32 °F. These conditions may not be reached through the wellbore, where the temperatures are particularly high; however, when the fluid is transported from the reservoir to the processing facility, it can lose temperature to the environment through the length of the flowline. Figure 3 adapted from (Usman, Olatunde, Adeosun, & Egwuenu, 2012) shows a general system of the subsea production at deepwater and ultra-deepwater levels.



**Figure 3. Sea bed of a subsea production system. Adapted from (Usman et al., 2012)**

Tying marginal field production of small reservoirs to platforms for larger reservoirs is a common practice to offset unjustifiable costs. Nowadays, Floating Production Storage and Offloading (FPSOs) are commonly used for this kind of production as shown in Figure 3 adapted from (Usman et al., 2012). A number of drilling centers composed of different equipment as it is shown in Figure 4 adapted from (FMCTechnologies, 2010), which include subsea trees, manifold, Jumpers, Umbilical Termination Assembly (UTA), and a Flowline End Termination (FLET). The FLET is the equipment that supports the flowlines that are tied back to the FPSO as shown in Figure 3 adapted from (Usman et al., 2012).





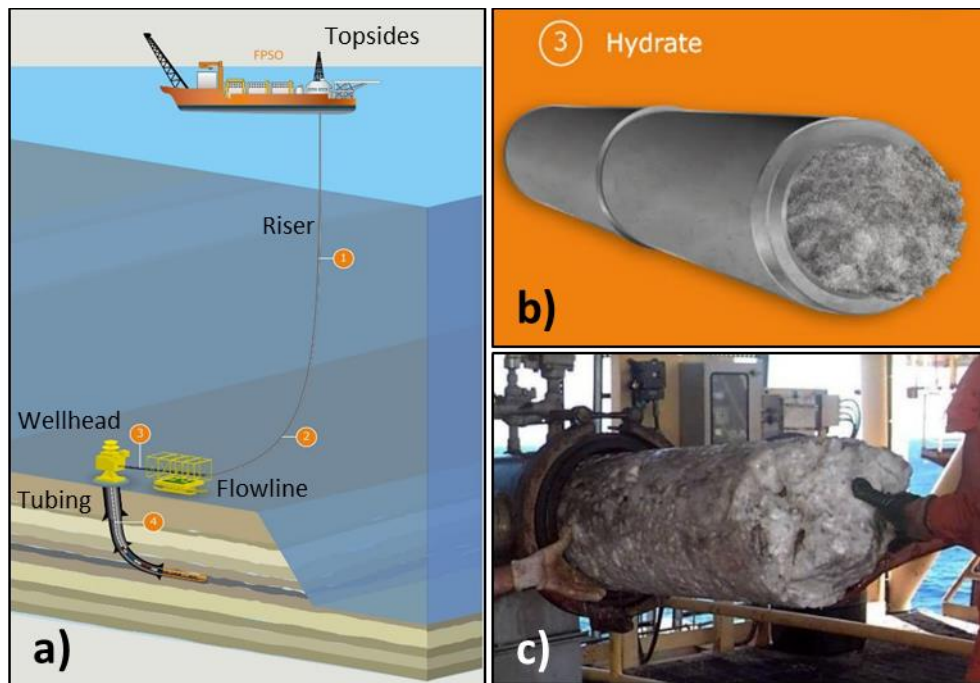
**Figure 4. General arrangement of a drilling center. Adapted from (FMCTechnologies, 2010)**

Flowline lengths vary depending on how far the target processing facility is from the reservoir or how far the fluid should be transported after it is processed. The flowline can reach several miles (Reith & Lasgstrom, 2015). Therefore, due to all these complex systems, many challenges need to be addressed. This section will discuss hydrate formation issues encountered in the whole process (drilling and production), and study them to understand the phenomenon and methods commonly used to prevent and/or mitigate.

## **2.1 Hydrate Formation in Upstream (Drilling and Production)**

Gas hydrates can form at any point of the production process from the wellbore to the topside, as long as the system reaches the necessary conditions, including high pressure, low temperature, light gas concentration and water concentration. Depending on the system, there may be some points more susceptible to hydrate formation than others.

A good comparison of two different systems is the seafloor versus the wellbore; the seafloor contains all the subsea equipment that can reach temperatures as low as 40° F while the wellbore annulus can reach temperatures as high as 200° F (Feng, 2011). Figure 5 adapted from (Chaudhari, 2016; Galvão, 2016) shows the general production scheme from the wellbore to the topside and a case of hydrate formation in a flowline.



**Figure 5. a, b) Offshore production system, adapted from (Galvão, 2016), c) hydrate formation at campos Basin (Brazil), in 2001, adapted from (Chaudhari, 2016).**

During drilling operations, hydrates can lead to blockages in tubing, affecting valves and the operation of the Blowout Preventers (BOP). Hydrates also can block other orifices that contain limited to no circulation. In a study conducted by Ward (Ward *et al.*, 2003), the fluid temperature was measured at the mud line depth to monitor the effects of low temperatures. A sensor was deployed inside the bottomhole assembly during drilling

operations to obtain real-time data. It was found that low fluid temperatures in conjunction with high pressures, as experienced during deepwater drilling, cause gas hydrate formation that results in hazardous scenario, such as the plugging of the BOPs or the risers.

On the other hand, hydrate formation can also start in places with minimal or no circulation including Kill line, choke valves or locations close to the BOP (Feng, 2011).

Due to the environmental conditions, subsea equipment between the wellhead and the delivery systems is more vulnerable to hydrate formation. Flowlines used to transport the fluid from the reservoir to the processing facilities, and those used to transport the fluid after the processing facilities to the final point in the delivery system, are exposed to longer heat transfer times, which is ideal for hydrate formation (Wilfred & Appah, 2015). This can be a problem either in normal operations or at shut-down and restart scenarios due to gas hydrate blockages leading to unexpected operational and safety problems (Sloan *et al.*, 2010). Although one of the biggest concerns related to hydrate formation is the cost associated with prevention, mitigation, and recovery, there is also a safety concern since it can lead to safety and environmental consequences. This event may be considered having a very low probability of failure as it has large number of preventive barriers that need to fail. However, events involving hydrate formation can still be accompanied with very high consequences which ultimately lead to high risk.

## **2.2 Safety Aspects of Hydrates in the Oil and Gas Industry**

The main safety aspects to consider during drilling and operations in the oil and gas industry is plugging.

Plugging (Amodu, 2008; Sloan Jr & Koh, 2007): there are different scenarios where environmental and operational issues can lead to hydrate formation in different equipment. This equipment might include Blowout Preventers (BOP), where a plugging can build up well pressure and interfere with the proper function of the BOP (when the plugging is located in BOP's ram cavity). Plugging can also form at the choke and kill-line, making it difficult to use these lines in well circulation, and between the drill string and the BOP, which can lead to problems when complete closing of the BOP is necessary. Finally, plugging can also form in the wellhead and many equipment after it including manifolds, risers, pipelines, Jumpers, and flowlines. Hydrates plug-in in any of the aforementioned equipment are usually controlled or removed through different strategies depending on the scenario.

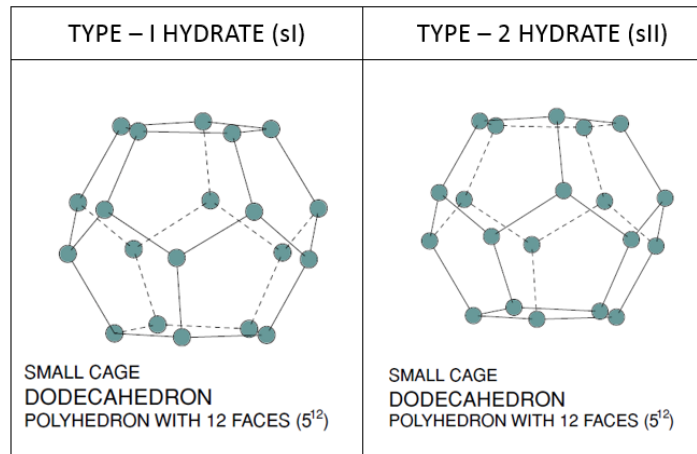
### **2.3 Thermodynamic Models to predict Hydrate Formation**

In the early 1810s, Humphry Davy found evidence that some gases could form solid compounds with water, and these were suspected to be hydrates. Later on, John Faraday proved the existence of hydrates through experiments. In 1930, Hammerschmidt concluded that some of the blockages in the oil and gas industry could be caused by hydrate formation (in gas transmission lines) (Sloan Jr & Koh, 2007), especially at temperatures above the freezing point. After this discovery, the interest and efforts to understand the hydrate phenomena started to increase with each decade as was shown by Sloan (Sloan, 2005).

Based on the research results, three different structures of hydrates were determined based on the type and the various sizes of the guest molecules, which allow

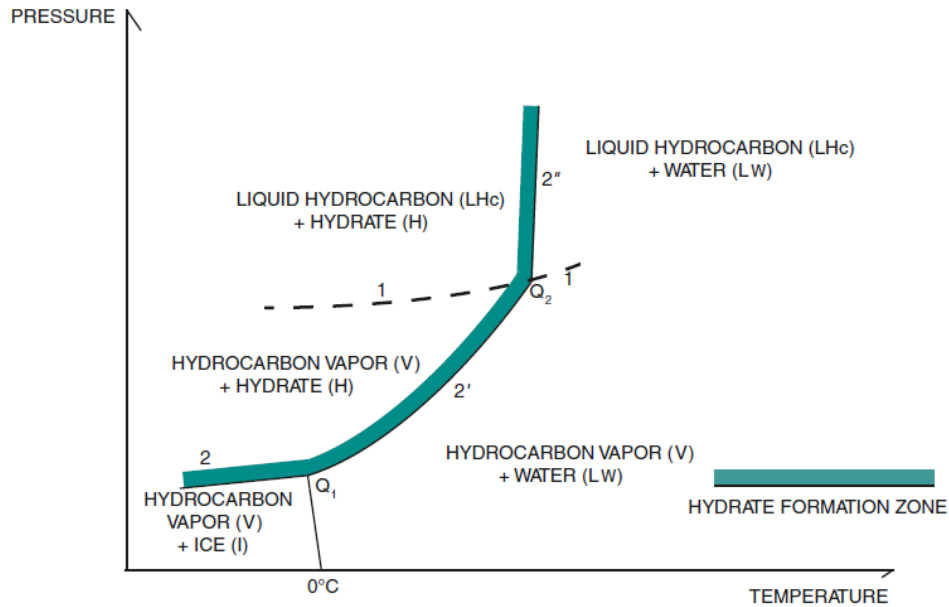
different cage arrangements, especially because of the number of water molecules necessary to capture the guest molecule is different. The hydration number is defined as the ratio of water-to-guest molecules. The most common structures of hydrates include (Giavarini & Hester, 2011):

- Structure I (sI): It is the smallest repeating crystal unit, which is a body-centered cubic lattice composed of 46 water molecules with 6 large cages and 2 small cages. Gases that commonly form sI hydrates include methane, ethane, CO<sub>2</sub>, and H<sub>2</sub>S. The hydrate number for full occupancy is 5.75 (46/78). See Figure 6 (left) adapted from (Giavarini & Hester, 2011).
- Structure II (sII): The unit cell is a face-centered cubic lattice composed of 136 water molecules with 8 large cages and 16 small cages. Gas molecules that commonly form sII hydrates include propane and I-butane, and those that form small sII hydrate structures include hydrogen, helium, and nitrogen. The hydrate number for full occupancy and small sII structures is 5.67 (136/24) and for large sII structures is 17. See Figure 6 (right) adapted from (Giavarini & Hester, 2011).
- Structure H (sH): The unit cell has a hexagonal lattice composed of 34 water molecules with 3 different types of cages: 3 small cages, 2 medium cages, and 1 large cage. One of the gas molecules that commonly forms sH hydrates is methylcyclohexane. However, the formation only happens with the help of a second small gas molecule (*i.e.*, methane), which is needed to stabilize the small and medium cages present in this structure.



**Figure 6. Small cage of a hydrate type 1 and 2. Adapted from (Giavarini & Hester, 2011).**

Figure 7 reprinted with permission from (Giavarini & Hester, 2011) shows an example of a typical phase diagram for pure hydrocarbons that form hydrates. The curve defines the points where the hydrates are stable, and it is called the hydrate stability curve. The hydrate stability curve is composed of two main regions (Giavarini & Hester, 2011): 1) the hydrate stability region, which is represented by the left region of the line (generally low temperatures and high pressures); and 2) the right region of the line, in which theoretically the hydrates cannot be stable. The curve has two quadruple points, Q1 and Q2, where four phases coexist. In the case of Q1, the four coexisting phases include Liquid water ( $L_w$ ), Ice (I), Hydrate (H), and Hydrocarbon Vapor (V), while for Q2, the coexisting phases are Liquid water ( $L_w$ ), Hydrate (H), Hydrocarbon Vapor (V), and Liquid Hydrocarbon ( $L_{HC}$ ).



**Figure 7. A typical P-T diagram for a pure hydrocarbon (larger than methane). Reprinted with permission from (Giavarini & Hester, 2011)**

The fundamentals of the current thermodynamic models were established by formulating hydrate thermodynamic property prediction methods. Different methods have been developed since 1951, either by doing experiments, correlations and/or models, for instance, those done by Kobayashi and Katz (Kobayashi & Katz, 1953), or studies such as those recently completed by Harmens and Sloan (Harmens & Sloan, 1990) and Hou (Hou, Hester, Sloan, & Miller, 2003). All these studies were focused on binary (such as hydrocarbon-water systems) and ternary systems. The most recognized and useful way to generate the phase diagram is by determining the equilibrium of the three phases (Lw-H-V). These diagrams allow one to define under what conditions of pressure and temperature hydrates can form for a given gas and water composition. The two existing methods for determining the equilibrium of the three phases are the gas gravity method and the

distribution coefficient method ( $K_{vsi}$ ) method. One disadvantage of the gas gravity method is that it cannot be used to calculate the hydrate composition. However, in 1959, van der Waals and Platteuw developed one of the earliest but most remarkable approaches used in the development of the method for determining the equilibrium of the three phases currently used, which allows for the calculation of the hydrate composition. This method uses statistical thermodynamics to predict equilibrium conditions including intermolecular potentials using microscopic properties at a given pressure and temperature. For many years, this method has been refined by different scientists, giving a good estimation of the hydrate phase equilibrium (Sloan Jr & Koh, 2007).

Nowadays, there are different commercially available software programs used for hydrate formation prediction. These programs use models based on the statistical thermodynamic approach with some modifications that increase the accuracy of the model. For instance, the basis for the PVTsim (version 13) (Calsep, 2015) is the chemical potential and the minimization of Gibbs Free Energy.

Ballard and Sloan (Sloan Jr & Koh, 2007) developed a study to compare the accuracy of the different commercial hydrate programs. They found that between the different programs, the average absolute error in the temperature is confined to a range between 0.4 to 0.66 kelvin degrees, which is acceptable in the engineering world. However, the current changes to the oil and gas composition associated with the new reservoirs and the field life, bring new challenges related to the accuracy of the models available, which introduces a degree of uncertainty into the calculations when making selections, for example the salt content composition has changed over time. Nevertheless,



in 2014, Shahnazar (Shahnazar & Hasan, 2014) performed an extensive review on the experimental and modeling approaches where she found that, from the total number of papers reviewed, the modeling categories are distributed as follows: thermodynamic models (50% ), gas gravity (31%) and, finally, statistical and neural network approaches (19%). Shahnazar concluded that further studies on statistical and neural network approaches should be considered and should have specific qualities including: 1) necessary variables; 2) increased accuracy; and 3) a “Faster and more robust neural network algorithm should be used rather than the typical ones.”

#### **2.4 Kinetic Models of Hydrate Formation**

Kinetic models help to determine when and where the hydrate may form, by understanding the growing and agglomeration process as a function of time. During the last decade, the oil and gas industry has been exploring the possibility of moving from hydrate avoidance techniques towards risk management techniques. There are many reasons that support this change. For instance, some systems have a phase equilibria (hydrate avoidance) without enough data to analyze and conclude if hydrate formation is probable or not. Some studies found that, even under the right conditions for hydrate formation (over the hydrate equilibrium curve), hydrates do not form for a period of time (Ribeiro & Lage, 2008; Sloan, 2005). Therefore, analyzing a system using hydrate avoidance purely based on thermodynamics could have some limitations. Thus, a risk management approach helps to study the hydrate formation as a function of time. The basis of risk management is the quantification of the hydrate kinetics (Sloan, 2005) that are able to enter in the hydrate formation region during operations. Nevertheless, in order

to implement risk management strategies, it is fundamental to understand the kinetics of hydrates (Ribeiro & Lage, 2008).

