ASSESSING THE POTENTIAL OF USING HYDRATE TECHNOLOGY TO CAPTURE, STORE AND TRANSPORT GAS FOR THE CARIBBEAN REGION

A Dissertation

by

JEROME JOEL RAJNAUTH

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

DOCTOR OF PHILOSOPHY

December 2010

Major Subject: Petroleum Engineering

Assessing the Potential of Using Hydrate Technology to Capture, Store and Transport

Gas for the Caribbean Region

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Approved by:

Co-Chairs of Committee,	Maria Barrufet
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ABSTRACT

Assessing the Potential of Using Hydrate Technology to Capture, Store and Transport
Gas for the Caribbean Region. (December 2010)

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Co-Chairs of Advisory Committee: Dr. Maria Barrufet
Dr. Gioia Falcone

Monetizing gas has now become a high priority issue for many countries. Natural gas is a much cleaner fuel than oil and coal especially for electricity generation. Approximately 40% of the world's natural gas reserves remain unusable because of lack of economic technology. Gas produced with oil poses a challenge of being transported and is typically flared or re-injected into the reservoir. These are gas transportation issues we now face.

Gas hydrate may be a viable means of capturing, storing and transporting stranded and associated gas. For example, stranded gas in Trinidad could be converted to gas hydrates and transported to the islands of the Caribbean. This study will seek to address some of the limitations from previous studies on transporting natural gas as a hydrate while focusing on small scale transportation of natural gas to the Caribbean Islands. This work proposes a workflow for capturing, storing and transporting gas in the hydrate form, particularly for Caribbean situations where there are infrastructural constraints such as lack of pipelines. The study shows the gas hydrate value chain for transportation of 5 MMscf/d of natural gas from Trinidad to Jamaica. The analysis evaluated the water required for hydrate formation, effect of composition on hydrate formation, the energy balance of the process, the time required for formation, transportation and dissociation and preliminary economics.

The overall energy requirement of the process which involves heating, cooling and expansion is about 15-20% of the energy of the gas transported in hydrate form. The time estimated for the overall process is 20–30 hrs. The estimated capital cost to capture and transport 5 MMscf/d from Trinidad to Jamaica is about US$ 30 million. The composition of the gas sample can affect the conditions of formation, heating value and the expansion process.

In summary, there is great potential for transporting natural gas by gas hydrate on a small scale based on the proposed hydrate work flow. This study did not prove commerciality at this time, however, some of the limitations require further evaluations and these include detailed modeling of the formation time, dissociation time and heat transfer capabilities.

DEDICATION

To my mother and my entire family, for their great support and encouragement throughout this work

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisors, Dr. Maria Barrufet and Dr. Gioia Falcone, for their encouragement, support and guidance throughout my time at Texas A&M University. Their knowledge and suggestions were very useful throughout this work. Thanks to Dr. Walter Ayers and Dr. Mahmoud El-Halwagi for serving on my committee.

NOMENCLATURE

CIP	Cross Island Pipeline
CNG	Compressed Natural Gas
H&V	Huron & Vidal
IPP	Independent Power Plant
LDC	Local Distribution Company
LNG	Liquefied Natural Gas
NGL	Natural Gas Liquids
PT	Pressure Temperature
SPE	Society of Petroleum Engineers
SRK	Soave Redlich Kwong
UK	United Kingdom
US	United States
VIP	Vacuum Insulation Panel
MMscf	Million standard cubic feet
MMT	Million tonnes
HP	Horse Power

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CHAPTER I

INTRODUCTION

1.1 Problem Overview

1.1.1 Worldwide

There are many problems and challenges associated with the ways of transporting natural gas. It is estimated that 40 % World's Gas Reserves are stranded (Fleisch, 2006). We define stranded gas here as gas reserves that are not economically viable to produce with current gas transportation technologies.

In general LNG and Pipelines are not economic transportation modes for stranded gas. LNG requires about 1–3 tcf gas and investments in excess of a billion dollars while pipelines are limited by distance and construction timeline.

In many cases associated gas that is produced with oil is either re-injected or flared. Small amounts of shallow gas reserves can be exploited to meet domestic markets or smaller markets.

This dissertation follows the style of *SPE Journal*.

1.1.2 Trinidad

Some of the present challenges Trinidad and Tobago faces are:

- In Trinidad there are stranded gas reserves both on land and offshore.
- Some of the fields produce associated gas which is presently being re-injected.
- There is need for other economic ways of capturing and transporting natural gas on a small scale.
- There is need to transport natural gas from Trinidad to other small islands since there exists a Caribbean regional market for natural gas.

Fig. 1 shows the map of Trinidad and Tobago with some of the stranded gas fields with potential production rates in the range 0.5 MMscf/d to 5 MMscf/d estimated from well test data.

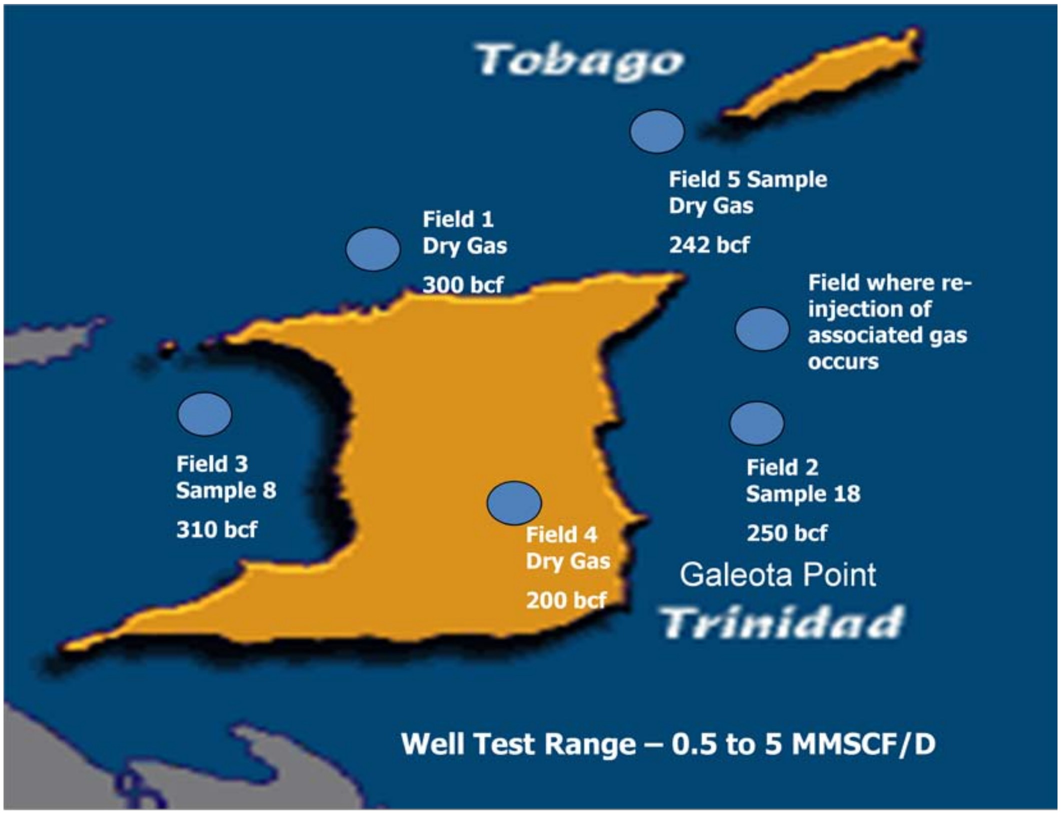

Fig. 1–Stranded Gas Fields in Trinidad with Reserves (Ministry, 2007)

Fig. 2 below shows the chain of Caribbean Islands where there are great potential for natural gas small scale markets.

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Fig. 2–Chain of Caribbean Islands for Possible Gas Transportation (Caribbean, 2008)

Table 1 below captures the gas usage for power generation of some of the major players in the Caribbean region. Jamaica and Barbados are two possible markets for natural gas. Jamaica requires 55 MMscf/d while Barbados about 8.3 MMscf/d for power generation.

Table 1–Some Caribbean Countries Power Generation Needs (Energy, 2008)

Country	Electricity Consumption 2006	Gas Usage 2006
	Billion kilowattshr	MMscf/d
Cuba	12.89	117.39
Jamaica	6.1	55.55
Dominican Republic	11.81	107.56
Puerto Rico	22.17	201.90
Barbados	0.91	8.29
Bahamas	1.79	16.30

1.2 Caribbean Gas Pipeline

Over the last decade, there have been numerous proposals and initiatives to have an Intra Caribbean gas pipeline to supply natural gas to many of the Caribbean Islands. This has never been materialized because of technical, geopolitical and jurisdictional issues. The technical challenges are associated with the sea floor topography of the Caribbean Sea which includes five basins separated by underwater ridges and mountains and two ocean trenches. Below are some highlights of past proposals for gas transportation in the Caribbean:

- In 2002- 2003, there was a proposal for an Intra Caribbean Gas Pipeline at a cost $600 MMUSD, 596 miles long, and 20” to 10” of pipe diameter.
- In 2007 Trinidad Government agreed to supply natural gas to Jamaica. But to date there is still no economic way of transporting natural gas to Jamaica.

- In 2009 – National Gas Company of Trinidad & Tobago proposed to build a 12” pipeline from Trinidad to Tobago at a cost of $80 MMUSD and 33.5 miles long. Presently a feasibility study is being done.

1.3 Introduction

The need for new methods for gas transportation is the challenge that drives the development of hydrate technology for storing and transporting natural gas (Masoudi and Tohidi, 2005). The ability of natural gas to form hydrate in combination with water is a very interesting and useful concept (Makogon, 1997) which could be widely utilized in the industry. An important feature of hydrates is their high storage capacity. 180 volume units of gas at standard conditions can potentially be packed into 1 volume unit gas hydrate crystals.

For many years natural gas hydrates have been a nemesis to the petroleum industry causing blockages in pipes and equipments. Since then, there has been great interest to understand and avoid the formation of hydrate during the transportation of gas. Now, the gas hydrate concept can be used to capture, store and transport natural gas. Natural gas hydrates are ice-like crystalline solids formed from a mixture of water and natural gas subjected to high pressure and suitable low temperature conditions (400-1200 psia and 33-40 F). These conditions are found in the permafrost and under the ocean floor. Hydrates consist of geometric lattices of water molecules containing cavities occupied by lighter hydrocarbons or other type of gaseous components for e.g. nitrogen or carbon dioxide.

Transporting gas in the form of a gas hydrate can prove to be very useful in the supply chain of natural gas to meet future energy demand. Thus major challenges exist in effectively capturing, storing, transporting and utilizing form of energy while meeting the world's diverse economic, political, and environmental needs. Technological advancement in utilizing gas hydrate as means of transporting natural gas could be a key component in capturing stranded, associated gas and in some cases unconventional gas. There is still about 40% of natural gas stranded reserves to be monetized.

1.4 Previous Work on Gas Transportation by Hydrate

Over the last couple of decades several studies were done focusing on large scale transportation of natural gas in hydrate form.

The previous studies on transporting gas as a hydrate include:

- Three main studies were done in:
    - UK (1996) by Advantica (Fitzgerald and Taylor, 2001)
    - Norway (1990) by NTNU (Norwegian University of Science and Technology) (Gudmundsson, Parlaktuna and Khokhar, 1994)
    - Japan (2001) by Mitsui Engineering (Taylor and Dawe, 2003)
- There were also several small scale laboratory studies.

The limitations and challenges of previous studies for applicability to large scale operations include:

(i) Very large amounts of water are needed in hydrate formation since on the average 852 bbls are required per MMscf. Therefore a sufficient water supply is therefore required.

(ii) There are problems associated with separating and packing hydrate particles for storage, transporting and dissociation. In previous work (Fitzgerald and Taylor, 2001), the hydrate was formed in a slurry form and then transferred to another vessel for dehydration and then another for transportation.

(iii) For hydrate formation, large formation vessels would be required since a lot of water is needed to capture natural gas for transport.

(iv) Quite a large amount of heat removal required during hydrate formation. The produce heat must be removed from the reaction vessel to ensure the formed hydrate do not dissociate.

(v) Energy is required for dissociation of the hydrate back to water and free gas.

(vi) Most of the previous studies focused on simple gases such as methane and ethane. Most natural gas has much more components than just methane and ethane and hence the composition can have significant impact on hydrate formation.

(vii) Gas transportation by hydrate has always been compared with LNG which is a proven technology and requires about 1–3 tcf gas for development. There is always comparison made with LNG in terms of storage capacity and economics.

(viii) In the formation of the hydrate, there would be a higher input pressure and temperature of gas directly from the well than conditions used in previous studies and laboratory experiments**.** Therefore there is need to lower the pressure and temperature of the gas from wellhead conditions to hydrate formation conditions.

1.5 Objectives of this Study

The objective of the study is to design an integrated scheme to transport natural gas in hydrate form Trinidad to the Caribbean islands. The study will show the gas hydrate value chain for transportation of 5 MMscf/d of natural gas from Trinidad to Jamaica. The work will propose a workflow for capturing, storing and transporting gas by hydrate technology. The analysis will evaluate the water required for hydrate formation, effect of composition on hydrate formation, the energy balance of the process, the time required for formation, transportation and dissociation and preliminary economics.

1.6 Conclusions

(i) There is need for new methods of natural gas transportation.

(ii) Stranded gas and associated gas reserved need to be captured economically.

(iii) Transportation of natural gas from Trinidad to the other Caribbean islands is needed.

(iv) Presently, LNG and pipeline are not economic means of gas transportation for the island.

(v) The study will design an integrated scheme to transport natural gas in hydrate form Trinidad to the Caribbean islands.

1.7 Structure of Dissertation

In Chapter II, gas transportation methods are reviewed emphasizing the need for new methods of gas transportation. The review identifies the pros and cons of the existing gas transportation modes of LNG and pipeline and introduces the gas hydrate as a potential way of transporting natural gas.

Chapter III gives details of the methodology used in this study. This chapter describes the thermodynamic model used the study and details of a sensitivity analysis evaluating the effects of the critical elements of pressure, temperature, gas composition and water on hydrate formation.

In Chapter IV details of the proposed solutions are discussed including upscaling from laboratory experiments, description and discussion of the proposed hydrate formation vessel, insulation required and the expansion process.

Chapter V evaluates the entire hydrate process with particular focus on energy balance, timing of each process and economic evaluation using hydrate technology to capture and transport 5 MMscf/d from Trinidad to Jamaica which is about 10% of the gas needs of Jamaica.

The next chapter (Chapter VI) focuses on a proposed work flow using two representative samples from Trinidad. This analysis shows the industrial application using hydrate technology and highlights the differences using the two distinct samples for gas transportation in hydrate form.

CHAPTER II

GAS TRANSPORTATION METHODS

Chapter I gave an overview of the problem associated with capturing and transporting stranded gas in Trinidad and Worldwide. Chapter I also clearly stated the objectives of the study. Now Chapter II focuses on evaluating the present gas transportation methods and introducing gas hydrate as a potential for capture and transporting stranded gas reserves.

2.1 Introduction

Natural gas is a versatile form of non-polluting fuel. With just over a dozen nations accounting for 84% of the world-wide production, access to natural gas has become a significant factor in international economics and politics. The major difficulty in the use of natural gas is transportation and storage because of its low density. Despite this, natural gas production has seen tremendous growth over the years. This has been due to large amount of natural gas reserves, and the wide variety of uses of natural gas and carbon dioxide emissions from natural gas energy generation are 30–40% less than coal.

In the past, the natural gas recovered in the course of producing petroleum could not be profitably sold, and was simply flared. This wasteful practice is now illegal in many countries. The most common method for transporting natural gas was high pressure in underground pipelines. Additionally, countries now recognize that value for the gas may be achieved with LNG, CNG, or other transportation methods to end-users in the future. In many cases the gas is now re-injected back into the formation for later recovery. Transportation is now a very important and key role in the supply chain for natural gas and the big challenge is to transport gas to markets at the lowest cost with minimal environmental risks. Now re-gasification at the market is important when selecting the mode of transportation of natural gas.

The efficient and effective movement of natural gas from producers to consumers requires an extensive and elaborate transportation system. In many instances, natural gas produced from a particular well will have to travel a great distance to reach its point of use. Transportation of natural gas is closely linked to its storage, as well; should the natural gas being transported not be required at that time, it can be put into storage facilities for when it is needed.

The factors affecting the type of gas transportation used include gas reserves, time frame to monetize the gas, the distances to the markets, investments and infrastructure available and gas processing. Stricter environmental laws' including the prevention of flaring gas has now pushed for ways to monetize associated gas. The possible ways of transporting natural gas to markets are pipelines, liquefied natural gas, gas to solids (hydrate), and other gas to commodity methods. Gas reserves are in the range of 6500 tcf but what is extremely significant is the 40% or 2500 Tcf that is considered stranded gas. These small pockets of gas reserves are found mainly in Russia, Qatar, Australia, Alaska and Trinidad (Fleisch, 2006). There is normally a large amount of associated gas that is re-injected or flared however nowadays many countries have banned the flaring of natural gas in large quantities. There is therefore a thrust for economic ways of transported stranded gas. Some of the gas transportation technologies (Rajnauth, Ayeni and Barrufet, 2008) are discussed.

2.2 Present Gas Transport Technologies

2.2.1 Pipelines

For many years pipelines have been the most convenient way to transport natural gas. Today pipeline transportation still remains a significant mechanism for gas delivery to markets. The transportation system for natural gas consists of a complex network of pipelines, designed to quickly and efficiently transport natural gas from its origin, to areas of high natural gas demand. Compressor stations are positioned along the pipeline route to maintain an efficient gas transportation process. Pipelines can measure anywhere from 6 to 56 inches in diameter. The completion of the 56” Cross Island Pipeline (CIP) in Trinidad makes it one of the largest diameter pipelines in the world (Pipeline, 2008). Pipelines are operated at pressures normally > 700 psig and this depends on the age of the pipeline and construction material used. The installation cost of pipelines range from US $1-6 million per mile. The actual price depends on factors such as the diameter, whether offshore or onshore, mountains or flat land, and distance. The technology for pipeline has evolved in terms of pipeline material, installation techniques, supervisory control and data acquisition (SCADA), surveillance, and automation systems (Verghese, 2003)

2.2.1.1 Pipeline Transportation Process

Pipeline networks are composed of several pieces of equipment that operate together to move products from location to location. The main elements of a pipeline system include:

- Initial Injection Station - is the beginning of the system, where the product is injected into the line. Storage facilities, pumps or compressors are usually located at these locations.
- Compressor/Pump Stations - Pumps for liquid pipelines and compressors for gas pipelines are located along the line to move the product through the pipeline. The location of these stations is defined by the topography of the terrain, the type of product being transported, or operational conditions of the network.
- Partial Delivery Station or Intermediate Stations - these facilities allow the pipeline operator to deliver part of the product being transported.
- Block Valve Station - These are the first line of protection for pipelines. With these valves the operator can isolate any segment of the line for maintenance work or isolate a rupture or leak. Block valve stations are usually located every 20 to 30 miles (48 km), depending on the type of pipeline. The location of these stations depends exclusively on the nature of the product being transported, and the trajectory of the pipeline and/or the operational conditions of the line.

- Station - This is a special type of valve station, where the operator can release some of the pressure from the line. Regulators are usually located at the downhill side of a peak.
- Final delivery station or Outlet stations/terminals - this is where the product will be distributed to the consumer. It could be a tank terminal for liquid pipelines or a connection to a distribution network for gas pipelines.

If there is a shutdown of the pipeline, the production from the well, processing and receiving terminals will also be shut down. Pipelines transportation faces risk of sabotage, other human and natural destruction. It is believed that pipeline transportation is uneconomic for reserves < 300 bcf (Fleisch, 2006).

2.2.1.2 Economics

Table 2 shows some of the proposed pipeline infrastructure around the world. This compiled data gives the sizes of pipeline, length of pipeline and the estimated cost (Rajnauth, Ayeni and Barrufet, 2008).

Table 2–Some Gas Pipelines with Estimated Cost

Pipeline	Size/ inches	Length / mile	Cost/ $US million
Trinidad to Tobago	No Data	176	550
Trans-Afghanistan	56	1044	3,500
Trans-Saharan Gas	No Data	2734	10,000
Kazakhstan gas	No Data	No Data	3,800
Medgaz pipeline- Algeria-Spain	48/24	470	1,350
Turkmen-China	Pipe network	4161	13,000

The estimated current pipeline cost is approx. US$3.28 million/mile. Again this cost may be dependent on several variables cited above.

2.2.1.3 Environment Considerations

Pipelines conveying flammable or explosive material, such as natural gas pose special safety concerns. Pipelines can be the target of vandalism, sabotage, or even terrorist attacks. In war, pipelines are often the target of military attacks, as destruction of pipelines can seriously disrupt enemy logistics. Since gas pipelines are an important asset of the economic development of almost any country, it necessary to have policies to ensure the safety of these assets, the population and environment where these pipelines run. Leak detection systems are necessary for gas pipeline systems.

There are also social problems that affect the operation of pipelines. In many countries, product theft is a problem for pipeline companies. It is common to find unauthorized extractions in the middle of the pipeline. In this case, the detection levels should be under 2 percent of maximum flow, with a high expectation for location accuracy (Pipeline, 2009). Different types of technologies and strategies have been implemented, from walking the lines, up to satellite surveillance. The most common technology to protect these lines from occasional leaks is known as Computational Pipeline Monitoring System. The potential for expanding the transport of natural gas by pipeline must be sought in innovative offshore engineering technologies; today the latter make it possible to develop subsea pipelines even at great depths with a high degree of safety. The current generation of pipelines has hindered the development of other natural gas transport technologies, with subsea routes at great depth on particularly uneven sea beds for the transport of gas volumes in the order of tens of millions of standard cubic meters per day.

The main limitation on the use of pipelines to transport natural gas lies in the need to cross the seas separating the producing country from the consuming country. Specifically, sea beds over 3,000-3,500 m deep with a particularly uneven morphology represent an enormous technological problem even today; in this case, too, this transport technology involves increased costs.

2.2.2 Liquefied Natural Gas

Liquefied natural gas or LNG is natural gas that has been converted to liquid form for ease of storage or transport. LNG is gas cooled to temperature of about -162 C and has a volume of 1/600 that of the gas at room temperature. LNG can be transported on land or by sea. It can be transported by specially designed cryogenic sea vessels (LNG vessels) or cryogenic road tankers. Prior to the liquefaction process, oxygen, carbon dioxide, sulfur compounds and water are removed. LNG is loaded onto ships and delivered to a re-gasification terminal, where the LNG is reheated and turned into gas. Re-gasification terminals are usually connected to a storage and pipeline distribution network to distribute natural gas to local distribution companies (LDCs) or Independent Power Plants (IPPs). A full LNG chain consists of a liquefaction plant, low temperature and pressurized transport ships and a re-gasification terminal. LNG provides a safe and efficient way of transporting natural gas over long distances, particularly from gas producing nations with insufficient pipeline infrastructures.

The LNG supply chain includes:

- Gas Production – the process of transporting gas from the reservoir to the LNG Plant.
- Gas Treatment – the removal of CO_2, H_2S, and dehydration
- LNG Production – the conversion of the natural to a liquid
- Shipping – Transporting the LNG from the plant to the markets by specialized ships
- LNG re-gasification terminals – the conversion of the LNG back to the gaseous phase
- Gas Utilization – the distribution of the gas to end users.

There are three main regions of LNG Exporters. These are the Atlantic Basin, Pacific and Middle East Exporters.

The Atlantic Basin region includes the exporters Trinidad, Algeria and Nigeria. There are presently 17 LNG trains and another 8 proposed trains. The train capacity ranges from 2.7 – 5 MMT/y and a cost per train between 0.83–1.5 billion USD.

The Pacific basin exporters of LNG include Indonesia, Malaysia, Australia, Brunei Darussalam, USA and Russia. These countries account for 33 LNG trains and 7 proposed new trains. The capacity of the trains varies between 1 and 3.75 MMT/y.

The Middle East exporters of LNG are Qatar, Oman and United Arab Emirates. This region accounts for 10 present LNG trains and 2 future trains. The capacity ranges from 1.6–4.4 MMT/y.

There are presently approximately 49 existing re-gasification terminals and 28 proposed terminals. LNG activities have been expanding and continue to expand. The conversion is 1 MMT/y LNG train is equivalent to 47.6 billion scf gas/y.

2.2.2.1 Economics

The most important infrastructure needed for LNG production and transportation is an LNG plant consisting of one or more LNG trains, each of which is an independent unit for gas liquefaction. Until 2003, LNG prices have closely followed oil prices. Since then, LNG prices to Europe and Japan have been lower than oil prices, though the link between LNG and Oil is still strong in contrast, recent prices in the US and UK markets have skyrocketed then fallen as a result of changes in supply and demand (Commercial, 2008).

Price arbitrage has not yet led to a convergence of regional prices and to a global market. For the time being, the market is a seller's market (hence net-back is best estimation for prices). The balance of market risks between the buyers (taking most of the volume risks through off-take obligations) and the sellers (taking most of the value risks through indexation to crude oil and petroleum products) is changing.

LNG projects are billion dollar projects. An estimated break down of the cost of the entire LNG process for a typical train (3 MMT/y) is shown below (Morgan, 2006) in **Table 3**.

Table 3–Breakdown of LNG Costs for Typical Train (5 MMT/y)

	Average Cost/ US Billion
Gas Gathering	1-1.5
Liquefaction (1 train)	1-1.5
Ships (5) @ $180 million	0.9
Re-gasification	0.5
Total	3.4 -4.4

2.2.2.2 Environmental Considerations

LNG is non-toxic, odorless, non-explosive and non-flammable in its liquid state. In fact, it will only burn after it has been re-gasified and mixed in the proper proportion with air. Natural gas burns only within the narrow range of a 5 to 15 volume percent gas-to-air mixture. Liquefied natural gas has about 45 percent the density of water, so if spilled onto a waterway, it will stay on top of the water until it evaporates into the atmosphere. Maintaining LNG safety is a top priority for several federal and state agencies, including the U.S. Coast Guard.

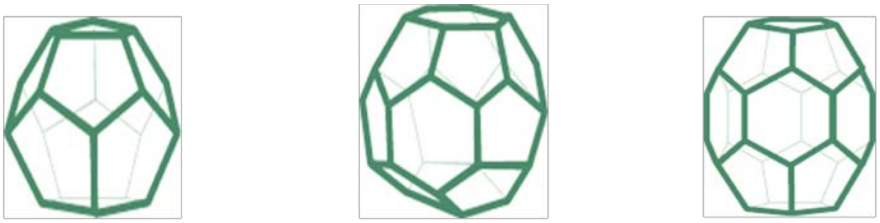
2.2.2.3 Re-gasification

Re-gasification terminal are very costly and countries have to consider this huge investment cost. At the re–gasification terminal, LNG is unloaded from LNG vessels and stored in insulated tanks at atmospheric pressure and a temperature of minus 162° C. For distribution the LNG is warmed to a point where it reverts to its gaseous state. The heat to re-gasify the LNG is provided both by sea water, using the heat naturally stored in the sea, and by turbine flue gases, using an energy recovery system. After the re–gasification process, the gas will be sent through a pipeline to the pipeline network. There are now ships that have re-gasification capabilities. Recently ship-to-ship transfer transfers have been carried out and involved the transfer of LNG from the LNG re-gasification vessel (LNGRV) to a conventional LNG carrier.

2.3 Gas Hydrate as a Potential Gas Transportation Mode

2.3.1 What Is Gas Hydrate?

Natural gas hydrates are ice-like crystalline solids formed from a mixture of water and natural gas subjected to high pressure and suitable low-temperature conditions. These conditions are found in the permafrost and under the ocean floor. Hydrates consist of geometric lattices of water molecules containing cavities occupied by light hydrocarbons and other types of gaseous components for such as nitrogen, carbon dioxide, and hydrogen sulfide.



