Feasibility Study of Transporting Natural Gas as Gas Hydrate

by

Nursyakilla binti Mohd Azman

Dissertation submitted to the
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CERTIFICATION OF APPROVAL

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Approved by,

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TRONOH, PERAK

SEPTEMBER 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NURSYAKILLA BINTI MOHD AZMAN

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ABSTRACT

Gas hydrates are clathrates, where a gas molecule is being caged by a host molecule with no chemical bonding. Hydrocarbons are noted to be able to create hydrate. There is a certain condition where the hydrate can be formed. Seen as a potential gas source, it is also has the potential to be used as a medium of transporting natural gas in solid form. For that, a feasibility study is to be conducted to see its economic feasibility. A process is suggested in transforming the natural gas to gas hydrate. The economics of the proposed process is evaluated, and comparison to LNG is being done. Marin transportation analysis is also conducted to see the feasibility of transporting hydrate by sea. From the economic analysis on the process, fixed capital and operating cost of hydrate plant is less than LNG liquefaction plant by. From the transportation cost analysis, it is concluded that natural gas hydrate (NGH) shipping is a good alternative for small-volume transport on short distance, where LNG can be uneconomical.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Hydrates are an example of a chemical compound called clathrate, in which a host lattice traps a smaller guest molecule inside the 'cage'. The guest molecule acts to stabilize the lattice structure of the compound. Gas hydrate can be found naturally in the Artic, beneath the permafrost as well as underneath the ocean floor at certain water depth (Demirbas, 2010; Carrol, 2009).

Formation of gas hydrate is favored by these condition; surroundings with low temperature and high pressure, the present of a former gas hydrate and sufficient amount of water (Demirbas, 2010).

Initially a nuisance to the natural gas processing and transporting process as it forms and builds up inside the pipeline thus plugging the pipeline; there is an increase of interest in studying the properties and usage of gas hydrate. Some research has been done to emulate the formation of gas hydrate and making it as an option to transport and store natural gas, in hope that it will be made as a viable option in transporting natural gas to the customer.

1.2 Problem Statement

According to American Petroleum Institute (API), the forecasted demand for natural gas in 2010 decreases a little before the demands continues to grow from 2012 to 2016 (American Petroleum Institute, 2009). (Please refer to Fig A1 for the graph to see the projection demand of natural gas). Globally, natural gas is commonly used as source for electricity and as world population increases, the consumption of natural gas will also increase. Supplies is said to be abundant worldwide, according to studies conducted by MIT (Connors, et.al, 2010). In the same study, one of the highlight is that the total delivery cost to international market is dependent to transportation cost, in which related to the distance of the route.

Methods used to transport natural gas are pipelines, liquefied natural gas (LNG), liquefied petroleum gas (LPG), compressed natural gas (CNG), gas- to-liquid, gas-to-commodity, gas-to-solid and gas-to-power. Pipelines are effective for short distance only; it is costly to build for a very long distance especially those of the subsea pipelines. The major way to transport natural gas is LNG using special tankers. The transportation cost of LNG has been reduced greatly due to the development in thermodynamic efficiency. The setbacks of LNG are the processing cost and it is not suitable for small- capacity shipping (Mokhatab, et.al, 2006; Speight, 2007). Another method currently under research is gas-to-solid, in which the natural gas is converted to solid form and transports them in ships. Gas hydrate is considered a good form for natural gas transportation.

A study made by Romanow in 2000 estimated that almost 60% world gas reserves are stranded reserves. Stranded reserves are reserves that are located far away from any processing plant in which transporting the gas to the end point (customer) is not feasible. Plus, the current trend for energy exploring is now moving to ultra-deep reserves where it calls for better technology and engineering knowledge. For these reserves, pipelines and LNG may not be a good choice as transportation option (Hidney & Parrish, 2006).

This study is to see the feasibility of transporting natural gas in forms of gas hydrate by performing an economic evaluation of a proposed gas hydrate process and evaluate the feasibility by comparing the economics with the major method which is LNG. The study would show the possibility of having a new method of transporting natural gas and serves as a starting point to explore other usage of hydrates.

1.3 Objective

The purpose of the study is:

i. To evaluate the economics of processing natural gas by converting it to gas hydrate via proposed process.
ii. To determine the feasibility of transporting natural gas in gas hydrate form.

1.4 Scope of study

The scope of the study comprises of:

i. Understanding the process of converting natural gas into gas hydrate.
ii. Economic evaluation of a proposed process.
iii. Economic feasibility of transporting natural gas in gas hydrate form using the proposed process as the processing route.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL REVIEW ON HYDRATES

Hydrocarbon of small-sized molecule, with sufficient amount of water and adequate condition can form hydrates. The inclusion of the 'guest' molecule inside the water lattice stabilizes the alignment of the host molecule, thus precipitate as solid (ice-like structure). The structure of the hydrates is divided into three namely Type I, Type II and Type H. Each structure has its own lattice structure and physical properties. Further research shows that there exists a relationship between sizes of the guest molecules and the types of lattice structure that it will form (Carrol, 2009). (Please refer Fig A2 for the chart that shows the relations between molecule size and type of lattice structure).

Aside from the three conditions needed for molecules to form gas hydrate, there are other factors that could improve the formation of gas hydrate. Multiple researches show that the factors are:

i. Turbulence

Agitation and stirring affected the rate of hydrate formation. In natural gas processing, the hydrate forms in pipeline section where the velocity is high and narrowing pipelines.

ii. Free water

Hydrate formation requires sufficient amount of water. The presence of free water could help enhancing the hydrate formation since it increases the gas-liquid surface interface, which is the nucleation site for the hydrate.

iii. Nucleation site

In a pipeline, an imperfection site (damaged or corroded) could be a good nucleation site for hydrate to form.

Commonly, the process route for natural gas hydrate transport is as in Fig 1 (Mannel and Puckett, 2008):

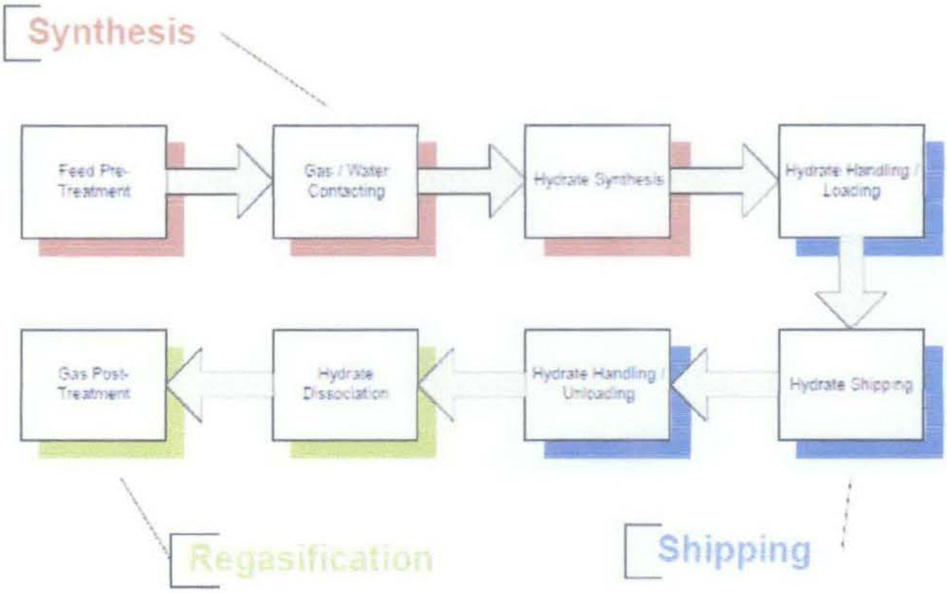


Fig 1 Process diagram for gas hydrate production

Many researches have been conducted to propose a feasible process route in converting natural gas into gas hydrate; the common process diagram as shown below (Danesh, et.al):