Although the hydrate kinetic process does not undergo any reaction (rather the structure is formed by hydrogen bonds), it can be represented by a crystallization process, which is defined by two steps: a nucleation process and a growth process (Sloan, 2005). Through nucleation, a supersaturated solution creates the right conditions to allow the generation of stable hydrate nuclei, which continuously grow during the growth step.

#### ***2.4.1 Hydrate Nucleation***

In 2008, Ribeiro and Lage (Ribeiro & Lage, 2008) developed state-of-the-art modeling for hydrate formation kinetics, in which they explained the hydrate formation as a “phase change process”, which is induced by a supersaturation environment, and described the process as a function of the Gibbs Free Energy. They found that if the ratio of the Gibbs Free Energy of the gas solved in the liquid to the Gibbs Free Energy of the hydrate is greater than 1, the aggregation of the water and gas molecules is favored. Also, the positive variation of the Gibbs Free Energy is associated with the separation of a new phase. Therefore, they concluded that the opposite results from the components of the Gibbs free energy of the system ( $G_{\text{sys}}$ ) is related to the size of the cluster.

In the early stages of the nucleation process, the system is highly dependent on the interfacial area. Because of this reason, it has been concluded that the most likely zone for nucleation is the gas-liquid interface. The key parameters associated to nucleation are: Gibbs Free Energy of the system ( $G_{\text{sys}}$ ); cluster radius ( $r$ ); critical radius ( $r_c$ ), which is the minimal stable radius; and nucleation time ( $t_{\text{nuc}}$ ), which is defined as “the time interval

between the establishment of super-saturation and the formation of the first clusters with  $r = r_c$  (Ribeiro & Lage, 2008).”

Many studies have been developed to prove the existence of the nucleation time and to understand its dependences with different operational conditions. For instance, in 1993, Skovborg *et al.* (Skovborg, Ng, Rasmussen, & Mohn, 1993) studied the nucleation time of different gases and their mixtures in a stirred reactor and found that “for a given pressure and temperature conditions, the value of  $t_{nuc}$  was observed to decrease when the stirring speed was raised”. Also, in 1987, Englezos *et al.* (Englezos, 1993) found that the nucleation time was highly sensitive to the operating temperatures. Thus, the driving force for hydrate nucleation was defined by Skovborg as a function of the chemical potential difference for water in the liquid and hydrate phases for specific operating conditions.

In 1994, Natarajan *et al.* (Natarajan, Bishnoi, & Kalogerakis, 1994) defined the driving force for hydrate nucleation as a function of the fugacity of the guest molecules at different phases (gas ‘ $f_{i,G}$ ’ and hydrate ‘ $f_{i,H}$ ’) and different conditions (operating and equilibrium). Based on this definition, the authors were able to propose a correlation to calculate the nucleation time ( $t_{nuc}$ ) for methane, ethane and carbon dioxide as follows:

$$t_{nuc} = K \left[ \frac{f_{i,G}(T_{OP}, P_{OP})}{f_{i,H}(T_{OP}, P_{eq})} - 1 \right]^{-m}$$

The parameters  $K$  and  $m$  depend on the properties of the guest molecule and the system where it is measured.

After reviewing the main parameters that determine the nucleation process, it is clear that, in order to have a good model of hydrate nucleation, it is critical to define the driving force correctly. In 2002, Kashchiev and Firoozabadi (Kashchiev & Firoozabadi, 2002) modified the existing definition and defined the driving force as the difference between the chemical potential of an old and new phase calling it super-saturation ( $\Delta g$ ) and expressed it as follows:

$$\Delta g = \mu_{GS} + n_w \mu_w - \mu_H$$

In this expression,  $\mu_{GS}$  and  $\mu_w$  are the respective chemical potentials of gas and water and  $n_w$  is the water molecule. Finally,  $\mu_H$  is the chemical potential of the unit.

In 2004, Anklam and Firoozabadi defined a new expression for the driving force of hydrate formation from gas multicomponent. This expression was developed based on the previous work done by Kashchiev and Firoozabadi, which is one of the expressions widely used.

$$\Delta g = n_w [\mu_w(T, P) - \mu_{w,H}(T, P, w)]$$

#### **2.4.2 Hydrate growth**

As Ribeiro and Lage (2008) described in their review, the system (oil, gas and water at low temperatures and high pressures) presents a decrement in the Gibbs Free Energy when the critical radius is overcome and the nucleus starts growing. As a result, a considerable increment of the gas consumption is introduced in the system, representing the transition between the nucleation and the growth stages.

After the growth stage starts, if a continuous flow of water and gas molecules reaches the crystal surface, the growth process is maintained. Although the hydrate formation does not involve a chemical reaction but a phase change process, the hydrate growth process is able to release energy in the form of heat. This increment of heat could negatively impact the driving force, increasing the hydrate decomposition.

In 1983, Vysniauskas and Bishnoi (Vysniauskas & Bishnoi, 1983) proposed the first hydrocarbon hydrate kinetic model based on a methane hydrate formation study developed in a stirred semi-bath reactor using cooling jacket. The system was operated at a constant pressure, and the temperature was controlled with a cooling system. The study measured the gas consumption as a function of time at different operating conditions, moving in certain intervals as follows:  $274 \leq T \text{ (K)} \leq 284$ , and  $3 \leq P \text{ (MPa)} \leq 10$ . The following semi-empirical expression estimates the methane consumption rate of the system during the growth process:

$$-\frac{dm_{gas}}{dt} = k_B A_S (\Delta T)$$

where  $m_{gas}$  represents the mass of the gas consumed,  $k_B$  is the reaction rate constant,  $A_S$  is the surface area of the interface, and  $\Delta T$  is the sub-cooling temperature difference.

Over the years many kinetic models have been developed by different authors, for instance: Englezos *et al.* model (Englezos, 1993), Skovborg and Rasmussen model (Skovborg *et al.*, 1993), Herri *et al.* model (Herri *et al.*, 1999), among others. However, one of the more recent studies was developed in 2007 by Boxall *et al.* (Boxall *et al.*, 2009), in which a kinetic model is proposed using Vysniauskas and Bishnoi as a fundamental

equation for the model. The model was named Colorado School of Mines hydrate kinetic (CSMHyK) and later incorporated the transient multiphase program, OLGA (Boxall *et al.*, 2009). The Boxall *et al.* model was developed under the following assumptions: “hydrate particles convert directly from emulsified water droplets, nucleation occurs at a sub-cooling temperature of 6.5 °F, and, once the hydrate is formed, the model assumes that these particles remain in the oil phase.”

Although the Boxall *et al.* model has been widely implemented in different companies, the kinetic model of hydrate formation is not fully understood, and the models are still associated with a high level of uncertainty, especially for the oil dominated systems.

## **2.5 Prevention, Mitigation and Remediation Techniques:**

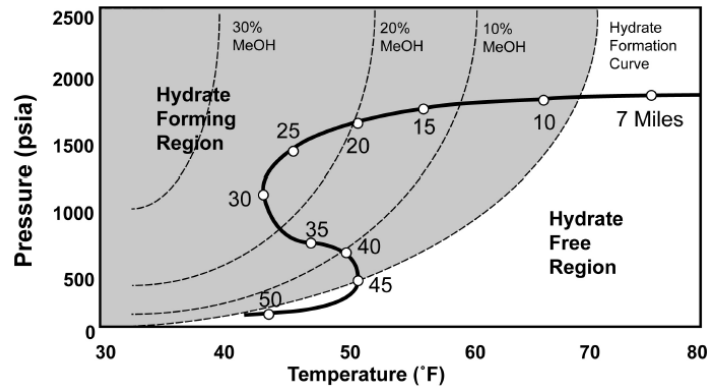
The oil and gas industry has recognized hydrate formation issues as one of the major concerns in flow assurance problems. Although the hydrate formation phenomena is not completely understood, academia and industry have been implementing different techniques. As it was mentioned by Kinnari *et al.* in 2014, there are three main parts of hydrate control: 1) the understanding of when and where a hydrate issue can be present (prediction), 2) knowing the preventive and mitigation strategies (methods) to implement depending on the system (prevention), and 3) knowing and being prepared to remediate the hydrate issue (problem-solving). These three components are known as the 3P’s of hydrate control (Kinnari, Hundseid, Li, & Askvik, 2014).

Some of the hydrate control techniques include chemical methods (use of inhibitors); thermal methods (insulation, direct electric heating, heat tracing, bundles); hydraulic methods (fluid displacement, gas sweep, depressurization, compression, and dense phase, pigging systems); and process solutions (gas dehydration, water cut reduction) (Kinnari *et al.*, 2014). Nevertheless, during the last decade, the oil and gas industry has widely implemented chemical and thermal methods as a part of their prevention strategies.

### **2.5.1 Chemical Methods (Inhibitors)**

The main function of hydrate inhibitors is modifying the equilibrium phase, the kinetics, and/or the agglomeration process by adding solutes to the water. The inhibitors can be classified as follows:

- A. Thermodynamic inhibitors (THI): The chemicals more commonly used in this category are methanol (MeOH) and monoethylene glycol (MEG) which shift the hydrate equilibrium curve to the left of the phase diagram, moving it to the extreme equilibrium conditions (low temperatures and high pressures) as shown in Figure 8 reprinted with permission from (Notz, 1994).



**Figure 8. Deep water pipeline with hydrate curve at different MeOH concentrations. Reprinted with permission from (Notz, 1994).**

The action mechanism is driven by a reaction between the methanol and water, reducing the water molecules available to interact with the light gases to avoid the hydrate formation. Nevertheless, there are some advantages and disadvantages associated with each one. Although MeOH is more effective, cost efficient, and has a low viscosity (which reduces the pump requirements), it possesses a large HSE risk, because it is highly volatile (flash point of 51.8 °F). An additional drawback of using methanol is that a too high methanol concentrations in the crude oil can exceed product specifications (50 ppm of MeOH) leading to quality problems. It is not uncommon to exceed these limits, because methanol cannot be removed from the crude oil in a cost effective way (Patel & Russum, 2010; Tian *et al.*, 2011). On the other hand, using MEG could be more expensive, it definitely possesses less risk. MEG has corrosion protective benefits, it can be recovered, and it is economically feasible, making it a long-term solution. Nonetheless, the



effectiveness depends on the good conditions which need to be assessed (Bui, 2016).

In general, the use of any type of THI can bring different drawbacks, for instance: high volume of inhibitor requirements (*i.e.*, 30 to 60% by volume of methanol based on aqueous phase) (Patel & Russum, 2010), contamination, scaling problems, safety concerns (MeOH), and reduction of the production rates (Tian *et al.*, 2011).

B. Low Dosage inhibitors (LDHI): There are two types of inhibitors under this category, including Kinetic Inhibitors (KI), which are able to retard crystal growth and/or nucleation for a specific period of time. This period of time is called “induction time” which depends on the subcooling temperature. Also, the AAs are surfactants that interrupt the formation of hydrate crystals through the active surface which are attached to the small particles (nucleus), preventing the agglomeration by creating a hydrophobic surface. During the last two decades, a large number of LDHIs have been studied as alternatives to replace THI and overcome certain issues associated to the use of THI. One of these issues involves the high inhibitor injection rate which requires a large storage capacity, which pose a safety concern for the system. Typical injection rates of LDH are around 0.5-2.0 % by volume (Patel & Russum, 2010).

Kinetic inhibitors (KI) are generally water soluble polymers, including polymers based in homo-polymers and copolymers of vinyl caprolactam (Vcap) (Chua *et al.*,

2012). Kinetic inhibitors are environmentally friendly and can be operated at low cost; these are some of the advantages of using KI. However, these inhibitors have a number of performance limitations in systems with high concentrations of H<sub>2</sub>S and CO<sub>2</sub> and high sub-cooling temperature, because the majority of KI available are not designed for severe conditions (Al-Eisa *et al.*, 2015).

On the other hand, AAs do not depend on sub-cooling temperatures, because, in this case, the system allows small crystals to form and disperse within the oil layers (Bui, 2016). However, these have two key limitations: a water cut range in which they are more efficient (40-60% water cut) and a topside emulsion formation which depend on the system conditions (Patel & Russum, 2010). Also, AAs have some other limitations, including salt concentration in the water, in which having a concentration between 1.5-3.0 wt.% of salts leads to poor performance, also high GOR values in gas condensate systems is other limitation (Patel *et al.*, 2011).

### **2.5.2 Thermal Methods (Insulation)**

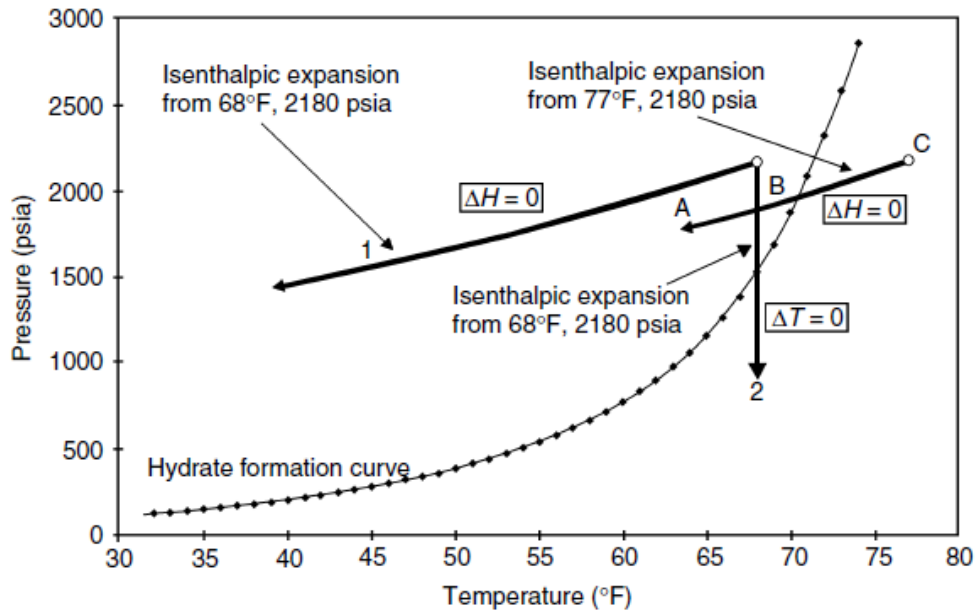
The intent of these methods relies on maintaining the temperature of the fluid over the hydrate formation temperature, preventing the system from falling within the hydrate equilibrium curve (hydrate zone). Different methods have been proposed in this category, however, the cost-benefit of their application is always a concern. Therefore, the application of these methods is frequently found in equipment close to the wellhead and/or short pipelines and flowlines. Thermal methods are often implemented during the earliest stages of the project. One of the common thermal methods used in industry are discussed below:

A. Insulation: the purpose of the insulation is to avoid heat transfer to the environment, maintaining the heat of the system using materials or fluids with low thermal conductivity. Materials, such as polyurethane, can be formed into layers with different thicknesses, depending on the requirements of the system (Wilfred & Appah, 2015). Also, the annulus can be filled with different fluids with low thermal conductivities. In a study developed by Owodunni *et al.* , the effectiveness of the insulating materials was found using flow conditions as prevention with the heat loss reduced at shut down conditions (Owodunni & Ajiienka, 2007).

### **2.5.3 Hydraulic Methods (depressurization)**

Depressurization is the common method used in this category, which involves dissociating the hydrate plug in-place. This method is part of the remediation measures, and it can be implemented in drilling or production operations. Also, it is simple to apply, and the expenses of the application are low.

The purpose of the depressurization process is to reduce the pressure, trying to place the system conditions outside of the hydrate zone (under the hydrate equilibrium curve). Depending on the hydrate plug location, the depressurization process can present isenthalpic rapid expansion (*i.e.*, through a valve) and very slow depressurization (*i.e.*, in a large volume pipeline) (Sloan Jr & Koh, 2007). Therefore, the hydrate becomes thermodynamically unstable. Figure 9 reprinted with permission from (Sloan Jr & Koh, 2007) shows a representation of both situations.



**Figure 9. Temperature changes as a result of depressurization (1) isenthalpic rapid expansion as through a valve, and (2) very slow depressurization, as in a large-volume region. Reprinted with permission from (Sloan Jr & Koh, 2007).**

The depressurization method used for hydrate remediation can be implemented from both sides of the blockage or only from one side. The choice of the method will depend on the configuration of the system (*e.g.*, flowline, wellbore, riser). Although depressurization from only one side of the blockage is possible, it is recommended to implement a two-side depressurization due to safety concerns (*i.e.*, to prevent that the hydrate plug becomes a high speed projectile). For systems where hydrate formation is expected and depressurization is considered a remediation alternative, this design should be defined in the earliest stages of the project, as a modification during production may not be feasible.