Structure I
5 small dodecahedral voids and six large tetradecahedral voids < 5.2 angstrom

Structure II
16 small dodecahedral voids and 8 large hexakaidecahedral voids 5.9-6.9 angstrom

Structure H
5 carbon atoms structure >6.9 angstrom

Fig. 3–Representation of Hydrate Types (Sassen, 1997)

Fig. 3 shows a simple illustration of the three types of hydrates. Gas hydrates are normally classified as structure SI, SII and H type gas hydrates. Structure I hydrates contain 46 water molecules per 8 gas molecules (Sassen, 1997). The hydrate number is 5.75. The water molecules form two small dodecahedral voids and six large tetra decahedral voids. These voids can hold only small gas molecules (methane, ethane) with molecular diameters not exceeding 5.2 angstroms. Structure II hydrates contains 136 water molecules per 24 gas molecules. The hydrate number is 5.67. The water molecules form 16 small dodecahedral voids and 8 large hexakaidecahedral voids. They may contain gases with molecular dimensions from 5.9 to 6.9 angstroms, such as propane, and isobutene. In this case structure II must form to accommodate the larger molecules (Makogon, 1981; Sloan, 1991). Structure H hydrates contains 34 water molecules per 6 gas molecules. The hydrate number is 5.67. This structure is large enough to hold molecules like iso-pentane, a branched-chain hydrocarbon molecule with five carbon atoms. Pentane (C_5H_{12}) and heavier hydrocarbons do not form hydrate because of their size (Carson and Katz, 1941).

The fit of the molecules within the cavities is important in determining the structure of the hydrate form. Therefore the composition of natural gas determines the type of gas hydrate structure formed.

Although gas hydrates resemble ice or wet snow, in appearance, but do not have ice's solid structure, are much less dense and exhibit properties that are generally associated with chemical compounds. Gas hydrates of interest to the natural gas industry are made up of lattices containing water molecules in different ratios with methane, nitrogen, ethane, propane, iso-butane, normal butane, carbon dioxide and hydrogen sulfide.

The cavities are at least partially occupied by small gas molecules such as CH_4, C_2H_6, C_3H_8, I-C_4H_{10}, n-C_4H_{10}, N_2, and CO_2 to stabilize the lattice structure (Tse and Bishnoi, 1994).

2.3.2 Possible Benefits of Gas Hydrate Technology

It may be possible that gas hydrate can provide an easier to produce, safer and cheaper to store method of capturing natural gas when compared to other transportation modes such as CNG and LNG. This may be a promising and attractive method of gas transportation. Gas hydrate has a high gas to solid ratio. 1 m^3 of hydrate contains 150-180 m^3 of gas per m^3 of water. The storage capacity depends on the structure of the hydrate formed whether structure I, II or H. The formation of these structures is dependent on the natural gas composition and the additive used. Some factors that affect storage capacity include incomplete cage filling, impurities and incomplete packing of the hydrate.

In this study, we would make reference to hydrates and not distinguish between the types of hydrates. However, the volume of hydrate I or hydrate II formed depends on the composition. Methane gives only hydrate I but for many of the samples in the analysis give varying volume percentages of hydrate I and hydrate II formed.

2.4 Conclusions

(i) Average pipeline cost is approximately US$3.28 million per mile (range 1-6 MMUSD/mile). This cost is dependent on diameter, whether onshore or offshore, mountains or flat land and distance.

(ii) LNG projects are billion dollar projects. For a 5 MMT/y LNG plant, it would cost approximately US$ 1.45 billion. Re-gasification plants are estimated at US$ 0.5 billion and an overall cost in the range of US $3–5 billion. These are too costly for inter island transport of natural gas.

(iii) LNG is too costly for capturing stranded gas. At least 1-3 tcf of gas is needed for a LNG project (Morgan, 2006). Stranded gas in Trinidad is in the reserve range of 200-300 bcf.

(iv) Gas hydrate can be a useful means of transporting natural gas. Gas hydrate can potentially provide an easier to produce, safer and cheaper method of capturing, storing and transporting natural gas. It has a fairly high gas to solid ratio. A lot of new knowledge on hydrate is obtained from studies of naturally occurring hydrates.

CHAPTER III

METHODOLOGY

Chapter II emphasizes the need for a new method of transporting natural gas especially for stranded gas and for small scale island transport. This chapter describes the methods used in this study. Information on the thermodynamic model used and details of a sensitivity analysis are discussed.

3.1 Introduction

This study seeks to accomplish the objectives by the doing the following:

(1) To do a sensitivity analysis using a commercial simulator (PVTSim, 2008) and includes:
    (i) Using 21 typical gas samples from Trinidad.
    (ii) Pressure, Temperature, Water conditions evaluated.
    (iii) Use results and calculations for further analysis.
    (iv) Evaluation of conditions for up-scaling from laboratory information.
(2) Address some of the limitations of previous work outlined above and propose possible solutions.
(3) Develop the proposed solutions by examining:
    (i) Process Analysis using one or two samples considering:
        - Up-scaling conditions
        - Energy required for the process

        - Time for formation, transportation and dissociation.
        - Economics analysis

    (ii) Available technology and equipment

(4) Evaluate the transportation of 5 MMscf/d of natural gas in hydrate form from Trinidad to Jamaica.

3.2 Hydrate Computations

The hydrate phase equilibrium calculations consider the different phases, namely gas, liquid water, ice, hydrate of structure I, hydrate of structure II.

Hydrates are formed when the hydrate state is energetically favorable as compared to a pure water state (fluid water or ice). The transformation from a pure water state to a hydrate state can be regarded as consisting of two steps:

1. Pure water (α) $\rightarrow$ empty hydrate lattice (β)
2. Empty hydrate lattice (β) $\rightarrow$ filled hydrate lattice (H)

where α, β and H are used to identify each of the three states considered. The β-state is purely hypothetical and only considered to facilitate the hydrate calculations. Which state is energetically favorable depends on which state has the lowest Gibbs energy. The difference between the chemical potential of water in the hydrate state (H) and in the pure water state (α) can be expressed as:

$$\mu^H - \mu^\alpha = (\mu^H - \mu^\beta) + (\mu^\beta - \mu^\alpha) \quad \textbf{(1)}$$

The first term on the right hand side ($\mu^H - \mu^\beta$) can be regarded as the stabilizing effect on the hydrate lattice caused by the adsorption of the gas molecules. This latter effect depends on the tendency of the gas molecules to enter into the cavities in the hydrate lattice. This tendency is in hydrate simulator expressed using a simple gas adsorption model.

A hydrate phase equilibrium curve represents the T, P values for which:

$$\mu^H - \mu^\alpha = 0 \quad \textbf{(2)}$$

At those conditions the hydrate state and the pure water state are equally favorable. To the left of the hydrate curve:

$$\mu^H - \mu^\alpha < 0 \quad \textbf{(3)}$$

And some of the water will be in a hydrate form at equilibrium. Whether this is a structure I or a structure II hydrate depends on which of the two structures has the lowest chemical potential in the presence of the actual gas components as potential guest molecules. To the right of the hydrate curve:

$$\mu^H - \mu^\alpha > 0 \quad \textbf{(4)}$$

i.e. at equilibrium at those conditions no hydrate can exist and the water will be in the form of either liquid or ice.

3.2.1 Hydrate PT Flash Calculations

Flash calculations are performed using an "inverse" calculation procedure outlined as follows:

(i) Initial estimates of the fugacity coefficients of all the components are established for all phases except the hydrate phases and any pure solid phases. This is done by assuming an ideal gas and ideal liquid solution, neglecting water in the hydrocarbon liquid phase and by assuming that any water phase will be pure water.

(ii) Based on these fugacity coefficients and the total overall composition (z_K, K = 1, N) from ideal solution (composition independent fugacity coefficients) a multi phase flash P/T is performed (Michelsen, 1989). The results of this calculation will be the compositions and amounts of all phases (except any hydrate and pure solid phases) based on the guessed fugacity coefficients, i.e.: x_{Kj} and β_j, $K = 1 \ldots n$, $j \neq$ hyd and pure solid. The subscript K is a component index, j a phase index, ß stands for phase fraction and N for number of components.

(iii) Using the Huron and Vidal (1979) model and the calculated compositions (x_{Kj}), the fugacities of all components in all the phases except the hydrate and pure solid phases are calculated: (f_{Kj}, K = 1… N, j ≠ hyd and pure solid).

(iv) Based on these fugacities (f_{Kj}, K = 1… N, j ≠ hyd and pure solid), mixture fugacities (f_K^{MIX}, K = 1…N) are calculated. For the non-water components, a mixture fugacity is calculated as the molar average of the fugacities of the given component in the present hydrocarbon phases. For water the mixture fugacity is set equal to the fugacity of water in the water phase.

(v) The fugacities of the components present in the hydrate phase are calculated using:

$$\ln f_k^H = \ln f_k^{MIX} + \theta \qquad ; \qquad k = 1 \ldots NHYP \tag{5}$$

where θ is a correction term identical for all components. θ Is found from

$$\ln f_k^{MIX} + \theta = \sum_{i=1}^{NCAV} \nu_i \ln\left(1 - \sum_{k=1}^{N} Y_{ki}\right) + \ln f_w^{\beta} \tag{6}$$

where w stands for water and β refers to the empty hydrate lattice.

and the expression for f_k^H is proposed by Van der Waals and Platteeuw (1959)

$$\ln f_w^H = \sum_{i=1}^{NCAV} \nu_I \ln\left(1 - \frac{\sum_{k=1}^{NHYD} C_{ki} \; f_k^H}{1 + \sum_{j=1}^{NHYD} C_{ji} \; f_j^H}\right) + \ln f_w^{EL} \tag{7}$$

where NHYD is the number of compounds present which may enter into the hydrate cavities and NCAV is the number of different cavities in the actual structure. Cki is an adsorption constant specific for a given component, k, in a given cavity, i, at a specified temperature. F_w^{EL} is the fugacity of water in a hypothetical empty hydrate lattice.

(vi) The hydrate composition is calculated using the expression:

$$\frac{x_K}{x_w} = \sum_{i=1}^{NCAV} \nu_i \frac{C_{Ki} \; f_K^H}{1 + \sum_{j=1}^{NHYD} C_{ji} \; f_j^H} \tag{8}$$

Which enables calculation of the fugacity coefficients? Non-hydrate formers are assigned large fugacity coefficients (ln = 50) to prevent them from entering into the hydrate phases.

(vii) Based on the actual values of the fugacity coefficients for all the components in all the phases (φ_{Kj}) and the total overall composition z_K an ideal solution (composition independent fugacity coefficients) multi phase flash is performed (Michelsen, 1988). The result of this calculation will be compositions and amounts of all phases (i.e.: x_{Kj} and , K=1,...,N, j=1,...,number of phases).

(viii) if not converged, repeat from 3.

3.2.2 Calculation of Fugacities in the Various Phases

To use the flash calculation procedure outlined above, expressions must be available for the fugacity of component i in each phase to be considered. The fugacity of component i in a solution is given by the following expression:

$$f_i = \varphi_i \; x_i \, P \tag{9}$$

where φ_i is the fugacity coefficient, x_i the mole fraction and P the pressure.

For the fluid phases φ_i is calculated from the selected equation of state. The mixing rule used for the a-parameter is either the classical Soave one or the one suggested by Huron and Vidal (1979).

For binary pairs of components of which at least one is polar, the classical mixing rules are often insufficient. The PVTSim hydrate module HYDSim can handle water, alcohol, glycols and salts. In PVTSim the mixing rule suggested by Huron and Vidal is used for most of the interactions with water, alcohols, glycols and salts. The H & V a-parameter mixing rule takes the following form:

$$a = b\left(\sum_{i=1}^{N}\left(z_i\,\frac{a}{b}\right) - \frac{G_\infty^E}{\ln 2}\right) \qquad \textbf{(10)}$$

where G_∞^E is the excess Gibbs energy at infinite pressure. G_∞^E is found using a modified NRTL mixing rule:

$$\frac{G_\infty^E}{RT} = \sum_{i=1}^{N} z_i\,\frac{\sum_{j=1}^{N}\tau_{ji}\,b\,z_i\,\exp\left(-\alpha_{ji}\,\tau_{ji}\right)}{\sum_{k=1}^{N} b_k\,z_k\,\exp\left(-\alpha_{ki}\,\tau_{ki}\right)} \qquad \textbf{(11)}$$

where α_{ji} is a non-randomness parameter, i.e. a parameter for taking into account that the mole fractions of molecules of type i around a molecule of type j may deviate from the overall mole fraction of molecules of type i in the mixture. When α_{ji} is zero, the mixture is completely random. The τ-parameter is defined by the following expression:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \qquad \textbf{(12)}$$

where g_{ji} is an energy parameter characteristic of the j-i interaction. The parameter b entering into the expression for G_∞^E is the b-parameter of the SRK-equation. The mixing rule used by Huron and Vidal (1979) uses the classical mixing rule for the b-parameter.

For a binary pair which can be described using the classical mixing rule, the local composition will not deviate from the overall composition, i.e. a_{ji} should be chosen equal to zero. By further selecting the following expressions for the interaction energy parameters:

$$g_{ii} = \frac{a_i}{b_i} \ln 2$$ **(13)**

$$g_{ji} = \frac{\left(b_i\ b_j\right)^{0.5}}{\left(b_i + b_j\right)} \left(g_{ii} \cdot g_{jj}\right)^{0.5} \left(1 - k_{ij}\right)$$ **(14)**

The H&V mixing rule reduces to the classical one. When the H&V mixing rule is used, these expressions are therefore used for g_{ij} and gii of binary pairs which do not require the advanced mixing rule.

The fugacities of the various components in the hydrate phases are calculated as described by Michelsen (1991)

Water:

$$\ln\ f_w^H - \ln_w^\beta = \nu_1\ \ln\left[\frac{N_0\ \left(1 - \theta\right)}{\nu_1}\right] + \nu_2\ \ln\left(\frac{N_0\ \theta}{\nu_2}\right)$$ **(15)**

Other Hydrate Formers:

$$f_K^H = \frac{N_K}{N_0\ C_{K2}\ \left(\theta + \alpha_K\ (1 - \theta)\right)} \qquad \textbf{(16)}$$

In these equations

f_w^β	fugacity of water in empty hydrate lattice
v_i	number of cavities of type i
N_0	number of empty lattice sites
θ	ratio of free large lattice sites to total free lattice sites
N_K	content of component k per mole of water
C_{Ki}	Langmuir constant
α_K	C_{K1}/C_{K2}

The determination of θ and x_i follows the procedure described by Michelsen (1991).

3.3 Sensitivity Analysis

3.3.1 Introduction

The main components in producing natural gas hydrate (whether for gas storage or for transportation), are water and natural gas, at low temperatures and high pressures. Each variable has a significant effect on the formation of gas hydrate. It is therefore critical to analyze the effect of each variable on hydrate formation to ascertain the best conditions required for a successful gas hydrate formation process.

This analysis evaluates the effect of these critical elements: temperature, pressure, gas composition, and water upon gas hydrate formation and summarizes the findings of a sensitivity analysis using varying natural gas compositions. Results show that the composition of the natural gas can affect the temperature and pressure required for formation of the hydrate. Even more significant is the effect of impurities in the natural gas on the pressure temperature (PT) curves of the hydrate. Carbon dioxide, hydrogen sulfide and nitrogen are the main impurities in natural gas affecting the hydrate formation. At a particular temperature, nitrogen increases the required hydrate formation pressure while both carbon dioxide and hydrogen sulfide lower the required hydrate formation pressure.

The quantity of water required for hydrate formation is an important variable in the process. The water to gas ratio vary depending on the composition of the natural gas and the pressure. Generally the mole ratio of water to natural gas is about 6:1; however, to achieve maximum hydrate formation an incremental increase in water or pressure may be required. This is an interesting tradeoff between additional water and additional pressure in obtaining maximum volume of hydrate and is shown in this analysis.

The objective of this study is to pre-design a system for transporting natural gas in hydrate form. As such a sensitivity analysis was used to investigate theoretically predicted hydrate formation PT boundaries from a thermodynamic model using a commercial simulator. The theoretical model was validated with selected experimental data to ensure that predictions were reasonable.

In this analysis, twenty one natural gas compositions of typical wells mainly from Trinidad (Ministry, 2007) are analyzed in order to estimate the process conditions to convert and transport 5 MMscf/d of gas in hydrate state to neighboring islands (e.g.). The natural gas streams obtained from these wells were, generally, sweet gases (without H_2S) and ranges in composition from C_1 to C_{10}. These samples are shown in **Table 4**. The expected production from these small producer wells are in the range of 0.5 MMscf/d to 5 MMscf/d. The most important design variables affecting the percentage of hydrate formed include: pressure, temperature, composition, and amount of water required to form hydrate.

Previous research work in this area included simple laboratory experiments and small scale pilot projects for hydrate formation using simple gases such as methane. Hence, it is important to determine the operational conditions, quantities and design variables for designing the gas hydrate formation for an upscale process. Gudmundsson, Parlaktuna and Khokhar (1994) deduced from their laboratory experiments that the conditions required for formation of the hydrate are 290 to 870 psia and 32 to 68 F. This experiment was conducted using methane. Another study (Gudmundsson et al., 1998) looked at two gas samples; pure methane and a gas mixture (92% C_1, 5% C_2, and 3% C_3).

The composition of the natural gas is an important factor when considering the temperature and pressure range to form natural gas hydrates. The formation conditions of 600 psia and 35 F were then chosen as it represents potential upscaling conditions deduced from experimental studies conducted by Okutani, Kuwabara and Mori (2007). Mole and volume % of hydrate formed will be shown.

Table 4–Natural Gas Composition from Trinidad/Mole %

Sample		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Dry Gas
Nitrogen	N_2	0.56	0.78	3.93	0.87	1.32	2.40	0.60	2.21	1.09	2.55	0.46	1.09	0.49	0.06	0.09	0.09	0.09	0.21	0.00	0.05	0.00
Hydrogen Sulphide	H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide	CO_2	3.92	2.84	2.98	3.75	0.90	0.64	3.64	1.12	1.73	0.44	6.11	1.73	5.84	0.10	0.31	0.58	0.68	0.94	0.37	0.02	0.00
Methane	C_1	92.09	92.04	88.29	87.77	88.02	88.37	87.48	86.21	85.20	85.04	77.25	85.20	78.07	96.82	93.42	91.65	89.55	94.70	92.28	99.63	99.00
Ethane	C_2	2.52	2.82	3.05	4.86	6.60	5.03	4.85	6.47	6.76	7.00	8.77	6.76	8.96	1.75	2.96	3.48	4.14	2.90	1.48	0.17	1.00
Propane	C_3	0.51	0.74	0.65	1.51	1.63	1.77	1.91	2.32	2.73	3.23	3.35	2.73	3.34	0.64	1.15	1.31	1.83	0.74	2.23	0.03	0.00
Isobutane	iC_4	0.10	0.14	0.24	0.31	0.20	0.65	0.34	0.44	0.36	0.32	0.75	0.36	0.71	0.18	0.34	0.30	0.63	0.15	0.70	0.01	0.00
N-Butane	nC_4	0.12	0.21	0.30	0.41	0.55	0.49	0.54	0.65	1.00	0.82	1.32	1.00	1.21	0.19	0.33	0.39	0.93	0.17	0.91	0.02	0.00
Isopentane	iC_5	0.05	0.10	0.14	0.19	0.17	0.20	0.21	0.25	0.30	0.16	0.44	0.30	0.35	0.08	0.15	0.16	0.53	0.06	0.79	0.01	0.00
N-Pentane	nC_5	0.04	0.08	0.14	0.12	0.21	0.15	0.16	0.18	0.38	0.20	0.69	0.38	0.50	0.06	0.11	0.16	0.47	0.05	0.09	0.02	0.00
Hexanes plus	C_{6+}	0.09	0.25	0.28	0.21	0.40	0.30	0.27	0.15	0.45	0.24	0.86	0.45	0.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hexanes	C_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.16	0.22	0.53	0.04	0.37	0.02	0.00
Heptanes	C_7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.25	0.28	0.38	0.02	0.30	0.00	0.00
Octanes	C_8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.18	0.39	0.18	0.02	0.25	0.00	0.00
Nonanes	C_9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.16	0.23	0.05	0.00	0.13	0.00	0.00
Decanes +	C_{10}^{+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.76	0.01	0.00	0.10	0.02	0.00

The molar concentrations of the natural gas analyzed are shown in **Table 4**. It was observed that they have carbon dioxide concentrations varying from 0.44 mol% (Sample 10) to 6.11mol% (Sample 11), C_1 concentration varying from 85.04 mol%

(Sample 8) to 99.63 mol% (Sample 20) and a ($C_2 + C_3 + iC_4 + nC_4 + iC_4 + nC_5 + iC_5 + C_6^+$) composition, varying from 1.0 mol % (Dry Gas) to 16.18 mol % (Sample 11).

3.3.2 Verification of Model

A thermodynamic model was used to estimate the conditions at which gas hydrates may form and in what quantities. Hydrates are formed when the hydrate state is energetically favorable as compared to a pure water state (fluid water or ice).

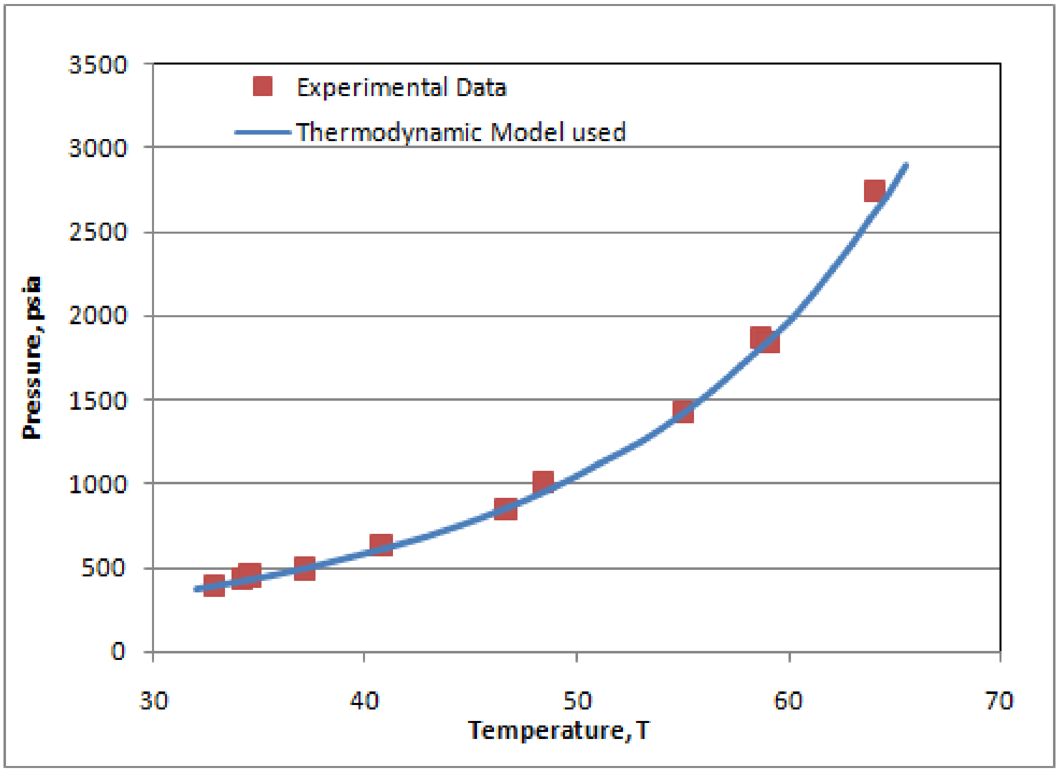


Fig. 4–Comparison of the Model Used with Experimental Data (Jagar and Sloan, 2001)

Fig. 4 above compares the thermodynamic model used in this study with experimental data for methane hydrate. The actual data matches closely with the mode used in this study. This validates the theoretical model and ensures reasonable predictions.

The following are the steps used in this sensitivity analysis:

(i) Inputted 21 gas compositions in commercial simulator and generate pressure/temperature data points.
(ii) Plotted PT curves for all samples.
(iii) Selected samples with lowest and highest PT curves. (Sample 11 and Sample Dry Gas)
(iv) Selected range of temperatures and pressures for analyzing both samples for different mole ratios. Ranges selected above PT curve.
(v) Used output from program to evaluate mole % of hydrate formed, volume %, and volume in ft^3, amount of gas stored in 1ft^3, weight of hydrate, tonnes, amount of water required and effect of composition on hydrate formation conditions.
(vi) Estimate the heating value of the gas before hydrate formation, gas captured in the hydrate form and the natural gas liquids (NGL) separated during hydrate formation.
(vii) Evaluate the latent heat of formation to be removed during hydrate formation for production range of 0.5 MMscf/d to 5 MMscf/d.

3.3.3 Natural Gas Hydrate Forming Conditions

The hydrate forming temperature/pressure for the twenty one natural gas streams given in **Table 4** is plotted in **Fig. 5.** This graph was developed on the basis of a large number of data points generated by computer using the PVTSim program. **Fig. 5** shows that the hydrate forming temperature/pressure relationship for natural gases is greatly influenced by the composition of the gas mixtures.

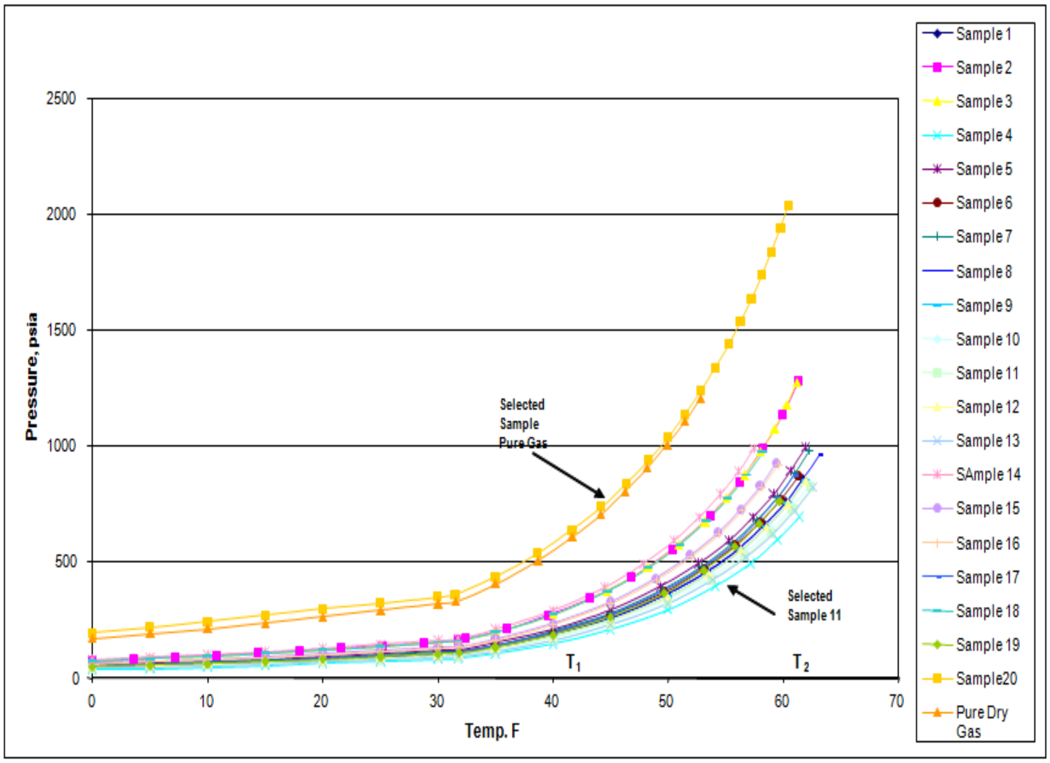


Fig. 5–Hydrate Forming Temperature/Pressure

The uppermost curve corresponds to the natural gas obtained from sample Dry Gas while the lowermost curve corresponds to the natural gas obtained from the Sample 11. At a fixed pressure, i.e. 600 psi sample 11 will form hydrates if the temperature is lower than T_2, while sample dry gas will form hydrate if T is lower than T_1.