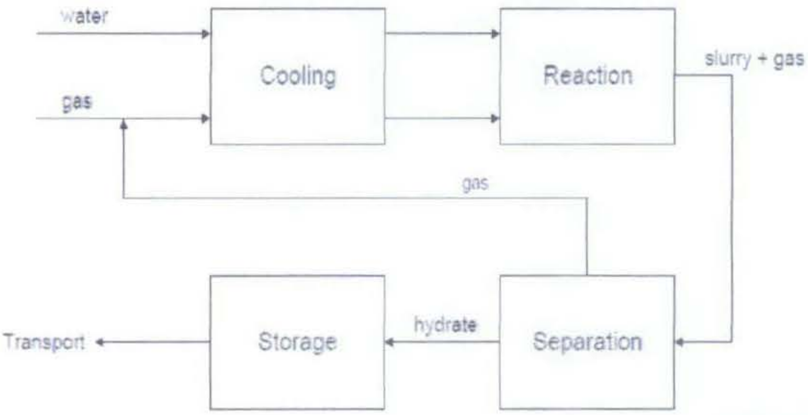


Fig 2 Process route for gas hydrate synthesis

2.2 Previous research on transporting natural gas as hydrates

Storing and transporting natural gas as gas hydrate has been researched extensively in Japan, Norway, England and US. (Please refer Fig A3 in the Appendix A for other process route being suggested by these nations). Researchers in Japan and Norway have come up with their own process route. In Japan, experimental plants have been set up by Mitsui Engineering and Shipbuilding Co., Ltd (MES) and have managed to produce natural gas hydrate in pellet form (Kanda, 2006).

Various economic feasibility studies have been reported. From the experimental plan built by MES Japan, they have concluded that it is feasible to transport natural gas as hydrates in some condition. They have come up with two cases for conceptual design and economic feasibility study. LNG ocean transport chain of same scale with the year's gas market price is used for comparison study. The result highlighted the initial cost for the hydrate transport chain is significantly lower (by 23-27%) than the LNG transport chain due to these reasons:

i. Equipment which made up the hydrate production plant is mostly a general merchandised product and relatively easy to obtain.
ii. Hydrate utilizes much higher storage temperature (close to room temperature) than LNG which needs to be store at (-162°C).
iii. Currently, hydrate ships are for small-volume transport. While the initial cost of hydrate ship is low, the feasibility of shipping hydrate reduces as the amount that needs to be exported is larger and the distance is bigger.
iv. Small LNG carrier is higher in unit cost than a normal-sized LNG ship carrier.

Please refer to Fig A4 in Appendix A for graphical representation of the findings. They also concluded that as their finding suggest, gas hydrate is feasible for smaller customer such as independent power producer and small gas provider in small cities.

Another research done by Mannel and Puckett in 2008 also highlights the same result as done by MES Japan. They had found that total annualized cost for LNG is lower than of hydrates because of the lower shipping cost due to greater energy density of LNG as compared to hydrate. For hydrates to make the same amount of energy being transported, more ships are needed, hence the increase in cost. LNG also gives better return of investment (ROI) than hydrates when the distance is greater. (Please refer to Fig A5 and Fig A6 in the appendix for the associated graph). Hydrates are deemed possible for short distance and small capacity.

As highlighted in Mannel's report, the feasibility study for transporting hydrates should consider these two components:

i. The costs associated with the synthesis and decomposition of natural gas hydrate.
ii. The costs of transporting the gas hydrate

Although the process diagram is basically the same, there is no established industrial synthesis for hydrates. Many of them are still in pilot testing stage and many research journals reported different technology to synthesis their end product. As noted by Hao Wenfeng in his journal, the current feasibility study that have been done is process specific, is conducted using small-scale reactors and has not yet address some problems that might occur during plant scale up (Hao, et.al, 2008).

2.3 General review on LNG

The most common way of transporting natural gas is by processing the gas into liquefied natural gas (LNG). Typically, LNG is consists of 85-95 percent of methane, the main component of natural gas. LNG is colorless, odorless, noncorrosive and nontoxic. The process of processing natural gas into LNG reduces the volume of the gas by the factor of 600. Ship carrier, tanker and pipeline are common ways to transport LNG to the intended customer. Currently, the market for LNG increases as the demand for natural gas increases across the globe. Japan has been the major LNG client for more than 30 years, and the market is growing steadily. Malaysia is the second largest exporter of LNG, behind Qatar in 2007. Below is a summary of properties of LNG in comparison with other fuel, as see in Table 1:

Table 1 Summary of Property Comparison of Some Fuels

Properties	**LNG**	**LPG**	**Gasoline**	**Fuel oil**
Flash Point (^{0}F)	-306	-156	-50	140
Boiling Point (^{0}F)	-256	-44	90	400
Flammability Range in Air (%)	5-15	2.1-9.5	1.3-6	N/A
Toxic	No	No	Yes	Yes
Carcinogenic	No	No	Yes	Yes
Flammable Vapor	Yes	Yes	Yes	Yes
Forms Vapor Cloud	Yes	Yes	Yes	No
Stored Pressure	Atmospheric	Pressurized (atmospheric if refrigerated)	Atmospheric	Atmospheric

The value chain for the natural gas processing into LNG involves these steps (Hidney & Parrish, 2006):

1. Natural gas treating (feed pretreatment)
2. Liquefaction cycle
3. Natural gas liquid condensate removal
4. Storage and loading

Process flowchart for common processes to transport natural gas can be found in Fig A7 in Appendix A. Natural gas that is being processed into LNG needs to be treated first before going into the liquefaction cycle. This is to avoid solid disposition inside the heat exchanger later.

Liquefaction plant is the heart of the LNG chain; it is the main section of the chain where the natural gas is being transformed into LNG. In the liquefaction plant, treated natural gas is being cooled down to cryogenic temperature, usually -132 0C, using a large cycle of refrigeration chain. Common methods for liquefaction cycle are Joule-Thompson expansion and expansion in an engine doing external work. The flow charts for both methods can be found in Appendix A, Fig A8.

The end product is either on ground storage or loaded for transport. Ground storage of LNG is a special storage tank which has two layer of wall for insulation. The tank employs auto-refrigeration process in which the boil-off LNG vapor is being released into the atmosphere, to keep the pressure inside the tank constant, preserving the cryogenic temperature inside the tank.

Tankers are used to transport LNG to fuel stations or remote land area. Special ships are used to transport the natural gas internationally while pipelines are for short distance transport. LNG ship carriers are highly sophisticated ship and since its first build in 1970s has undergone large advancement in order to satisfy the increasing demand of LNG. Only a few numbers of shipyard capable in constructing a LNG ship carrier. Although processing natural gas into LNG requires many rotating equipment under high pressure and low temperature, LNG has been widely used for natural gas transportation as the growth of the technology for the process in thermodynamics makes the process more economical for large-volume transport.