#### **2.5.4 Process Solution (water reduction)**

The basis of the process solution is to reduce the amount of water available to form hydrates, either in gas or oil systems. There are some challenges associated with the water removal process because hydrates can form even when water concentration is very low (ppm range). Also hydrates can form in the vapor space of multiphase systems. On the other hand, an approximate amount of 3 Barrel of Water Per Day (BWPD) is produced from the oil well (SPE-International, 2016), which requires a large process surface facility with high associated costs.

### **2.6 Hydrate Management Systems (HMS):**

Throughout the last two decades, companies have started to implement specific systems to manage the hydrate issues in their operations. Once a system is established, it becomes easy to evaluate its implementation and the risk associated to hydrate plugging, which is the fundamental problem in managing the hydrate formation (Kinnari *et al.*, 2014). As it was mentioned in Section 2.5 above, there are different methods to prevent, mitigate and remediate the hydrates, which can be incorporated into the HMS. Currently, the system includes different components, such as topside processing facilities, metering, monitoring, hydrate formation prediction (simulations), operator analysis based on the metering and simulations (human knowledge and intervention), application and control of the preventive methods (THI and/or LDHI), mitigation and remediation methods. However, there is not a unique HSM. Every company implements the most convenient methods for their facilities due to their unique operational discipline, resources, and, most

importantly, their own product compositions, which makes it difficult to standardize an HMS.

Companies have customized their own HMS based on their experience and resources. For instance, OneSubsea (Schlumberger) uses MEG, which is a THI, as the primary preventive method to avoid hydrate formation (Lupeau, Smith, Seng, & Grzelak-OneSubsea, 2016), while Halliburton uses LDHI, which needs a constant vigilance of the data-flows and conditions for every part of the system (Patel, 2015). The two previous examples provide a comparison between hydrate avoidance versus hydrate management (or risk management), in which the hydrates are allowed to form as small crystals but are controlled by interrupting their growth process (KHI) or the agglomeration process (AAs). Therefore, the factors that may influence the overall risk in one (OneSubsea) HMS are not the same in another HMS (Halliburton).

**Table 2. Qualitative comparison of the avoidance approach vs. risk management approach systems**

<b>Component</b>	<b>Avoidance Approach (THI)</b>	<b>Risk Management (LDHI)</b>
Hydrate formation prediction (simulations)	1) Dependence on the thermodynamic models: <b>(High)</b> 2) Dependence on the Kinetic Models <b>(Low)</b>	1) Dependence on the thermodynamic models: <b>(High)</b> 2) Dependence on the Kinetic Models <b>(High)</b>
Operators analysis based on the metering and simulations	<b>High</b>	<b>High</b>
Metering	<b>High</b>	<b>High</b>
Monitoring	Level of Vigilance <b>(Medium)</b>	Level of Vigilance <b>(High)</b>

**Table 2 Continued**

<b>Component</b>	<b>Avoidance Approach (THI)</b>	<b>Risk Management (LDHI)</b>
Human interface level	<b>Medium</b>	<b>High</b>
Hydrate formation allowed	<b>NO</b>	<b>YES</b>
Level of safety	<b>Safer approach</b>	<b>Less safe approach</b>
Operating expenditure (OPEX)	<b>High</b>	<b>Medium</b>

Table 2 shows differences between the two approaches, in which each component has different uncertainties. An example of the uncertainties associated with each HMS is mentioned by Lupeau A. *et al.* (2016). He explained the HMS of OneSubsea where the system starts in the PureMEG that is the regeneration process located in the topside of the facilities and is used to recover the MEG up to 95% as shown in Figure 10 adapted from (Lupeau et al., 2016):



**Figure 10. Schematic of OneSubsea Hydrate Management Systems. Adapted from (Lupeau et al., 2016).**

As the author mentioned, measurements, in general, are fundamental to assess the risk associated with hydrate plugging, especially the wet-gas water or water cut measurements. These measurements bring a lot of challenges related to the technologies available. Lupeau A. *et al.* also mentioned that, “significant changes in water properties (*i.e.*, salinity) will affect the water measurement accuracy of any device;” therefore, recorded data through the field life is essential. Currently, the Vx PHASEWATCHER device is being used to measure different flow rates, because it is an inline flowmeter that is able to measure three-phase flow rates (oil, water, and gas). However, OneSubsea developed a new device called AQUAWATCHER (conductivity probe) in which the principle is a microwave reflection measurement. This device has a lower uncertainty in measuring water composition. Nevertheless, Lupeau A. *et al.* mentioned that the parameters that operators want to monitor, in order to have effective operation, are all



related to flow rate (gas, condensates, vapor water, condensate water, and formation water) and salinity.

These measurements will then be used to continually simulate the flow using the incorporated software called OLGA, which will help the operator to identify any alert of hydrate formation and also help to determine the amount of inhibitor needed. The inhibitor is delivered into the flowline through a system involving different equipment: chemical injection unit (topside), umbilical, and chemical injection valve, among others. In general, an HMS is a highly complex system that involves different factors with real time operations, which can accumulate uncertainty in the final calculation of the risk associated with hydrate plugging. Figure 11 adapted from (Grzelak & Bussell, 2015), shows a representation of the accumulating and compounding uncertainties (Grzelak & Bussell, 2015).

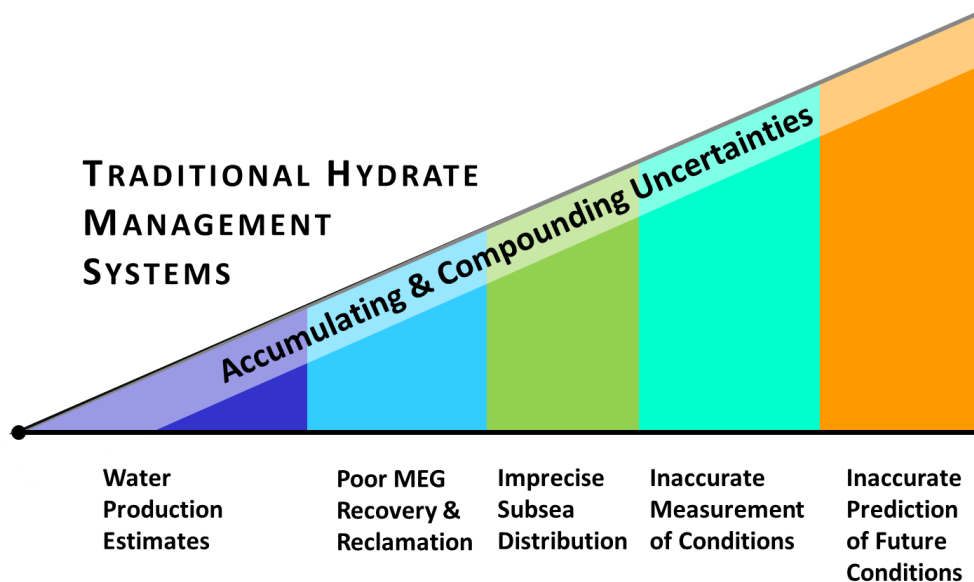


Figure 11. Accumulating and Compounding Uncertainties. Adapted from (Grzelak & Bussell, 2015).

## **2.7 Quantitative Risk Analysis and Probabilistic Approach:**

Cost-benefit is the main driving factor to look for a different approach to control the issues associated with hydrate formation (Sloan, 2005). This is reasonable since the ultimate objective of any operator company is to produce oil and gas in a cost effective way. However, any approach to control hydrate formation has an inherent risk that can lead to different consequences, including economic, environmental, and/or health (human losses). Thus, each company has their own risk appetite in which the risk acceptance level will vary. Consequently, it becomes important to know the total risk associated with the HMS in a comprehensive manner.

As it was mentioned in section 2.6, the HMS has different components. Therefore, in order to understand the total risk associated with the system, it is necessary to know the risk associated with each component.

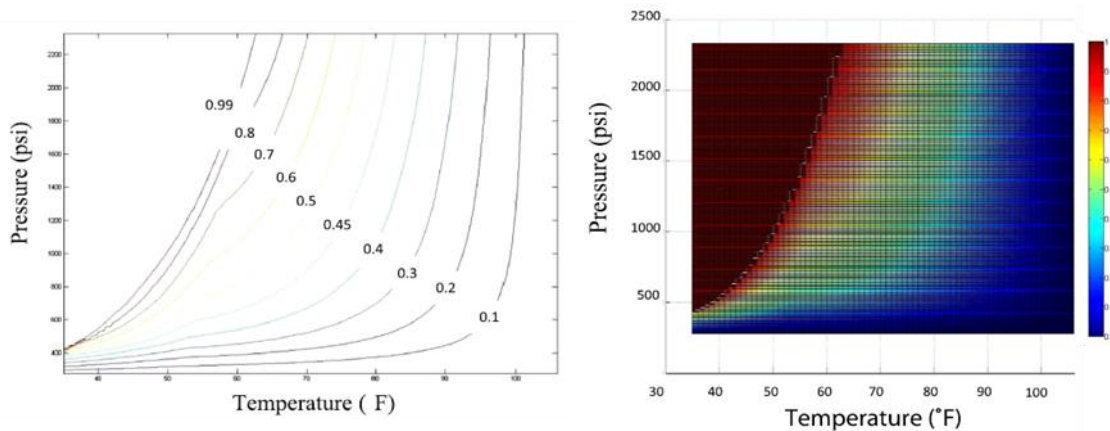
Predicting when and where the hydrate might form, poses a large uncertainty due to the inaccurate models used to develop this analysis. Currently, the most used model to predict hydrate risk is called CSMHyFAST, which is incorporated into a transient flow simulator (OLGA) and is able to calculate different aspects of the hydrate phenomena in oil dominated systems, including nucleation (formation), growth parameters, pressure drop and relative viscosity. In 2012, Zerpa (Zerpa, Sloan, Koh, & Sum, 2012) defined a risk criteria based on the gas hydrate model. This risk criteria is defined by three performance measures: pressure drop, volume fraction of the hydrate particles, and relative viscosity. Also, it was divided into three risk levels (low, intermediate, and high) as listed in Table 3.

**Table 3. Risk criteria for a qualitative assessment (Zerpa *et al.*, 2012).**

<b>Risk Level</b>	<b>Pressure drop <math>\Delta P_{flowline}</math> (psi)</b>	<b>Volume particle of the hydrate <math>\Phi_{hyd}</math></b>	<b>Relative viscosity <math>\mu_r</math></b>
Low	$\Delta P_{flowline} < 300$	$\Phi_{hyd} < 0.10$	$\mu_r < 10$
Intermediate	$300 < \Delta P_{flowline} < 500$	$0.10 < \Phi_{hyd} < 0.40$	$10 < \mu_r < 100$
High	$\Delta P_{flowline} > 500$	$\Phi_{hyd} > 0.40$	$\mu_r > 100$

Similarly, in 2015, Chaudhari (Chaudhari, 2016) developed a study on hydrate risk quantification in oil and gas production focused on oil dominated systems named CSMHyK; this model is still in an early stage. Chaudhari concluded that, although the risk criteria established by Zerpa in 2012 is a good approximation, it might not be applicable to others systems such as oil dominated. Therefore, it can be confirmed that this risk model is still limited and is not based on a probabilistic approach.

The aforementioned risk models depend on certain inputs, including the hydrate equilibrium curve (phase diagram) that is obtained from different thermodynamic models which, at the same time, hold a level of uncertainty. For instance, in 2015, a study developed by Herath *et al.* proposed a basic probabilistic method to determine the hydrate equilibrium curve, not derived from point values but from probabilistic curves outside of the hydrate zone, for any given operational condition. Figure 12 reprinted with permission from (Herath *et al.*, 2015), shows the probability of hydrate formation within the operating range.



**Figure 12. General phase diagram with probability curves under the hydrate equilibrium (left); Phase diagram of 99% CH<sub>4</sub> and 1% C<sub>2</sub>H<sub>6</sub> with the probability representation under the hydrate equilibrium (right). Reprinted with permission from (Herath, Khan, Rathnayaka, & Rahman, 2015)**

A probabilistic approach allows for a better understanding of the problem and its associated uncertainties. Therefore, it is also necessary to understand the kinetic and flow models using probabilistic approaches. A study completed by Herath and Faisal, in 2016, implemented a probabilistic approach during the design phase in order to prevent hydrate formation (Herath, Khan, & Yang, 2016). However, there is not one study that integrates the whole Hydrate Management System and determines the probability of hydrate plugging in the system while integrating all the components of the HMS. Thus, the present study proposed a framework as the first step towards this direction.

### 3 PROPOSED FRAMEWORK

This section describes the proposed framework for modeling the operational risk of the Hydrate Management System (HMS), which is composed of three areas. The framework includes an integration of pure deterministic methods with probabilistic techniques through the application of Bayesian Networks (BN). This approach will help identify the interdependencies among the individual interfaces, processes, and their components related to hydrate risk management. The outcome of this framework will provide a better understanding of how individual components might affect other components as well as the whole hydrate management system.

#### 3.1 Framework: “Modeling Operational Risk of Hydrate Management Systems Using Bayesian Networks”

This basic framework was developed as part of modeling the operational risk in a hydrate management system. The proposed approach will help identify interfaces among the different components of subsea systems and determine their conditional dependencies with the purpose of modeling and managing the risk of hydrate formation and providing a tool for better decision making. This basic framework (Figure 13) is further divided into three main areas of study:

##### 3.1.1 Area 1 (*Scenario definition and causal & consequence modeling*)

This area focuses on defining the subsea scenarios. Depending on how well the scenarios are defined, the dependencies between the different components will be easy to understand.

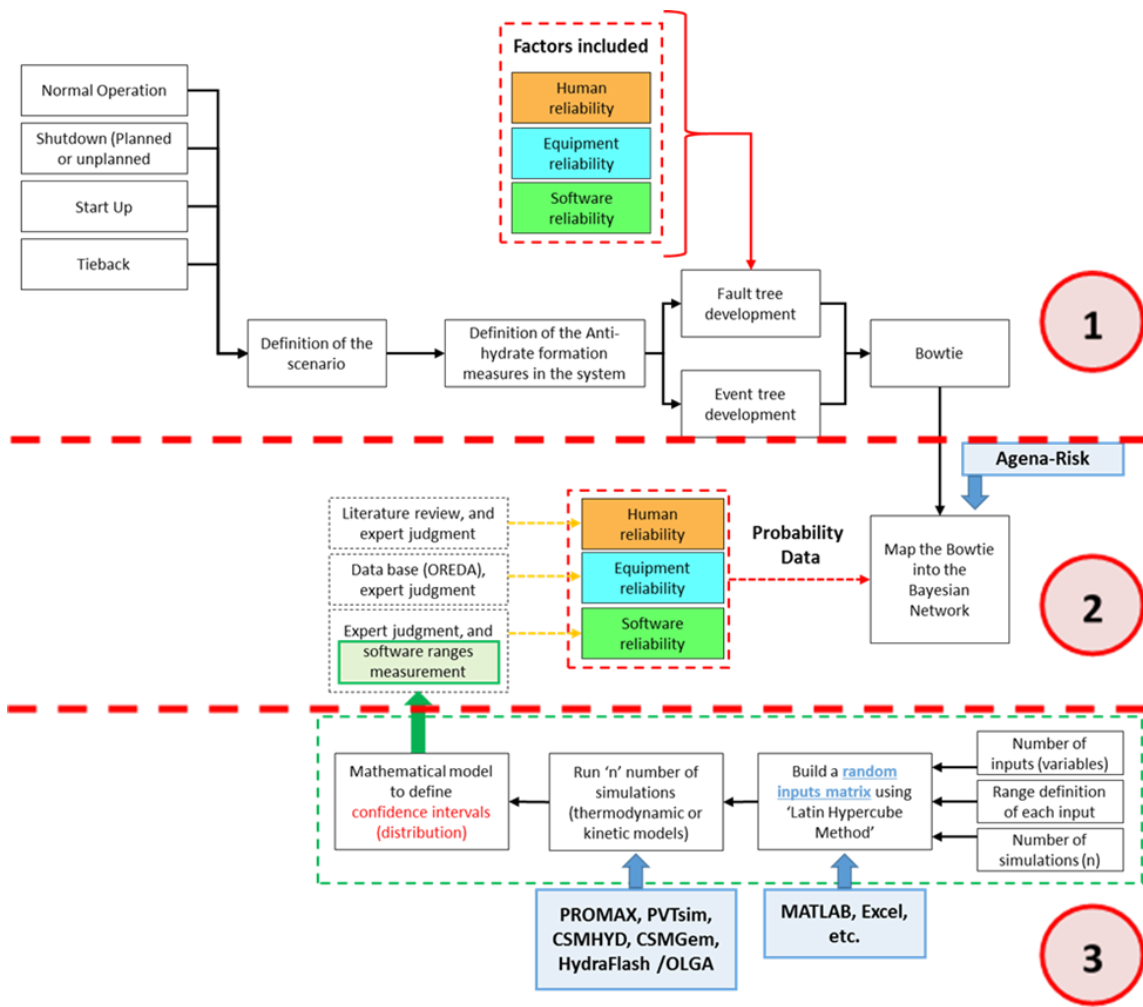


Figure 13. Modeling operational risk of hydrate management

### 3.1.1.1 Scenario Definition

This study is focused on the production operations from wellhead to topside, including equipment such as the Christmas tree, jumpers, manifolds, flowlines, risers, and topside processes. The scenario can include different equipment based on the activity involved, such as normal operations, shutdown, or start up. For example, an unplanned well shutdown can be caused by different reasons, including failure of any subsea

equipment (hydraulic leak or electrical failure), High-High (HH) or Low-Low (LL) on pressure and temperature alarm systems, failure in subsea control equipment, or software failure, among others. Hydrate formation is one of the biggest concerns during an unplanned shutdown, because the equipment becomes cold due to the temperature of the surrounding environment. This phenomenon is commonly known as a thermal-related risk (Ellerton & Chauvet, 2009). During an unplanned shutdown, there may not be enough time to implement the whole procedure to depressurize, inhibit, or purge, which helps avoid hydrate formation (Ellerton & Chauvet, 2009). In such a case, the absence of the aforementioned procedures can allow the trapped fluids to reach the conditions necessary for hydrates to form.