The samples with the highest and lowest PT curves are shown in **Fig. 6** and the selected range of temperatures and pressures for analyzing both samples for different mole ratios. Ranges selected above PT curve. The PT profiles of all other samples fall between these two extremes.

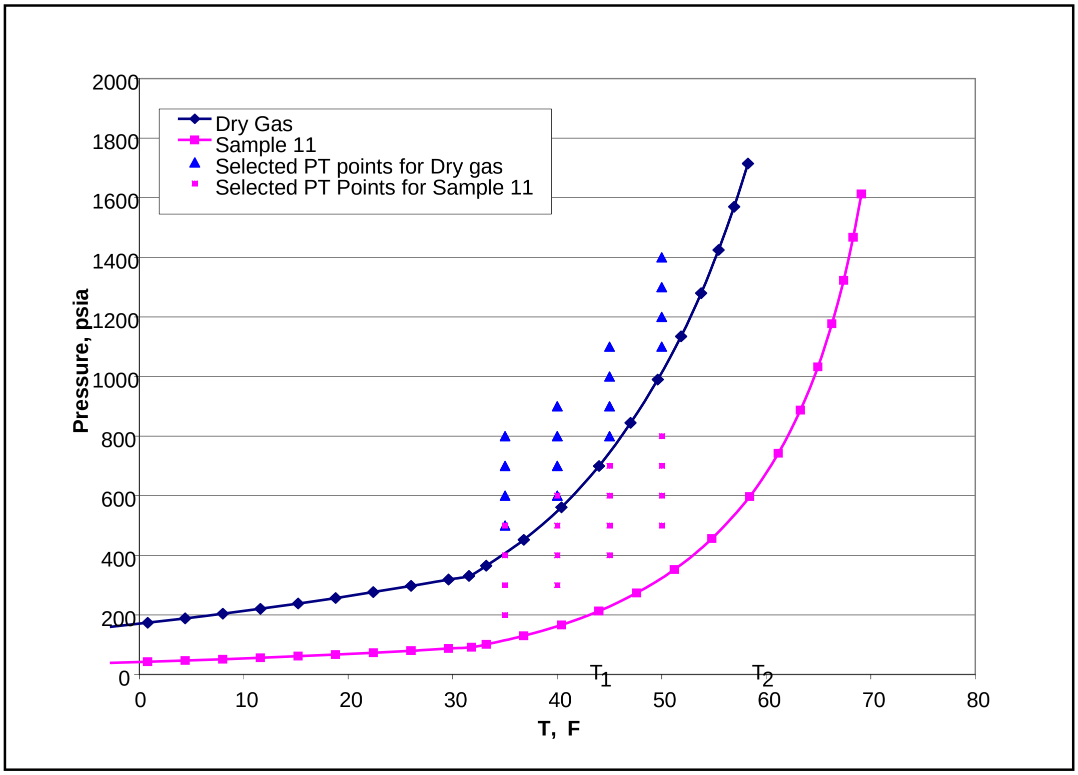


Fig. 6–Theoretical Hydrate Forming Temperature/Pressure (Equilibrium Curves) for Sample 11 and Dry Gas Sample

It was also observed that at a fixed temperature, the higher methane content (Dry Gas) in the natural gas increases the pressure of hydrate formation. Similarly, the higher propane concentrations in the sample (Samples 11) lower the formation pressure of the hydrate at a fixed temperature.

3.3.4 Effect of Composition on Hydrate Formation Pressure

Fig. 7 shows the effect of the light components ($N_2 + CO_2 + C_1$) on hydrate formation pressures at temperatures of 40 F, 45 F and 50 F. The points, in **Fig. 7**, correspond to the natural gas streams shown above. It is observed that as the ($N_2 + CO_2 + C_1$) composition varied from 84 mol% to 99 mol%, the hydrate formation pressure increases from 161.5 psi to 572.1 psi at 40 °F. Similar trends can be seen at the temperatures 45 F and 50 F.

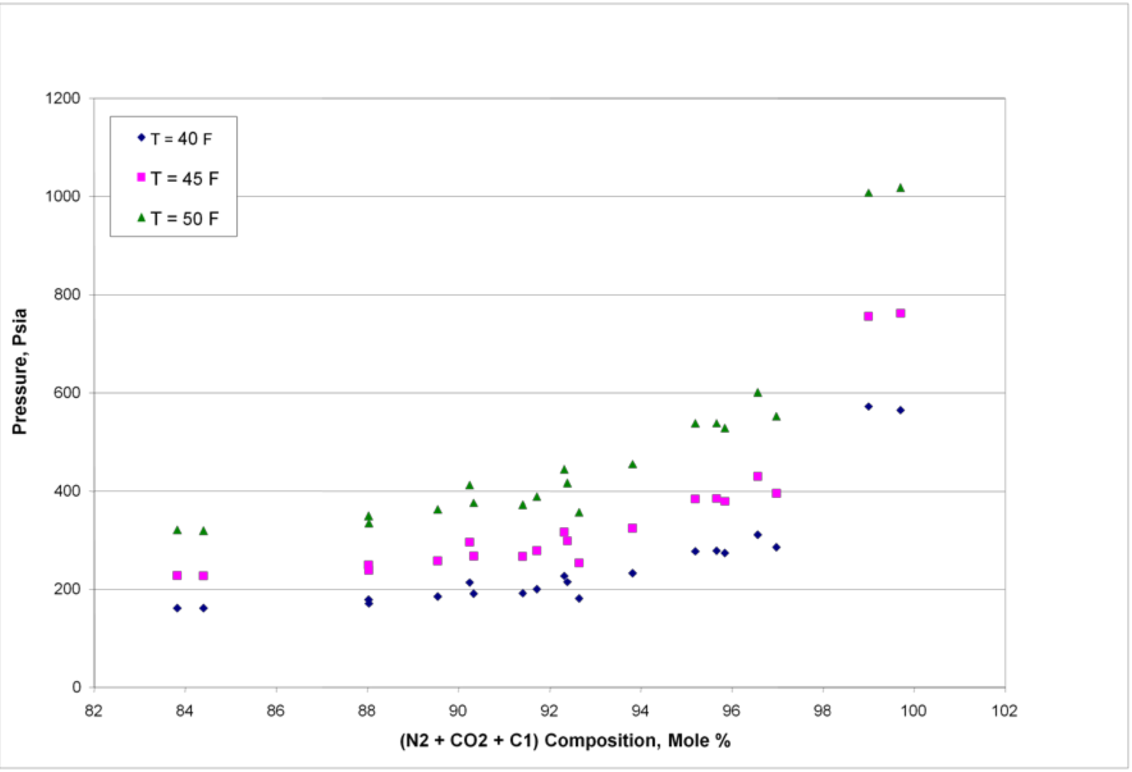


Fig. 7–Hydrate Formation Pressure for Different Compositions (Light Components) from the 21 Samples

The influence of the heavier is opposite to that observed in **Fig. 7** i.e., varying (C_2 + C_3 + iC_4 + nC_4 + iC_5 + nC_5 +C_{6+}) concentration from 0.3 mol% to 16.2 mol%, the hydrate formation pressure decreases from 565.2 psi to 161.4 psi approximately, at 40 F**.**

3.3.5 Further Analysis Using Two Selected Samples

From the twenty one samples two samples were selected for further analysis. These samples are Sample 11 and Sample Dry Gas as seen above. Composition of Sample 11 and Sample Dry Gas are shown in **Table 4**. A range of temperatures and pressures above the equilibrium line were selected for analysis of the two selected samples using a water-gas mole ratio from 1:1 to 6:1. These ranges are also illustrated in **Fig. 6** and were selected to identify PT points above the equilibrium line to evaluate a hydration formation trend as PT changes. For each of the temperatures selected four 100 psia increment pressure points were chosen above the equilibrium line. The effect of water content on hydrate formation and pressure and temperature effects on storage capacity are shown.

3.3.6 Effect of Mole Ratio on Amount of Hydrate Formed

The effect of the water content on volume of hydrate formed was simulated at 40 F, 45 F and 50 F and at pressures varying from 300 psi to 800 psi for Sample 11 and 600 psia to 1400 psia for Sample Dry Gas.

This effect was analyzed considering the following levels of the mol water phase/mol feed ratio, 1:1, 2:1, 3:1, 4:1, 5:1 and 6:1. Numerical examples of this analysis are given in **Table 5** for the Sample 11, which has the lower (N_2 + CO_2 + C_1) natural gas composition and in **Table 6** for the Sample Dry gas, which has the higher (N_2 + CO_2 + C_1) natural gas composition. **Table 5** and **Table 6** show the V_{GAS}/ (V_{GAS}+V_{HYD}) ratio as a function of temperature, pressure and mol water phase/mol feed ratio.

V_{GAS} represents the volume of gas at the particular temperature and pressure specified in the table cell. V_{HYD} represent volume of hydrate with gas at standard condition. A V_{GAS}/ (V_{GAS}+V_{HYD}) ratio of 0.444 indicates 44.4% of free gas at a particular temperature and pressure to be captured in hydrate formed. The empty cells to the left of the data in the table correspond to PT points very close to or below the equilibrium line and as a result no hydrate is formed. (*) The empty cells to the right correspond to PT points not chosen for the sample as they correspond to point's way above the equilibrium line and therefore is no significant change in volume of hydrate formed.

Table 5–Effect of Water Content on Volume of Hydrate Formed for Sample 11

T, F	Mole Ratio	Pressure, psia					
		300	400	500	600	700	800
		V gas/ (Vgas+Vhyd)					
40	1	0.974	0.965	0.955	0.946	See note above (*)	See note above (*)
	2	0.940	0.919	0.897	0.875		
	3	0.931	0.854	0.817	0.782		
	4	0.987	0.750	0.699	0.647		
	5	0.850	0.710	0.505	0.435		
	6	0.830	0.809	0.134	0.054		
45	1	No hydrate	0.965	0.956	0.946	0.935	See note above (*)
	2		0.920	0.899	0.877	0.856	
	3		0.870	0.821	0.786	0.752	
	4		0.840	0.730	0.655	0.607	
	5		0.810	0.690	0.450	0.391	
	6		0.780	0.650	0.420	0.095	
50	1		No hydrate	0.957	0.946	0.937	0.926
	2			0.900	0.880	0.859	0.837
	3			0.850	0.780	0.757	0.725
	4			0.820	0.730	0.620	0.573
	5			0.780	0.700	0.570	0.370
	6			0.750	0.660	0.531	0.331

Table 6–Effect of Water Content on Volume of Hydrate Formed for Sample Dry Gas

T, F	Mole Ratio	Pressure, psia								
		600	700	800	900	1000	1100	1200	1300	1400
		V gas/ (Vgas+Vhyd)								
40	1	0.9497	0.9408	0.9318	0.9228	See note above (*)	See note above (*)	See note above (*)	See note above (*)	See note above (*)
	2	0.8847	0.8657	0.8469	0.8284					
	3	0.7974	0.767	0.738	0.7103					
	4	0.6741	0.6319	0.5933	0.5581					
	5	0.4866	0.4352	0.3917	0.3546					
	6	0.1669	0.1227	0.0912	0.0684					
45	1	No hydrate	No hydrate	0.9329	0.924	0.9151	0.9062			
	2			0.8491	0.831	0.8132	0.7958			
	3			0.7418	0.7144	0.6884	0.6637			
	4			0.5989	0.5639	0.532	0.5028			
	5			0.3996	0.3622	0.3301	0.3024			
	6			0.1021	0.0778	0.0596	0.0460			
50	1			No hydrate	No hydrate	No hydrate	0.9077	0.899	0.8904	0.8818
	2						0.7988	0.7822	0.7659	0.7502
	3						0.6683	0.6451	0.6232	0.6025
	4						0.5088	0.4821	0.4578	0.4355
	5						0.3094	0.285	0.2638	0.2451
	6						0.0532	0.0418	0.0329	0.0259

From **Table 5** and **Table 6,** it can be observed that the $V_{GAS}/(V_{GAS}+V_{HYD})$ ratio decreases by (i) increasing the water content at fixed temperature and pressure and (ii) increasing the pressure at fixed temperature and mole ratio. This means that the volume of hydrate formed increases when the pressure and water content increases. For a fixed P and T the volume of hydrate reaches a maximum as the moles of water increases. Beyond that further additions of water will result in free water liquid phase. For a fixed mole ratio the volume of gas decreases due to compressibility effect.

Fig. 8 shows the maximum mole % of hydrate formed for different mole ratio (water to gas) for 600 psia and 35 F for the dry gas sample.

Mole ratio of 6:1 give the best results about 99.5% while a mole ratio of 1:1 give about 58%. A similar mole % trend was seen for Sample 11.

Fig. 9 shows the maximum volume % of hydrate formed for different mole ratio (water to gas) for 600 psia and 35 F for the dry gas sample.

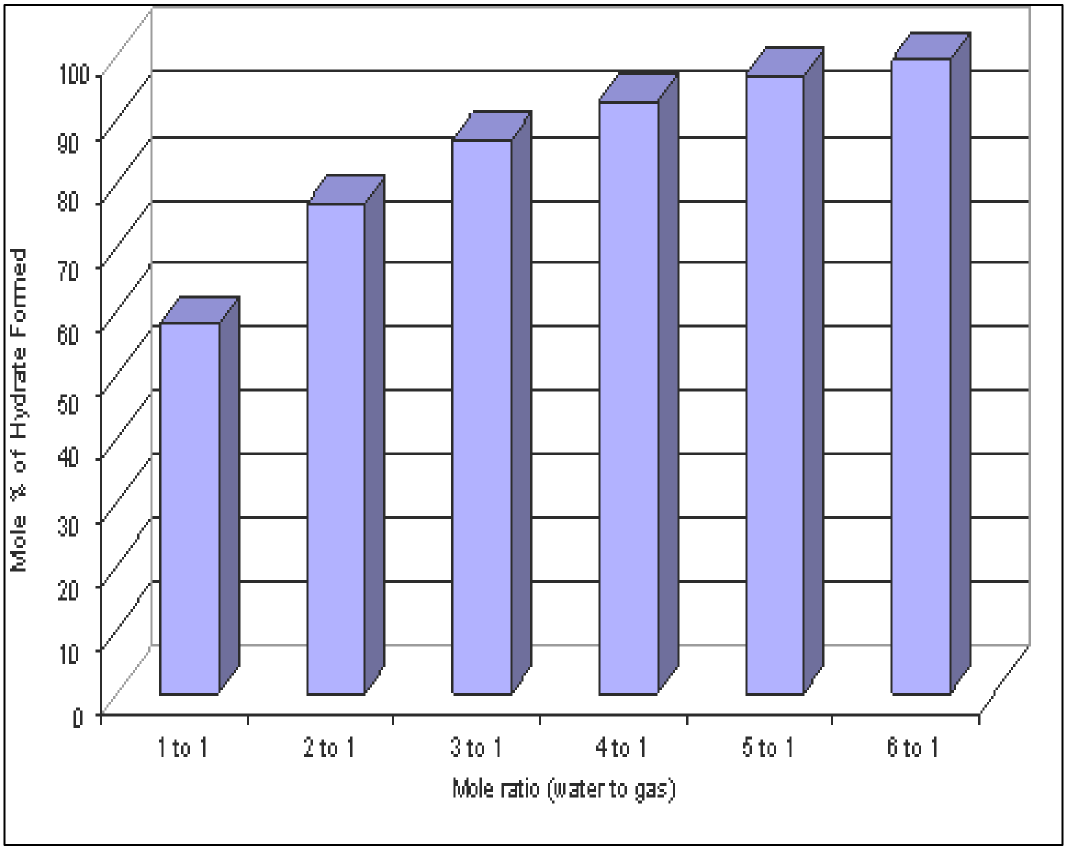


Fig. 8–Maximum Mole % of Hydrate Formed for Different Mole Ratios (600 psia and 35 F)

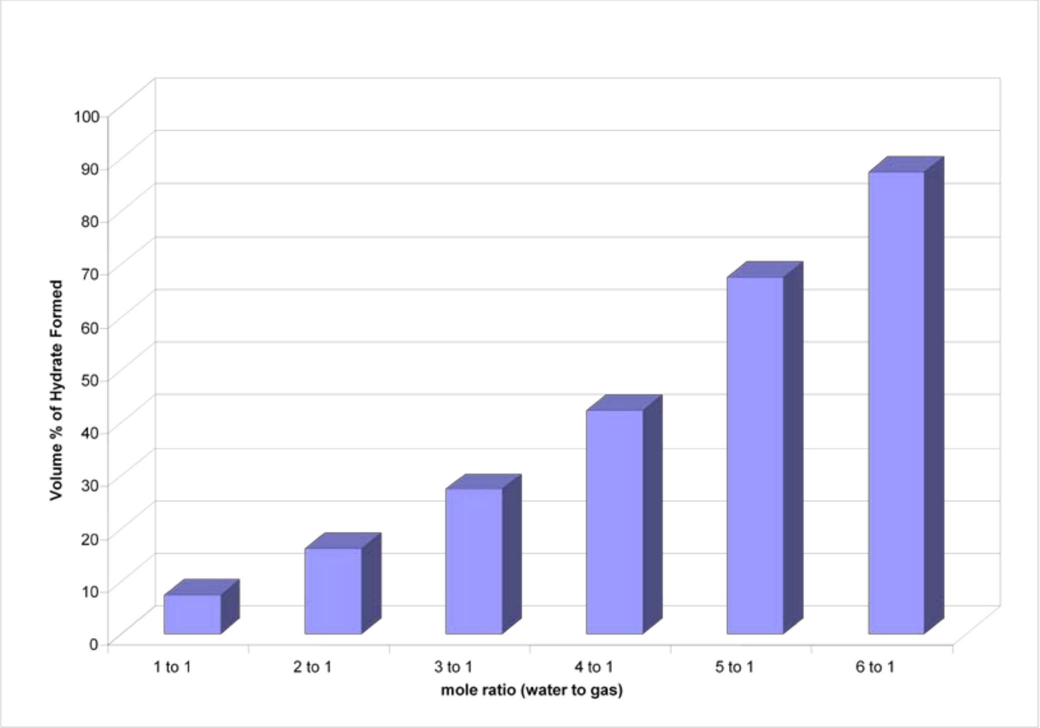


Fig. 9–Maximum Volume % of Hydrate Formed for Different Mole Ratios (600 psia and 35 F)

A water to gas mole ratio of 6:1 provide the best results with 87.4% hydrate formed while a mole ratio of 1:1 gives about 7.3%. The remaining 12.6 % represent free gas to be captured in hydrate form. The free gas can be captured by additional water or by increasing the pressure which increases the storage capacity of the hydrate. A similar trend was seen for Sample 11 with 94.53 volume % of hydrate formed at 600 psia and 35 F. It is therefore necessary to obtain 100% volume of sample 11 hydrates to transport to potential market. The initial conditions were 35 F, 600 psia and 6:1 mole ratio and 94.53 volume % of hydrate formed.

For a fixed temperature of 35 F and sample 11, the minimum pressure to obtain 100% gas in hydrate form is 719 psia at water to gas mole ratio of 6:1. Additionally the pressure can be reduced to 600 psia but the water to gas ratio has to be increase to 6.1 to 1. For a gas rate of 5 MMscf/d, this represents an additional 68 bbls/d of water. This results in a 1.6% increase in water.

The additional pressure required can be translated to work by the system. The calculation is shown below:

Initial Volume = 94%

Final Volume = 100%

Thus

$$\frac{V_f}{V_i} = \frac{1}{0.94}$$

$$\boldsymbol{dW = -PdV} \tag{17}$$

$$\boldsymbol{W = \int_{vi}^{vf} PdV} \tag{18}$$

$$\boldsymbol{W = nRT\ ln\frac{v_f}{v_i}} \tag{19}$$

This assumes isothermal work.

where

W	work done by the system, Btu
P	pressure, psia
V	volume
n	no of moles of gas
T	Temperature, R
R	Gas constant, Btu/lbmole^{-1}R^{-1}

T 494.67 R (35 F)

R 1.986 Btu/lbmol^{-1}R^{-1}

n 13182 moles of gas (See calculation in section 3.3.9)

$$W = 13182\ x\ 1.986\ x\ 494.67\ x\ ln(\frac{1}{0.94})$$

$$W = 720811\ Btu$$

3.3.7 Effect of PT on Storage Capacity of the Hydrate

The storage capacity of hydrates makes them attractive for gas transportation. Hydrates have a high gas to solid ratio of 150-180 scf in 1cf (Masoudi and Tohidi, 2005). The volumetric content of gas in the hydrate state depends on the composition and density (Makogon and Holditch, 2002).

The storage capacity sample calculation for sample 2 at 800 psia and 50 F is shown below. The data in **Tables 7** and **8** below will be used in the sample calculations and shows four phases: vapor, liquid, Hyd-I and Hyd–II.

Table 7–Simulator Output of Composition in Mole % (800 psia and 50 F)

	Total	Vapor	Liquid	Hyd-I	Hyd-II
H_2O	85.714	0.018	0.049	86.408	86.279
N_2	0.124	3.531	0.268	0.104	0.102
CO_2	0.536	1.356	0.835	0.378	0.633
C_1	12.539	93.355	23.1	12.879	11.439
C_2	0.694	0.402	0.533	0.23	1.012
C_3	0.216	0.024	0.106	0	0.364
iC_4	0.044	0.004	0.036	0	0.075
nC_4	0.059	0.04	0.593	0	0.098
iC_5	0.027	0.705	25.528	0	0
nC_5	0.017	0.349	16.795	0	0
C_6	0.03	0.217	32.157	0	0
Total	100.00	100.00	100.00	100.00	100.00

Table 8–Results from Flash Calculations (800 psia and 50 F)

	Total	Vapor	Liquid	Hyd-I	Hyd-II
Mole%	100	0.63	0.09	40.07	59.22
Weight%	100	0.61	0.31	39.52	59.56
Volume, ft³/lb-mol	0.36	8.05	1.65	0.31	0.32
Volume%	100	13.82	0.4	34.44	51.34
Density, lb/ft³	49.8098	2.1941	38.2203	57.1607	57.7879
Molecular Weight	18.15	17.67	62.98	17.9	18.25

Since the water to gas mole ratio is 6 to 1, therefore

100 moles = 14.29 gas + 85.71 water

<u>The breakdown of gas moles in each phase is shown below:</u>

$$n_g = \frac{(100 - mole\%\ H_2O\ in\ vapor) x\ mole\%\ vapor}{100} = \frac{(100 - 0.018)\ x\ 0.63}{100} = 0.63$$

$$n_{g/water} = \frac{(100 - mole\%\ H_2O\ in\ liquid)x\ mole\%\ vapor}{100} = \frac{(100 - 0.049)\ x\ 0.09}{100} = 0.09$$

$$n_{g/HydI} = \frac{(100 - mole\%\ H_2O\ in\ HydI)x\ mole\%\ vapor}{100} = \frac{(100 - 86.41)\ x\ 40.07}{100} = 5.45$$

$$n_{g/HydI} = \frac{(100 - mole\%\ H_2O\ in\ HydII)x\ mole\%\ vapor}{100} = \frac{(100 - 86.28)\ x\ 59.22}{100} = 8.13$$

$$Total\ moles\ of\ gas = 0.63 + 0.09 + 5.45 + 8.13 = 14.29$$

where:

n_{gas}	no of moles of free gas
$n_{g/water}$	no of moles of gas in water
$n_{g/hydI}$	no of moles of gas in Hydrate I
$n_{g/hydII}$	no of moles of gas in Hydrate II

<u>The total moles of gas in hydrate are:</u>

$n_{g/totalhyd} = 5.45 + 8.13 = 13.57$, which represents 94.96%?

<u>The moles of free gas are:</u>

$n_g = 0.63$, which represents 4.4%

<u>The volume in ft^3 in calculated below:</u>

$$Volume(ft^3) = Volume(\frac{ft^3}{mol})\ x\ moles$$

$$V_g = 8.05\ x\ 0.63 = 5.072\ ft^3$$

$\mathrm{V_{water}} = 1.65 \text{ x } 0.09 = 0.1485 \text{ ft}^3$

$\mathrm{V_{HydI}} = 0.31 \text{ x } 40.07 = 12.42 \text{ ft}^3$

$\mathrm{V_{HydII}} = 0.32 \text{ x } 59.22 = 18.95 \text{ ft}^3$

$\text{Total} = 5.072 + 0.1485 + 12.42 + 18.95 = 36.592 \text{ ft}^3$

The volume % of free gas is therefore 13.9 % $(\frac{5.072}{36.592})$

where:

V_{gas}	volume of free gas
V_{water}	volume of gas in water
V_{HydI}	volume of gas in Hydrate I
V_{HydII}	volume of gas in Hydrate II

The following is the calcultion for volume of gas stored in scf:

Amount of gas transported in hydrate in scf:

$$\boldsymbol{V = \frac{n_g R T_{sc}}{P_{sc}}} \qquad \textbf{(20)}$$

$$V = \frac{13.572 \text{ x } 10.73 \text{ x } 520}{14.73} = 5151.4 \text{ scf}$$

Amount of gas stored in 1 ft^3 hydrate:

$$\frac{5151.4}{18.95 + 12.42} = 164.2\, scf$$

The storage capacity results for Sample 11 are shown in **Fig. 10** below. **Fig. 10** shows increasing pressure results in an increase in storage capacity of the hydrate at the selected pressures and temperatures shown in **Fig. 6** and a mole ratio of 6.1 (gives the best results). It can be seen for 40 F, storage capacity increases from 153 scf in 1 cf to 163 scf in 1cf as pressure increases from 300 psia to 600 psia.

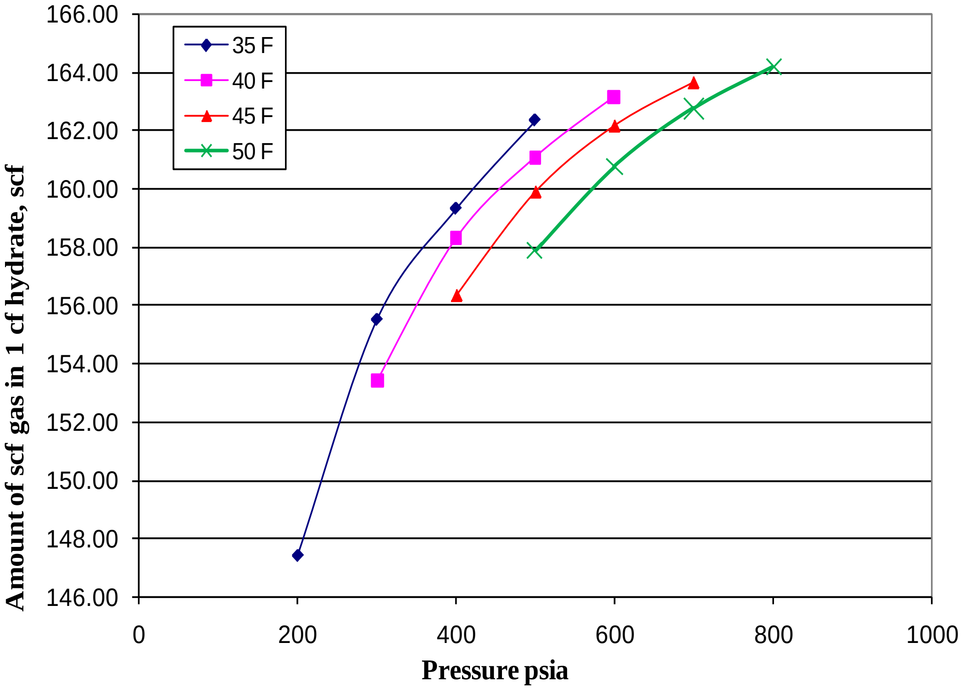


Fig. 10–Effect of Temperature and Pressure on Storage Capacity of Hydrate with 6:1 Mole Ratio for Sample 11

The storage capacity results for Sample Dry Gas are shown in **Fig. 11** below. **Fig. 11** shows increasing pressure results in an increase in storage capacity of the hydrate at 35, 40, 45 and 50 F. It can be seen for 40 F, storage capacity increases from 166.8 scf in 1 scf to 170.2 scf in 1 cf as pressure increases from 600 psia to 900 psia.