There have been very few accidents related to LNG in operation as well as during transport. This can be attributed to stringent safety and hazard precaution at place as well as the properties of LNG itself.

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY AND ACTIVITIES

The study can be divided into two sections; each with its own activities. The sections are:

i. Cost in association with synthesis of the hydrates.
ii. Cost in association with transporting the hydrates.

Under the first section, the activities are as listed:

i. Coming up with a new process to synthesis gas hydrate. This is done by understanding the kinetics of the process and comparison with proposed process flow in literature.
ii. Finding the capital investment of the proposed process. This includes finding price of the raw materials, energy consumption of each equipment and equipment cost.
iii. Evaluate the economics of the process and comparison with LNG.

Under the second section, the activities are as listed:

i. Finding the initial cost of shipping. These include the cost of the ship, other cost related to transferring the end products.
ii. Finding the transportation cost of hydrates.
iii. Comparison between the transportation cost of hydrates with transportation cost of LNG. For this, the distance and volume to be transported is kept constant to ease the comparison

CHAPTER 4
RESULT AND DISCUSSION

4.1 PROCESS SUGGESTION AND FLOWSHEET

A flow sheet for the hydrate formation process has been developed. There are three component that makes up the process; reactor, separator and freezer. These three makes up the main process line for the process of transforming the natural gas to gas hydrate. Shown below is the current flow sheet for the process.

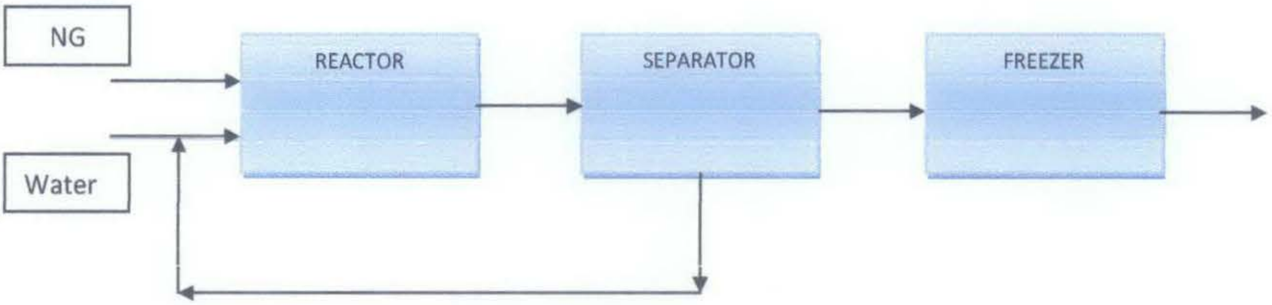


Fig 3 Suggested process flow sheet

The reactor is the heart of the process; this is where the reaction took place. The natural gas and water are being fed into the reactor. The natural gas molecule will then being absorbed inside the water hydrate cage and form natural gas hydrate. The end product is slurry of gas hydrate with excess water. The separator separates the excess water from the product, where the water is recycled back into the reactor. The recycled water acts to improve the efficiency of the process by reducing the overall water feed used as well as improving the nucleation rate of the process, since some hydrate seed may be inside the water. The hydrate is then sent to the freezer, to cool down the hydrate to storage temperature, before being stored and shipped.

When the reaction takes place, there will be some heat released due to the formation of the hydrate. The heat released will be captured by the refrigeration cycle outside of the reactor. Refrigerant R-134a is used as the cooling fluid in the cycle. R-134a absorbs the heat released inside the reactor, keeping the temperature inside the reactor constant.

The refrigeration cycles doubly acts as heat absorber for the reactor as well as the refrigerator for the freezer. The fluid enters the compressor and enters the condenser. This liquid refrigerant then enters the throttle valve, undergoing expansion. The cooled fluid then enters the storage section, where it acts as cooling medium for the freezer. The slightly cool fluid then enters the reactor, to absorb the heat from the hydrate formation reaction and once again enters the compressor to complete the cycle.

4.2 Assumptions for the suggested process

The basis of the calculation is 2 million ton per year of natural gas processed. In order to complete the material balance as well as simplify the calculation, some assumptions are being made.

1. The natural gas fed into the reactor is entirely made of methane.

   Although in nature, natural gas contains some other type of alkane, especially ethane and propane, it is much easier to observe the reaction if there is only one reaction occurs (only one species is being reacted). Plus, many data and correlations published for the reaction of natural gas and water to form hydrate uses pure methane as their main feed.

2. Type of crystal structure of the hydrate formed is structure sII.

   According to Sloan (2008), although a pure methane gas forms sI-type hydrate, a small impurity of the gas (inclusion of small amount of propane and ethane in the gas) could change the hydrate structure into a sII-type hydrate. In nature, the natural gas contains small amount of ethane and propane, thus it is better to predict that the formed crystal is a sII-type hydrate structure.

3. The hydration number of the hydrate formed follows Villard's Rule.

   Villard's Rule states that the dissociable hydrate compounds that forms from the reaction of water and natural gas can be expressed by the formula $M + 6\ H_2O$, where M is the molecule of the respective gas (Sloan, 2008). Although is not ideally accurate, this approximation is good for initial calculation.

4. Many physical properties of the hydrate follow the properties of a water ice. A hydrate crystal with all cavities filled for a sI and sII structure consists of 85 mol% of water. Due to nonstoichiometric nature of hydrate, the amount of water can be variably higher than 0.85 (Sloan, 2008). With this amount of water, it is safe to assume that some properties of the hydrate (such as density of the hydrate) can be same as the properties of ice.

4.3 Operating parameter of the proposed process

The choice of the parameter is based on the kinetics of the reaction as well as comparison with proposed processes by other research. The relationship between pressure and temperature for pure methane is shown by Fig 4, suggested by Sloan et.al in 2001.