The total time from the moment of shutdown until the system reaches hydrate formation conditions is defined as the “cooldown time.” Therefore, operators use the cooldown time to solve the situation, which is usually around 20 hours. The cooldown time is broken into three different times (Bai & Bai, 2012): a) ‘No touch time’- hydrate mitigation is not necessary. This is around four hours and is used to prepare the plan in case the operation is not recovered. B) ‘Light touch time’- methanol is injected into dead leg areas: for example, trees, well tubing and tree jumpers. C) ‘Displacement time’- live crude content in the flowlines is displaced. The whole process involves technical and management components that need to be studied as a general picture in order to identify causation and be able to control it. A similar situation happens at every scenario, like normal operations.

### ***3.1.1.2 Definition of formation avoidance measures in the system***

Based on the scenario and case study, the formation avoidance measure could be different. It might include not only one measure but also a combination of different measures, including Hydrate Inhibitors (THI and LDHI), Electrical Heating (DEH and ETH), and Isolation Systems. However, the developed framework is designed to assess the operational risk associated with the hydrate management systems used to control hydrate formation through the life of the field, rather than assessing the engineering design. Certainly, the design parameters will be taken into account, as part of the inputs in some of the simulations, in order to estimate the amount of inhibitor required to ensure straightforward operations.

### ***3.1.1.3 Fault tree development***

Fault tree analysis is a deductive method that helps identify ways in which hazards can lead to incidents (Crowl and Louvar 2011). The analysis starts with a well-defined incident (top event) and works backwards towards the different intermediate or basic events that can lead to the incident. Considering that hydrate formation events are highly complex phenomena that depend on many variables, either technical or managerial, it is important to understand the basic event or events that can lead to failure due to hydrate formation (plugging).



The top event considered in this study is defined as a loss of control, which can lead to an uncontrollable hydrate formation and might form a plug. Therefore, the proposed factors to include in the fault tree are human, equipment and software reliabilities. Most of the hydrate management systems used across the oil and gas industry



include a considerable level of human intervention, such as monitoring operational variables, competencies, and communication. Thus, human reliability can represent the basic event of the hydrate management system. The equipment reliability of the inhibitor injection, including pumps, valves, lines (topside), control systems, dynamic or static umbilical, distribution module, etc. should be included in the total measure of the risk. Finally, the software reliability is highly important to estimate the inhibitor composition necessary to prevent hydrate formation and to predict when and where hydrates will form. However, thermodynamic models and kinetic models do not always perform an accurate prediction. Although current thermodynamic models are accurate enough, they are not suitable to predict hydrate formation under changing oil and gas compositions, such as high salt content and ultrahigh pressures/deep waters. In addition, the kinetic mechanism of hydrate formation is not fully understood yet. Therefore, the existing hydrate kinetic models are not highly precise, which can bring some uncertainty into the system. The reliability of this calculation might depend on different factors, including the input quality, model uncertainty, and the competencies of the person (or group of people) developing the simulation calculation.

The mathematical and probabilistic development is driven by the combination of the component failures, the cut sets (basic events), and the way these events are interconnected by the logic gates (Ericson, 2015). The most common gates used in process safety systems are AND and OR, which are defined as follows (Table 4):

Table 4. AND & OR gates definition (Ericson, 2015).

Gate	Symbol Representation	Definition	Math expression
AND		The output occurs if both inputs occur	$P(1 \text{ AND } 2) = P(1)*P(2) = P(1)+P(2)$
OR		The output occurs if one out of both inputs occurs	$P(1 \text{ OR } 2) = P(1)+P(2)-[P(1)*P(2)]$

There are more logic functions, including Priority AND, Exclusive OR, and Inhibit. However, for this approach only AND & OR are used. The calculations become complex when there are more than two component failures or cut sets.

#### 3.1.1.4 Event tree development

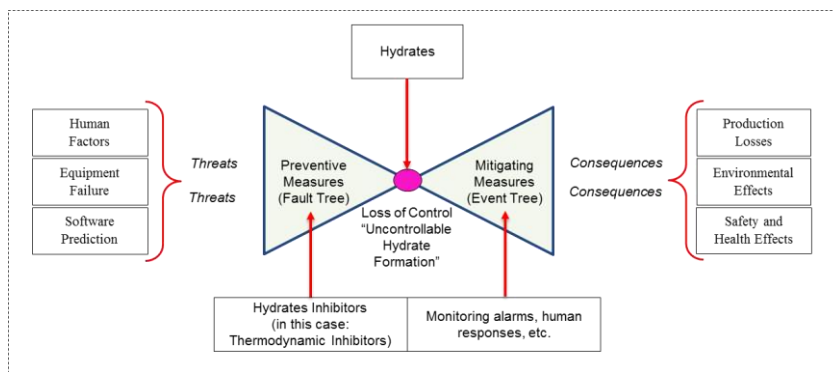
Event tree analysis is a logical technique that helps to determine the event sequences for a specific situation through a single initiating event. In process safety, event trees are widely used to determine the initiating event and identify all possible consequences that can lead to a failure.

The initiating event considered in this study is defined as a loss of control leading to uncontrollable hydrate formation. The mitigation barriers included in the event tree are related to the subsequent actions needed to reduce and control the possible consequences. Therefore, event trees will be different depending on established procedures in each company and for each possible scenario. The possible events to include in the event tree

are alarm monitoring, human interventions (human factors), emergency shutdowns, and the hydrate depressurizing process, among others.

### 3.1.1.5 Bowtie development

Bowtie analysis (Fenton & Neil, 2012) is a combination of two types of operational risk models: fault tree (left side) and event tree (right side). The threats and consequences are tied together using the resulting hazardous event (represented by the knot).



**Figure 14. Hydrate formation Bowtie.**

The proposed bowtie analysis for hydrate formation is included in the framework where some of the threats involved are related to human, equipment, and software reliabilities. The possible consequences considered are production losses and environmental, safety, and health effects.

### 3.1.2 Area 2 (Bowtie mapping as Bayesian Network )

The second area is focused on mapping the bowtie into a Bayesian Network using AgenaRisk or any other suitable software in order to quantify the risk of hydrate formation, including different components of the system.

The biggest challenge in risk assessment is to estimate small and reliable probabilities for rare, catastrophic events (*i.e.*, rupture of a flowline due to an uncontrollable hydrate formation) (Fenton & Neil, 2012). These events do not allow accumulation of enough data to determine their frequency (Fenton & Neil, 2012). Therefore, a value of these small and rare probabilities can be estimated by applying a causal model in the system of interest. A causal model, such as a bowtie, estimates the probability of a rare, catastrophic event through a number of connected processes that prevent, control, or mitigate the event. It is desirable to estimate that probability, for example through a bowtie (Fenton & Neil, 2012). Thus, mapping a bowtie into a Bayesian Network helps to develop statistical/probabilistic modeling and to identify the direct dependencies of the system.

### ***3.1.3 Area 3 (Software uncertainty measurements )***

This area is mainly focused on studying the possible uncertainties associated with each software calculation performed during the operation of the hydrate management system. Depending on the subsea scenario, it could involve thermodynamic or kinetic calculations using different software, including PVTsim, Multiflash, CSMGem, PROMAX, and OLGA (Hydrate Package).

Although the hydrate formation has been described as a deterministic problem, and almost all thermodynamic and kinetic models are deterministic, the uncertainties related to their outcomes need to be estimated when used to support operational decisions. Uncertainty is frequently expressed as a probability distribution, which specifies the likelihood of the possible outcomes. Uncertainty comes from diverse sources and can be

divided into six different classes: inherent randomness, measurement error, systematic error, natural variation, model uncertainty, and subjective judgment. Therefore, the most important type of uncertainty associated with this problem is related to the models, because as mentioned before, the hydrate formation mechanism is not completely understood. Hence, it is valid to mention that the existing kinetic models are an unrefined abstraction of the natural system. Although there is not a clear path to estimate the uncertainties in complex systems, there are some that can be evaluated in order to identify a suitable approach for each system such as (Uusitalo, Lehtikoinen, Helle, & Myrberg, 2015): expert assessment, model sensitivity analysis, model emulation, temporal or spatial variability in the deterministic models, multiple models, and data-based approaches.

Therefore, the framework (Figure 13) proposes to apply a model sensitivity analysis or uncertainty analysis (if available) as a first approach. In a sensitivity analysis, the model inputs are varied to determine how the model outputs respond so inputs that produce the most significant changes in the outputs can be identified. However, only the uncertainty in the model inputs can be accounted for in this approach and not the intrinsic uncertainties in the model's structure (*i.e.*, model approximations, functional relationships between variables) (Uusitalo *et al.*, 2015). Thus, other approaches to obtain the uncertainty in the model's structure can be part of this studies too.

### **3.1.3.1 Sensitivity and uncertainty analysis**

A common practice in developing a sensitivity and uncertainty analysis is using a Monte Carlo method. However, considering the complexity of the thermodynamic and kinetic hydrate models, the framework proposes to use a Latin Hypercube method to build

a random input matrix. The Latin Hypercube method is a modification of a Monte Carlo method in which the number of models to run ( $n$ ) is lower and, at the same time, representative. The last step is to implement a mathematical model to define the probability distribution.

## 4 RESULTS AND DISCUSSION

In this chapter, the proposed framework for determining the risk of hydrate formation to a subsea process was applied to a hypothetical case study. The main objective of this exercise was to establish a proof of concept and show how this framework could be applied in industry. This case study was also intended to identify areas of improvement that can be used to define a path forward for this research.

The case study was built from data obtained in a literature review and the test system was a hypothetical chemical injection skid for a subsea production system. Therefore, a few assumptions were made to define the conditions of the case study. These assumptions will be defined at the time they are used.

### 4.1 Case study

The test system consists of an oil and gas field developed via a single wellhead and a single flowline. The flowline transports natural gas from a satellite platform to a process facility. The process uses injection of thermodynamic inhibitors together with thermal isolation (polyethylene isolation layer with thickness equal to  $5 \times 10^{-4}$  inches) as preventive method for controlling hydrate formation. The asset uses a chemical injection skid for supplying the thermodynamic inhibitor. The company that operates the asset has a hydrate management system in place, which is implemented by the engineers and operators. Table 5 and Table 6 list the equipment used in the case study and the conditions and parameters are provided in Table 7, Table 8, and Table 9 (Wilfred & Appah, 2015).

**Table 5. Top side equipment considered.**

Topside	
Equipment	Description
Pump and Line	Transports the inhibitor from the storage to the injection system
Regular Valve	Chemical injection pump discharge valve
Control systems	Part of the chemical injection skid which is located on deck

**Table 6. Subsea equipment considered.**

Topside	
Equipment	Description
Dynamic umbilical	Transports the inhibitor from the storage to the injection system
Distribution module	Distributes the inhibitor as needed over the seabed
Subsea control system	Control the distribution of the inhibitors over the sea bed
X-mas tree	Stack of valves installed on a wellhead to provide a controllable interface between the well and production facilities (Chemical injection points)
Flowmeter and water sensor	Measure the flowrate and water concentration on the system. This information is used to calculate the required inhibitor rate.

**Table 7. Boundary Conditions (Wilfred & Appah, 2015).**

Parameters	Description	Units
Fluid inlet pressure at satellite platform	1,800	Psia
Fluid inlet temperature at satellite platform	82.4	°F
Minimum arrival temperature at processing facility	78.8	°F
Minimum arrival pressure at processing facility	1,200	Psia
Design fluid flow rate	8,605,440	m <sup>3</sup> /d
Maximum turndown	4,302,720	m <sup>3</sup> /d



**Table 8. Natural Gas Composition (Wilfred & Appah, 2015).**

Gas Composition	Mole Percent
N <sub>2</sub>	0.16
CO <sub>2</sub>	1.02
H <sub>2</sub> O	0.39
C <sub>1</sub>	75.42
C <sub>2</sub>	7.65
C <sub>3</sub>	4.27
n-C <sub>4</sub>	8.42
n-C <sub>5</sub>	2.67

**Table 9. Temperature along the flowline length (Wilfred & Appah, 2015).**

Temperature of the system in function of the length								
Length (miles)	0.62	1.24	1.86	2.49	3.10	3.73	4.35	4.97
Temperature (°F)	80.6	78.8	77	74.3	71.6	68	63.5	60.8

The general assumptions for this case study are:

- The injection system does not have any spare equipment.
- There is only one flowmeter and water sensor for the whole system.
- All failure rates provided use year as a base.
- Inhibitor concentration 10% mol.

## 4.2 Framework application & results

**Area 1:** The scenario conditions, parameters, and preventive measures are defined in section 4.1. The fault tree developed from the case study is shown in Figure 15.

The top event is defined as a loss of control that could lead to an “uncontrollable hydrate formation.” It is assumed that there are two main threats, or events that immediately lead to the top event; “failure of hydrate formation detection (A)” and “failure of hydrate formation control (B).” Both components must fail in order the top event to occur. Therefore, these two events (components) are interconnected by an AND gate as shown in Figure 15.

**A. Failure of hydrate formation detection:** When assessing hydrate formation, the first step is the evaluation of the phase diagram (or envelope) of the system. This diagram is commonly used to define the operating zones, which is useful for determining the conditions at which hydrates can be present on the system at a given conditions. Instruments such as flowmeters and water sensors are used to obtain information from seabed conditions to create the phase diagram at regular intervals, especially when conditions of the fluid change (*e.g.*, water composition). Therefore, the reliability of those sensors is key when assessing the risk of hydrate formation. One additional factor to consider is that all the changes in the operating variables are monitored by humans. Subsea control room operators must respond to critical alarms caused by changes to the main variables beyond a predetermined operating window (operating outside this envelope, could result in entering the zone of hydrate formation). The failure of this component “A” involve the three factors proposed in the framework: a) *human* response failure; b) *equipment* failure; and c) *software* failure. In this case the components are interconnected

using an AND gate, because even if two of the components fail the detection can still be successful.

- i. **Human response failure** (failure to respond to excursions outside operation envelope of T, P and other variables): as part of the HMS, there is a high dependence on monitoring many variables, for example monitoring pressure trends. In this case, a pressure drop could be caused by hydrate formation and the operator should be able to recognize this type of events. Typically, there are three basic events associated with human response failure: (1) signal is not monitored (operator lost attention); (2) communication error (*i.e.*, there was not adequate communication of the actions to be taken); and (3) signal interpretation failure (there was a misunderstanding of the variables shown in the monitor).
- ii. **Equipment failure**: as mentioned in the previous chapter, flow rate and water concentration measurement are key parameters that need to be continually monitored to detect the conditions that could lead to hydrate formation. However, there are many threats that could result in instrument failure including corrosion, erosion, vibration, restrictions, and blockages. Since these sensors provide information for assessing the possible formation of hydrates, the failure of the flowmeter and the water content sensors was also incorporated as part of the system analyzed in this case study. In Figure 15 below, the respective failure for these instruments have

been assumed to depend on three basic events: Setting error (4 and 8); Rule violation (5 and 9); and hardware failure (6 and 7).