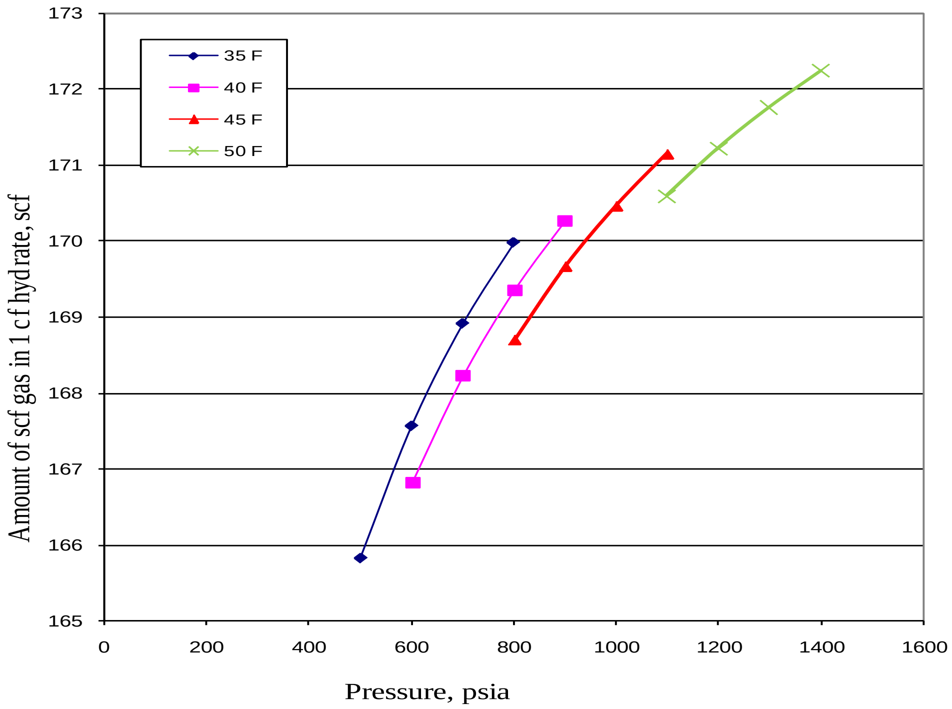


Fig. 11–Effect of Temperature and Pressure on Storage Capacity of Hydrate with 6:1 Mole Ratio for Dry Gas

3.3.8 Estimation of Mole Ratio Mole Required for All Samples

As indicated earlier, the formation conditions of 600 psia and 35 F were then chosen as it represents potential upscaling conditions deduced from experimental studies conducted by Okutani et al, 2007. The water to gas mole ratios for all samples was estimated for conditions of 600 psia and 35 F using the commercial simulator. This was done by changing the mole ratio at this specific temperature and pressure until 100 % volume of hydrate is formed. The results are shown in **Table 9** below. If excess water is used in the formation of the hydrate (7:1 mole ratio), a hydrate phase and aqueous phase is obtained.

Table 9–Actual Water to Gas Mole Ratio for All Samples (600 psia and 35 F)

Sample	Mole Ratio
Sample 1	6.284
Sample 2	6.264
Sample 3	6.32
Sample 4	6.23
Sample 5	6.22
Sample 6	6.26
Sample 7	6.21
Sample 8	6.25
Sample 9	6.16
Sample 10	6.24
Sample 11	6.10
Sample 12	6.16
Sample 13	6.05
Sample 14	6.28
Sample 15	6.18
Sample 16	6.10
Sample 17	6.09
Sample 18	6.29
Sample 19	6.11
Sample 20	6.31
Sample Dry Gas	6.29

The results show the range of mole ratio from 6.1:1 to 6.32:1 above the 6:1 mole. For 5 MMscf/d, this represent an additional 68–218 bbls of water required when considering all samples. This is an additional 1.6–5.1% change in water needed. Commercial flow meters are capable of handling such this % change. It is important to note that while the mole ratios do not change substantially, the actual water needs will change greatly with the amount of MMscf/d of gas processed.

3.3.9 Estimation of Water Required for Hydrate Formation

Using the mole ratio estimated (**Table 9**) the amount of water required for capturing a certain volume of gas was estimated. The amount of water required for gas rates in the range of 0.5MMscf/d to 5 MMscf/d for dry gas sample with a mole ratio of 6.29:1 were evaluated.

This was calculated as follows:

$$\boldsymbol{n_g = \frac{V_g P_{sc}}{RT_{sc}}} \tag{21}$$

$$\boldsymbol{\frac{n_w}{n_g} = 6.29} \tag{22}$$

$$\boldsymbol{n_w = \frac{\rho_w V_w}{MW_w}} \tag{23}$$

$$\boldsymbol{V_w = \frac{6.29 n_g MW_w}{\rho_w}} \tag{24}$$

where

n_g	moles of gas
V_g	volume of gas, 0.5 MMscf
P_{sc}	standard pressure, 14.71 psi
R	gas constant, 10.73 $\mathrm{ft^3 psi R^{-1} lbmol^{-1}}$
T	standard temperature, 520 R
n_w	moles of water
MW_w	molecular weight water, 18

p density of water, 62.48 lbm/ft^3

Vw volume of water, bbls

For 0.5MMscf/d

$$n_g = \frac{500000x14.71}{10.73x520} = 1318$$

$$V_w = \frac{6.29\ x\ 1318\ x\ 18}{62.48\ x\ 5.615} = 425\ bbls$$

For capturing 0.5MMscf of dry gas sample, 425 bbls of water is required.

3.3.10 Estimation of Heating Values of Gas Samples

The heating values of all samples were estimated:

(i) To use in energy balance calculations for entire process since it gives an indication of the amount of energy transported in the gas.

(ii) To determine gas acceptance at markets around the world or whether further gas processing required. This is important since gas is sold based on its heating value.

The heating value was calculated simply by multiplying the ideal heating values of the individual component by the mole fraction which gives a simply approximation. A sample of this calculation is shown below in **Table 10** and for this sample the heating value is estimated to be 1053 Btu/scf**.**

Table 10–Heating Value Estimation for a Typical Sample

		Mole Fraction	Ideal Heating Value	Heating Value in Sample
			Btu/scf	Btu/scf
Nitrogen	N_2	0.87	0	0
Hydrogen Sulfide	H_2S	0.00	637.1	0
Carbon Dioxide	CO_2	3.75	0	0
Methane	C_1	87.77	1010	886.47
Ethane	C_2	4.86	1769.7	86.00
Propane	C_3	1.51	2516.1	37.99
Iso-butane	iC_4	0.31	3251.9	10.08
N-Butane	nC_4	0.41	3262.3	13.37
Is pentane	iC_5	0.19	4000.9	7.60
N-Pentane	nC_5	0.12	4008.9	4.81
Hexanes plus	C_{6+}	0.21	4755.9	9.99
Hexanes	C_6	0.00	4755.9	0
Heptanes	C_7	0.00	5502.5	0
Octanes	C_8	0.00	6248.9	0
Nonanes	C_9	0.00	6996.5	0
Decanes +	C_{10}^{+}	0.00	7742.9	0
Total		100		1056.33

Gas may be transported to different regions around the world and therefore would be required to meet that region's heating value standard. The accepted heating value range accepted in the US is in the range 966–1120 Btu/scf. For Europe, the range is 940–1204 Btu/scf and for Japan 1065–1160 Btu/scf is required.

3.4 Overview of Proposed Solutions

It is proposed that the same vessel used to form the hydrate be also used for storage and transport to its delivery point. The "one vessel" concept is very useful to avoid moving the solid hydrate from vessel to vessel for storage and transportation, reduce costs, since no additional facility is needed for dissociation at the final destination, and allow water re-cycling. Using one vessel for formation, storage, transportation and dissociation of the hydrates gives operational flexibility for temporary storage and transportation. In the absence of pipeline infrastructure, hydrates could be transported in the vessel, by truck, railway or ship.

The formation of natural gas hydrate yields a high latent heat of formation that must be removed to prevent dissociation. To this aim, the formation vessel could be equipped with heat exchange tubes, extending the full length of the vessel, to facilitate heat transfer from the vessel. The heat exchange tubes not only aid the heat removal process. They also: (i) supply heat for later dissociation of hydrate, after formation and storage/transportation, and (ii) provide additional surface area for more effective hydrate formation.

Heat from the surrounding can transfer into the formation vessel and increase its temperature, causing dissociation of the hydrate as it forms. Insulation is therefore necessary to minimize heat transfer with the surroundings.

Some of the reasons for the “one vessel concept” are:

(i) Avoid moving the hydrates to storage and transportation vessel.
(ii) Temporary Storage
(iii) Reduction in facility cost.
(iv) No additional facility cost at the gas destination.
(v) Water can be re-used.
(vi) Reduction in environmental concerns.

This work proposes a workflow for capturing, storing and transporting gas in the hydrate form, particularly for situations where there are infrastructural constraints such as lack of pipelines. These applications of gas hydrate technology can have potential benefits to the oil and gas industry in Trinidad and Tobago.

3.5 Conclusions

(i) Generally the higher the methane percentage in the gas sample the higher the hydrate formation pressure at a fixed temperature.

(ii) Generally the higher the propane concentration in the natural gas, the lower the hydrate formation pressure at a fixed temperature.

(iii) Impurities affect the hydrate formation pressure/temperature equilibrium line. Carbon dioxide and Hydrogen sulfide reduces the pressure/temperature equilibrium while nitrogen increases it.

(iv) The range of hydrate storage capacities obtained in this analysis was 147-172 scf in 1cf of gas. The values were consistent with the literature values of 150-180 scf in cf of hydrate. The sample with the higher methane content (dry gas sample) give the higher storage capacity range of 166-172, while the sample with the lower methane content (sample 11) give a storage capacity range of 153-163 for temperatures 35, 40, 45 and 50 F.

(v) The mole ratio (hydrate number) is approximately 6; however, the actual hydrate number depends on the composition, temperature and pressure. The

$V_{GAS}/(V_{GAS}+V_{HYD})$ ratio is a useful ratio to illustrate the gradual reduction in free gas (forming the hydrate) as mole ratio, temperature and pressure changes.

(vi) To obtain 100% volume of hydrate, there is a tradeoff between addition water and increasing pressure. In this case, it was a compromise between an additional 119 psia and 68 bbls/d of water for transporting 5 MMscf/d. In this case, the additional pressure represents compression work done on the system (approximately 720811 Btu).

(vii) Most of the gas samples meet US and Europe heating value standards.

CHAPTER IV

PROPOSED SOLUTIONS

The previous chapter discussed the methodology of the study. This chapter will discuss details of the proposed solutions for the problems highlighted previously. The emphasis would be on upscaling from laboratory experiments, size, heat exchange capabilities and insulation of the proposed hydrate vessel and the details of the required expansion process.

4.1 Upscaling from Laboratory Experiments

This section discusses the condition for upscaling hydrate formation from laboratory experiments. **Table 11** below shows the summary of the comparison between two laboratory experiments and potential upscaling conditions. Experiment 1 used ethane gas with a formation temperature of 38 F and pressure of 366 psia (Zhong and Rogers, 2000). This experiment had a formation time of 3 hours and a surface area to volume ratio of 0.4. Experiment 2 had hydrate formation conditions of 35 F and 600 psia and used methane gas (Okutani, Kuwabara and Mori, 2008). The formation time in this experiment was 5.75 hours (more conservative) with a 0.4 surface area to volume ratio. In the experiments, the surface area is the internal chamber wall of vessel.

The upscaling conditions were assumed to be similar to experiment 2 since the dry gas sample used in this analysis had similar composition (99% methane). Also most natural gas samples have significantly more methane than ethane components.

Table 11–Comparison of Hydrate Formation Conditions

	Experiment 1	Experiment 2	Upscale
Composition	Ethane	Methane	99% Methane
Temperature, F	38	35	35
Pressure, psia	366	600	600
Formation Time, hr	3	5.75	6
Ratio of Surface Area / Volume	0.4	0.4	0.4

It is assumed that in the hydrate process design, the formation conditions will be 35 F and 600 psia, the hydrate formation time is estimated to be about 6 hours and a surface area to volume ratio of at least 0.4 will be used.

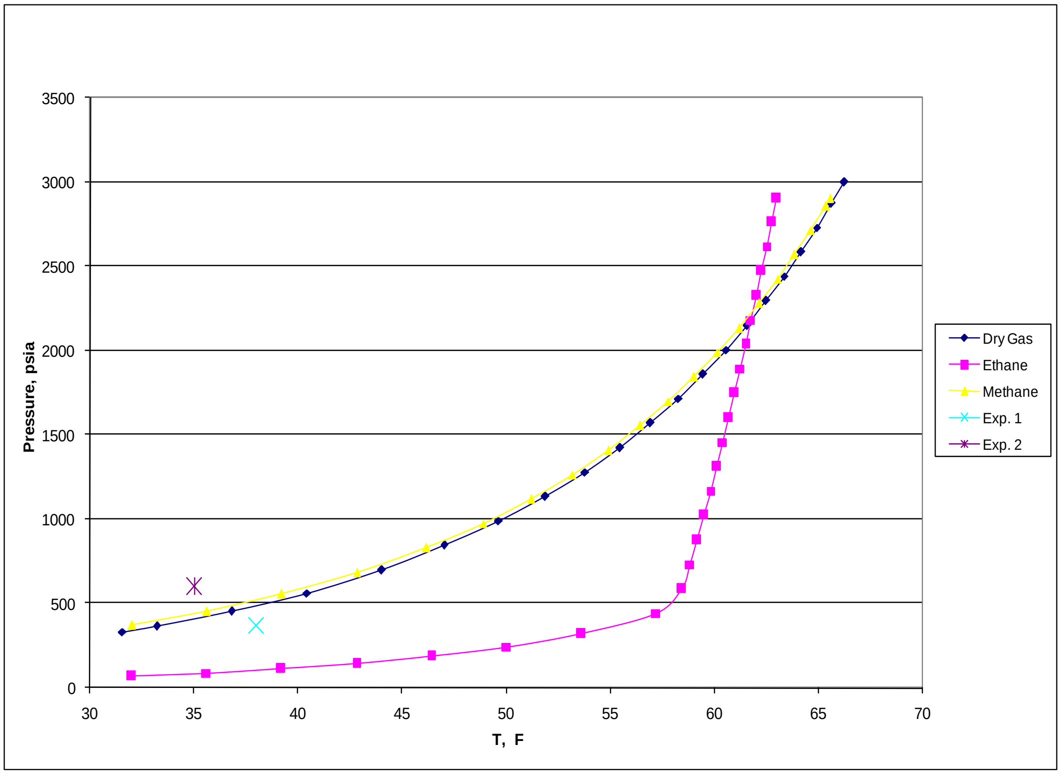


Fig. 12–PT Curves for Samples Used in Exp. 1 and 2 and Conditions of Hydrate Formation

The above **Fig. 12** shows the hydrate PT curve comparison for methane and ethane hydrate used in experiment 1 and 2 and the dry gas sample to be used in the industrial upscaling. It can be seen that both dry gas sample and methane hydrates have very similar PT curves. Also the formation condition for experiment 1 lies below the PT curves for methane and dry gas sample. Hence these conditions cannot be used for upscaling and thus the hydrate formation conditions of experiment 2 would be used in this study for hydrate formation.

In summary, to achieve formation rates similar to laboratory experiment 2, the following should be met:

(i) A surface area to volume ratio of at least 0.4
(ii) Similar temperature and pressure (35 F and 600 psia)
(iii) Similar Composition (Methane)

4.2 Hydrate Vessel

This analysis will give some basic description of the proposed hydrate vessel. It is not the intention here to give detailed design of vessel since it is out of the scope of this study. Some of the parameters discussed are size, water and hydrate levels in the vessel, heat exchange capabilities and insulation that are required to estimate the energy balance, time of the process and economics.

4.2.1 Sizing

The rationale for sizing of hydrate vessel is as follows:

(i) Consideration of the expected production rates – 0.5 to 5 MMscf/d

(ii) The size of the vessel must be capable to handle minimum production rate of 0.5 MMscf/d.

(iii) The assumption of length is 3 times diameter is used for sizing of the vessel. This is typical industry practice.

(iv) To ensure that the surface area to volume ratio of at least 0.4. This ratio is used from the upscaling from laboratory experiments.

For 0.5MMscf natural gas the total hydrate volume at 600 psia and 35 F is 2984 ft^3

Using the Assumption that the Length is 3 times Diameter, then L = 33 ft and D = 11 ft

From

$$\frac{\pi D^2 L}{4} = 2984 \qquad \textbf{(25)}$$

This vessel gives a surface area to volume ratio of 0.446.

Fig. 13 shows the side and end views of the proposed hydrate formation vessel.

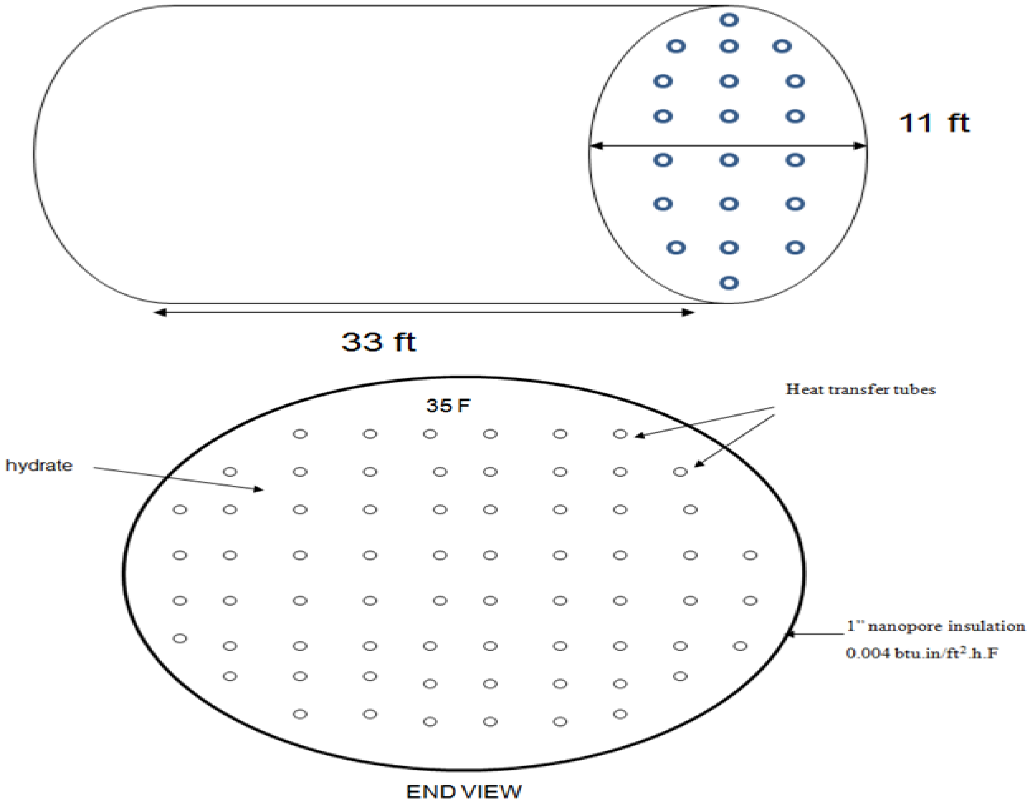


Fig. 13–Hydrate Formation Vessel Showing Side and End Views

Several possible sizes of vessels were evaluated for various gas production rates to determine the surface area to volume ratio. The only sized vessel that gives the required surface area of at least 0.4 for upscaling is the 11ft x 33 ft cylindrical vessel capable of storing 0.5 MMscf of gas which is commercially available. Therefore to transport 5 MMscf/d, 10 vessel would be required each transporting 0.5 MMscf each.

4.2.2 Water and Hydrate Levels in Vessel

It is necessary to estimate the water and hydrate levels in the vessel. It is important that the hydrate does not fill the entire vessel but some space is left at the top

(3.5%). This would allow gas released during the dissociation process of the hydrate to rise at the top of the vessel and removed.

The water level for hydrate formation and the hydrate level is estimated as follows:

The volumes and % of vessel filled for various heights in the hydrate vessel were evaluated and plotted in **Fig. 14**.

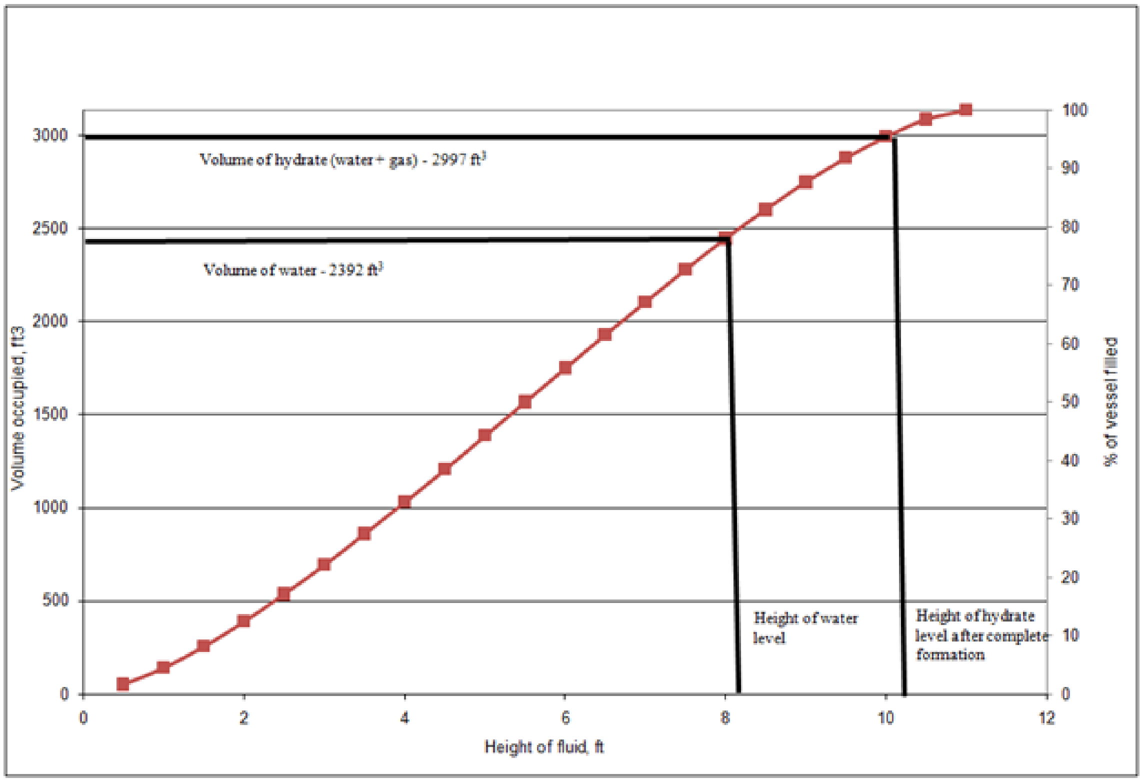


Fig. 14–Plot of Volume and % Filled vs. Height in Hydrate Vessel for 0.5 MMscf

4.2.3 Heat Exchange Design of the Vessel

The formation vessel should be equipped with heat exchange tubes, extending the full length of the vessel, to facilitate heat transfer from the vessel. The heat exchange tubes not only aid the heat removal process but they also: (i) supply heat for later dissociation of hydrate, after formation and storage/transportation, and (ii) provide additional surface area for more effective hydrate formation.

4.2.3.1 Size and No. of Tubes Required for Heat Removal

This section evaluates the possible sizes and amounts of heat exchange tubes required for removal of heat in the hydrate vessel. Several sizes of tubes were evaluated to determine the most appropriate size for the vessel. The following are the steps used in the estimation of the number of tubes required for different tube sizes (Standards, 1999) and in this example brine is used as the heat removal fluids, however many refrigerants can be used:

(i) Estimate the overall flow rate of water required to absorb the latent heat of formation using the following equation -

$$\boldsymbol{Q = mC_p(T_2 - T_1)} \qquad \textbf{(26)}$$

where

m is the mass flow rate/cycle,

Q is the heat to be removed,

Cp is the heat capacity of the fluid,

change in temperature is the difference between the hydrate formation temperature and the temperature of the flowing fluid.

Q = 3.15 x 10^7 Btu

c_p = 0.7643 Btu/lb-F

T_2 = 35 F

T_1 = 30 F

m = 987166 gal/cycle

(ii) Estimate the flow rate for different tube sizes using standard recommended velocities for each tube size. These tubes velocities range from 2-8 ft/s.

Using 1” heat transfer tubes

The total flow rate through the 1” tubes is

$$\boldsymbol{q = \frac{2.448 v \pi D^4}{4}} \tag{27}$$

where

D internal diameter of tube, ft

v velocity, ft/s

For v = 8 ft/s and D = 0.834 ft

q = 817.3 gal/hr

(iii) Assuming a time of hydrate formation of 6 hours, the amounts of fluid (gals) for each tube size is then estimated.

For a 6 hrs

q = 817.36 x 6 = 4903.8 gal/cycle

(iv) The amount of tubes is then estimated from the overall flow divided by the individual tube flow.

No of 1” tubes required to remove latent heat is

$$n = 987166 / 4903.8 = 202$$

Similar calculations were done for other tube sizes and are shown in **Table 12**. Also shown in the table are the volumes of the various tubes. This indicates the amount of physical space the tubes take up in the vessel.

Table 12–No. of Tubes and Volume of Tubes for Different Tube Sizes

OD, in	Velocity	Water Flow rate, q	No of tubes	Volume of tubes
	ft/sec	gal/hr		ft^3
0.25	2	2.1	79375.7	892.9
0.375	3	19.2	8548.0	216.4
0.5	4	65.5	2510.3	113.0
0.625	5	154.7	1063.4	74.8
0.75	6	300.6	547.4	55.4
0.875	7	516.8	318.3	43.9
1	8	817.3	201.3	36.2

The 1” tubes were selected for the following reasons:

(i) The least amount of tubes to remove the latent heat of formation.

(ii) The least space taken up in the vessel with an overall volume of 36.2 ft^3.

For geometry purposes 240 tubes would be used in the hydrate formation vessel. The surface area to volume ratio increases using the heat transfer tubes in the vessel (0.446 to 0.58). This can impact the analysis of the formation time and as a result is a limitation using the upscaling formation time.

The actual volume available for gas and water to come into contact is the volume of the vessel less the volume of the tubes (3143–36 ft^3) is 3107 ft^3.

4.2.3.2 Tube Spacing in the Vessel

Fig. 15 shows the end view of the vessel with a section of tube spacing.