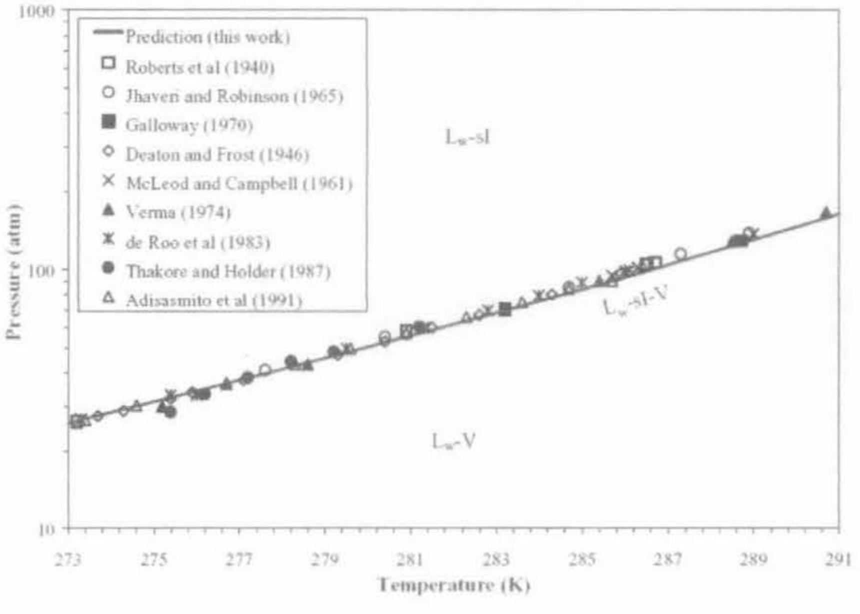


Fig 4 P-T relationship for pure methane

From Fig 4, relationship between pressure and temperature are linear. The higher the operating temperature, the pressure required to nucleate a methane hydrate increases as well. It also shows that for pure methane gas, there could be only one hydrate structure form, which is sI. However, the relationship between pressure and temperature as well as phase structure of the hydrate gets complicated when mixtures of gas are in the system. In reality, natural gas is consists of mixtures of methane, ethane, propane and some inert gas. Small addition of impurities of the gas could change the crystal structure, as well as the phase structure of the system. Different pressure can also affect the phase diagram of hydrate. The effect of pressure and gas mixture to the phase diagram can be illustrated below, as shown in Fig 5.

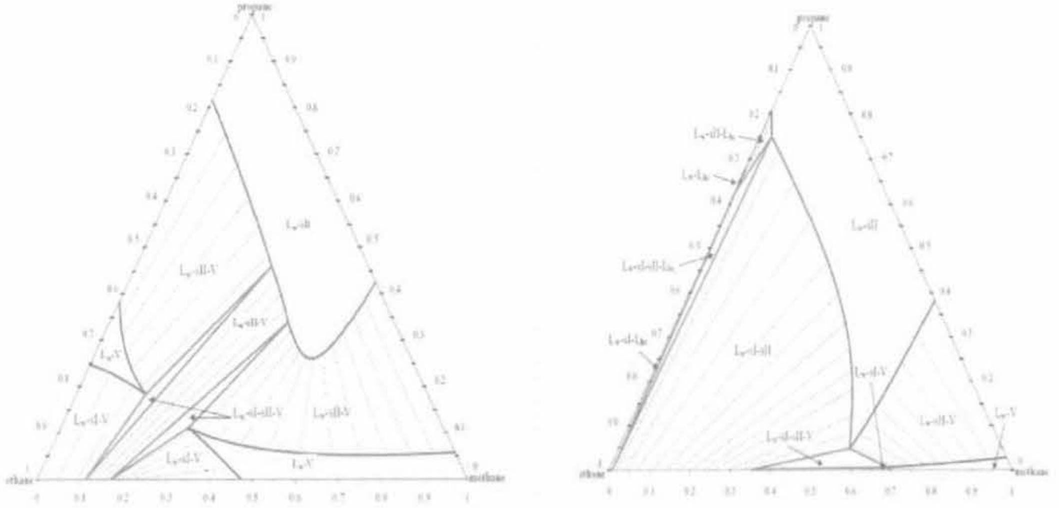


Fig 5 Phase diagram of methane + ethane + propane at 277.6K with different pressure; 11atm (left) and 15atm (right)

For that, in order to obtain a feasible operating pressure and temperature for the hydrate process, a good understanding of hydrate formation is needed. Comparison with different proposed process also helps in choosing the operating temperature. The table below shows reported operating pressure and temperature proposed by different literature.

Table 2 Reported operating temperature and pressure by different proposed process

Proposed Process	Operating Temperature	Operating Pressure
Japan (MES 2002)	275 K	50 atm
BG	283-288 K	60-90 bar
Norwegian	283 K	50 bar
Javanmardi et.al	300 K	60 bar

4.4 Reactor selection and design

Reactor is the heart of the process, as this is where all reaction to transform the feed into the intended product. A good choice of reactor helps in making sure that the reaction takes place smoothly.

Two common type of reactor are CSTR and PFR. The advantage and application of each reactor is shown in the Table below.

Table 3 Comparison of CSTR and PFR

TYPE OF REACTOR	APPLICATION	ADVANTAGES	DISADVANTAGES
Continuous Stirred Tank Reactor (CSTR)	• Operated at steady state • Perfectly mixed • Uniform temperature throughout the reactor	• Good temperature control • Low operating cost and maintenance cost • High selectivity • Highly uniform product	• Large volume • Residence time cannot be control due to reactant coming and leaving continuously.
Plug Flow Reactor (PFR)	• Large scale operation • Fast reaction • High temperature reaction	• High volumetric unit conversion • Run for long period of time without	• Temperature is hard to control • Maintenance cost is higher than CSTR.

	- Good for gas polymer	maintenance

Hydrate formation requires high pressure and low temperature. A large volume of water needs to be used in order to fully transform all gas feed into hydrate. A reactor with an easy temperature control would help maintaining the temperature inside the reactor, as the increase of temperature inside the reactor would decreases the efficiency of the process. For these reasons, the best choice for reactor would be CSTR.

As indicated by Hao et.al, stirring velocity and time has significant impact on the reaction rate of hydrate growth. The findings are shown in Fig 6 and Fig 7 below.

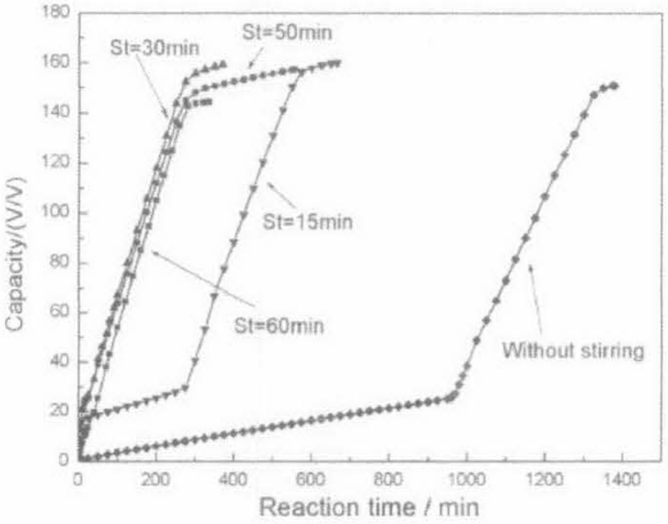


Fig 6 Effect of different stirring time on reaction rate (stirring velocity = 320 rpm, P = 5.0 MPa)

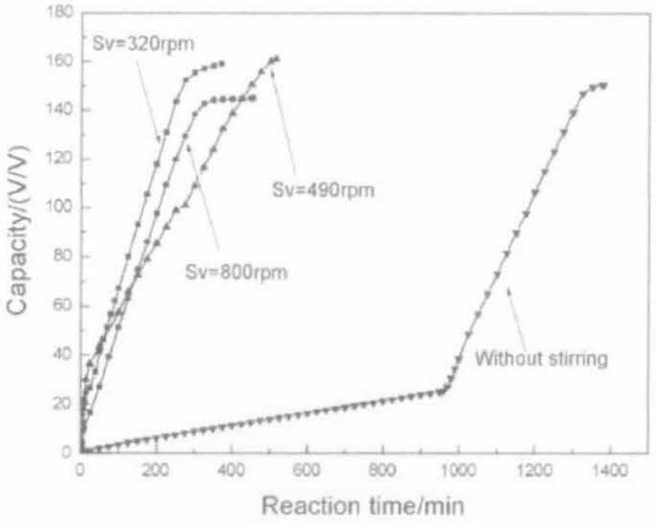


Fig 7 Effect of different stirring velocity on reaction rate (Stirring time = 30 min, P =5.0 MPa)

From both figures, it can be concluded that agitated or stirred reactor is a good choice for large capacity process as it quickens the reaction rate of the process. The conclusion derived from Fig 7 is that increasing the stirring time decreases the reaction time and increases the capacity, but too long stirring time is also not good, as it again increases the reaction rate for the process. No stirring or too short stirring time do not help the process to attain good diffusion effect, but too long stirring time will decompose the formed hydrate, hence increasing operation cost.