- iii. **Software failure:** software can fail due to many causes; however, for this academic exercise, a simplification was made and only three of those causes were considered as part of the failure events. Figure 15 shows that these causes are interconnected using an OR gate. Here, incorrect inputs, calculation uncertainty, and employee competence are the three reasons considered in this study. Their respective basic events are shown in Figure 15: incorrect inputs - failure of electronic devices and instrument measuring uncertainty (10 and 11), employee skills – wrong understanding and wrong interpretation (12 and 13), uncertainty of the models (14 and 15).

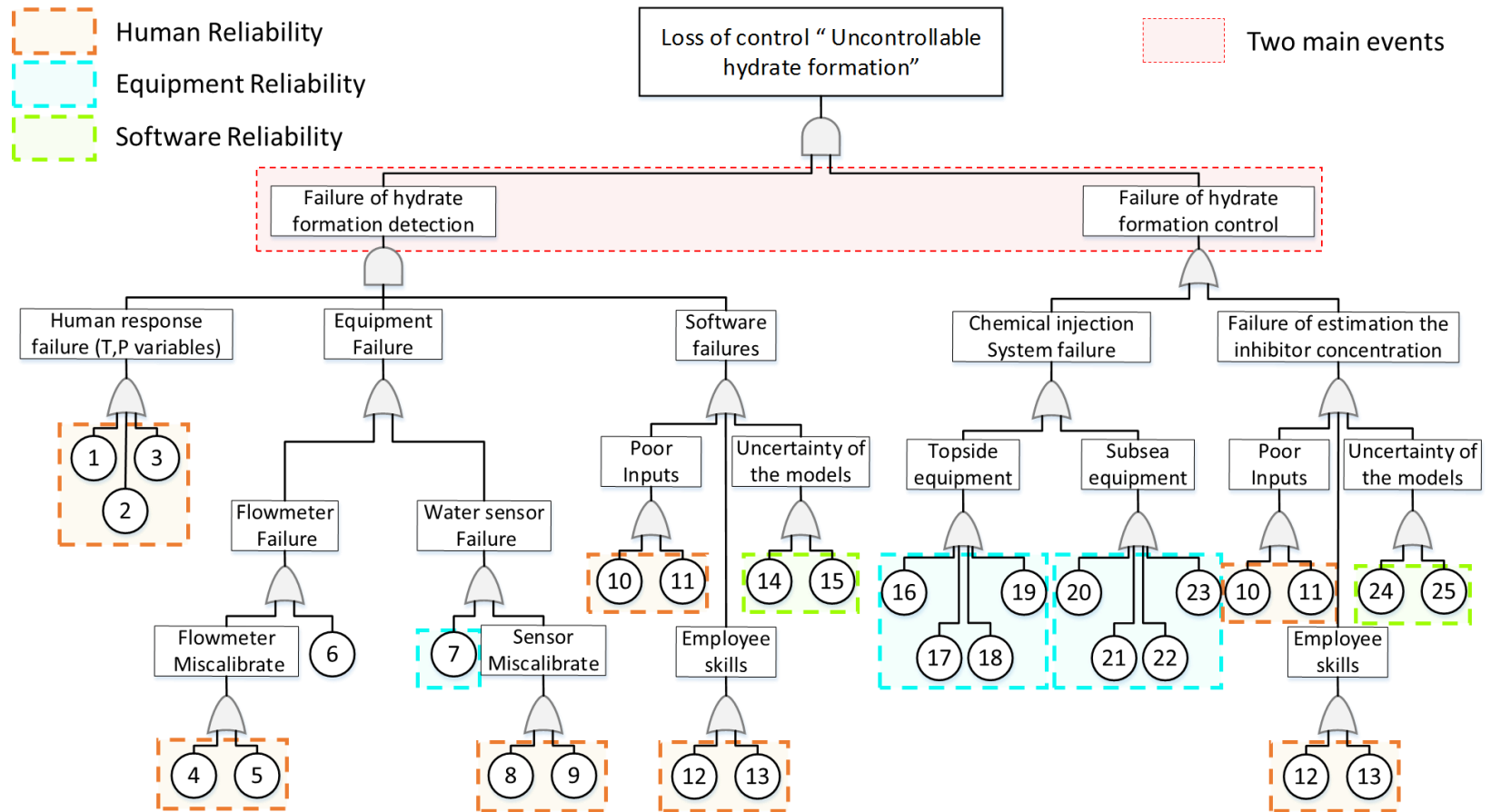
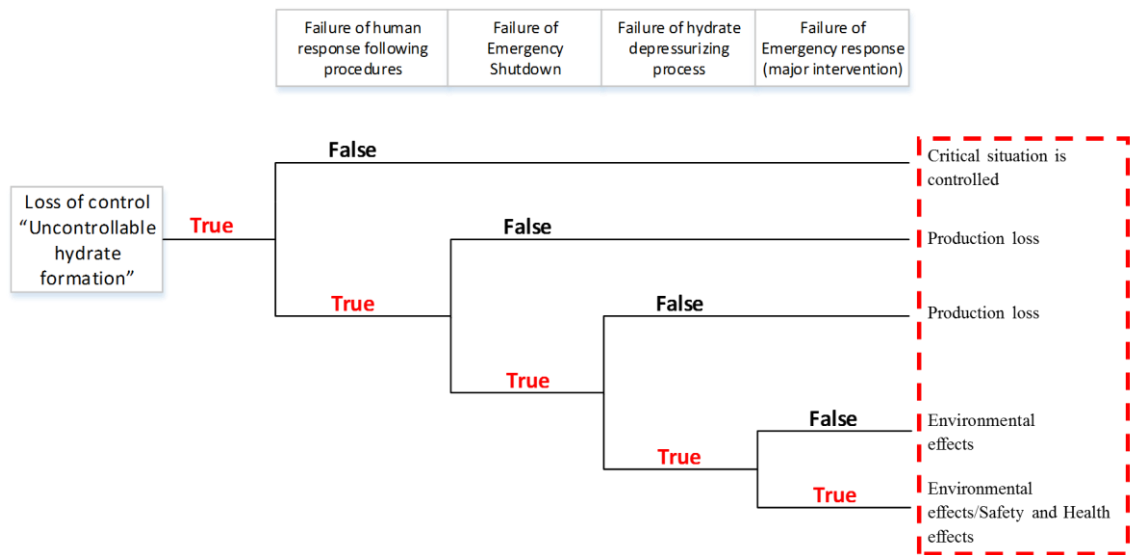


Figure 15. Hypothetical case study fault tree including different factors that can influence hydrate management.

**B. Failure of hydrate formation control:** this component can fail if the chemical injection systems fail or if there is a wrong estimation of the hydrate inhibitors concentration needed to control the hydrate formation. Because, if any of the two subcomponents fail the component fail. Hence, it is interconnected with and OR gate.

- i. **Chemical injection system failure:** as it was defined previously, the inhibitor injection system consists of subsea and topsides systems. Failure of the topsides system involves the following basic events: pump failure (16); chemical injection discharge valve failure (17); distribution line failure (18); control system failure (19). On the other hand, the failure of the subsea system involves the following basic events: dynamic umbilical failure (20). Note event at high concentrations of inhibitor there are reports of hydrate formation inside the umbilical (20); distribution module failure (21); subsea control failure (22); X-Mas tree failure / injection system failure (23). For these type of failures, it is assumed that if any of equipment mentioned above fail, the flow of inhibitor into the system is interrupted.
- ii. **Failure to estimate the inhibitor concentration:** incorrect inputs and operator competence is considered to influence in this event (10, 11, 12 and 13). The only different is that the uncertainty of the software is measured including inhibitor composition.

Event tree development: An event tree for this case study is shown in Figure 16. The initiating event is defined as a loss of control leading to an “uncontrollable hydrate formation.” In order to mitigate the consequences, certain operational procedures are defined as part of the response. The event tree has been developed from literature review and from inputs provided by flow assurance specialists from industry. Note that an event tree can vary significantly from company to company, as these event trees are dependent on the specific scenarios considered and the specific hydrate mitigation protocols / procedures followed by each company. Once the initiating event occurs, it can lead to different consequences including asset damage and safety and environmental impact, depending on the operational procedures and technologies used. On the other hand, if the right-hand side barriers (mitigations) work as intended, the initiating event can be controlled. Once hydrate is formed, part of the remediation process is to identify the location of the plug and initiate a recovery process to remove this plug.



**Figure 16. Hypothetical case study event tree, including different events after the initiator event, "Uncontrollable hydrate formation."**

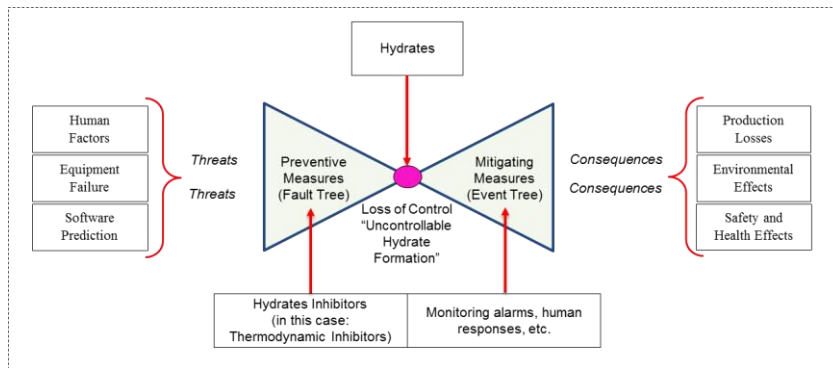
In this case study “following procedures” is the first barrier on the right-hand side of the mitigation system. This barrier depends on human factors related to training, experience, and ability to react to similar situations. Part of the procedure could involve hydraulic methods and depressurization processes without a full shutdown of the system. However, as any other barrier requiring human intervention, this barrier is not 100% reliable. The second mitigation action is the activation of the “emergency shutdown system”, which can be activated automatically or directly by the operator. The reliability of the emergency shutdown system is considered high. The third mitigation barrier considered is the so called “hydrate depressurization process”, which is a field procedure implemented to remove and/or dissociate the hydrate blockage in the system. Finally, the last barrier considered is the “emergency response (major intervention)”, which involves all the processes implemented in response to an environmental spill.

*Bowtie into development:* The bowtie approach is an integration of the fault tree and the event tree. Since the top event and the initiator event are the same for both the causal model (Fault tree - Figure 15) and the consequence model (Event tree –Figure 16), both can be linked to get a bowtie of the general hydrate management system for the hypothetical case study.

Figure 17, shows a bowtie representation of the hypothetical hydrate management system. The left-hand side of the bowtie includes the preventive controls and the right-hand side the mitigation controls. If the left-hand side controls (preventive measures) fail



and the conditions of the systems are within the zone where hydrate formation is possible, then it is possible that the system will form a plug. This event is represented in the bowtie by the “knot”, which is defined as an AND gate between the probability of hydrate formation and the probability of the failure preventive measures per year.



**Figure 17. Hydrate formation Bowtie.**

**Area 2: Bowtie mapping as Bayesian Network.** The next step in the process to model the operational risk of the HMS is to map the bowtie in a Bayesian Network using AgenaRisk and assign probability data as follows:

Human reliability: the information used in all the basic events related with human reliability, are based on the assumption that the human factors associated to any operation in offshore systems are similar. Therefore, the probabilities of the basic event related to human factors including “Signal is not monitored”, “signal interpretation failure”, “communication error”, “setting error”, and “rule violation” are assumed as the same values used by Zeng (Zeng, 2015), which were obtained from literature review and input from experts. In order to obtain probability values for basic events not included in Zeng’s

thesis, the same approach was implemented using the parents' nodes information as shown in Figure 18. For the probability calculation of the basic event "employee skills" different parent nodes were included such as supervision, procedure, competence, working under pressure, communication and risk perception. The parent nodes (human factor nodes) were ranked following a TNormal distribution with 5 level: very low, low, medium, high, and very high. The influence of each parent node over the child node is weighted using an expression available in AgenaRisk (Weighted Mean). The weights scale used is defined from 1 to 5, in which 5 is assigned to the human factor with more importance. For this case study the weight value is assigned based on engineer judgment as it is show in the Table 10. The probability calculation of the "employee skills" is shows in Figure 19.

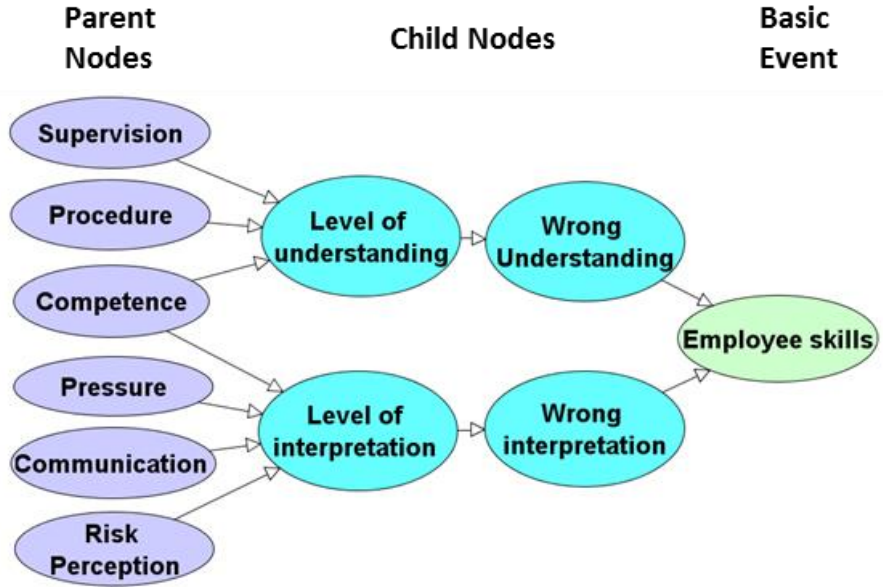


Figure 18. Parent and child nodes of the "employee skills" basic event.

Table 10. Weight values of child nodes.

Employee skills (Software reliability)		
Child nodes	Parent nodes	Weight
Level of understanding	Competence	5
	Supervision	2
	Procedure	4
Level of interpretation	Competence	5
	Working under Pressure	1
	Communication	4
	Risk perception	2

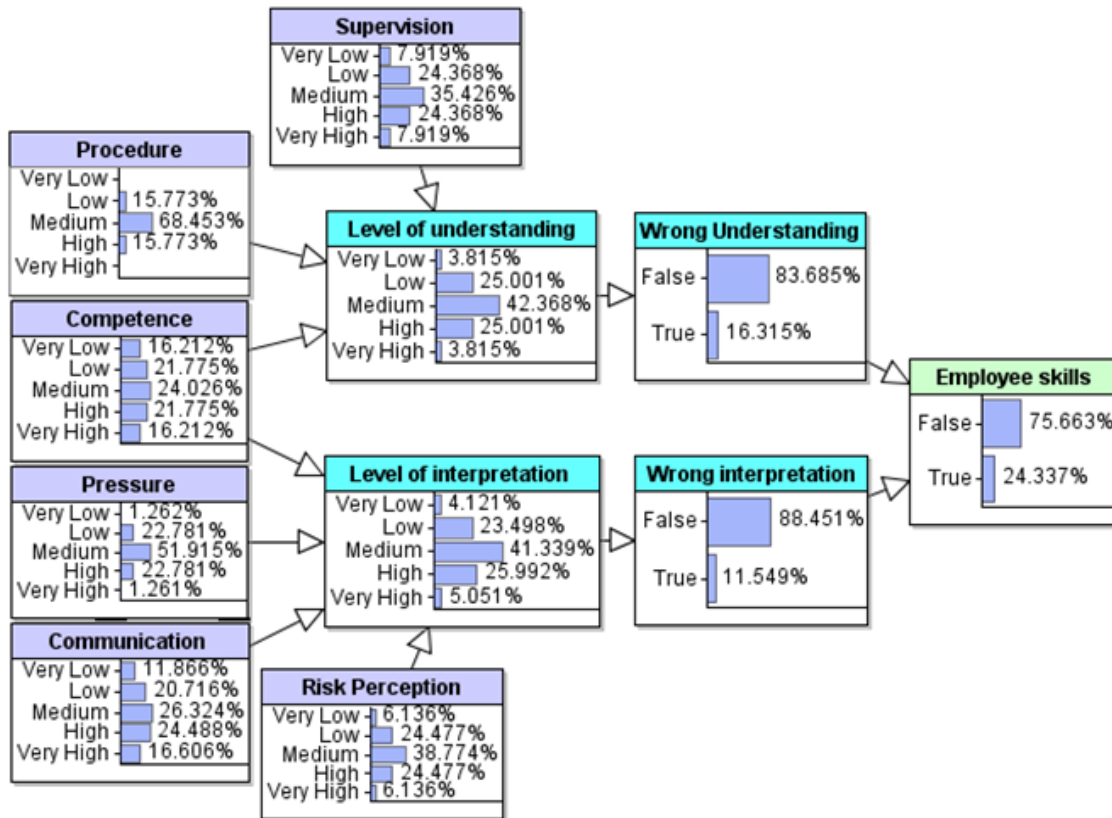


Figure 19. Probability calculation of the basic event "employee skills."