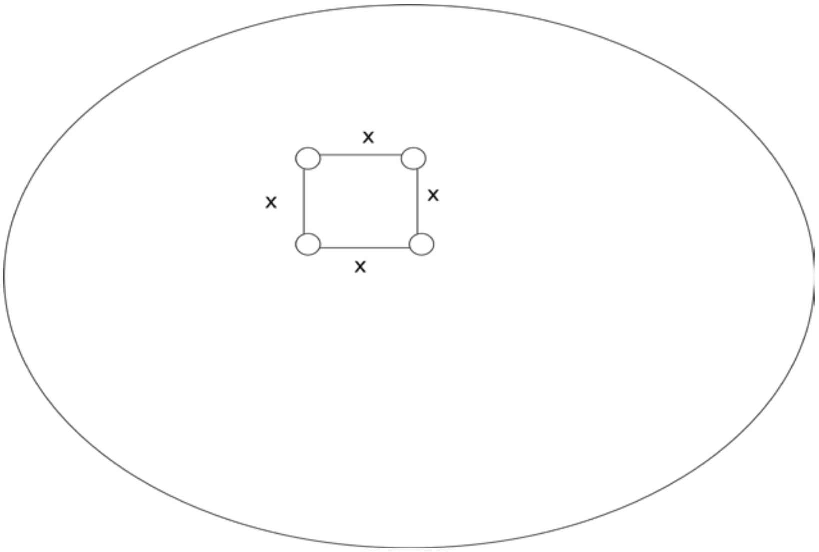


Fig. 15–Section of the Tube Spacing within the Vessel

The object of this exercise is to determine x which is the distance between two heat exchange tubes in the hydrate vessel **(Fig. 15)**. This is important in modeling the time of dissociation of the hydrate.

The distance x between two tubes was estimated and the value of x was found to be 6.55 inches. Details are shown in Appendix A.2.

4.2.4 Vessel Insulation

Heat from the surrounding can transfer into the formation vessel and increase the temperature of hydrate, causing dissociation of the hydrate as it forms. Insulation (e.g. NanoPore) is therefore necessary to minimize heat transfer with the surroundings. NanoPore thermal insulation provides exceptional performance with a very low overall thermal conductivity of 0.004 Btu.in/ft^2.h.F. Because of its unique pore structure, NanoPore thermal insulation can provide thermal performance greater than conventional insulation materials (NanoPore, 2010). Fiber glass has a thermal conductivity of 0.347 Btu.in/ft^2.h.F, expanded polystyrene 0.208 Btu.in/ft^2.h.F and polyurethane a value of 0.173 Btu.in/ft^2.h.F. About 240 btu/h of heat gained from the surroundings must be removed when using 1” thickness NanoPore material, compared to 4.35 x 10^7 btu/hr without any insulation.

Using

$$\boldsymbol{Q = \frac{kAdt}{s}} \qquad \textbf{(28)}$$

K = thermal conductivity (0.004 Btu.in/ft^2.h.F)

A = surface area (1330.5 ft^2)

dt = temperature change (80-35=45 F)

S = Insulation thickness (in)

For S = 1 i.e. 1” NanoPore insulation

$$Q = \frac{0.004x1330.5x45}{1}$$

$$Q = 239.5\ Btu/hr$$

Table 13–Heat Gain Using NanoPore Insulation

NanoPore Thickness	Heat Gain
in	btu/hr
0	1902602.5
1	239.5
2	119.7
3	79.8
4	59.9
5	47.9

In **Table 13,** other NanoPore thicknesses with corresponding heat transfer are shown. When one considers economics, the 1” NanoPore insulation will be quite adequate. The low (240 btu/hr) heat transfer into the hydrate vessel is not significant enough to cause any significant increase in temperature of the hydrate. The overall temperature rise in 24 hrs in the hydrate vessel is only 0.055 F. This was calculated as follows:

For 1 hr

$$\boldsymbol{\Delta T = \frac{Q}{mc_p}} \qquad \textbf{(29)}$$

where

Cp = heat capacity of hydrate (10.82 Btu/lbmole.F)

n = no of moles (9602)

Q = heat transfer (239.5 Btu/hr)

$\Delta \mathrm{T} = 0.002$ F in 1 hr.

4.2.4.1 Description of Insulation

NanoPore thermal insulation is a porous solid that is prepared by one of several processes which yield both low density and small pores (NanoPore, 2010). Because of its unique pore structure, NanoPore thermal insulation can provide thermal performance unequalled by conventional insulation materials. In the form of a vacuum insulation panel (VIP), NanoPore thermal insulation can have thermal resistance values as high as R40/inch which is 7-8 times greater than conventional foam insulation materials.

Due to unique structure, its conductivity can actually be lower than air at the same pressure. Its superior insulation characteristics are due to the unique shape and small size of its large number of pores. Gas molecules within the matrix experience what is known as the Knudsen effect, which virtually eliminates exchange of energy in the gas, effectively eliminating convection and lowering overall thermal conductivity. NanoPore Insulation may be used over a wide temperature range from below cryogenic (<-196 °C) to high temperatures (>800 °C).

4.3 Expansion Process

For capturing natural gas from the wellbore, an expander would be used to expand the gas from wellhead conditions to hydrate formation conditions. The wellhead condition may be in the range of 1800 psia and 170 F and therefore expansion and cooling is necessary to form hydrates.

4.3.1 Expander

Turboexpanders offer the high power level, operating temperature and pressure ratio solutions for energy recovery and refrigeration.

The need of the expander in this study is to extract energy from gas stream and hence reduce the pressure and temperature required for hydrate formation.

The operation of the expander is governed by the following principles:

The total energy of the system is the sum of the work done and the heat added.

$$\boldsymbol{dU = dW + dQ} \qquad \textbf{(30)}$$

where

U internal energy of the system

W work done on the system

Q heat added to the system

The work done by the system is

$$\boldsymbol{dW = -pdV} \qquad \textbf{(31)}$$

where

p pressure of the system

V volume in the system

and

The amount of energy the system gains by heat is

$$\boldsymbol{dQ = TdS} \qquad \textbf{(32)}$$

where

T temperature of the system

dS the change in entropy

The change in energy or enthalpy is given by:

$$\boldsymbol{H = U + pV} \qquad \textbf{(33)}$$

this gives

$$dH = dU + pdV + Vdp$$

and the expression for work is therefore:

$$\boldsymbol{W = \Delta H - T\Delta S} \qquad \textbf{(34)}$$

The work the gas performs in the expander is gain from its enthalpy and the gas cools in the expander.

For an ideal case, the isentropic process (no change in entropy and 100% efficient),

$$\Delta \mathrm{S} = 0$$

and

$$\boldsymbol{W = \Delta H} \qquad \textbf{(35)}$$

For non ideal case

$\mathrm{W} = \Delta \mathrm{H} - \mathrm{T}\Delta S$ and

$$\boldsymbol{\Delta S = \frac{1}{T} dH - \left(\frac{V}{T}\right) dp} \qquad \textbf{(36)}$$

The efficiency of the expander is related to the enthalpy by the following expression:

$$\boldsymbol{\Delta H = \frac{Q}{\eta} (\frac{T_2}{T_1})} \qquad \textbf{(37)}$$

where

T_2 output temperature after expansion

T_1 initial temperature

η expansion efficiency

For different expansion efficiencies the output temperatures are different.

The HP developed by the expander (Simms, 2009) can be estimated by:

$$\boldsymbol{Power = \Delta H \ x \ wx \ \eta} \qquad \textbf{(38)}$$

where

w is the gas flow rate

A sample calculation of this is shown in Chapter V.

4.4 Environmental Considerations

If during shipping the hydrate vessel falls into the ocean, it is expected that once the vessel remains sealed and intact there would not be any significant effect on the hydrate in the vessel. While the temperature of ocean water changes and would be expected to be lower than the atmospheric temperature, the heat transfer into the vessel is expected to be lower than when the transportation was at atmospheric temperature. So in this case there would be no effect on the hydrate in the vessel. Similarly case is expected for land transportation of hydrate.

It must be remembered that pressure vessels are designed to operate safely at a specific pressure and temperature technically referred to as the "Design Pressure" and "Design Temperature". A vessel that is inadequately designed to handle a high pressure constitutes a very significant safety hazard. Because of that, the design and certification of pressure vessels is governed by design codes such as the ASME Boiler and Pressure Vessel Code in North America. The safe design, installation, operation, and maintenance of pressure vessels in accordance with the appropriate codes and standards are essential to safety and health.

4.5 Conclusions

(i) In this study, the pressure and temperature to form the hydrate is similar to conditions use in a previous experimental study.

(ii) The size of the hydrate formation vessel was chosen to be 11 ft x 33 ft cylinder for 0.5 MMscf/d. This was most appropriate size based on the required surface area to volume ratio of at least 0.4.

(iii) The vessel would be 75% filled with water required to form 0.5MMscf natural to hydrate. When hydrate formation is complete the vessel will be 96.5% filled leaving 3.5% space free. This free space helps when the hydrate is dissociated and the gas rises and is removed.

(iv) The size of the heat transfer tube proposed is 1” and the amount of 1” heat transfer tubes required is estimated at approximately 240 for the 11 ft x 33 ft cylindrical vessel.

(v) The spacing of the tubes is estimated to be 6.55 in between each tube.

(vi) NanoPore insulation provides superior insulation characteristics to other insulation materials. NanoPore thermal insulation provides exceptional performance with a very low overall thermal conductivity of 0.004 btu.in/ft^2.h.F.

(vii) The expander is useful to extract energy from gas stream and thereby reducing temperature and pressure of the gas stream to hydrate formation conditions (600 psia and 35 F).

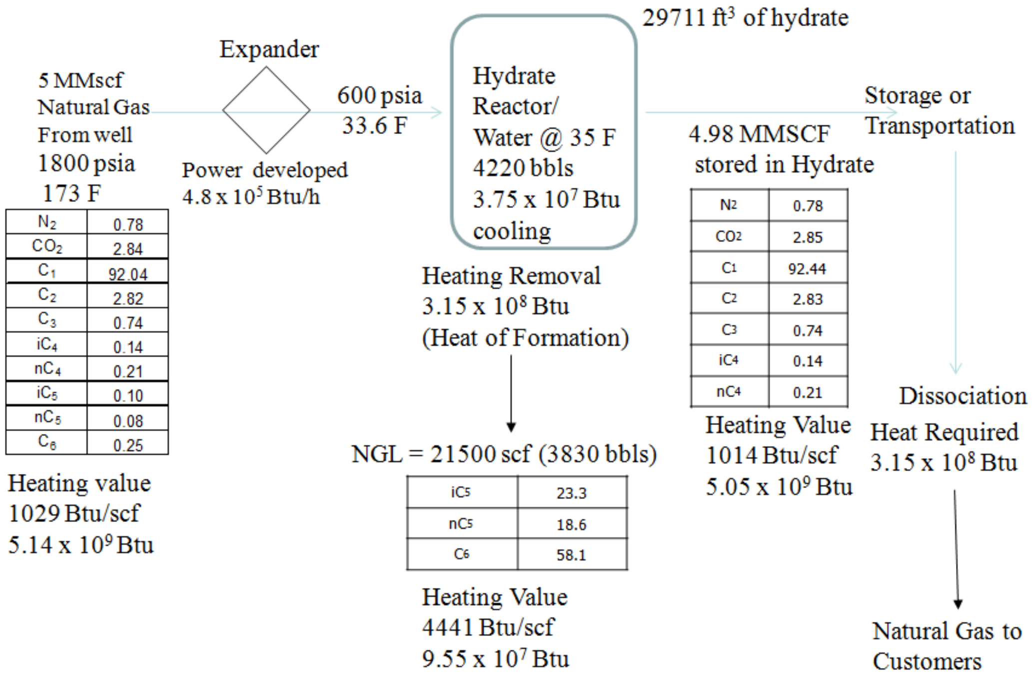
CHAPTER V

HYDRATE PROCESS ANALYSIS

Chapter IV provided design details of the proposed hydrate vessel together with other new concepts of using expander and NanoPore insulation. With this information, Chapter V would give details of the entire hydrate process work flow with particular focus on energy balance, time of each process and economic analysis.

5.1 Energy Balance for the Hydrate Process

The hydrate process energy requirements are shown for Sample 2 in **Fig. 16** below for 5MMscf/d. The heating value of the gas before and after hydrate formation is shown. This is particularly important since the gas is sold based on the heating value. Gas from the well is passed through an expander to lower the temperature and pressure suitable for hydrate formation.



N_2	0.78
CO_2	2.84
C_1	92.04
C_2	2.82
C_3	0.74
iC_4	0.14
nC_4	0.21
iC_5	0.10
nC_5	0.08
C_6	0.25

iC_5	23.3
nC_5	18.6
C_6	58.1

N_2	0.78
CO_2	2.85
C_1	92.44
C_2	2.83
C_3	0.74
iC_4	0.14
nC_4	0.21

Fig. 16–Hydrate Process Showing Energy Balance

The power developed by the expansion process is 4.8 x 10^5 Btu/h. After the expansion the natural gas is pumped into the hydrate vessel with 4220 bbls of cold water. The cooling requirement for water is also shown in the figure. The formation of hydrate results in large amount of heat of formation that must be removed during the process.

The natural gas composition may have heavier components (C_5 or higher), as in the case of Sample 2. In the hydrate formation process, only C_1 to C_4 are captured, and the higher components (C_5 and higher) separate in the process as natural gas liquids (NGL). In this case 3830 bbls of NGL is separated out with a heating value of 4441 Btu/scf and is useful energy.

The same amount of energy removed during the formation of the hydrate is same energy requirement for dissociation.

5.1.1 Heating Value

The heating value of Sample 2 is estimated to be 1029 Btu/scf and this is shown below in **Table 14**. For 5 MMscf of gas, the heating value translates to 5.14 x 10^9 Btu.

Table 14–Heating Value Estimation for Sample 2 Before Hydrate

		Mole Fraction	Ideal Heating Value	Gas mix before hydrate
Sample	2		Btu/scf	Btu/scf
Nitrogen	N_2	0.78	0.0	0.0
Carbon Dioxide	CO_2	2.84	0.0	0.0
Methane	C_1	92.04	1010.0	929.6
Ethane	C_2	2.82	1769.7	49.9
Propane	C_3	0.74	2516.1	18.6
Iso-butane	iC_4	0.14	3251.9	4.6
N-Butane	nC_4	0.21	3262.3	6.9
Iso-pentane	iC_5	0.10	4000.9	4.0
N-Pentane	nC_5	0.08	4008.9	3.2
Hexanes	C_6	0.25	4755.9	11.9
Heptanes	C_7	0.00	5502.5	0.0
Octanes	C_8	0.00	6248.9	0.0
Nonanes	C_9	0.00	6996.5	0.0
Decanes	C_{10}	0.00	7742.9	0.0
Total		100		1028.6

Table 15 shows the heating value of the gas stored in the hydrate is estimated at 1014 Btu/scf with 29711 ft^3 of hydrate being formed.

Table 15–Heating Value Estimation for Sample 2 in Hydrate

		Mole Fraction	Ideal Heating Value	Gas mix in hydrate
Sample 2 in hydrate			Btu/scf	Btu/scf
Nitrogen	N_2	0.78	0.0	0.0
Carbon Dioxide	CO_2	2.85	0.0	0.0
Methane	C_1	92.44	1010.0	933.6
Ethane	C_2	2.83	1769.7	50.1
Propane	C_3	0.74	2516.1	18.7
Iso-butane	iC_4	0.14	3251.9	4.6
N-Butane	nC_4	0.21	3262.3	6.9
Total		100		1013.9

The natural gas liquids may separate during the hydrate process for sample 2 and provides useful energy. The heating value of the NGL is estimated at 4441 Btu/scf. This is shown in **Table 16**.

Table 16–Heating Value Estimation for Natural Gas Liquid (NGL)

		Mole Fraction	Ideal Heating Value	Gas mix in hydrate
Sample 2 NGL			Btu/scf	Btu/scf
Iso-pentane	iC_5	23.26	4000.9	930.4
N-Pentane	nC_5	18.60	4008.9	745.8
Hexanes	C_6	58.14	4755.9	2765.1
Heptanes	C_7	0.00	5502.5	0.0
Octanes	C_8	0.00	6248.9	0.0
Nonanes	C_9	0.00	6996.5	0.0
Decanes	C_{10}	0.00	7742.9	0.0
Total		100.00		4441.3

5.1.2 Expansion

The expansion process must also ensure the gas sample remains in the single phase region of the phase diagram, which is important in the design process. From the wellhead, the gas flows through a turbo-expander, which causes the gas temperature to drop to 35 F, and the pressure to drop to 600 psia, assuming an efficiency of 85% or 90% depending on the sample.

Table 17–Horse Power Generated and Outlet Temperature for Various Expansion Efficiencies

Efficiency	100%	95%	90%	85%	80%
Inlet, Enthalpy, Btu/lb-mol	574.7	574.7	574.7	574.7	574.7
Outlet, Enthalpy, Btu/lb-mol	-487.8	-434.6	-381.5	-328.4	-275.3
Change Enthalpy, Btu/lb-mol	1062.5	1009.3	956.2	903.1	850
HP, Btu/hr	584375	527359.25	473319	422199.3	374000
Outlet Pressure, psia	600	600	600	600	600
Outlet Temperature, F	19.4	25	30.3	35.5	41.3

The power developed by the expander and the outlet temperatures are shown in **Table 17**. The data in the table were obtained from the commercial simulator. An efficiency of at least 85% is required to obtain an outlet temperature of 35 F, required for hydrate formation. This generates 1.01 x 10^7 Btu of energy. Below is a sample calculation of power from the expander:

$$Power = \Delta h \times w \times \eta_e$$

where:

Δh = change in enthalpy, btu/lbmole,

w = flow rate, lbmole/hr

η_e = expander efficiency, %

For an 85% efficiency, Δh = 903.1 btu/lbmole and w = 550 lbmole/hr

$Power_{\exp ander}$ = 422199.3 Btu/hr

Some commercial expanders can have up to 90% expansion efficiency (TurboExpander, 2010).

5.1.3 Hydrate Formation

5.1.3.1 Water Cooling Requirements

The cooling requirement of water is estimated as follows.

The water enthalpies before and after the cooling are obtained NIST chemistry webBook (Themophysical, 2008).

The sensible heat of cooling is estimated from

$$Q_{water} = m(H_i - H_f) \qquad \textbf{(39)}$$

where

Q	sensible heat of cooling
m	no of moles of gas mix
H_i	initial enthalpy of water
H_f	final enthalpy of water

Sample calculation

For 5 MMscf/d gas mix, 79037.9 moles of water is required for hydrate formation

Water cooling from 60 F to 35 F is to be carried out.

m = 83046

H_i = 506.9 Btu/lbmole

H_f = 86.46 Btu/ lbmole

Q = 83046 (506.9 – 54.91)

Q = 37535961 Btu/d

$Q = 3.75 \times 10^7$ Btu/d

5.1.3.2 Latent Heat of Formation Estimation

During the formation of the hydrate large amount of heat is given out which must be removed to ensure the hydrate formed do not dissociate. The latent heat of formation is estimated based on the mole fraction of the gas as a weighting factor of the heat of formation of the gas components (Makogon, 1981) shown in **Table 18.**

Table 18–Estimation of Latent Heat of Formation

			Heat of Formation	Gas Mix
Sample	1		kJ/mol gas	kJ/mol gas
Nitrogen	N_2	0.56	0.00	0.00
Hydrogen Sulphide	H_2S	0.00	0.00	0.00
Carbon Dioxide	CO_2	3.9	66.00	2.59
Methane	C_1	92.00	54.20	49.9
Ethane	C_2	2.52	81.80	2.06
Propane	C_3	0.51	129.20	0.66
Iso-butane	iC_4	0.10	133.20	0.13
N-Butane	nC_4	0.12	133.20	0.16
Iso-pentane	iC_5	0.05	0.00	0.00
N-Pentane	nC_5	0.04	0.00	0.00
Hexanes plus	C_6+	0.09	0.00	0.00
Total		100		55.51

The latent heat of formation of the gas sample is 55.51 kJ/mol gas (63 Btu/scf).

For 5 MMscf/d gas of sample, the latent heat is calculated as follows.

Latent heat of formation of the hydrate

= Btu/scf gas x 5 MMscf/d

= 63 x 5,000,000

= 3.15 x 10^8 Btu/d

5.1.3.3 Heat Gain through Insulation

NanoPore thermal insulation provides exceptional performance with a very low overall thermal conductivity of 0.004 btu.in/ft^2.h.F. About 240 Btu/h of heat gained from the surroundings must be removed when using 1” thickness NanoPore material, compared to 4.35 x 10^7 Btu/hr without any insulation.

5.1.3.4 Summary of Cooling Requirement (Hydrate Formation)

Table 19 summarizes the cooling requirement for formation of hydrate for 5 MMscf/d. The largest energy requirement is removal of the latent heat of formation which is approximately 3.15 x 10^8 Btu/d. Heat gain through insulation is at about 2880 Btu/d. Overall the total cooling requirement for hydrate formation for 5 MMscf/d is 3.53 x 10^8 Btu.

Table 19–Summary of Energy Requirement for Hydrate Formation

Process	Btu/d
Latent Heat of Formation	3.15×10^8
Water Cooling	3.75×10^7
Gain through Insulation	2.88×10^3
Total	3.53×10^8

5.1.4 Hydrate Dissociation

For hydrate dissociation, it estimated that the same amount of latent heat removed during the formation process is required. In this case, 3.15×10^8 Btu/d is required for dissociation of gas hydrate storing 5 MMscf/d.

5.1.5 Summary

The overall energy requirement for the process is about 15-20% of the energy value of the gas transported in hydrate form.

5.2 Time Breakdown for the Hydrate Process

The hydrate value chain time breakdown is show in **Fig. 17** below. The formation time is estimated as six (6) hours. The time for transportation to the market (Jamaica) ranges from 10 to 20 hours depending on the location of the well in Trinidad and the location of the actual destination in Jamaica. About 3.6 hours are estimated for the time of dissociation of the hydrate and details are shown below.

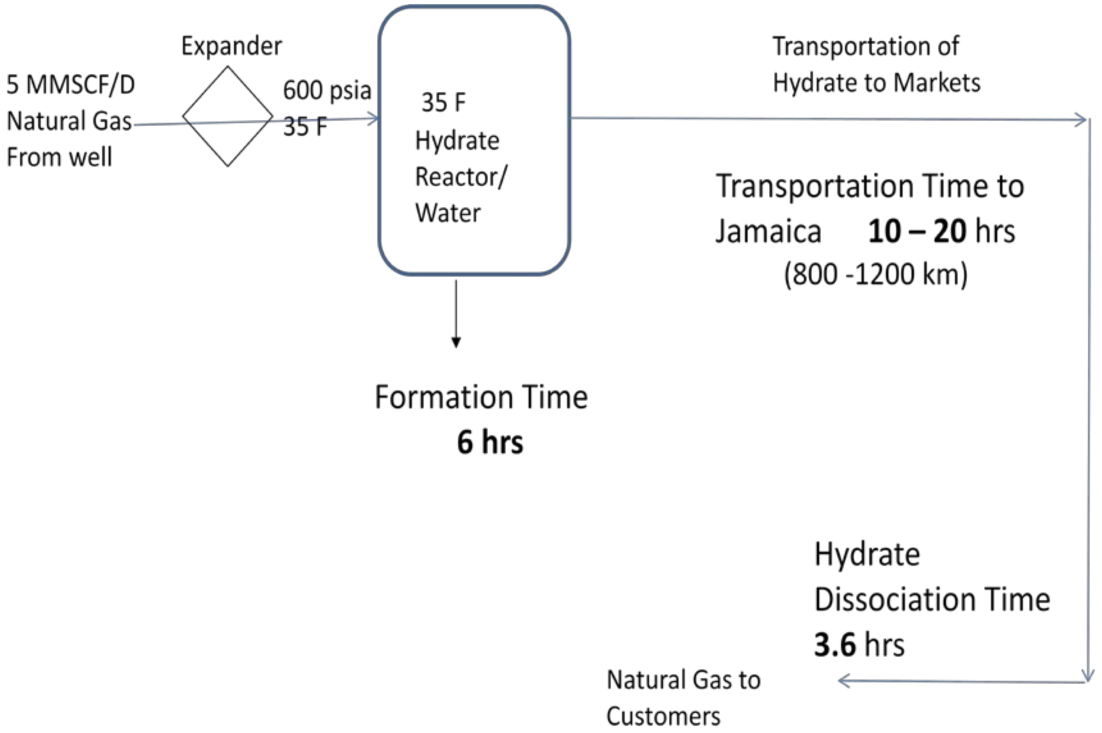


Fig. 17–Time Breakdown for Hydrate Process

5.2.1 Formation Time

The formation time was estimated from laboratory experiments with similar conditions to that for upscaling. The details of this are shown in section 6.1. The formation time for 0.5 MMscf is shown in **Fig. 18**. Note the shape of the curve is s shape indication a low rate of formation at the start, then an increase in formation rate followed by a drop in rates nearing the end of the formation of hydrate cycle.

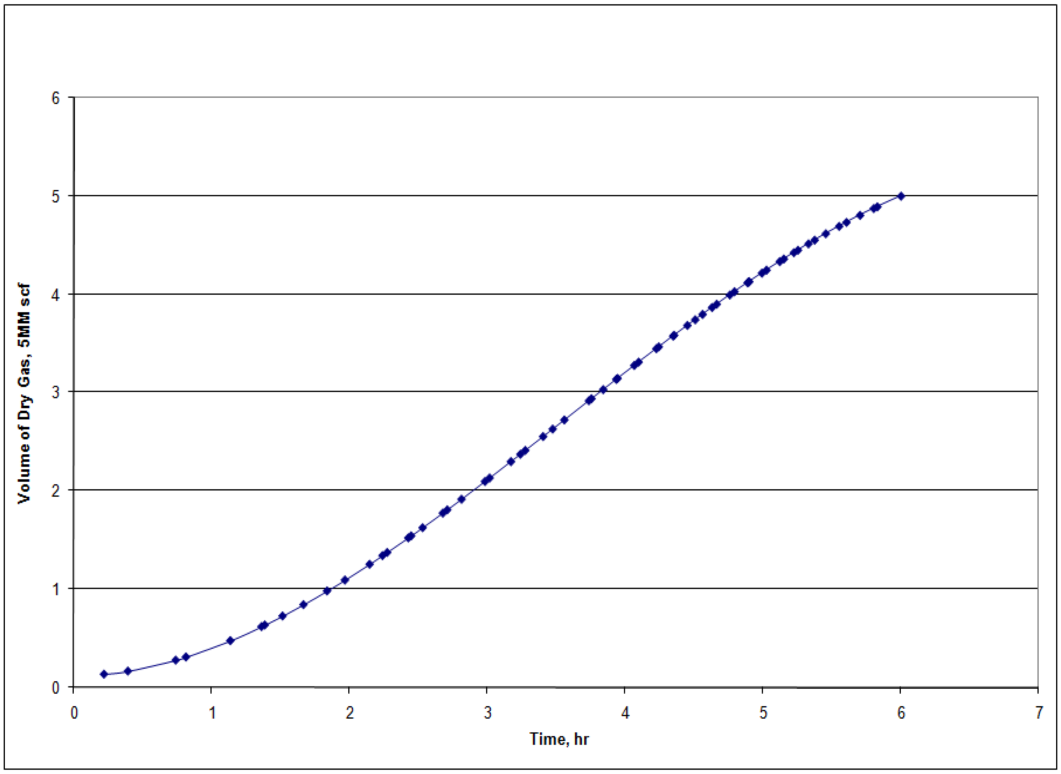


Fig. 18–Formation Time for 5 MMscf

5.2.2 Transportation Time

The actual transportation time from production of hydrate in Trinidad to the market in Jamaica depends mainly on:

(i) The actual distance between the well location in Trinidad and the market destination in Jamaica. For e.g. if the gas well is off the east of Trinidad, the transportation time is longer than for a well location on the west coast or north coast. A similar situation would be seen at the market destination. Therefore it would take a longer time if it is necessary to move around the island.