From Fig 8, stirring velocity is also important to hydrate formation process. Static and too high stirring velocity does no good for the process. Stirring generally helps the process to enter growth period rapidly. No stirring lowers down the diffusion rate of the hydrate, which lengthens the reaction rate. Too high stirring velocity does not help much in increasing the diffusion rate either.

A research on potential energy savings in hydrate plant by Daimichi et.al of University of Tokyo reveals that energy consumption in the reactor and by the stirrer decreases with the increasing rate of reaction rate.

Large liquid-gas surface contact area increases hydrate nucleation rate. This is because it is on the two-phase boundary film where the nucleation starts. In order to increase the surface contact area, the feed gas should be dispersed in fine bubbles. A bubble diffuser, as well as membrane should be able to disperse the gas. Bubble diffuser has higher operating cost due to energy consumption, while membrane has large upfront investment. For the purpose of this process, membrane is used.

After deciding the type of reactor for the process, the next step is to design the reactor. The volume of the reactor can be obtained by determining the rate of the reaction. To estimate the rate of reaction, the equation proposed by Englezos (Englozes et.al, 1987) is used:

$$R = 4\pi K \mu_2 (f - f_{eq}) \qquad \text{Equation 1}$$

Where R is rate of hydrate formation, K is the empirical kinetic parameter, μ_2 is the second moment of the particle size distribution of hydrate crystal in the reactor, f is fugacity of the gas in the reactor and f_{eq} is fugacity of the equilibrium pressure for hydrate in the reactor temperature.

Fugacity required for the calculation is obtained by using virial equation estimation. The second moment of the particle size distribution is obtained using these two equations (Englezos et.al, 1987)

$$\mu_0 = \frac{3M(N - N_{eq})}{4\pi V \rho r^3} \qquad \text{Equation 2}$$

$$\mu_2 = 4r^2 \mu_0 \qquad \text{Equation 3}$$

Where μ_n is nth moment of particle size distribution, M is the molecular mass of the hydrate, N is the number of moles of gas in the solution at reactor condition, N_{eq} is number of moles of gas at equilibrium pressure in reactor temperature, V is the volume of water for the number of moles calculated above, ρ is density of hydrate and r is the mean particle radius for the hydrate crystals in the reactor.

The number of moles of gas in the solution can be solved using Henry's Law. The empirical kinetic parameter K is the reaction rate constant for hydrate formation. A research one by Bergeron et.al which determines the reaction rate constant of methane hydrate formation reveals that reaction rate constant increases with temperature following Arrhenius relationship, with activation energy of 323 kJ / mol. Using Arrhenius equation, the reaction rate constant for the proposed process can be determined.

After obtaining the reaction rate, the volume of the reactor can be obtained by this relationship:

$$V = \frac{Q}{R}$$

Equation 4

Where R is reaction rate for the proposed process calculated in equation 1, and Q is the flow rate of the gas into the reaction.

Membrane area size needs to be estimated. At first, permeate flow rates per unit area were calculated using Fick's law.

$$N_i = \frac{\varepsilon}{z} \Delta P_i$$

Equation 5

Where N_i is the flux of methane through membrane, ε is the permeability of the membrane to methane; P_i is the partial pressure difference across the membrane. One assumption made is that the hydrate formation occurs fast enough that the partial pressure on the water side of the membrane was negligible compared to the high pressure of gas side of the membrane. Permeated gas flow rate is calculated by the number of moles per second gas flow of the intended capacity. This permeated gas flow times the permeate flow per area will give the area of membrane needed.

Agitator power requirement is calculated by the following equation. Agitator power depends on the geometry of the agitator itself and type of reactor.

$$P = N_p \rho N^3 \frac{D^5}{g_c}$$

Equation 6

Where P is power requirement for the agitator, N_p is the dimensionless power number, ρ is density of the fluid inside the reactor, D is the agitator diameter, and g_c is gravitational constant.

4.5 Separator choice and sizing

To separate excess water from the hydrate, a separator is used. The type used in the process is a mechanical-physical separator, which is a decanter. Decanter uses the principle of settling and sedimentation in separating the particle from the fluid. The difference of density between water and hydrate is being used in order to separate hydrate from water. One assumption made is that the hydrate crystal is big enough and in large amount in which during settling, these particles would interfere with the motion of individual particles. For that, equations used for hindered settling can be used.

Settling velocity can be determined as equation shown below.

$$v_t = \frac{gD_p^{\,2}(\rho_p - \rho_l)}{18\mu}(\epsilon^2 \varphi_p) \qquad \text{Equation 7}$$

Where v_t is settling velocity, g is gravitational force, D_p is the diameter of the particle, ρ_p is density of particle, ρ_l is density of the fluid, μ is viscosity of the fluid, ε is volume fraction of the liquid, φ_p is empirical correction factor. Both ε and φ_p can be calculated using these equations.

$$\varepsilon = \frac{(\frac{\omega_f}{\rho_f})}{\left(\frac{\omega_f}{\rho_f}\right) + (\frac{\omega_p}{\rho_p})} \qquad \text{Equation 8}$$

$$\varphi_p = \frac{1}{10^{1.82(1-\varepsilon)}} \qquad \text{Equation 9}$$

Where ω_f is weight percent of the fluid in the slurry, ρ_f is density of the fluid, ω_p is weight percent of the particle in the slurry, ρ_p is density of the particle. After calculating the settling velocity, the area of the decanter can be estimated.

4.6 Freezer sizing

Freezer is used to cool down the hydrate to storage temperature. This is to ease the transport of hydrate. Here, the volume of freezer is calculated. The intended temperature for storage is 258.15 K. The refrigeration cycle provide the cooling medium for the freezer.

The time needed to freeze down the hydrate is approximated by Plank's model.

$$t = \frac{L\rho}{T_{tf} - T_d}\left(m\frac{Y}{h} + n\frac{Y^2}{k}\right) \qquad \text{Equation 10}$$

Where t is freezing time, L is latent heat of freezing of the product (latent heat of freezing for ice is 6013.4 kJ / kmol) , T_{tf} is initial freezing point for the product, T_d is the temperature of the cooling medium, Y is characteristic length for the freezer, h is surface heat transfer coefficient, k is thermal conductivity of the product, m and n are geometric coefficient. After the freezing time is calculated, the volume of the freezer can be obtained.

4.7 Final operating detail

The complete process flowchart for the proposed process is shown as Fig 8 below.