Equipment Reliability: the failure rate values were gathered from OREDA (Technology, Society, Norges teknisk-naturvitenskapelige, & Dnv, 2015). OREDA's failure rates are calculated based on the assumption that the failure rate function is constant and independent of time. Therefore, the failure rates are assumed to be exponentially distributed. Also, the failure rates are given as "failures per million hours." Thus, the failure rate is converted to "failures per year" by multiplying it by  $8,760 \times 10^{-6}$ . The equipment failure is modeled as a continuous distribution using built-in functions available in AgenaRisk. The failure rates of the flowmeter and water sensor were assigned based on engineering judgment.

**Area 3:** Software uncertainty measurements. As mentioned in section 3.1.3., the Latin Hypercube method was used to develop the sensitivity analysis. This method partitions each input distribution into N intervals of equal probability and selects one sample to form each interval. In this case study, the inputs were the gas composition without and with inhibitor concentration (components 8, and 9, respectively as shown in Table 8). The method was applied to two systems, one with only the gas and another containing hydrate inhibitor.

A Latin Hypercube built-in code in MATLAB was used to generate a random matrix of the simulations inputs to generate the hydrate equilibrium curve. The default input distribution in MATLAB is a uniform distribution. The command used in MATLAB to generate the two different random sampling matrices (with and without inhibitor) is:

- X is defined as the random matrix [X=lhsdesign (n, p, 'interactions', k)], where n is the number of desired simulations, p is the number of variables to use in the Uncertainty analysis, and k is the number of iterations needed to improve the design.
- For this case study, n=100, p<sub>without</sub>=8, p<sub>whit</sub>= 9, k=10 and two matrices (100X8) and (100X9) are generated. Each variable contains 100 different points between 0 and 1 (uniformly distributed).

	A	B	C	D	E	F	G	H	I
1	x1 (N2)	x2 (CO2)	x3 (H2O)	x4 (C1)	x5 (C2)	x6 (C3)	x7 (n-C4)	x8 (n-C5)	x9 (MeOH)
2	0.6843	0.3358	0.2627	0.6124	0.7176	0.5444	0.4381	0.2327	0.5901
3	0.6969	0.4434	0.6201	0.5091	0.4653	0.6813	0.5107	0.1625	0.5449
4	0.5490	0.5058	0.2460	0.9432	0.5794	0.9178	0.5934	0.8894	0.2662
5	0.0495	0.8006	0.3812	0.8509	0.5516	0.9919	0.3931	0.6822	0.7445
6	0.7903	0.0929	0.6681	0.1485	0.7640	0.9786	0.5520	0.2998	0.7193
7	0.8091	0.2505	0.0833	0.4406	0.0372	0.3943	0.0462	0.6165	0.6917
8	0.8534	0.0108	0.9851	0.2906	0.8803	0.4062	0.2075	0.3433	0.7575
9	0.4263	0.6882	0.8653	0.1556	0.3791	0.0535	0.1767	0.5242	0.3583
10	0.3944	0.7333	0.8062	0.3275	0.1395	0.2245	0.5702	0.0721	0.4853
11	***	***	***	***	***	***	***	***	***

**Figure 20. Random matrix "with inhibitor."**

Figure 20 shows a representation of the random matrix, where all the 100 values for each variable have values between 0-1.

Therefore, in order to define the inputs for the simulation to run in PVTsim, a range with a minimum and a maximum for each variable is defined (the % is assumed based on engineering judgment, considering a reasonable composition change in a period of time) to represent the variability as follows:

- Without inhibitor: the variability defined for almost all the components is (+/-) 30% of the value. However, the variability defined for water is (+/-) 90%.

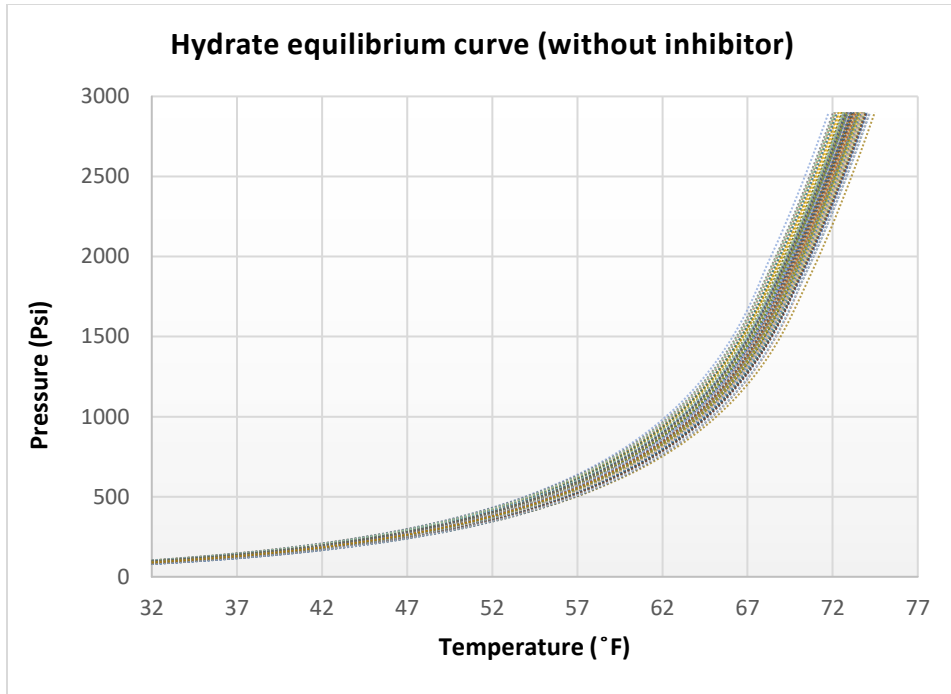
- With inhibitor: the variability defined for almost all the components is (+/-) 30% of the value. However, the variability defined for water is (+/-) 90% and for the inhibitor concentration is 50%.

The inputs for each simulation are calculated using the following formula (Oyana & Margai, 2015):

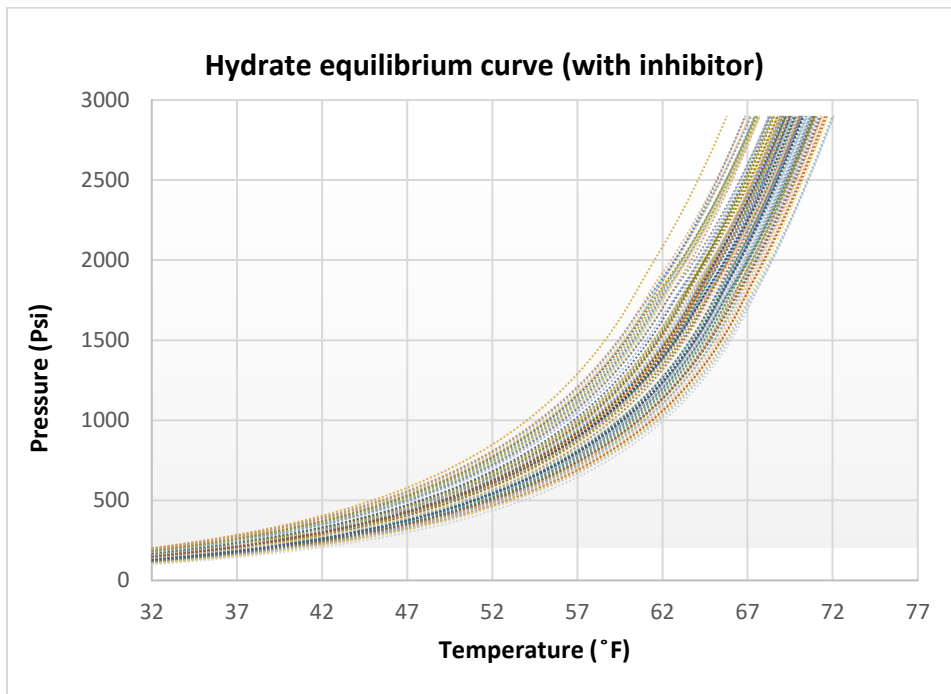
$$Y_{n \times p} = RAND(X_{n \times p}) * (MAX - MIN) + MIN$$

Where  $X_{n \times p}$  represents any of the random values from 0 to 1 for each simulation and each composition. The matrix is normalized before running the simulation on PVTsim.

The hydrate equilibrium curve is generated 100 times for each system (with and without inhibitor) using PVTsim. It is used Soave-Redlich-Kwong (SRK) as an equation of state, because it calculates the fugacity for Natural gases more accurately than using the Peng-Robinson equation (N. R. Kim, Ribeiro, & Bonet, 2008). Figure 21 and Figure 22, show the equilibrium curves without and with inhibitor, respectively.



**Figure 21. Hydrate equilibrium curves (without inhibitor) using PVTsim Nova.**



**Figure 22. Hydrate equilibrium curves (with inhibitor) using PVTsim Nova.**

All the curves (n=100) obtained for each case, with and without inhibitors, were used to perform an uncertainty analysis and estimate the total model output uncertainty. This output uncertainty results from the uncertainty associated to the parameters in the model. The following statistical calculations were used to estimate the uncertainty of the model outputs (Reder, Alcamo, & Flörke, 2017):

$$E(Y) = \frac{1}{n} \sum_{i=1}^n y_i$$

$$V(Y) = \frac{1}{n-1} \sum_{i=1}^n (y_i - E(Y))^2$$

Where  $(y_i)$  is the model output for the  $i^{th}$  sample of the LHS, and  $E(Y)$  represents the mean and  $V(Y)$  the variance. Also, the coefficient of variation (CV) is calculated and used as a measure of model output, giving a good estimation of the model output uncertainty (Reder *et al.*, 2017).

$$CV = \frac{\sigma}{\mu} = \frac{\sqrt{V(Y)}}{E(Y)}$$

Because these statistics calculations are usually applied to models that generate a single point value as output and not a curve of values (in this case 24 points), two main assumptions were defined for implementing the statistic calculation to measure the uncertainty to the hydrate equilibrium curve:

- The statistical calculations were applied to each variable independently developing two different calculations, where  $(y_i)$  can take two values, the output temperature, and the output pressure of a “n” number of curves.



- It is assumed that each one of the 24 points in the curve correspond to each other in all the curves obtained (n=100), which means that: point 1 from the curve 1 correspond to point 1 from the curve 2, and so on for all one hundred curves and for each point.

Considering the two assumptions aforementioned, Table 11 show the statistic calculation for both cases (with and without inhibitor).

**Table 11. Uncertainty estimation of the hydrate equilibrium curve.**

Hydrate equilibrium curve <u>without</u> inhibitors		Hydrate equilibrium curve <u>with</u> inhibitors	
Temperature - CV	0.65%	Temperature - CV	1.95%
Pressure - CV	6.20%	Pressure - CV	17.25%

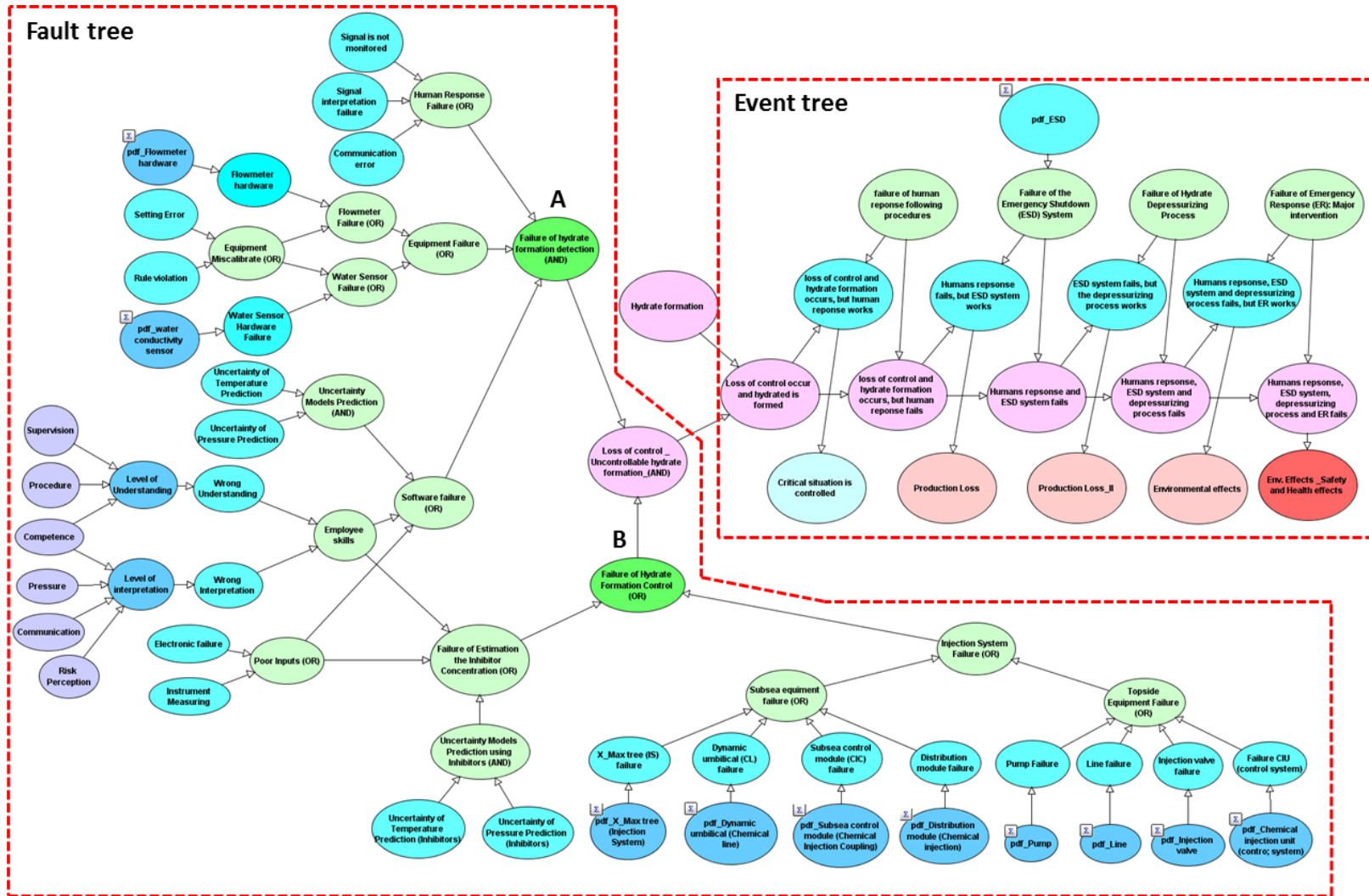


Figure 23. Bowtie mapping in a BN using AgenaRisk.