(ii) The type of sea vessel used to transport the hydrate. The vessel can be built to meet the specific needs and thus with constantly improving technology there are faster and faster vessels.

If one considers an average vessel speed of 25 knots (46 km/hr) and the transporting distance ranging from 800 – 1200 km and hence the estimated for transportation of 10 to 20 hrs.

5.2.3 Dissociation Time

The dissociation time at the market is another key aspect to the overall gas hydrate value chain. Dissociation of the hydrate can be done through depressurization of hydrate or increasing temperature of the hydrate. In this study we only consider hydrate dissociation by increasing temperature.

Faster dissociation rates would be facilitated by the heat transfer tubes that traverse the entire vessel. Hot water can be pumped through the tubes thereby increasing the temperature of the hydrate and facilitating dissociation. The dissociation temperature is estimated at 42 F for the dry gas sample from **Fig. 19**. The PT curve shown in **Fig. 19** shows the formation temperature and possible dissociation temperature. It is important to note here that dissociation temperature may be different for different gas samples. The key therefore is to heat the hydrate to dissociation temperature 42 F and estimate the overall time while accounting for phase change.

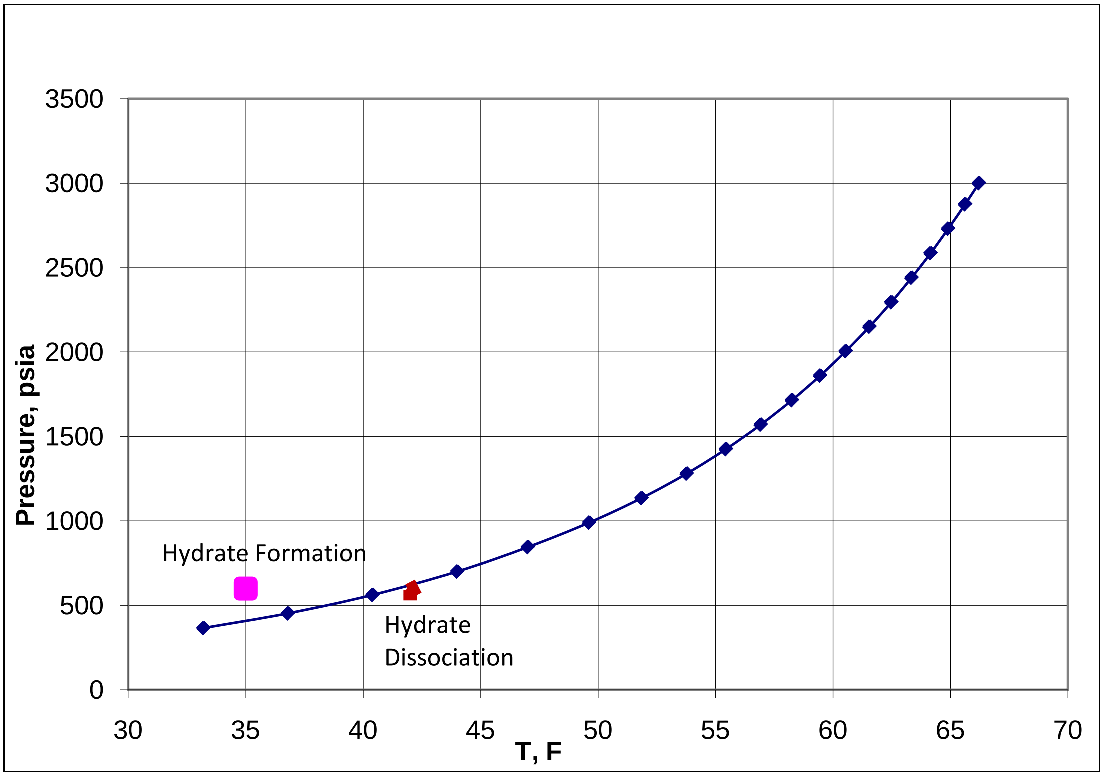


Fig. 19–PT Curve for Dry Gas Sample Showing Hydrate Formation and Dissociation Conditions

The model used here for estimation of dissociation is one developed to estimate the dissociation time of a hydrate plug (Hong, Gruy and Herri, 2006). A similar concept is seen between both the hydrate plug and a circular region around the heat transfer tube in the hydrate vessel.

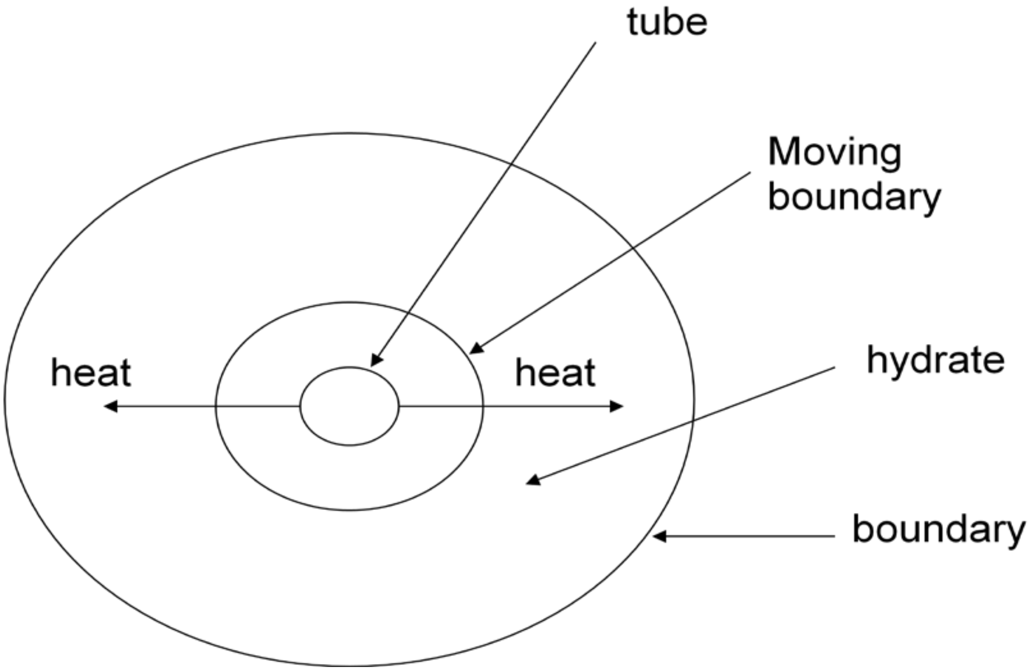


Fig. 20–Dissociation Schematic for One Heat Exchange Tube

Fig. 20 shows the heat transfer from one tube outwards dissociating the hydrate as a moving front. In this study heat transfer is the determining step of dissociation (Hong, Gruy and Herri, 2005).

Assumptions of the model:

(i) Pressure is homogeneous in the hydrate

(ii) Hydrate around the heat transfer tubes are dissociated radially and axial dissociation is neglected.

(iii) The temperature drop across the tube wall is negligible.

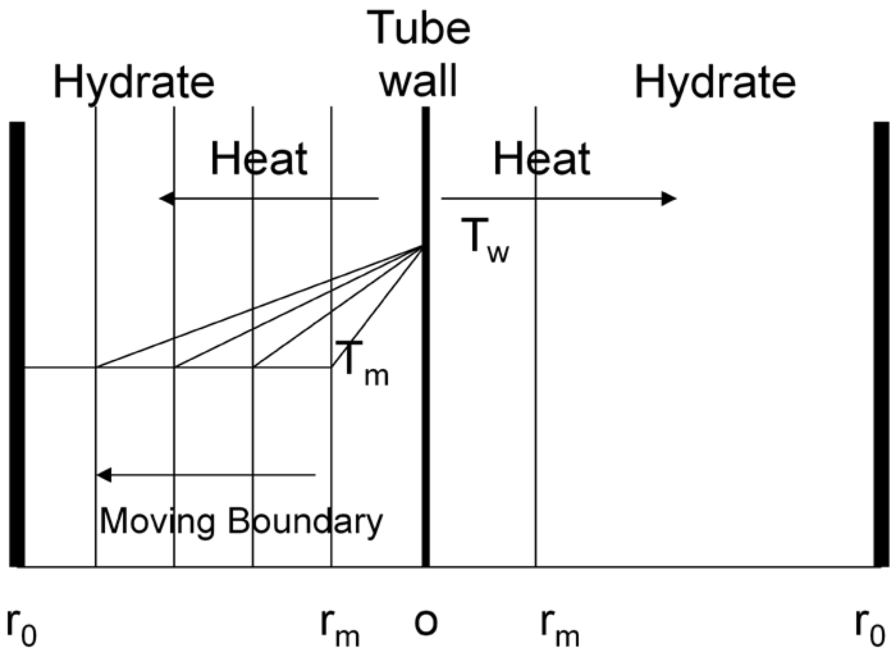


Fig. 21–Hydrate Dissociation with Moving Boundary

Fig. 21 shows the schematic of hydrate dissociation with moving boundary.

At time $t > 0$, the outer surface of the heat transfer tube is maintained at a temperature T_w

So, the initial condition of this system is

$T = T_i$, $t = 0$, **(40)**

and the boundary conditions are

$T = T_w$, $r = r_0$, $t > 0$, **(41)**

$$-K_L \frac{dt}{dr} = (1-\varepsilon)\rho_H L \frac{dr_m}{dT}, \; r = r_m, \; r_m < r_0, \; t > 0$$

(42)

$T = T_m, r = r_m$, $t > 0$ **(43)**

The enthalpy function H is a function of temperature T

$$\boldsymbol{H = \int_{T_i}^{T} \rho_L c_L dT + \rho_H L(1-\epsilon) f(T)} \quad \textbf{(44)}$$

where

$$\mathbf{f}(\boldsymbol{T}) = \begin{cases} \boldsymbol{0}, & \boldsymbol{if\ T < T_m} \\ \boldsymbol{1}, & \boldsymbol{T \geq T_m} \end{cases} \quad \textbf{(45)}$$

Another form of the enthalpy is

$$\boldsymbol{\frac{\partial H}{\partial t} = \rho_L c_L \frac{\partial T}{\partial t}} \quad \textbf{(46)}$$

As the phase change is realized, a discontinuity in H is observed.

Substituting H into the heat equation, we obtained the equation of the phase change in a cylindrical two dimensional region with radial symmetry as follows:

$$\boldsymbol{\frac{\partial H}{\partial t} = K_L \left\{ \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} \right.} \quad \textbf{(47)}$$

The melting of the hydrate described by equations (45) can be written in the following non-dimensional form as:

$$\boldsymbol{\frac{\partial H^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial r^*} + \frac{1}{r}\frac{\partial T}{\partial r^*}} \quad \textbf{(48)}$$

The dimensionless variables are defined by:

$$\boldsymbol{t_D^* = \frac{K_L t_D}{r_0^2 \rho_L C_L}} \quad \textbf{(49)}$$

$$\boldsymbol{L^* = \frac{L\rho_H(1-\epsilon)}{\rho_L c_L (T_w - T_m)}} \quad \textbf{(50)}$$

$$\boldsymbol{T_0^* = \frac{(T_0 - T_m)}{(T_m - T_w)}} \quad \textbf{(51)}$$

The numerical results from this scheme indicate that the dimensionless melting time t: for the circular cylinder may be approximated by the following expression:

$$\boldsymbol{t_D^*} = (\mathbf{0.14} + \mathbf{0.085}\boldsymbol{T_0^*}) + (\mathbf{0.252} - \mathbf{0.0025}\boldsymbol{T_0^*})\boldsymbol{L^*}$$

(52)

The dissociation time estimated from the equation was 3.6 hrs for a 3.3 inch radius around the heat exchange tube **(Fig. 22)**. With the possibility of flowing hot water through all the tubes at the same time, we can therefore estimate the total time of hydrate dissociation as 3.6 hrs. Approximately 3500 gallons of water at 80 F would flow through the 1” tubes during the 3.6 hrs dissociation period. One can therefore imagine the length of time it would take for dissociation without heat transfer tubes in the hydrate vessel. Details are shown in Appendix A.3. The following terms are used in the equations above:

c_L	heat capacity of liquid water, btu/lb F
ϵ	Porosity of hydrate, %
H	enthalpy, btu/lb
K_L	thermal conductivity of liquid water, btu/ft.h.F
L	heat of dissociation of hydrate, btu/lb
M	molar mass, kg/mol
r	radial coordinate, ft
r_0	radius of hydrate around heat tube, ft
r_m	radial position of phase change boundary, ft
t	time, hr
t_D	dissociation time, hr

T	temperature, F
T_0	initial temperature, F
T_m	dissociation temperature, F
T_w	external tube wall temperature, F

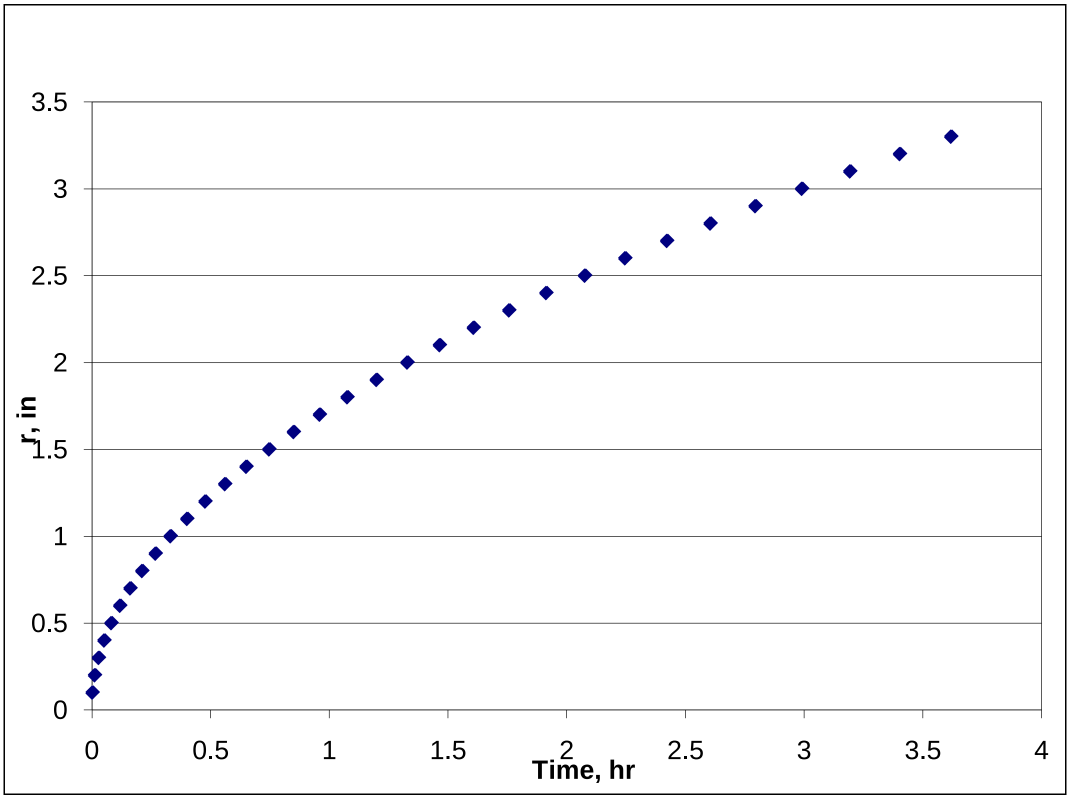


Fig. 22–Time of Dissociation for Moving Boundary

5.3 Economics

5.3.1 Overiew

The economics of the gas hydrate process is shown in **Fig. 23**. The expander cost is $1.5 million. The estimated cost to capture 5 MMscf/d is about US$4.4 million which includes the cost of 10 vessels with insulation and the heat transfer tubes for each. Additionally a refrigeration unit is required and this is estimated to cost about US$ 219,000.

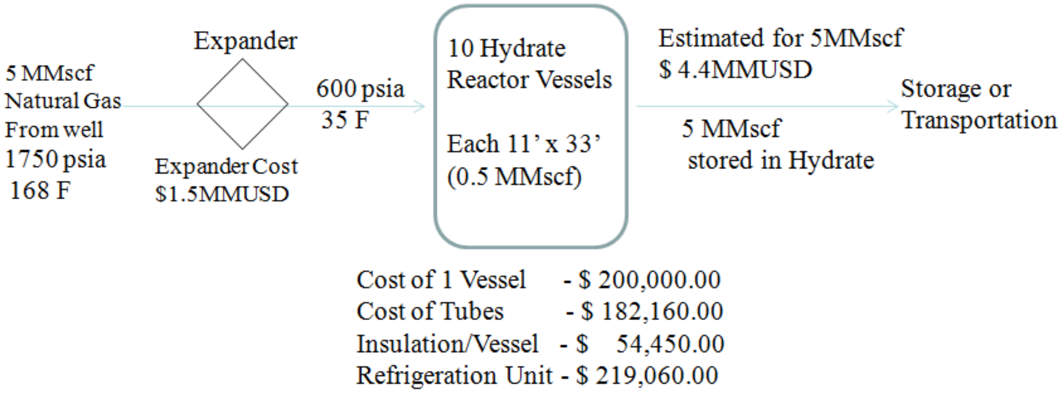
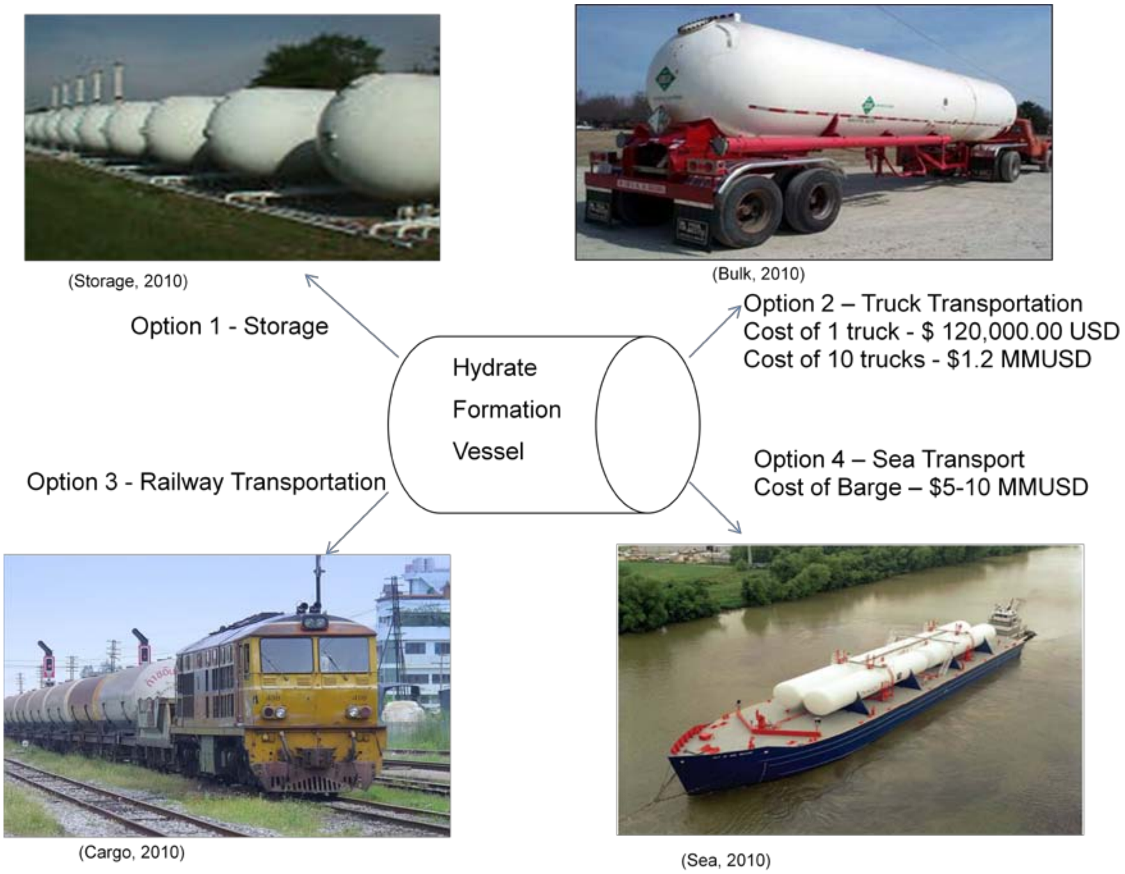


Fig. 23–Estimated Cost Breakdown for Hydrate Process

The cost for the transportation options are shown in **Fig. 24**. To transport 10 hydrate vessels by truck is estimated to be about $1.2 MMUSD. However to transport by sea using a barge can cost anywhere between 5 and 10 MMUSD.



(Storage, 2010)

(Bulk, 2010)

(Cargo, 2010)

(Sea, 2010)

Fig. 24–Estimated Cost for Different Vessel Transportation Modes

5.3.2 Scheduling

To have a constant supply of 5 MMscf/d to Jamaica, it is estimated that 30 vessels and 2 barges are required. This is estimated from the time breakdown discussed in section 5.2.

5.3.3 Cost Summary

The estimated capital cost of supply 5 MMscf/d natural gas is shown in **Table 20** below. The total cost is approximately US$ 30 million.

Table 20–Capital Cost Summary for Transporting 5 MMscf/d Gas

Quantity	Item	$ MMUSD
1	Expander	1.5
30	Hydrate Vessel	13.08
2	Refrigeration Unit	0.44
2	Barges	15
	Total	30.02

Table 21 shows a summary of net income for transporting 5 MMscf/d using an average gas price of US $5.00 estimated from gas prices over the last few months. The yearly income is about 9.1MMUSD and 182 MMUSD for the life of the well.

Table 21–Net Income Summary

Gas Transported	Estimated Life of well
Price of Gas	$5.00 Mscf
Income per day	$25,000.00
Income/year	$9,125,000.00
Estimated Life of well	20
Income/ well life	$182,500,000.00

There are operating costs associated with the hydrate process. Some of these costs include raw materials, labor, utilities, maintenance and repairs, insurance, operating supplies, administrative and contingency. These were not quantified in this study.

5.4 Conclusions

(i) To have a constant and adequate supply of 5 MMscf/d of natural gas, thirty hydrate vessels and two or three barges may be required since the overall process time can vary from 20–30 hrs.

(ii) Commercial expander can have an efficiency of up to 90%. Therefore the selected expander efficiency must allow the expansion of the gas to the required hydrate formation conditions. The power developed by the expander is of the magnitude 4.2×10^5 Btu/h.

(iii) The cooling requirement for the hydrate formation (5MMscf/d) was estimated to be 3.5×10^8 Btu/d. About 89% of this requirement is from the latent heat of formation.

(iv) For dissociation of the hydrate, 3.15×10^8 Btu/d is required; this represents the same amount of latent heat removed during hydrate formation.

(v) Time analysis shows six hours for hydrate formation, 10-20 hours estimated for transportation and 3.6 hours estimated for dissociation.

(vi) The estimated capital cost of to transport 5 MMscf/d to Jamaica is approximately US $30 million.

(vii) Using an average gas price of US $5, the net income is 9.1 MMUSD per year.

CHAPTER VI

POTENTIAL INDUSTRIAL APPLICATION

Now we have seen the details of the work flow in Chapter V, this chapter would compare the industrial application of this work to two distinct gas samples. One sample (dry gas) is mainly methane and the other (Sample 2) has components up to C_6. This would highlight some of the effects of composition on the gas hydrate work flow.

6.1 Overview

Over the past decade, gas hydrates have stimulated significant interest and triggered fundamental research. Primarily, the focus has been on hydrate blockage in pipelines, and on naturally occurring gas hydrates. However, gas hydrates can be useful in many different ways that can be pertinent to our industry, thanks to their unique structural packing where only certain molecules can enter the gas hydrate cavities. Among the several potential uses of gas hydrate technology are gas separation, transportation and storage of natural gas, desalination, and carbon dioxide disposal. In particular, it is possible to: (i) separate the heavier components (pentane and higher) from natural gas, and (ii) capture, store and transport natural gas.

This study proposes a workflow for capturing, storing and transporting gas in the hydrate form, particularly for situations where there are infrastructural constraints such as lack of pipelines. These applications of gas hydrate technology can have potential benefits to the oil and gas industry.

6.2 Introduction

The need for new methods for gas transportation is the challenge that drives the development of hydrate technology for storing and transporting natural gas (Masoudi and Tohidi, 2005). The ability of natural gas to form hydrate in combination with water is a very interesting and useful concept (Makagon, 1997) and can be widely utilized in the industry. Gas hydrates can be regarded as a safe and easy way of capturing gas, storing and transporting associated, stranded and flared gas (Berner, 2003).

The objective of this chapter is to show useful industrial applications that rely on gas hydrate technology, based on selected gas samples (**Table 22**). These applications include situations when:

(i) Gas storage is required, and so natural gas is converted to gas hydrate and stored for future use.

(ii) Natural gas hydrate technology provides an attractive method to capture and transport natural gas on a small scale.

(iii) In the hydrate process of capturing natural gas, heavy components (C_5 and above) are separated out as Natural Gas Liquids (NGL), while C_1 to C_4 are stored in hydrate form.

The proposed workflow will be discussed using two representative gas samples (‘Dry gas’ and ‘Sample 2’). The former is basically pure methane, whereas sample 2 has the heavier C_5 and C_6 components. It is assumed that these gases are produced from a given field, at a given rate.

Table 22–Natural Composition of the Two Gas Samples (Mole %)

	N_2	H_2S	CO_2	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	C_6
Dry Gas	0.00	0.00	0.00	99.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Sample 2	0.78	0.00	2.84	92.04	2.82	0.74	0.14	0.21	0.10	0.08	0.25

Expansion of the gas from wellhead conditions is necessary to trigger hydrate formation, depending on the properties of the gas. This will be shown in this analysis with the two selected samples.

In the hydrate formation process, only the C_1 to C_4 alkane components of natural gas are captured. C_5 and higher components are separated out as natural gas liquids. This is a particularly useful concept, especially in cases when the lighter components of natural gas are needed for power generation, and the heavier components can have a negative impact on gas turbines. This concept is illustrated below with the Sample 2 case.

The formation of natural gas hydrate yields a high latent heat of formation that must be removed to prevent dissociation. To this aim, the formation vessel could be equipped with heat exchange tubes, extending the full length of the vessel, to facilitate heat transfer from the vessel. The heat exchange tubes not only aid the heat removal process but they also: (i) supply heat for later dissociation of hydrate, after formation and storage/transportation, and (ii) provide additional surface area for more effective hydrate formation.

As we have seen that the proposal is to use the same vessel used to form the hydrate be also used for storage and transport to its delivery point. The “one vessel” concept is very useful to avoid moving the solid hydrate from vessel to vessel for storage and transportation, reduce costs, since no additional facility is needed for dissociation at the final destination, and allow water re-cycling. Using one vessel for formation, storage, transportation and dissociation of the hydrates gives operational flexibility for temporary storage and transportation. In the absence of pipeline infrastructure, hydrates could be transported in the vessel, by truck, railway or ship.

6.3 Gas Expansion

Below are the steps used in the analysis of gas expansion prior to hydrate formation:

(i) To achieve the hydrate formation conditions (600 psia and 35 F), expansion process was evaluated by the commercial simulator.

(ii) Phase envelopes were obtained for all samples using a commercial simulator.

(iii) The actual wellhead conditions of two selected samples were used in this analysis.

(iv) The simulator was used to determine the temperature of gas after expansion with a fixed hydrate formation pressure (600 psia).

(v) Pressure and Temperature of gas after expansion is plotted on the phase envelope diagram to indicate the phase at this time.