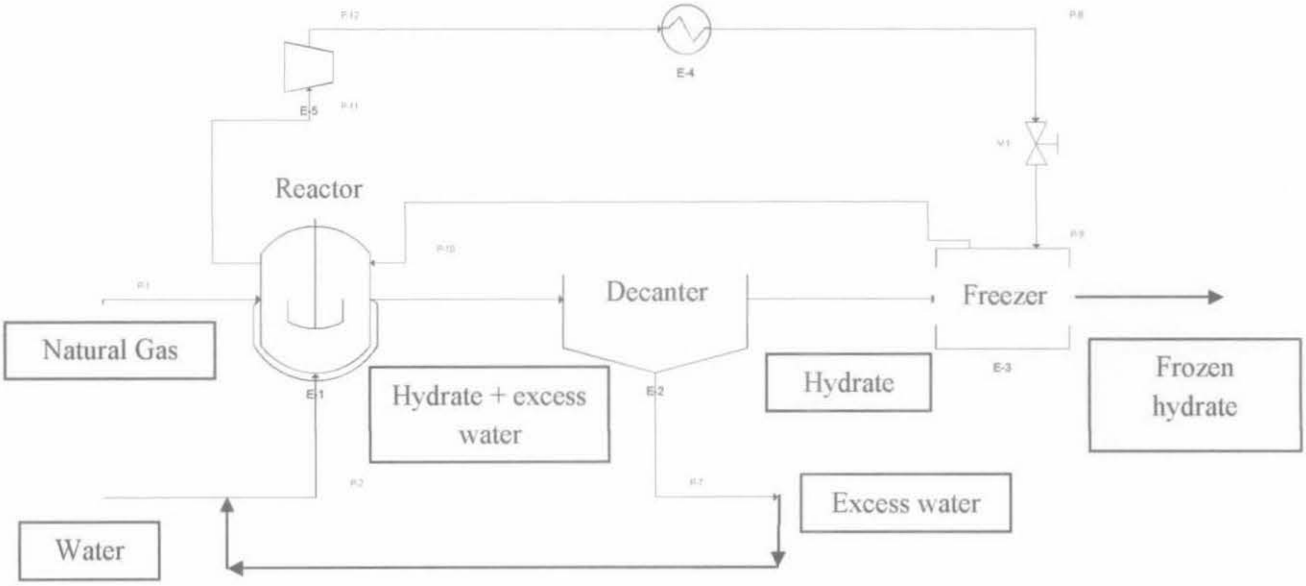


Fig 8 Complete process flowchart for the proposed process

Operating parameter for the proposed process is summarized as below:

Table 4 Operating parameter of the proposed process

OPERATION PARAMETER	
Pressure of reactor	60 bar
Temperature of gas feed	300K
Temperature of water feed	300K
Temperature of stored hydrate	258K
Plant life	20 years
Operation days	330 days

The lists of main equipment as well as its sizing details are as shown below:

Table 5 List of equipment and its sizing detail

EQUIPMENT	SIZE	UNIT
Propeller	1767.67	kW
Compressor	35555.05	kW
Heat exchanger	9431.27	m^2
Reactor	98509.73	m^3
Freezer	43.34	m^3
Decanter	58.67	m^2
Membrane	28862.78	m^2

4.8 Economic evaluation of the process

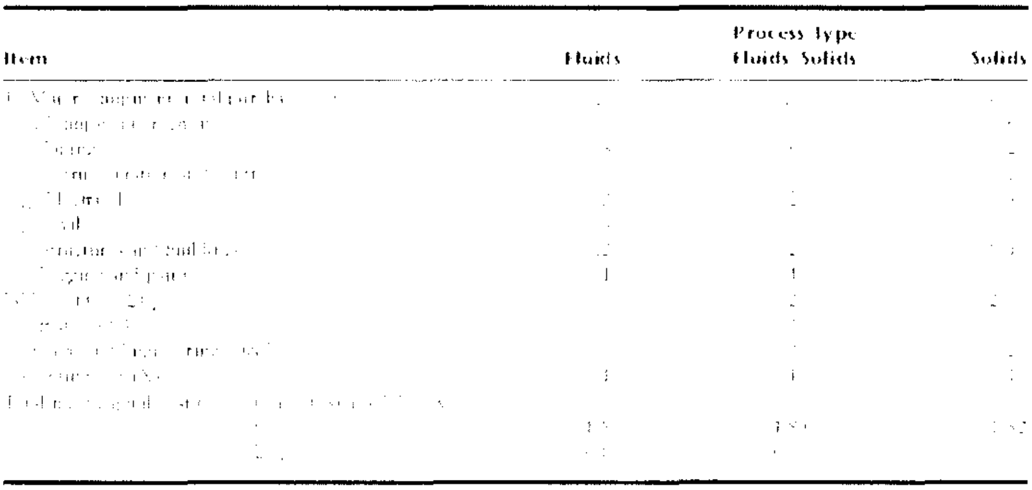
4.8.1 Fixed capital cost

From the sizing of the equipments as well as other cost to run the plant, the economics of the plant can be evaluated. This analysis could determine the feasibility of the proposed process in transporting natural gas as hydrate.

Fixed capital is the cost of setting up the plant. This includes:

1. The fixed battery limits investment – the cost of the plant itself.
2. The modification and improvements that must be made to the site infrastructure, known as offsite investment
3. Engineering and construction cost.
4. Contingency charge

For fixed capital of this plant, the detailed factorial estimate technique is used. Typical factors used in estimating fixed capital cost are shown in the Fig 9 below.



Item	Fluids	Process Type Fluids Solids	Solids

Fig 9 Typical factors used in detailed factorial estimate (Sinnott)

Preliminary estimated total cost for installing equipment is available in books. This factor is made for equipment made from carbon steel. To make the estimation to be more accurate, the material factor is used, shown as Fig 10 below. The data used CE index at 2006 – 478.6. The CE index at May 2011 is 618.3. The cost will be corrected for inflation. The exchange rate of US Dollar to RM is 3.17

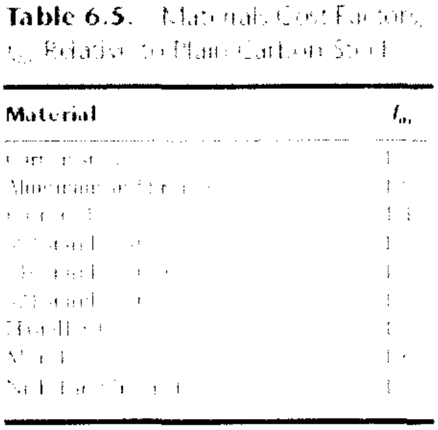


Table 6.5. Materials Cost Factors, f_m, Relative to Plain Carbon Steel

Material	f_m
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

Fig 10 Factor to estimate equipment cost of different material of construction

The estimated equipment cost for the proposed process is shown in Table below:

Table 6 Estimated cost for main equipments for proposed process

EQUIPMENT	SIZE	UNIT	ESTIMATED COST (RM MILLION)
Propeller	176.767	kW	0.49
Compressor	35555.05	kW	1.66
Heat exchanger	9431.27	m^2	12.66
Reactor	98509.73	m^3	40.47
Freezer	43.34	m^3	0.81
Decanter	58.67	m^2	0.10
Membrane	28862.78	m^2	75.07