Fault tree (A)

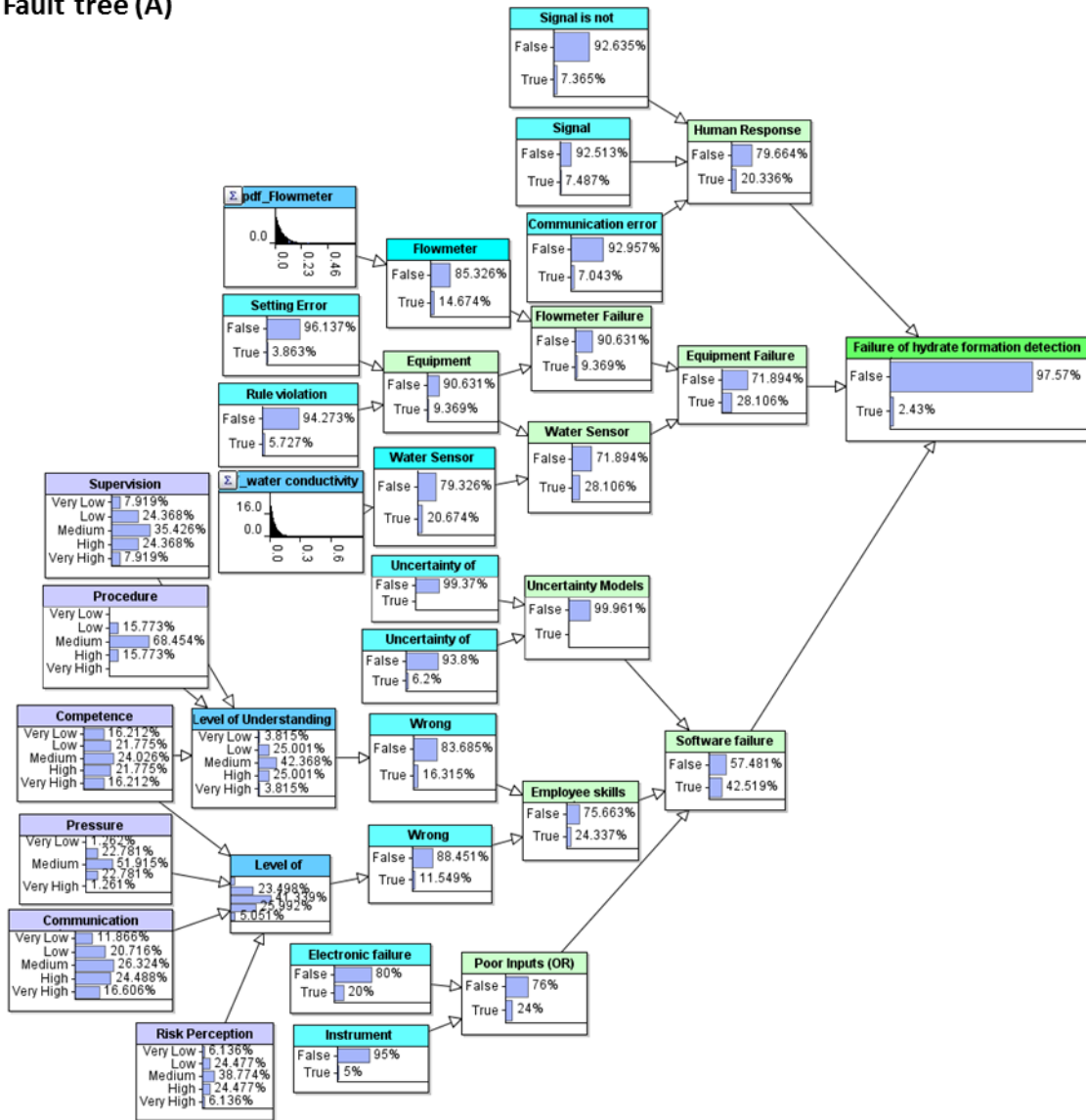
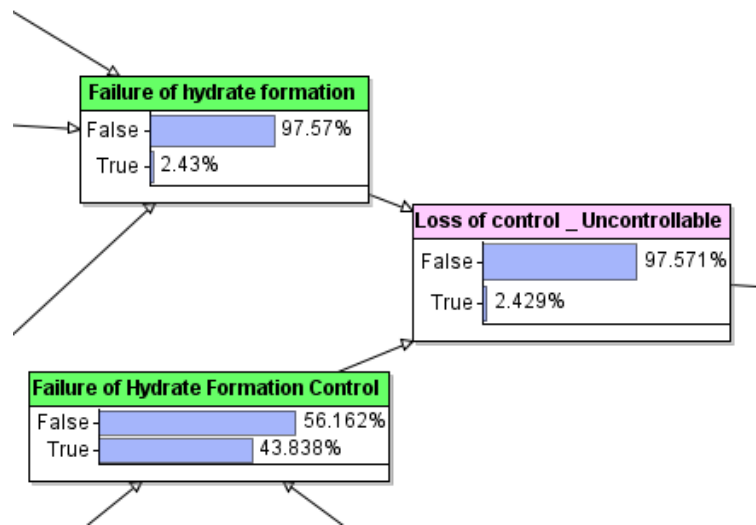


Figure 24. Fault tree event modeled in AgenaRisk as a BN: "Failure of hydrate detection."

Figure 23 shows the bowtie mapped in a Bayesian Network using AgenaRisk. The part outside the square shows the fault tree, and the part inside shows the event tree. The bowtie shows some relations between two of the events: Poor inputs and Employees skills.



Figure 24 shows the model of one of the main events of the fault tree “Failure of hydrate detection”. The probability of the detection of hydrate would fail is 0.0247 in a year, which is reasonable considering that this event is frequently presented without being detected. Also, Figure 25 shows the model of the second main event of the fault tree “Failure of hydrate formation control”. The probability of the systems to control hydrate formation would fail is 0.438 in a year. Although the reason why this value is high can be due to the information used in the exercise, the literature has reported that the knowledge of the operators and inputs are key components contributing to the increase the reliability of the entire HMS.



**Figure 26. Probability of loss of control "Uncontrollable hydrate formation."**

The probability of loss of control calculated by the model is 0.0242 (Figure 26), which means that the probability that the preventions system fails is 0.0242 in a year. According with the temperature profiles along the flowlines length showed in Table 9, the

temperature can take values up to 60.8°F at 5 miles from the satellite platform. Therefore, using the hydrate equilibrium curve (Figure 22), suggests that the conditions fall over the hydrates zone. Thus, it is assumed the probability of hydrate formation is 1. Figure 27 shows the event tree model with the probability of the consequences, which is the final outcome of the framework proposed, as show in the Table 12:

**Table 12. Probability of the consequences of the case study.**

<b>Consequences</b>	<b>Probability</b>
Loss of production I	0.0036401
Loss of production II	2.9904E-6
Environmental Effects	3.2895E-7
Environmental Effects/ Safety and Health effects	3.3227E-9

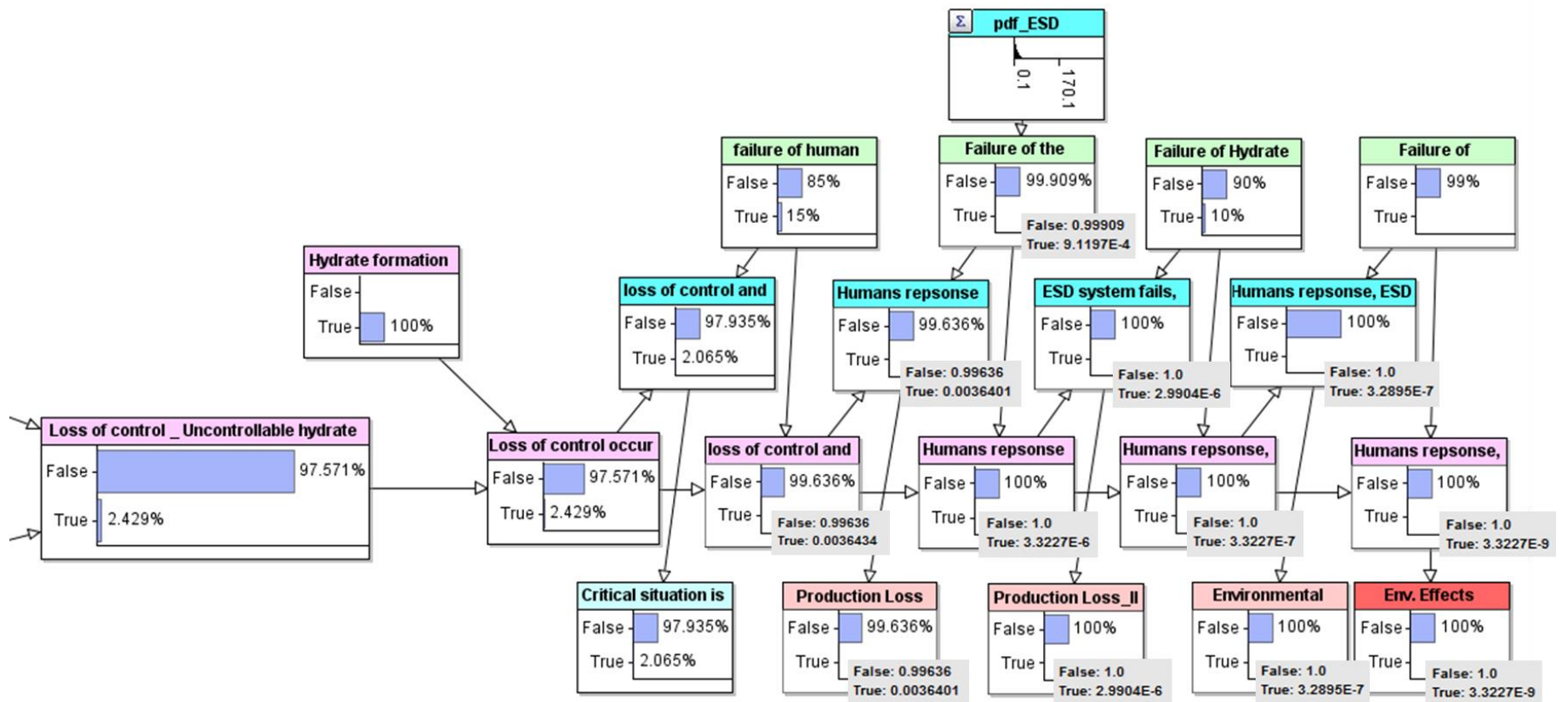


Figure 27. Event tree modeled in AgenaRisk

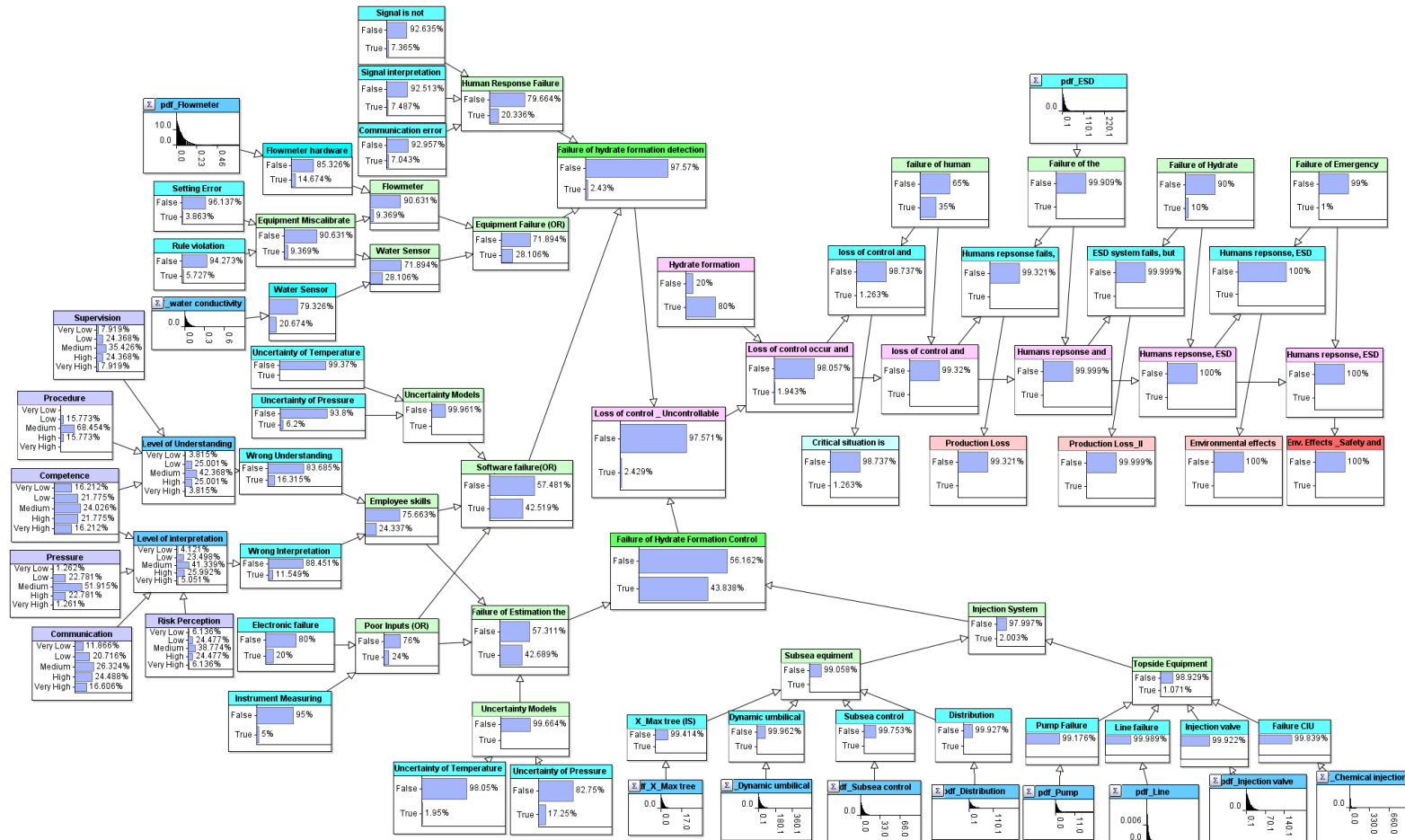


Figure 28. Bowtie modeled as a BN in AgenaRisk.



Locating the obtained probabilities within a generic risk matrix, all the consequences probabilities seems to fall into a reasonable range. For instance, using the matrix below (Figure 29) reprinted with permission from (Herath et al., 2016), loss of production is categorized as a possible event, which is the biggest concern of the hydrate formation. Also, environmental, safety and health effects are categorized as very unlikely, these results are aligned with experts experience that have mentioned that this kind of events are rare.

		Consequences				
		Negligible (0-2)	Minor (2-4)	Moderate (4-6)	Critical (6-8)	Catastrophic (8-10)
Probability	Very Likely (1-0.1)	Medium	High	High	Very High	Very High
	Likely (0.01-0.1)	Medium	Medium	High	Very High	Very High
	Possible (0.001-0.01)	Low	Medium	Medium	High	Very High
	Unlikely (0.0001-0.001)	Low	Low	Medium	High	High
	Very Unlikely (<0.0001)	Low	Low	Low	Medium	High

Figure 29. Risk matrix. Reprinted with permission from (Herath et al., 2016).

## 5 CONCLUSIONS AND FUTURE WORK

### 5.1 Conclusions

Hydrate formation is one of the principal flow-assurance challenges associated with offshore subsea oil and gas production systems in deepwater operations as hydrates can cause severe flow assurance problems. Operating companies have implemented different methods to prevent and mitigate the formation of hydrates. Although hydrate formation has the potential for causing safety and environmental consequences, it is difficult to establish a relationship between hydrate formation and these events as the evidence is not easy to identify. A more visible problem associated with hydrate formation is production deferment and asset damage in subsea systems, which causes millionaire losses.

Although hydrate formation phenomenon has been known for many years, a full understanding of the mechanism of formation of hydrates does not exist and hence, its risk of is difficult to quantify. Since, one of the key premises of science is that you cannot control what you cannot measure, this research proposed a framework for modeling the operational risk of a hydrate management system implemented on subsea production systems. The framework includes three different factors: human reliability, equipment reliability, and software reliability:

The advantages of the proposed framework include:

- Provides a methodology for obtaining quantitative data that can be used in quantitative risk assessments;
- The framework identifies preventive measures for hydrate control and estimates the probability of failure of these preventive measurements and the probability of occurrence for different consequences including production loss, environmental effects, safety and health effects.
- The proposed framework using a Bayesian Networks provides a structured visualization of the relationship between operating variables & conditions, operating procedures, reliability of control & preventive measures, and the probability of hydrate formation and its potential consequences. The use of this framework was tested with a hypothetical case study, which was developed as a proof of concept. The probabilities calculated using this framework along with the Bayesian Networks model were reasonable based on a general risk matrix (refer to Section 4.2). The results from this study provide a good starting point for further developing the proposed framework for a specific hydrate management system.
- Results from the uncertainty analysis developed show that model output uncertainty in both cases of study, without and with inhibitor, are low. This is reasonable because thermodynamic models are accurate enough from an engineering perspective. However, it was observed that the model output uncertainty with inhibitors increased about 11% in the pressure calculation, which suggest that the uncertainty change depends on the composition

During the development of this thesis, there were a considerable number of discussions with experts, which led to one important finding:

Nowadays, the oil and gas industry is looking to decrease or remove the use of inhibitors as part of the hydrate management system. One of the reasons is that the chemicals used as inhibitors are difficult to remove from the production stream, which affects its quality. The possible alternative is to use operating methods including hydraulic methods such fluid displacement, small depressurization, and compression methods. Therefore, the question now remains: is the hydrate management system becoming relying more on human with this approach?