6.4 Dry Gas Sample Analysis

The process flow in **Fig. 25** illustrates the capture of 5 MMscf of dry gas from one producing well in hydrate form. The wellhead conditions are considered to be 1750 psia and 168 F. From the wellhead, the gas flows through a turbo-expander, which causes the gas temperature to drop to 35 F, and the pressure to drop to 600 psia, assuming an efficiency of 85% (note that some commercial expanders can exhibit up to 90% efficiency).

These new pressure and temperature values represent the inlet conditions to the hydrate reactor vessel. Note the heating value of the dry gas is the same before and after hydrate formation (1018 Btu/scf). The sample's heating value was estimated from the heating values of the sample's components, using the composition shown in **Table 22**.

The amount of water required for the process was estimated at 6.29:1 mole ratio of water to gas for the Dry gas sample. This was determined from a sensitivity analysis shown in Chapter III and highlighted in **Table 23**. A total of 4261 bbls of water is therefore required to capture the 5MMscf of gas.

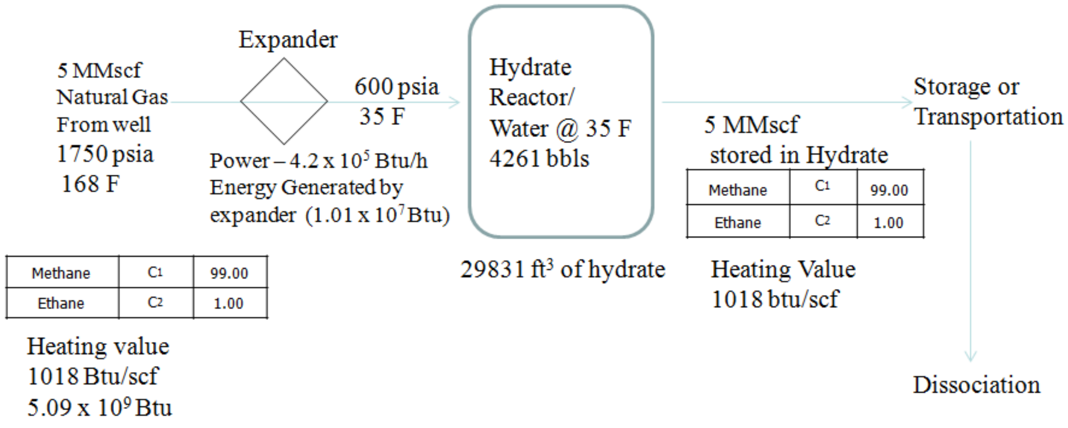


Fig. 25–Gas Hydrate Process Flow for the Dry Gas Sample

Table 23–Heating Value Estimation for Dry Gas Sample

			Ideal Heating Value	Heating Value Gas mix before hydrate	Heating Value Gas mix in Hydrate
Sample Dry gas		Mol %	Btu/scf	Btu/scf	Btu/scf
Methane	C_1	99.00	1010.0	999.9	999.9
Ethane	C_2	1.00	1769.7	17.7	17.7
Total		100		1018	1018

Fig. 26 shows the expansion process with corresponding energy exchange for the ideal process (isentropic and 100% efficient) and for the actual process at various expander efficiencies. On the secondary axis of the graph is the outlet temperature that corresponds to a given efficiency. The figure presents the variation in enthalpy and entropy for the expansion process considering several expansion efficiencies. At 100% efficiency (Isentropic process), entropy is constant but the value increases as efficiency

decreases. The work the gas performs is gained from its enthalpy and the gas cools rapidly in the expander. The expansion process must also ensure the gas remains in the gaseous phase.

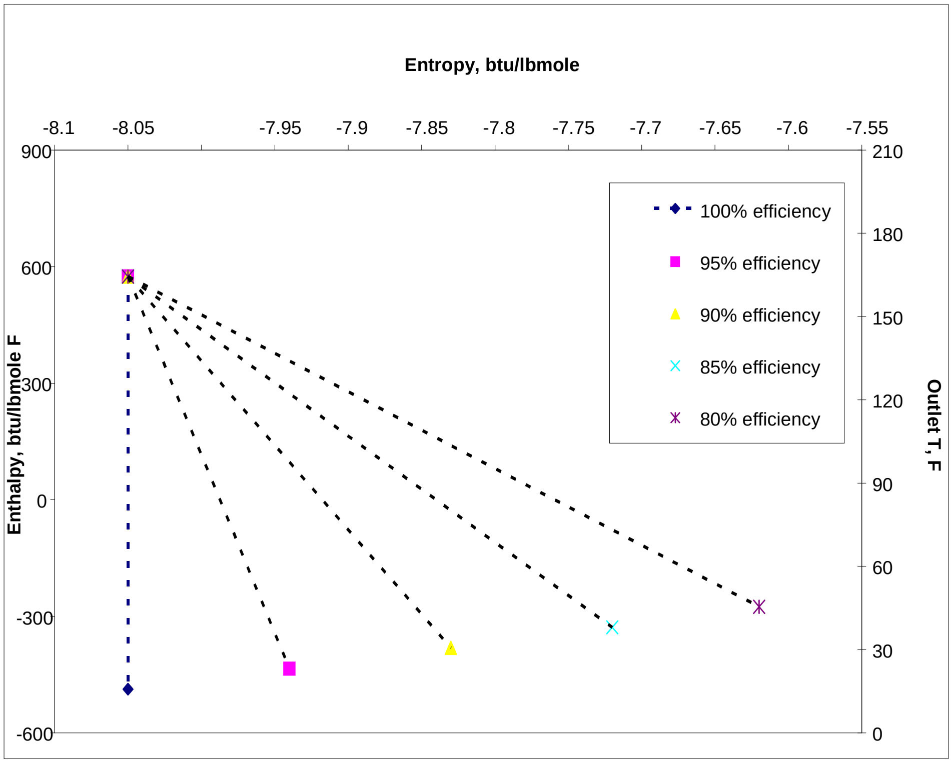


Fig. 26–Expansion Process for Dry Gas Sample

Table 24–Horse Power Generated and Outlet Temperature for Various Expansion Efficiencies for Dry Gas

Efficiency	Power	Outlet Temperature
%	Btu/h	
100	584375.0	19.4
95	527359.3	25
90	473319.0	30.3
85	422199.3	35.5
80	374000.0	41.3

The power developed by the expander and the outlet temperatures are shown in **Table 24**. An efficiency of at least 85% is required to obtain an outlet temperature of 35 F, required for hydrate formation. This generates 1.01 x 10^7 Btu of energy. Below is a sample calculation of power from the expander which was shown in Chapter V.

$$Power = \Delta h \times w \times \eta_e$$

where:

Δh = change in enthalpy, btu/lbmole,

w = flow rate, lbmole/hr

η_e = expander efficiency, %

For an 85% efficiency, Δh = 903.1 btu/lbmole and w = 550 lbmole/hr

$Power =$ 422199.3 Btu/hr

Some commercial expanders can have up to 90% expansion efficiency, which is adequate for both samples to process 5MMscf/d with only one expansion stage.

Fig. 27 shows the phase diagram for Dry Gas sample, with the wellhead and outlet conditions for varying expansion efficiencies. It can be seen that gas remains in the gas phase region during the expansion process. Note that this sample is mainly pure methane and does not exhibit a phase envelope.

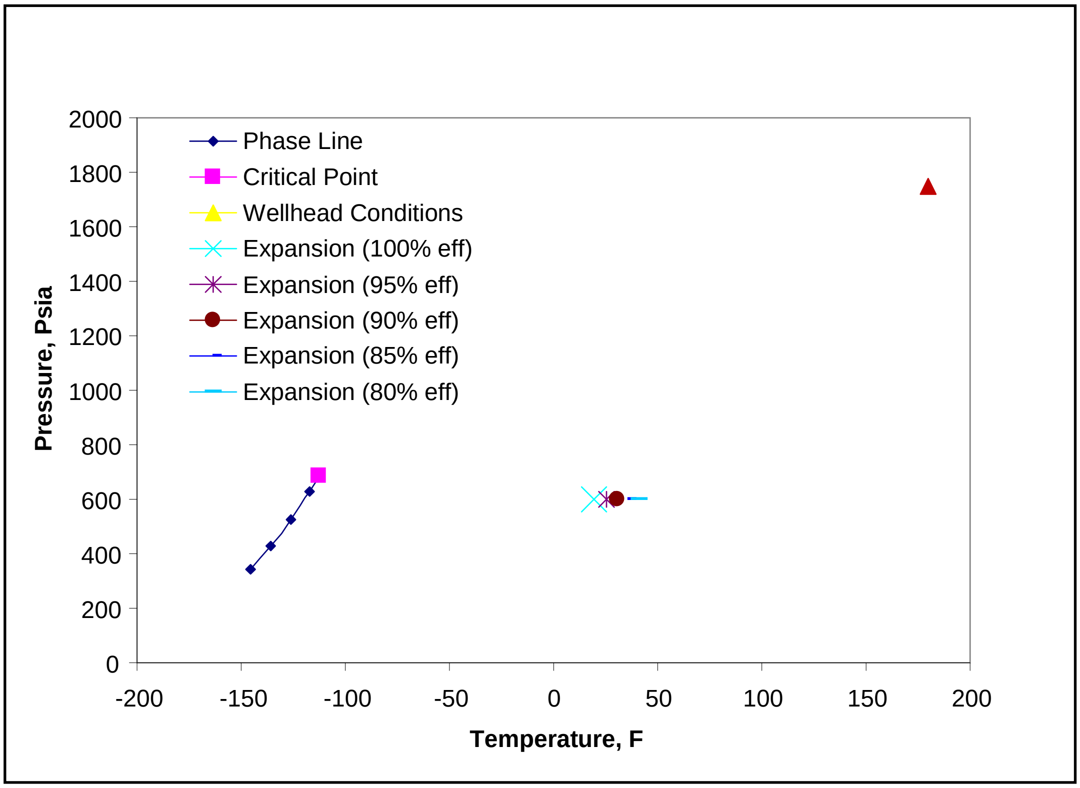


Fig. 27–Phase Diagram for the Dry Gas Sample

6.5 Sample 2 Analysis

The process flow in **Fig. 28** illustrates the capture of 5 MMscf of Sample 2 gas in hydrate form. The computed heating value of the gas was 1029 Btu/scf before the hydrate formation, and 1014 Btu/scf after. This is because the hydrate formation separates the heavier components (> C5) as useful natural gas liquid. 0.02 MMscf (3829 bbls) of natural gas liquids are obtained with a heating value of 4441 Btu/scf while 4.98 MMscf natural gas (C_1 to C_4) is stored in hydrate form. The heating values of the samples are shown in **Tables 25, 26 and 27** below. These include Sample 2 before and after hydrate formation, and the natural gas liquids separated during hydrate formation. The amount of water required for the process was estimated a 6.264:1 mole ratio of water to gas. A total of 4220 bbls of water is therefore required to capture 4.98 MMscf of gas.

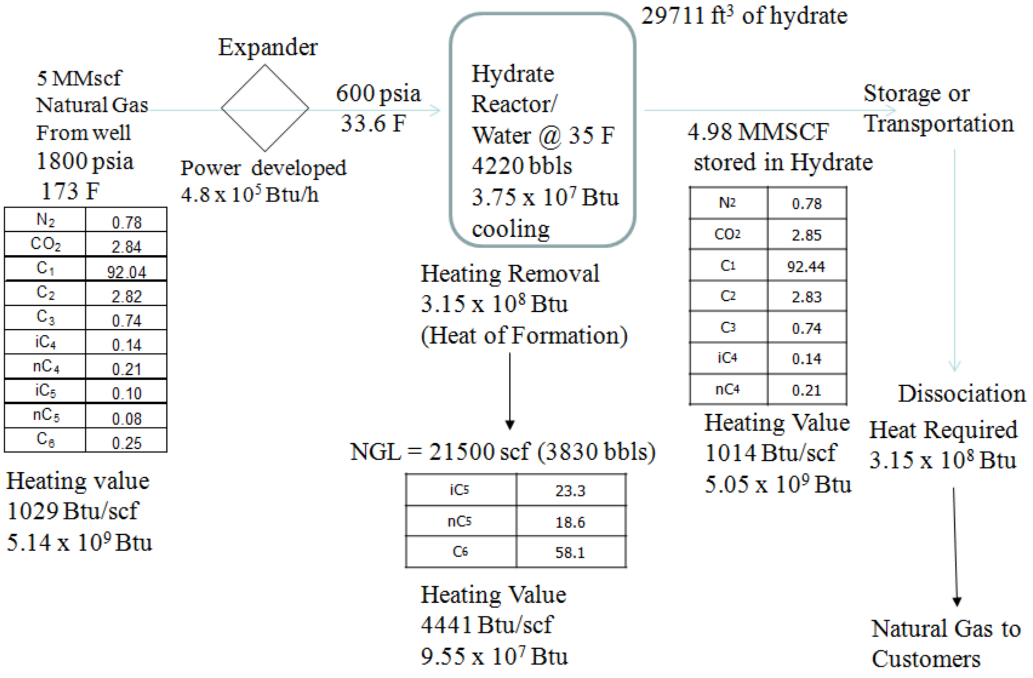


Fig. 28–Gas Hydrate Process Flow for Sample 2

The actual wellhead conditions in this case are 1800 psia and 173 F which is slightly different from the Dry Gas Sample. The expansion turbine extracts the potential heat energy from the gas, causing it to cool drastically from 173 F to 35 F.

Table 25–Estimation of Heating Value of Sample 2 Before Hydrate Formation

Sample 2 before hydrate formation			Ideal Heating Value	Gas mix before hydrate
		Mol %	Btu/scf	Btu/scf
Nitrogen	N_2	0.78	0.0	0.0
Carbon Dioxide	CO_2	2.84	0.0	0.0
Methane	C_1	92.04	1010.0	929.6
Ethane	C_2	2.82	1769.7	49.9
Propane	C_3	0.74	2516.1	18.6
Iso-butane	iC_4	0.14	3251.9	4.6
N-Butane	nC_4	0.21	3262.3	6.9
Iso-pentane	iC_5	0.1	4000.9	4.0
N-Pentane	nC_5	0.08	4008.9	3.2
Hexanes	C_6	0.25	4755.9	11.9
Total		100		1029

Table 26–Estimation of Heating Value of Sample 2 After Hydrate Formation

Sample 2 after hydrate formation			Ideal Heating Value	Gas mix in hydrate
		Mol %	Btu/scf	Btu/scf
Nitrogen	N_2	0.78	0.0	0.0
Carbon Dioxide	CO_2	2.85	0.0	0.0
Methane	C_1	92.44	1010.0	933.6
Ethane	C_2	2.83	1769.7	50.1
Propane	C_3	0.74	2516.1	18.7
Iso-butane	iC_4	0.14	3251.9	4.6
N-Butane	nC_4	0.21	3262.3	6.9
Total		100		1014

Table 27–Estimation of Heating Value of Natural Gas Liquids for Sample 2

Natural Gas Liquids			Ideal Heating Value	NGL Heating Value
		Mol %	Btu/scf	Btu/scf
Iso-pentane	iC_5	23.3	4000.9	930.5
N-Pentane	nC_5	18.6	4008.9	745.8
Hexanes	C_6	58.1	4755.9	2765.1
Total		100.0		4441

Fig. 29 shows the expansion process with corresponding energy exchange for the ideal and the actual processes.

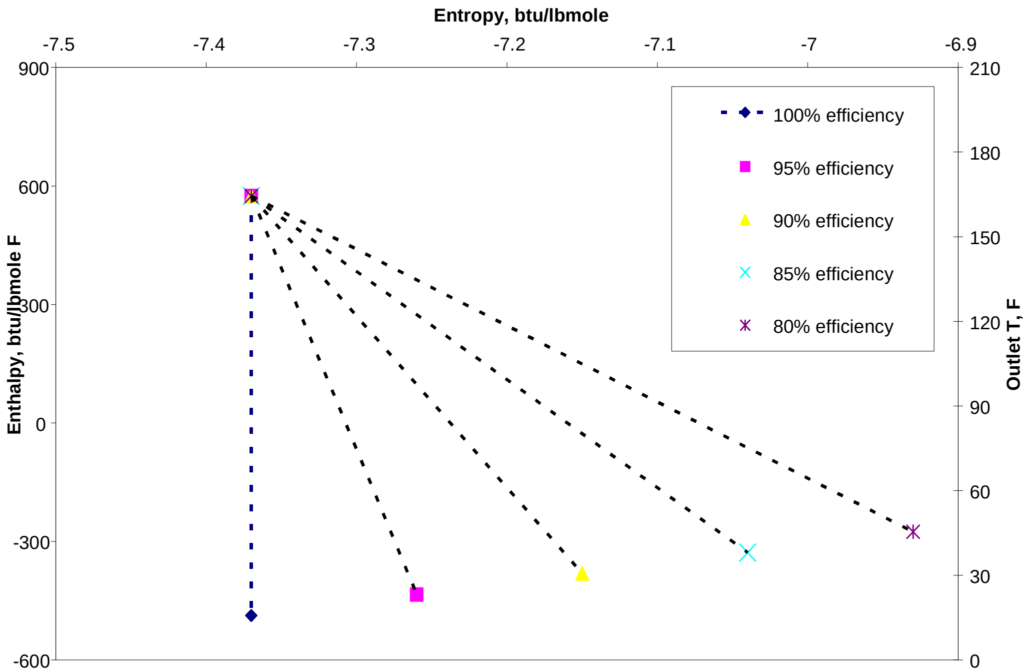


Fig. 29–Expansion Process for Sample 2

The power developed by the expander and the outlet temperatures are shown in **Table 28**. At least 90% efficiency is required to have an outlet temperature of 35 F required for hydrate formation in this case. This generates 1.29 x 10^7 Btu of useful energy.

Table 28–Horse Power Generated and Outlet Temperature for Various Expansion Efficiencies for Sample 2

Efficiency	Power	Outlet Temperature
%	btu/h	
100	593615.0	23.14
95	536294.0	28.33
90	481338.0	33.61
85	429352.0	38.91
80	380336.0	44.22

Fig. 30 shows the phase diagram for the Dry Gas sample with wellhead and outlet conditions, and with varying expansion efficiencies. Note that at 100% efficiency, the gas is very close to the two phase region.

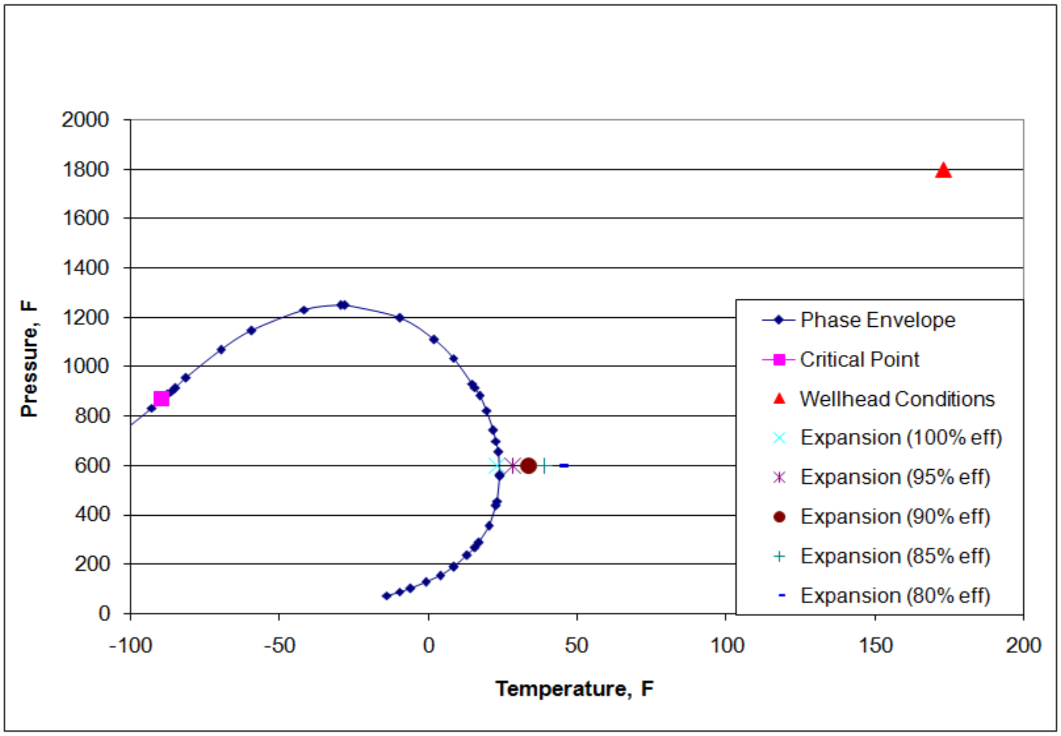


Fig. 30–Phase Diagram for Sample 2

6.6 Hydrate Formation

The next stage after gas expansion/cooling is the hydrate formation. Natural gas from the expander, together with cold water, enters the reactor vessel at 35 F, and approximately 29831 ft^3 of hydrate is formed. The formation of natural gas hydrate yields a high latent heat of formation which must be removed to prevent dissociation.

It is proposed that the same vessel used to form the hydrate could also be used for storage and transport to its delivery point, whether the gas is for domestic use or international markets.

The natural gas composition may have heavier components (C_5 or higher), as in the case of Sample 2. In the hydrate formation process, only C_1 to C_4 are captured, and the higher components (C_5 and higher) may separate in the process as natural gas liquids (NGL). This is not the case with the Dry gas sample, which is primarily methane, with 1% ethane. **Fig. 31** shows the density difference between water, hydrate and NGL during the process.

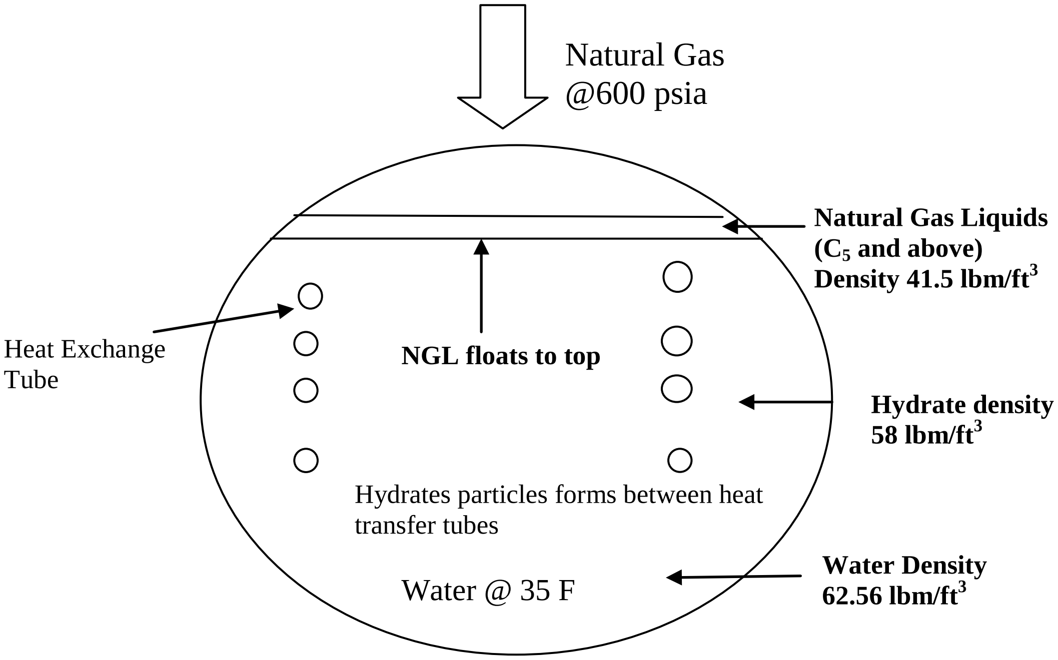


Fig. 31–Densities of Water, Hydrate and NGL

This separation method can be very useful for capturing lighter components necessary for efficient power generation. Some small amounts of higher components might have a negative effect on gas turbine systems. According to Ginter, Simchick and Schlatter (2001), there are problems with the presence of higher molecular weight components found in natural gas, as they can condense at low temperature, and appear as droplets in fuel supply, thus increasing the tendency for self-ignition. This also affects the flame position and combustion stability.

Once the hydrate formation is complete, temporary storage or transportation may be required.

6.7 Storage of Hydrates

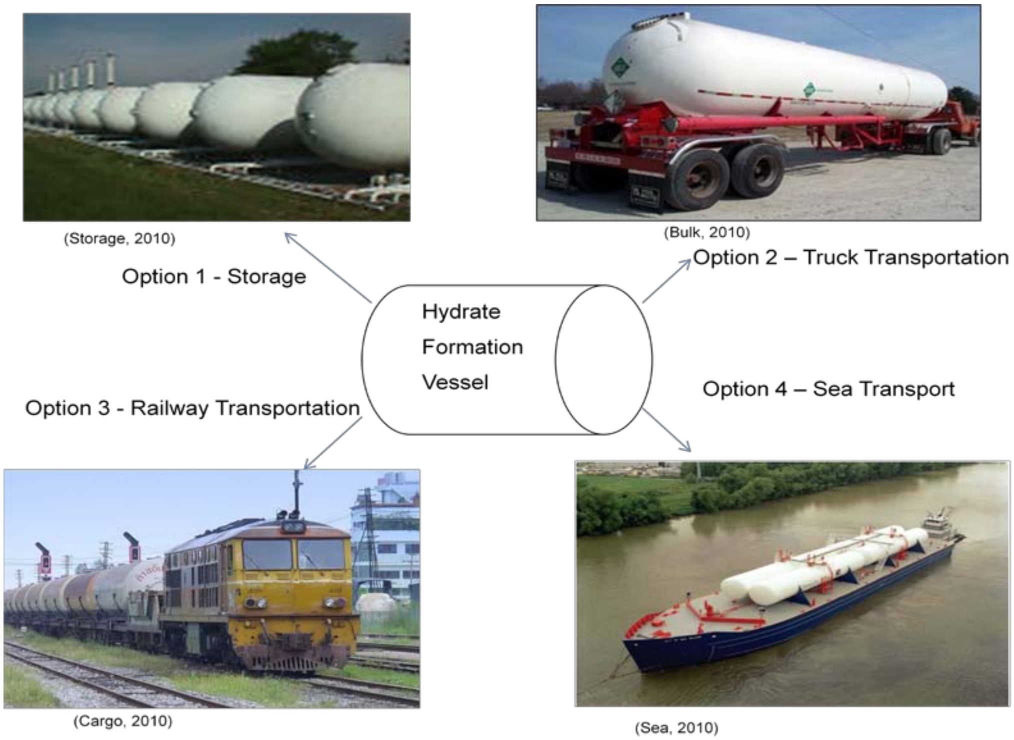
If gas storage is required, the same formation vessel could be used to store the hydrate. Depend on the storage time additional cooling may be required to remove heat gain from the surroundings. Heat gain at a rate of 240 Btu/hr must be removed. To this aim, the fixed heat transfer tubes in the vessel can be used, in combination with a small refrigeration unit. **Fig. 32** shows the conceptual storage system of gas hydrate, which can be used for possible storage for land based power plants. Several storage vessels could be stacked side by side while awaiting hydrate dissociation to provide natural gas for users such as power generation.

6.8 Transportation of Hydrates

Transporting gas hydrate can be done both by land and by sea in order to deliver natural gas. A small refrigeration system may be required to remove heat gained from the surroundings. The same formation vessel can be used can to transport hydrate using a trucking system, as shown in **Fig. 32**.

For remote fields, where only rail road transportation is available, gas hydrate could be transported by train in the formation vessels **(Fig. 32)**.

For transportation by sea, the hydrate storage vessels could be placed in a container for protection, and transported to small-scale markets for short to medium distances **(Fig. 32)**. According to Gudmundsson et al. (1998), natural gas hydrate transportation by sea is best suited for distances up to 12000 km.