Using the factors in Table, the fixed capital for this plant is estimated. The factor used is for fluid-solid process type. The total cost is calculated using this equation. The fixed capital calculated for the process as well as fixed capital for LNG liquefaction plant is given as Table 7 below:

$$C = \sum_1^M C_{e_{i,CS}}\left[\left(1+f_p\right)f_m + \left(f_{er} + f_{el} + f_i + f_c + f_s + f_l\right)\right] \quad \text{Equation 11}$$

Table 7 Comparison of fixed capital cost for proposed process and LNG

Fixed capital cost (RM million)	210
Fixed capital cost for LNG (RM million)	400
% savings	47.5

The estimated total fixed capital investment for the proposed process is RM 210 million. For the same basis of operation, the main process plant for LNG which is liquefaction plant costs RM 400 million (Economides, 2005). The difference of fixed capital cost for both plants is 47.5 percent. The difference can be attributed to several reasons. LNG liquefaction plant uses many rotating equipment and uses specialized equipment, which is costly in terms of building and installation. Cooling down gas to cryogenic temperature would require many compressors in the refrigeration cycle. Although the technology for LNG is quite advance, this high-technology process generally costs a lot since it uses special equipment. In comparison, the equipment used in hydrate plant is readily available in market, and uses less rotating equipment. The technology behind hydrate is still quite low, as the hydrate process is still under extensive research. This could be the contributing factor of small fixed capital for hydrate process in comparison to LNG.

4.8.2 Operation and Maintenance cost

Operation and management cost for the proposed plant can be estimated from the equation given (Douglas, 1988).

$$O\&M = 1.031\,(raw\ materials + utility) + 0.186\,(onsite) + 2.13(operating\ labor) + 0.0256\,(revenue)$$

Equation 11

The price of natural gas in Malaysia (industrial tariff) is RM 15/mmBtu. The electricity tariff for industrial tariff (medium) is taken as RM 0.30/kWh. Water tariff is taken as RM 1.34 / m^3. For onsite cost, the fixed capital is being divided by the plant useful life, which is 20 years. The labor cost per day for one person is set at RM 100. The required manhour/day-processing step can be estimated by this equation (Douglas, 1988).

$$Operating\ labor = \exp\left(2.791 + 0.234\ln(capacity)\right) \qquad \text{Equation 12}$$

Where capacity is stated as ton of natural gas fed into the reactor per day. It is assumed that for this wok, six processing steps are required. Dividing the equation with six will give the number of labor needed. The table that shows the summary of calculation for hydrate and LNG is shown in Table below.

Table 8 Comparison of operating cost of hydrate and LNG

UNIT	**PRICE/UNIT**	**TOTAL PRICE/DAY (RM THOUSANDS)**	
		NGH	**LNG**
Cost of natural gas	15	45454.55	45454.55
Cost of electricity	0.3	11.52	92.20
Operating labor	100	13.50	13.50
Revenue	5.61	62454.55	62454.55
Onsite	-	19.94	60.61
O&M cost (RM million)		48.51	48.68

Operating cost for hydrate is slightly smaller compared to LNG. LNG due to the usage of many rotating equipments, utilizes more electricity than hydrate plant. Based on operating cost, it can be concluded that hydrate and LNG has comparable value.

4.8.3 Transportation of natural gas

This section is to evaluate the feasibility of transporting natural gas in hydrate form. The transportation type under study is marine transportation. The data of shipping cost is shown below as Table 9.

Table 9 Details for shipping of NGH and LNG

DETAILS	**NGH**	**LNG**
Capital cost of one ship	80 million USD	400 million USD
Size of the capacity	250000 m^3	266000 m^3
Speed	15.4 knots	19 knots

The capital cost for a LNG ship is very expansive compared to NGH ship. LNG ship carrier is a specialized ship with very advance technology in place and in need of skilled labor, which can be very costly.

One of the effects that can be seen for this study is the number of ship required to carry specific demand to the customer. The amount of methane inside LNG and hydrate differs greatly. 1 m^3 of LNG contains 600 m^3 of methane, while 1 m^3 of NGH contains 170 m^3 of methane. If there is a specific energy demand, the amount of methane that both ships can carry will influence the number of ships required to carry the capacity. Fig 11 shows the relationship between demand and number of ships required to carry the capacity specified.

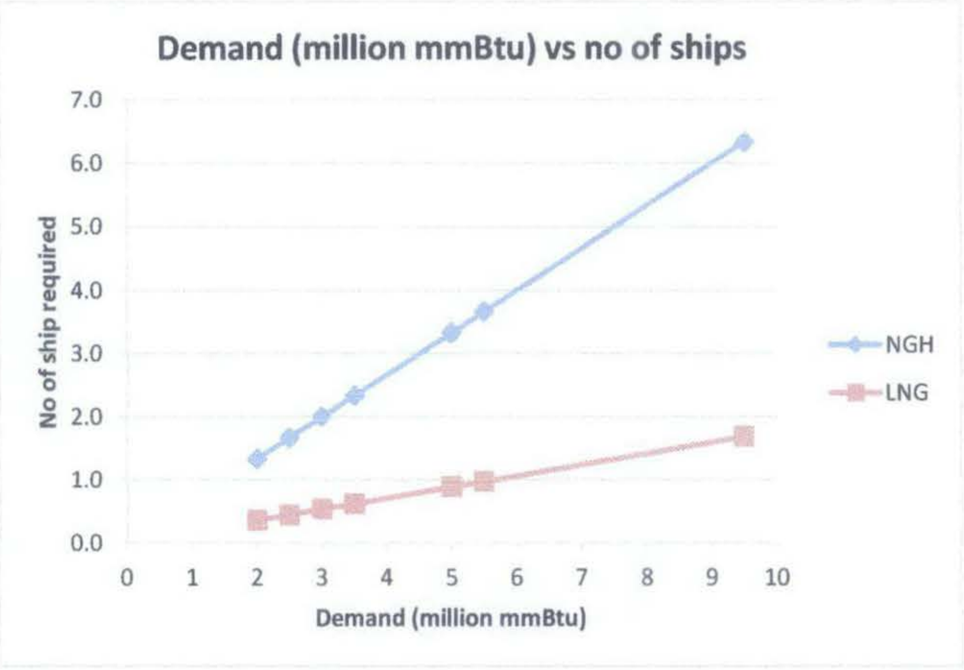


Fig 11 Relationship between energy demand and number of ships required.

From Fig 11, the number of ships required to carry specific amount of energy demand by customer increases greatly for NGH ships, as opposed to LNG ships. The amount of energy in NGH and LNG is directly related in the amount of methane inside, which has significance difference between the two. This causes the different no. of ships requirement to carry the specified demand. For example, at 6 million mmBtu, LNG ship required is 1, while NGH ship required is 4. The increasing number of ships required to deliver the required energy demand may increases the capital cost as well as operating cost, which may look unpromising. But there is large capital cost difference between the two ships.

Another analysis done is the number of days required for one NGH ship and LNG ship to reach the destination. Using the speed of the ships, the days required to reach destination is obtained. Due to the difference of power between the ships, the number of days needed for one ship to complete certain distance differs. The result can be seen in Fig 12 below.