## **5.2 Future work**

This work was developed based on a hypothetical case study using different assumptions. Therefore, it is recommended to implement the framework proposed using a real case scenario to have a better understanding of its implementation.

Develop an uncertainty analysis for the kinetic models using Latin Hypercube Sample, in order to estimate the total uncertainty of model output identifying the most influential parameters, the model can be optimized.

## REFERENCES

- Al-Eisa, R. M., Elanany, M. S., Al-Majnouni, K. A., Al-Jabran, A. A., Al-Ajwad, H. A., Abba, I. A., & Al-Malki, A. R. (2015). Kinetic Hydrate Inhibitors for Natural Gas Fields: Rational Design and Experimental Development. *Saudi Aramco Journal of Technology*.
- Amodu, A. A. (2008). *Drilling through gas hydrate formations: possible problems and suggested solutions* (Doctoral dissertation, Texas A&M University).
- Anklam, M. R., & Firoozabadi, A. (2004). Driving force and composition for multicomponent gas hydrate nucleation from supersaturated aqueous solutions. *The Journal of chemical physics*, *121*(23), 11867-11875.
- Ballard, A. L., & Sloan Jr, E. D. (2004). The next generation of hydrate prediction: Part III. Gibbs energy minimization formalism. *Fluid Phase Equilibria*, *218*(1), 15-31. doi:<http://dx.doi.org/10.1016/j.fluid.2003.08.005>
- Bhandari, J., Abbassi, R., Garaniya, V., & Khan, F. (2015). Risk analysis of deepwater drilling operations using Bayesian network. *Journal of Loss Prevention in the Process Industries*, *38*, 11-23. doi:<http://dx.doi.org/10.1016/j.jlp.2015.08.004>
- Bollavaram, P., & Sloan Jr, E. D. (2003, January). Hydrate plug dissociation by method of depressurization. In *Offshore Technology Conference*. Offshore Technology Conference..
- Boxall, J., Davies, S., Koh, C., & Sloan, E. D. (2009). Predicting when and where hydrate plugs form in oil-dominated flowlines. *SPE Projects, Facilities & Construction*, *4*(03), 80-86.
- Brustad, S., Løken, K. P., & Waalmann, J. G. (2005, January). Hydrate Prevention using MEG instead of MeOH: Impact of experience from major Norwegian developments on technology selection for injection and recovery of MEG. In *Offshore Technology Conference*. Offshore Technology Conference.
- Bui, L. (2015). Hydrate Prevention - Methanol or Glycol? Which is More Effective? Retrieved from <http://oilpro.com/post/6185/methanol-glycol-which-more-effective>
- Calsep. (2015). PVTSIM NOVA. Retrieved, from <http://www.calsep.com/about/pvtsim-nova.html>

- Chaudhari, P. N. (2016). *Development of hydrate risk quantification in oil and gas production* (Doctoral dissertation, Colorado School of Mines. Arthur Lakes
- Chua, P. C., Kelland, M. A., Hirano, T., & Yamamoto, H. (2012). Kinetic hydrate inhibition of poly (N-isopropylacrylamide) s with different tacticities. *Energy & Fuels*, 26(8), 4961-4967.
- Clark, L. W., & Aanderson, J. (2007, January). Low Dosage Hydrate Inhibitors (LDHI): Advances in Flow Assurance Technology for Gas Production Systems. In *International Petroleum Technology Conference*. International Petroleum Technology Conference.
- Daraboina, N., Malmos, C., & von Solms, N. (2013). Synergistic kinetic inhibition of natural gas hydrate formation. *Fuel*, 108, 749-757.
- Englezos, P. (1993). Clathrate hydrates. *Industrial & Engineering Chemistry Research*, 32(7), 1251-1274.
- Ericson, C. A. (2015). *Hazard analysis techniques for system safety*. John Wiley & Sons.
- Feng, M. (2011). *The Temperature Prediction in Deepwater Drilling of Vertical Well* (Doctoral dissertation, Texas A&M University).
- FMCTechnologies. (2010). Shell Mars B - West Boreas Retrieved from [http://www.fmctechnologies.com/en/SubseaSystems/GlobalProjects/NorthAmerica/US/ShellMarsB\\_WestBoreas.aspx?tab={892F84B4-BF15-4AF7-AEB1-D16B4600AAA8}#](http://www.fmctechnologies.com/en/SubseaSystems/GlobalProjects/NorthAmerica/US/ShellMarsB_WestBoreas.aspx?tab={892F84B4-BF15-4AF7-AEB1-D16B4600AAA8}#)
- Fenton, N., & Neil, M. (2012). *Risk assessment and decision analysis with Bayesian networks*. Crc Press.
- Frostman, L. M., Thieu, V., Crosby, D. L., & Downs, H. H. (2003, January). Low-dosage hydrate inhibitors (LDHIs): reducing costs in existing systems and designing for the future. In *International Symposium on Oilfield Chemistry*. Society of Petroleum Engineers.
- Galvão, Q. (2016). Flow Assurance and Artificial Lif. Retrieved from <http://www.qgep.com.br/static/enu/garantia-de-escoamento-e-elevacao-artificial.asp?idioma=enu>
- Giavarini, C., & Hester, K. (2011). *Gas hydrates: Immense energy potential and environmental challenges*. Springer Science & Business Media.

- Grzelak, E., & Bussell, B. (2015). Intelligent Hydrate Management (8). Retrieved from <http://gpaeurope.com>
- Gudmundsson, J. S. (2002, May). Cold flow hydrate technology. In *4th international conference on gas hydrates* (pp. 19-23).
- Harmens, A., & Sloan, E. D. (1990). The phase behaviour of the propane-water system: A review. *The Canadian Journal of Chemical Engineering*, 68(1), 151-158.
- Herath, D., Khan, F., Rathnayaka, S., & Rahman, M. A. (2015). Probabilistic estimation of hydrate formation. *Journal of Petroleum Science and Engineering*, 135, 32-38. doi:<http://dx.doi.org/10.1016/j.petrol.2015.08.007>
- Herath, D., Khan, F., & Yang, M. (2016). Risk-based winterization to prevent hydrate formation in northern harsh environment. *Ocean Engineering*, 119, 208-216.
- Herri, J. M., Gruy, F., Pic, J. S., Cournil, M., Cingotti, B., & Siquin, A. (1999). Interest of in situ turbidimetry for the characterization of methane hydrate crystallization: Application to the study of kinetic inhibitors. *Chemical Engineering Science*, 54(12), 1849-1858.
- Huo, Z., Hester, K., Sloan, E. D., & Miller, K. T. (2003). Methane hydrate nonstoichiometry and phase diagram. *AIChE journal*, 49(5), 1300-1306.
- Johnsen, H. K. (1990, September). *Hydrates, - The Start of a Chain Reaction Leading to the Piper Alpha Disaster?* Paper presented at the IChemE Symposium, London. Retrieved from [http://www.icheme.org/~media/Documents/Subject%20Groups/Safety\\_Loss\\_Prevention/Hazards%20Archive/S122%20-%20Piper%20Alpha%20Lessons/S122-02.pdf](http://www.icheme.org/~media/Documents/Subject%20Groups/Safety_Loss_Prevention/Hazards%20Archive/S122%20-%20Piper%20Alpha%20Lessons/S122-02.pdf)
- Joshi, S. V., Grasso, G. A., Lafond, P. G., Rao, I., Webb, E., Zerpa, L. E., ... & Sum, A. K. (2013). Experimental flowloop investigations of gas hydrate formation in high water cut systems. *Chemical Engineering Science*, 97, 198-209. doi:<http://dx.doi.org/10.1016/j.ces.2013.04.019>
- Kashchiev, D., & Firoozabadi, A. (2002). Driving force for crystallization of gas hydrates. *Journal of crystal growth*, 241(1), 220-230.
- KBC. (2016). Multiflash, PVT Modeling and Flow Assurance Software. Retrieved from [http://www.kbc.com/images/documents/technology/2016\\_Multiflash.pdf](http://www.kbc.com/images/documents/technology/2016_Multiflash.pdf)
- Kim, J., Noh, Y., Chang, K., & Chang, D. (2016). Determination of hydrate inhibitor injection rate for flowlines based on Monte Carlo method. *Journal of Loss*

*Prevention in the Process Industries*, 44, 62-72.  
doi:<http://dx.doi.org/10.1016/j.jlp.2016.08.012>

- Kim, J., Noh, Y., Ryu, J., Seo, Y., & Chang, D. (2016). Determination of hydrate inhibitor injection rate based on the life-cycle cost of the injection facility and mitigating measures. *Journal of Natural Gas Science and Engineering*, 34, 552-562. doi:<http://dx.doi.org/10.1016/j.jngse.2016.07.030>
- Kim, N. R., Ribeiro, P. R., & Bonet, E. J. (2008). Study of hydrates in Drilling Operations: A Review. *Brazilian Journal of Petroleum and Gas*, 1(2).
- Kinnari, K., Hundseid, J., Li, X., & Askvik, K. M. (2014). Hydrate management in practice. *Journal of Chemical & Engineering Data*, 60(2), 437-446.
- Kobayashi, R., & Katz, D. (1953). Vapor-liquid equilibria for binary hydrocarbon-water systems. *Industrial & Engineering Chemistry*, 45(2), 440-446.
- Lou, X., Ding, A., Maeda, N., Wang, S., Kozielski, K., & Hartley, P. G. (2012). Synthesis of effective kinetic inhibitors for natural gas hydrates. *Energy & Fuels*, 26(2), 1037-1043.
- Lupeau, A., Smith, M. T., Seng, L. Y., & Grzelak-OneSubsea, E. Hydrate Management: Managing Uncertainty & Risk through Enhanced Measurement. Retrieved from [http://www.tuvnel.com/assets/content\\_images/7.2\\_OneSubsea.pdf](http://www.tuvnel.com/assets/content_images/7.2_OneSubsea.pdf).
- Manning, M. (2016). Offshore oil production in deepwater and ultra-deepwater is increasing. Retrieved from <https://www.eia.gov/todayinenergy/detail.php?id=28552>
- Mazloun, S., Chapoy, A., Yang, J., & Tohidi, B. (2011, July). Online monitoring of hydrate safety margin. In *Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011)* (pp. 17-21).
- Natarajan, V., Bishnoi, P. R., & Kalogerakis, N. (1994). Induction phenomena in gas hydrate nucleation. *Chemical Engineering Science*, 49(13), 2075-2087.
- Owodunni, O. L., & Ajienka, J. A. (2007, January). Use of Thermal Insulation to Prevent Hydrate and Paraffin Wax Deposition. In *Nigeria Annual International Conference and Exhibition*. Society of Petroleum Engineers.
- Oyana, T. J., & Margai, F. (2015). *Spatial analysis: statistics, visualization, and computational methods*. CRC Press.



- Patel, Z. D. (2015) *Meeting the Hydrate Challenge - Expert Viewpoint/Interviewer: U. Intelligence*. Meeting with experts. Retrieved from <http://analysis.upstreamintel.com/>.
- Patel, Z. D., Dibello, M., Fontenot, K., Guillory, A., & Hesketh-Prichard, R. (2011, January). Continuous application of anti-agglomerant Idhi for gas-condensate subsea tieback wells in deepwater gulf of mexico. In *Offshore Technology Conference*. Offshore Technology Conference.
- Patel, Z. D., & Russum, J. (2010). Flow assurance: Chemical inhibition of gas hydrates in deepwater production systems. Retrieved from <http://www.offshore-mag.com/articles/print/volume-70/issue-6/subsea/flow-assurance-chemical-inhibition-of-gas-hydrates-in-deepwater-production-systems.html>
- Reder, K., Alcamo, J., & Flörke, M. (2017). A sensitivity and uncertainty analysis of a continental-scale water quality model of pathogen pollution in African rivers. *Ecological Modelling*, 351, 129-139.
- Reith, C., & Lasgstrom, K. (2015). Reliable Subsea Oil & Gas Transportation Syte,ms. Retrieved from <https://www.slideshare.net/CharlieReith/reliable-subsea-oil-gas-transportation-paper-presentation-slides-6-november-2015>
- Ribeiro, C. P., & Lage, P. L. (2008). Modelling of hydrate formation kinetics: State-of-the-art and future directions. *Chemical Engineering Science*, 63(8), 2007-2034.
- Rocha, L. A. S., Junqueira, P., & Roque, J. L. (2003, January). Overcoming deep and ultra deepwater drilling challenges. In *Offshore Technology Conference*. Offshore Technology Conference.
- Schlumberger. (2017). dbrHydrate Fluid Analysis Software. Retrieved from [http://www.slb.com/services/characterization/reservoir/core\\_pvt\\_lab/fluid\\_lab\\_services/fluid\\_lab\\_software/dbrhydrate\\_software.aspx](http://www.slb.com/services/characterization/reservoir/core_pvt_lab/fluid_lab_services/fluid_lab_software/dbrhydrate_software.aspx)
- Shahnazar, S., & Hasan, N. (2014). Gas hydrate formation condition: Review on experimental and modeling approaches. *Fluid Phase Equilibria*, 379, 72-85.
- Skovborg, P., Ng, H. J., Rasmussen, P., & Mohn, U. (1993). Measurement of induction times for the formation of methane and ethane gas hydrates. *Chemical Engineering Science*, 48(3), 445-453.
- Sloan, E. D. (2005). A changing hydrate paradigm—from apprehension to avoidance to risk management. *Fluid Phase Equilibria*, 228, 67-74.

- Sloan, E. D. (2010). *Natural gas hydrates in flow assurance*. C. A. Koh, & A. Sum (Eds.). Gulf Professional Publishing.
- Sloan Jr, E. D., & Koh, C. (2007). *Clathrate hydrates of natural gases*. CRC press.
- SPE-International. (2016). Controlling excess water production Retrieved from [http://petrowiki.org/Controlling\\_excess\\_water\\_production](http://petrowiki.org/Controlling_excess_water_production)
- Technology, S., Society, Norges teknisk-naturvitenskapelige, u., & Dnv, G. L. (2015). *OREDA : offshore and onshore reliability data handbook*.
- Tian, J., Bailey, C., Fontenot, J., & Nicholson, M. (2011, January). Low dosage hydrate inhibitors (LDHI): advances and developments in flow assurance technology for offshore oil and gas productions. In *Offshore Technology Conference*. Offshore Technology Conference.
- Tzotzi, C., Parenteau, T., Malmaison, F., Gainville, M., Siquin, A., Cassar, C., ... & Nord, P. J. M. A. (2014). Hydrate plug management full scale test: Hydrate plug dissociation in an electrically heated pipe in pipe. In *Proceedings of the 8th International Conference on Gas Hydrates (ICGH8-2014)*.
- Usman, M. A., Olatunde, A. O., Adeosun, T. A., & Egwuenu, O. L. (2012). Hydrate management strategies in subsea oil and gas flowlines at shut-in condition. *Petroleum and Coal*, 54(3), 191-202.
- Vysniauskas, A., & Bishnoi, P. R. (1983). A kinetic study of methane hydrate formation. *Chemical Engineering Science*, 38(7), 1061-1072.
- Ward, M., Granberry, V., Campos, G., Rausis, M., Sledz, M., Weber, L., ... & Romero, J. (2003). A joint industry project to assess circulating temperatures in deepwater wells. *SPE drilling & completion*, 18(02), 133-137.
- Webber, P. A., & Nagappayya, S. (2016). *U.S. Patent No. 9,410,073*. Washington, DC: U.S. Patent and Trademark Office.
- Wilfred, O., & Appah, D. (2015). Analyzing Thermal Insulation for Effective Hydrate Prevention in Conceptual Subsea Pipeline Design. *International journal of Current of Engineering and Technology*, 5(04), 2492-2499.
- Xiao, J. J., Shoup, G., Hatton, G., & Kruka, V. (1998, January). Predicting hydrate plug movement during subsea flowline depressurization operations. In *Offshore Technology Conference*. Offshore Technology Conference.

Zeng, M. (2015). *Integration of Human Factors in Offshore Blowout Risk Assessment* (Master thesis, Texas A&M University).

Zerpa, L. E., Sloan, E. D., Koh, C., & Sum, A. (2012). Hydrate risk assessment and restart-procedure optimization of an offshore well using a transient hydrate prediction model. *Oil and Gas Facilities*, 1(05), 49-56.