(Storage, 2010)

(Bulk, 2010)

(Cargo, 2010)

(Sea, 2010)

Fig. 32–Conceptual Options for Storage and Transporting Gas Hydrate

The final stage in the proposed workflow is dissociation, when the hydrate conditions are altered to return natural gas and water. This dissociation stage is done using the heat exchange tubes to transfer heat to the hydrate, causing re-gasification.

6.9 Dissociation of Hydrates

Hot water can be pumped through the heat exchange tubes in the vessel to facilitate hydrate dissociation. The same amount of heat of formation removed during hydrate formation is required to dissociate the hydrate to gas and water. In this case, 3.15 x 10^8 Btu must be supplied to dissociate the 29831 ft^3 of hydrate.

6.10 Conclusions

(i) The expansion process yields useful energy that can be used in many ways, including power generation.

(ii) The expansion efficiency required to obtain the natural gas at 35 F may vary from sample to sample. In this case, for dry gas sample, 85% efficiency was required, whereas 90% efficiency was needed for sample 2. Some commercial expanders can have up to 90% expansion efficiency.

(iii) The expansion process ensured that both the dry gas sample and sample 2 remain in the single phase region of the phase diagram, which is important in the design process.

(iv) The hydrate formation process separates out C_5 and higher as natural gas liquids, and captures C_1 to C_4. This is particularly important in cases where light components are needed for power generation.

(v) Gas hydrate can be used as a form of natural gas storage for future use, as in the case of power plants.

(vi) Using one vessel for hydrate formation, storage, transportation and dissociation could provide significant flexibility and hardware cost reduction.

(vii) Transportation of natural gas in the form hydrate by trucks, railway and sea can be considered especially in the absence of pipeline infrastructure.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Presently, LNG and Pipelines are not economic means of gas transportation for the Caribbean islands. LNG requires 1-3 tcf of gas and approximately US$ 2 billion. Pipeline cost is estimated at US $ 3.28 million/mile and a Caribbean pipeline faces several challenges that are technical, geopolitical and jurisdictional in nature.

Impurities affect the hydrate PT equilibrium. Carbon dioxide increases the PT equilibrium line while nitrogen reduces it. At a fixed temperature, the higher the % methane in the sample the higher the hydrate formation pressure while the higher the propane levels the lower the formation pressure. The storage capacities were higher for samples with higher % methane.

To obtain 100% volume of hydrate, there is a trade- off between using additional water or increase of the hydrate formation pressure.

The recommended size of the vessel is 11 ft x 33 ft cylindrical vessel for 0.5 MMscf of natural gas. The vessel would be equipped with 240 heat transfer tubes to remove the large heat of formation. The spacing of the tubes is estimated to 6.55 in between each tube. The vessel would be equipped with NanoPore insulation which provides exceptional performance with a low overall thermal conductivity of 0.004 Btu.in/ft.h.F.

The use of an expander is another proposal in this study. The expander would extract energy from the gas stream thereby reducing temperature and pressure to hydrate formation conditions. Commercial expanders have up to 90% efficiency.

To supply 5MMscf/d natural gas from Trinidad to Jamaica, it is estimated about 30 hydrate vessels would be required and two or three barges since the overall process time can vary between 20-30 hrs.

The cooling requirement for the hydrate formation is 3.5×10^8 Btu/d and for dissociation 3.15×10^8 Btu/d is required for 5 MMscf/d of natural gas. The overall energy requirement of the process is about 15-20% of the energy of the gas transported in hydrate form.

Time breakdown shows about 6 hours is estimated for hydrate formation, 10-20 hours for transportation from Trinidad to Jamaica and 4-5 hours for dissociation.

The estimated capital cost to capture and transport 5 MMscf/d to Jamaica is US$ 30 million using an average gas price of US$ 5/Mscf. If we consider a pipeline of US $ 1-6 million/mile, and a distance to Jamaica about 500-745 miles, then a pipeline from Trinidad to Jamaica would be estimated at > US$ 500 million. The operating costs were not quantified in the study.

The expansion efficiency required for different samples are different. For sample 2, 90% efficiency was required while the dry gas sample required an efficiency of 85%.

The heat transfer tubes not only aid in removal of heat from the hydrate formation process but also supply heat during the dissociation process.

The hydrate formation process could separate out C_5 and higher as natural gas liquids and captures C_1 to C_4. The capture of C_1 to C_4 in hydrate form is particularly useful for power generation where the lighter components are preferred.

Using the ‘one vessel” concept for hydrate formation, storage, transportation and dissociation would provide significant flexibility and cost reduction in capturing and transporting 5 MMscf/d of natural gas to Jamaica. This vessel concept not only facilitates transportation by sea but also by truck and railway for land transportation.

In summary there is great potential for transporting natural gas by gas hydrate on a small scale based on the proposed hydrate work flow. However this study did not prove commerciality.

The composition of gas is very important and such proper evaluation must be done to ensure the gas sample is adequate for transportation via gas hydrate. As explain earlier the natural gas must remain in the gaseous phase after expansion prior to hydrate formation.

The study addressed some of the challenges and problems encountered in previous studies. Using “One vessel” concept will ensure that the hydrate is not transferred from vessel to vessel and the water can be re-used after dissociation. The intention is to sell gas and not gas hydrate. Use several smaller vessels to form the hydrate and heat transfer tubes can be placed in the vessel to aid in heat removal during hydrate formation. Energy required for dissociation can be obtained from waste heat from power generation or heating by solar system.

Previous studies use mostly simple gases such as methane and ethane in their analysis however this study analyzed 21 typical gas samples from Trinidad. The focus was on small gas reserves or stranded gas and not large reserves required for transport by LNG**.** The actual wellhead conditions are much higher than the conditions used in laboratory experiment and as a result an expander will be used to expand the gas to hydrate formation conditions.

The main limitations and uncertainties of the study are:

(i) The research is applicable to transportation of natural gas from Trinidad to Jamaica. The distances and energy needs of the islands are small. The conditions such as climate in the Caribbean are quite different around world. The average temperature throughout the year is 80 F and this can impact on heating and cooling requirements.

(ii) The particular natural gas sample:

- May not meet heating value requirement
- May not remain in the single gas phase after expansion
- May require additional separation for samples with large amounts of impurities.

(iii) The study only assesses a gas rate of 5 MMscf/d and a higher gas rates may pose additional challenges. This study analyzes the work flow for one well flowing 5 MMscf/d. If there are multiple wells separate economic evaluation must be done for each well since the gas rate and wellhead conditions may be different.

(iv) The composition of the gas of the gas may change during the life of the well. This was not evaluated in this study. However, in this analysis a wide range of gas sample were captured and most of the sample had greater than 90 % methane. For these samples, no significant change is expected.

(v) The study did not analyze possible decline curves for the wells. However, wells can be schedule to come on stream at different times to meet the designated 5 MMscf/d for transportation.

(vi) This work did not evaluate the wellhead pressure decline with time. As the wellhead conditions change, the expansion process and hence the output condition would also change. This is recommended for further study.

(vii) The heat transfer using the heat exchange tubes in the vessel is an uncertainty of the study. During hydrate formation, hydrates builds up around the tubes and as such the heat transfer coefficients changes. This can be modeled as a moving boundary with time as hydrates build up around the tube in the vessel. This is recommended for future evaluation.

(viii) During hydrate formation and dissociation in the vessel, the study did not analyze the uncertainty in obtaining a constant temperature of the fluid as it flows through the tube. The sensitivity in temperature changed was not evaluated and can be done in a future study.

(ix) During dissociation, the pressure increases in the vessel and this can act on the heat transfer tubes, hydrates and internal walls of the vessel may result in some mechanical of the tubes. This was not evaluated in this study and is recommended for further work.

(x) The study did not quantify the development costs and these can have a tremendous impact on the overall economics.

The recommendations are:

(i) Further work is recommended on detailed design of the hydrate vessel considering all technical and environmental specifications. Also focusing on removal of NGL from hydrate vessel.

(ii) Additional work on possible hydrate formation process for samples with higher impurities and those samples that go into the two phase region during expansion. This would analysis of the separation requirements for these samples.

(iii) The study did not prove commerciality and as such further evaluations are required in modeling of the formation time, dissociation time and heat transfer capabilities. Some laboratory experiments can be performed to evaluate these variables using a small experiment vessel similar to the proposed design in this study (cylindrical vessel with heat transfer tubes).

(iv) There is some uncertainty in the study with the surface area for water to gas contact. To address uncertainty with gas to water contact area during hydrate formation, it may be worth to consider using several smaller vessels in cascade with smaller amounts of water. This may ensure free gas to get in contact with water in each vessel in cascade. This concept can be evaluated to determine its efficiency and cost effectiveness.

If additional work is to done in this area of research, some of the evaluations needed for a gas hydrate process are:

(1) The composition of the sample must be evaluated to:
    (i) Ensure heating value is within an acceptable range of 960-1120 Btu/scf.
    (ii) Ascertain if the sample is appropriate for gas hydrate process since the sample must remain in the gaseous phase after expansion. If the sample goes into the two phase region after expansion additional separation is required and this was not analyzed in this study.
    (iii) Determine dissociation temperature since each sample has a different PT curve. At a fixed pressure, the temperature at which the hydrate dissociates may be different.
    (iv) Look at change in fluid composition coming out of the well since this can affect the overall process.

(2) The exact amount of water for a particular volume of gas can be determined. The composition of the sample affects the mole ratio and hence the amount of water needed.

(3) Higher components of the natural gas such as pentane and higher are not captured in the hydrate and separated out as natural gas liquids (NGLs). This can provide additional fuel for many processes.

REFERENCES

Berner, D. Hydrates for Transportation of Stranded Natural Gas. 2003. Paper SPE 84225 presented at the 2003 SPE Annual Technical Conference and Exhibition, Denver 5– 8 October. SPE 84225-MS.

Bulk Truck and Transport. Paul Akers Inc., www.paulakers.com.Downlaoded Feb. 2010.

Cargo Transportation, www.thaitransit.com/srt-cargo-trans.html. Downloaded Feb. 2010.

Caribbean Region Map. www.maps.com. Downloaded March 2008.

Carson, B.D., and Katz, L.D. 1941. Natural Gas Hydrates. *AIMME Tech. Pub*. 1371.

Commercial Aspects of LNG. http://en.wikipedia.org/LNG. Downloaded Feb. 2008.

Energy. 2008. World Electric Power Generation and Usage. Energy Information Administration. http://www.eia.doe.gov. Downloaded March 2009.

Fitzgerald, A., and Taylor, M. Offshore Gas to Solids Technology. 2001. Paper SPE 81805 presented at the 2001 Offshore Europe Conference held in Aberdeen, Scotland, 4-7 September. SPE 81805-MS.

Fleisch, T. 2006. The end of Stranded Gas: The emergence of the Gas to Products Option. Paper SPE 112802 presented at 2006 SPE Distinguished Lecturer Series.

Ginter, D., Simchick, C., and Schlatter, J. 2001. Variability in Natural Gas Fuel Composition and its Effect on Combustion Systems. California: California Energy Commission.

Gudmundsson, J., Andersson, V., Levik, O., and Parlaktuna, M. 1998. Hydrate Concept for Capturing Associated Gas. Paper SPE 50598 presented at the 1998 SPE European Petroleum Conference held in the Hague, The Netherlands, 20-22 October. SPE 50598-MS.

Gudmundsson, J., Parlaktuna, M., and Khokhar, A. 1994. Storing Natural Gas as a Frozen Hydrate. *SPEPF* (February 1994): 69-73. SPE-24924-PA.

Hong, D.N., Gruy, F., and Herri, J.M. 2006. Experimental Data and Approximate Estimation for Dissociation Time of Hydrate Plugs. *Chem. Eng. Sci.* **61**: 1846–1853.

Huron, M. J. and Vidal, J. 1979. New Mixing Rules in Simple Equations of State for Representing Vapor-Liquid Equilibria of Strongly Non-ideal Mixtures. *Fluid Phase Equilibria* **3**: 255.

Jager, M.D. and Sloan, E.D. 2001. The Effect of Pressure on Methane Hydration in Pure Water and Sodium Chloride Solutions. *Fluid Phase Equilibria* **185**: 89.

Makogon, Y. 1981. Hydrates of Natural Gas. Tulsa: Penn Well Pub. Co.

Makogon, Y. 1997. *Hydrates of Hydrocarbon*. Tulsa: Penn Well Pub. Co.

Makogon, Y. and Holditch, S. 2002. Gas Hydrate as a Resource and a Mechanism for Transmission. Paper SPE 77334 presented at the 2002 SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 29 September-2 October. SPE-77334-MS.

Masoudi, R., and Tohidi, B. 2005. Gas Hydrate Production Technology for Natural Gas Storage and Transportation and CO_2 Sequestration. Paper SPE 93492 presented at the 2005 SPE Middle East Oil & Gas Show and Conference, Bahrain, 12-15 March. SPE 93492-MS.

Michelsen, M. L., 1989. Calculation of Multiphase Ideal Solution Chemical Equilibrium. *Fluid Phase Equilibria* **53**: 53–80.

Michelsen, M. L., 1991.Calculation of Hydrate Fugacities. *Chem. Eng. Sci*. **46**: 1192-1193.

Ministry. 2007. Resource Management Report. Port of Spain: Ministry of Energy and Energy Industries.

Morgan, J. LNG – What's Happening and Why! 2006. SPE 108824 available from SPE, Richardson, Texas.

NanoPore Thermal Insulation. NanoPore Incorporated, www.nanopore.com/products. Downloaded March 2010.

Okutani, K., Kuwabara, Y., and Mori, Y. 2007. Surfactant Effects on Hydrate Formation in an Unstirred Gas/Liquid System: An Experimental Study using Methane and Sodium Alkyl Sulfates. *Chem. Eng. Sci.* **63**: 183-194.

Pipeline. National Gas Company of Trinidad and Tobago, www.ngc.co.tt. Downloaded March 2008.

Pipeline Variable Uncertainty and their Effects on Leak Detectability. http://en.wikipedia.org/API_1149. Downloaded Feb. 2009.

PVTSim Software 2008. Version 18. Calsep.

Rajnauth, J., Ayeni, K., and Barrufet, M. 2008. Gas Transportation: Present and Future. Paper SPE 114935 presented at the 2008 CIPC/SPE Gas Technology Symposium Joint Conference, Alberta, Canada, 16–19 June. SPE 114935-MS.

Sassen, R. 1997. Gas Hydrate Gardens of the Gulf of Mexico. Texas A&M University Dept. of Oceanography. *Quarterdeck.* **5** (3): 3-4

Sea Transportation. Trans Ocean, www.transocean.com. Downloaded Feb 2010.

Simms. J. Fundamental of the Turboexpander: Basic Theory and Design. 2009. http://simmsmachineryinternational.com/Fundamentals%20of%20Turboexpanders.pdf. Downloaded March 2010.

Sloan, D.E., Jr. 1991. Natural Gas Hydrates. *JPT* **43 (**12): 1414-1417.

Standards of the Tubular Exchange Manufacturers Association, 8th Edition. 1999. Tarrytown, NY.

Storage Tanks. Gas Tex. Energy, www.gastexasenergy.com. Downloaded Feb. 2010.

Taylor, M., and Dawe, R. Fire and Ice. 2003. Gas Hydrate Transportation–A Possibility for the Caribbean Region. Paper SPE 81022 presented at the 2003 SPE Latin American and Caribbean Petroleum Conference held in Port of Spain, Trinidad, West Indies, 27-30 April. SPE 81022-MS.

Thermophysical Properties of Fluid Samples 2008. NIST Chemistry WebBook. http://webbook.nist.gov/chemistry/fluid.

Tse, C.W., and Bishnoi, P.R., 1994. Prediction of Carbon Dioxide Gas Hydrate Formation Conditions in Aqueous Electrolyte Solutions. *The Canadian Journal of Chemical Engineering* **32**(Feb): 119-124.

TurboExpander-Generator for Natural Gas Applications. GE Oil and Gas, http://www.geoilandgas.com/businesses/ge_oilandgas/en/prod_serv/prod/turboexpanders/en/index.htm. Downloaded March 2010.

Van der Waals, J.H. and Platteeuw, J.C. 1959. Clathrate Solutions. *Adv. In Chem.Phys*. **2**: 1-57.

Verghese, J. Options for Exploiting Stranded Gas-An Overview of Issues, Opportunities & Solutions. Paper SPE 84250 presented at the 2003 SPE Annual Technical Conference and Exhibition, Denver, Colorado, 5-8. SPE 84250-MS.

Zhong, Y. and Rogers, R.E. 2000. Surfactant Effects on Gas Hydrate Formation. *Chem. Eng. Sci.* **55**: 4175-4187.

APPENDIX A

A.1 Water and Hydrate Level in the Vessel

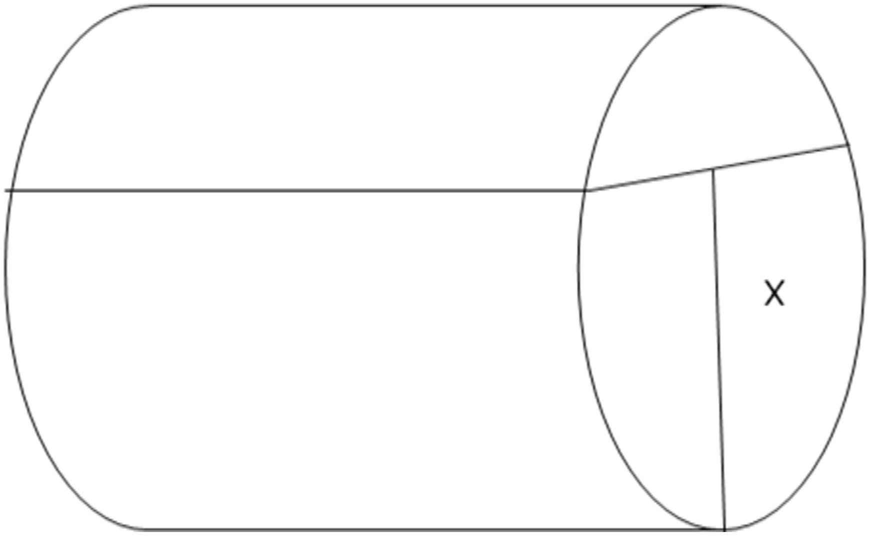


Fig. A.1–Hydrate Vessel Showing Water Level x

The object is to determine x which is the height of the water level for hydrate formation**.**

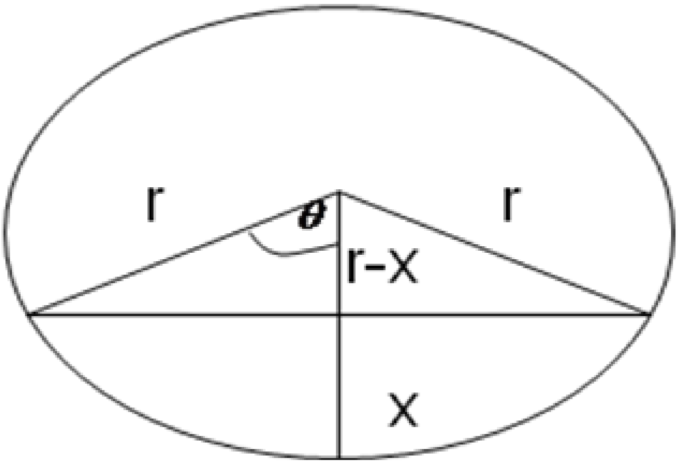


Fig. A.2–Mathematical Representation to Determine the Height x in the Vessel

The following are the steps used estimate the level in the hydrate vessel as the vessel fills up with water or hydrate:

(i) Determine the length of the base of the triangle

$$base_t = 2\sqrt{r^2 - (r - x)^2}$$

$$base_t = 2\sqrt{2rx - x^2}$$

(ii) Area of triangle

$$area_t = \frac{1}{2}bh$$

$$area_t = (r - x)\sqrt{2rx - x^2}$$

(iii) Use inverse cosine to estimate Θ

$$\theta = cos^{-1}(\frac{r-x}{r})$$

(iv) Area of sector

$$\frac{2\theta}{2\pi} = \frac{area_s}{\pi r^2}$$

$$\frac{2\cos^{-1}(\frac{r-x}{r})}{2\pi} = \frac{area_s}{\pi r^2}$$

$$area_s = r^2\cos^{-1}(\frac{r-x}{r})$$

(v) Area of hydrate at the end of tank

$$area_s - area_t$$

$$r^2\cos^{-1}\left(\frac{r-x}{r}\right) - (r-x)\sqrt{2rx - x^2}$$

(vi) Volume of hydrate

$$1 - [r^2\cos^{-1}\left(\frac{r-x}{r}\right) - (r-x)\sqrt{2rx - x^2}$$

Volume of hydrate for varying heights in vessel

$$1 - [r^2\cos^{-1}\left(\frac{r-x}{r}\right) - (r-x)\sqrt{2rx - x^2}$$

r = radius of vessel, 5.5 ft

x = height of water or hydrate in vessel, ft

When x = 0.5 ft, using above equation

Volume = 50.9 ft^3

Similar calculations were done for different for x values up to 11 ft. This is shown in **Table A.1**

Table A.1–Volume and Vessel Filling % as a Function of Height

x	Volume	Vessel Filling
ft	ft^3	%
0.5	50.89	1.62
1	141.88	4.52
1.5	256.84	8.19
2	389.45	12.42
2.5	535.76	17.08
3	692.85	22.09
3.5	858.38	27.37
4	1030.37	32.86
4.5	1207.06	38.49
5	1386.80	44.22
5.5	1568.05	50.00
6	1749.30	55.78
6.5	1929.04	61.51
7	2105.72	67.14
7.5	2277.71	72.63
8	2443.25	77.91
8.5	2600.34	82.92
9	2746.64	87.58
9.5	2879.25	91.81
10	2994.21	95.48
10.5	3085.21	98.38
11	3136.09	100.00

A.2 Tubing Spacing in the Vessel

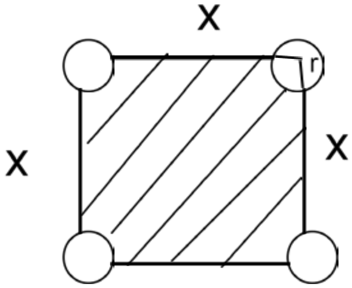


Fig. A.3–Spacing of tubes in vessel

The object of this exercise is to determine x which is the distance between two heat exchange tubes in the hydrate vessel **(Fig. A.3)**, this is important to determine the dissociation time.

The following method is used to estimate the value of x.

r_{tube} – radius of tube = 0.5 in

r_{circle} – radius of circle = 66 in

n – no of tubes = 240

Determine the Area of ¼ circle

$$\frac{\pi r^2}{4}$$

Calculate the Area of square

$$(2r + x)^2$$

Evaluate the Area of shaded region

$$(2r + x)^2 - (\frac{\pi r^2}{4} \times 4)$$

Determine the Area of tubes

$$\pi r^2 n \quad = 188.5$$

Calculate the Area of circle

$$\pi r^2 = 16286$$

Estimate the value of x using the following ratio

$$\frac{Area_{tube}}{Area_{circle-Area_{tube}}} = \frac{\pi r^2}{(2r+x)^2 - \pi r^2}$$

x = 6.55

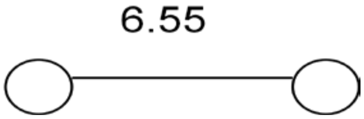


Fig. A.4–Spacing between heat transfer tubes

A.3 Dissociation Time

The melting of the hydrate can be written in the following non-dimensional form (Voller et al, 1981) as:

$$\frac{\partial H^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial r^*} + \frac{1}{r}\frac{\partial T}{\partial r^*}$$

The dimensionless variables are defined by:

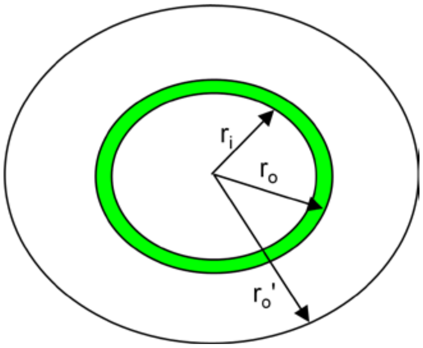
$$t_D^* = \frac{K_L t_D}{r_0^2 \rho_L C_L}$$

$$L^* = \frac{L\rho_H(1-\epsilon)}{\rho_L c_L (T_w - T_m)}$$

$$T_0^* = \frac{(T_0 - T_m)}{(T_m - T_w)}$$

The numerical results from this scheme indicate that the dimensionless melting time t: for the circular cylinder may be approximated by the following expression:

$$t_D^* = (0.14 + 0.085T_0^*) + (0.252 - 0.0025T_0^*)L^*$$



The main inputs in the model is shown below.

General Information:

T_{air}	296.15	F	Temp. of the Air
r_i	0.06951	ft	Inner Diameter of Inner Tube
r_o	0.08333	ft	Outer Diameter of Inner Tube
r_o'	0.38	ft	Outer Diameter of Outer Tube
Δz	11	ft	Increment of length
k	0.35	btu/ft.h.F	Thermal conductivity
V	14.96273		Volume of cylinder

Outer Shell Information (Hydrate)

C_{ps}	10.8	btu/lb F	hydrate heat capacity
T_{0s}	35	F	temp. of hydrate
A_s	0.431612	ft2	cross sectional area where hydrate is present
ρ_s	56.75	lb/ft3	density of hydrate
F_s	0	ft^3/s	volumetric flow rate of shell side fluid
k	0.283112	btu/ft.h.F	thermal conductivity of hydrate
V	14.2432	ft3	Volume of hydrate
Tm	42	F	temp. of dissociation

Tube Side Fluid Information (Water)

C_{pt}	1.00459	btu/lb F	hot water heat capacity
T_{0t}	80	F	hot water temp. inside tube
A_t	0.015171	ft2	cross sectional area where tube side fluid is present
ρ_t	62.43	lb/ft3	density of hot water inside tube
F_t	0.030381	ft3/s	volumetric flow rate of hot water inside tube
k	0.35	btu/ft.h.F	thermal conductivity of water

Table A.3–Time for Dissociation as r Increases from the Tube

r	td
in	hr
0.1	0.003
0.2	0.013
0.3	0.030
0.4	0.053
0.5	0.083
0.6	0.120
0.7	0.163
0.8	0.213
0.9	0.269
1	0.332
1.1	0.402
1.2	0.479
1.3	0.562
1.4	0.651
1.5	0.748
1.6	0.851
1.7	0.961
1.8	1.077
1.9	1.200
2	1.330
2.1	1.466
2.2	1.609
2.3	1.758
2.4	1.915
2.5	2.077
2.6	2.247
2.7	2.423
2.8	2.606
2.9	2.795
3	2.991
3.1	3.194
3.2	3.404
3.3	3.620

APPENDIX B

TECHNICAL PAPERS WRITTEN

SPE 114935
Gas Transportation: Present and Future
J. Rajnauth, K. Ayeni, and M. Barrufet, SPE, Texas A & M University

SPE 113811
Monetizing Gas: Focusing on Developments in Gas Hydrate as a Mode of Transportation
Jerome Rajnauth, SPE, Texas A&M University; Maria Barrufet, SPE, Texas A&M University

SPE 121281
CO_2 Hydrate: A possibility for future CO_2 disposal –
J. Rajnauth, SPE and M. Barrufet, SPE, Texas A&M University

SPE 131663
Hydrate Formation: Considering the effects of Pressure, Temperature, Composition and Water
J. Rajnauth, SPE, M. Barrufet, SPE, and G. Falcone, SPE, Texas A&M University

SPE 133466
Potential Industry Applications Using Gas Hydrate Technology
J. Rajnauth, SPE, M. Barrufet, SPE, and G. Falcone, SPE, Texas A&M University

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