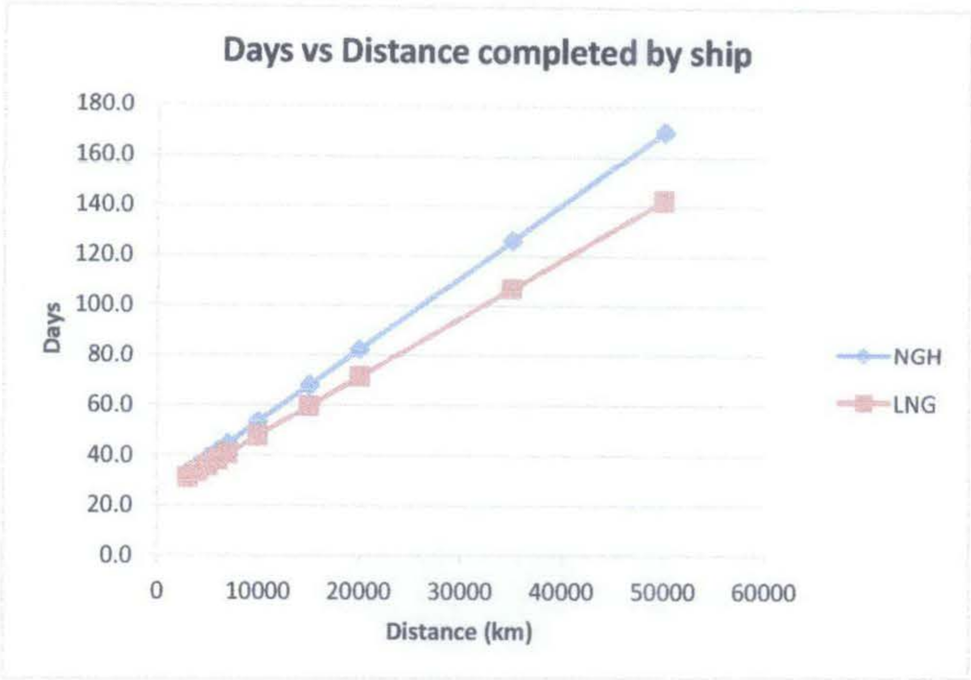


Fig 12 Relationship between distance of ship travel (going round) and days

From Fig 12, NGH ships require more days to reach the destination and coming back to the starting point compared to LNG ships. At distance less than 10 000 km, the days required to both ships to travel are comparable. After 10 000 km, with the increment of distance is greater, the gap between days required for NGH ship to travel with days required for LNG ship to travel is greater. Longer travel time will affect the shipping cost, especially the labor cost while on travel. This concludes that NGH is not suitable for long distance travel.

Another analysis done is the profit obtained by delivering the specified energy demand to customer. The number of ships needed will the ones calculated in Fig. The profit of natural gas is set at 9 USD per mmBtu. Here, the cost calculated takes into account the annual cost of operating the ship as well as annualized capital cost of the ship. The effect of travel distance is also added into the analysis. Fig 13 shows the relationship between profit and energy demand.

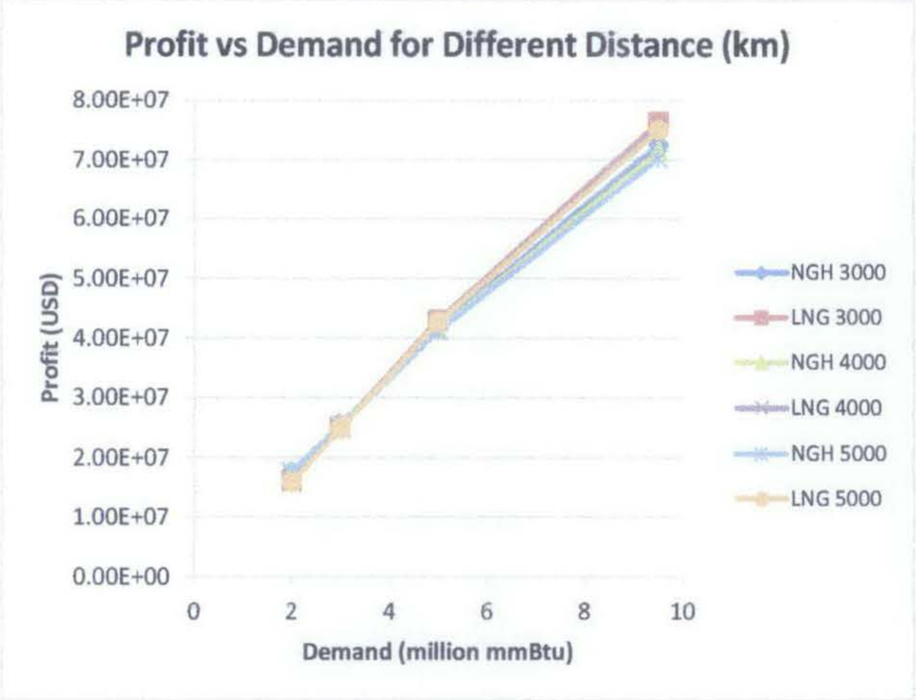


Fig 13 Relationship between profit and energy demand specified, on different distance.

As shown in Fig 12, profit for NGH and LNG depends strongly on the amount of energy demand by customer and the distance of the market from the port. This is because it influences the number of ship needed to supply the capacity, as well as the days required to ship these demands to the intended market. Large energy density for LNG as well as powerful ship makes LNG competitive in profit, especially for large demand and longer distance. NGH produces profit larger than LNG when the demand is less than 4 million mmBtu, which indicates the NGH can be a better alternative for small market transportation.

Conclusion that can be drawn from these three analyses is that transporting natural gas as gas hydrate does seems promising at this point. LNG remains the best choice to transport natural gas as the shipping technology advances makes LNG more economical for large-volume transport. NGH may be competitive for small to mid-size transportation, where the large capital cost for LNG does not seem competitive.

CHAPTER 5
CONCLUSION

5.1 CONCLUSION

Conclusions that can be drawn from the literature study are:

1. Natural gas is fast becoming a choice for fuel due to it being environment-friendly. The resource for natural gas is abundant and it can sustain the demand needed.

2. Many world reserves are stranded reserves. If these reserves can be tapped, the supply of the natural gas will increase greatly.

3. Current method of transporting natural gas such as pipelines and LNG might not be a feasible choice especially for small volume transportation.

4. Transporting natural gas in hydrate form seems like a viable choice. Previous research results show the possibility of gas hydrate being a method of transporting natural gas.

At the end of this project, the conclusions drawn are as follows:

1. A process flow chart has been proposed for transforming natural gas as gas hydrate. The operating parameter, choice of reactor, separator and freezer has been chosen.

2. The economics of the proposed process has been evaluated. Comparison with LNG is made to see any significant difference between the two processes. NGH has the advantage of low fixed capital cost and operating cost as oppose to LNG. Previous research has also arrived to the same conclusion

3. The preliminary feasibility of transporting natural gas as NGH has been conducted. Comparison with LNG is made to see any significant difference between the two

processes. NGH has the advantage of low capital cost for shipping, but the small value of energy in hydrate increases the number of ship required to deliver specified amount of natural gas to customer. LNG has the advantage of highly developed technology, large capacity and high amount of methane, which makes it suitable for large-volume transportation. NGH is then suitable for small to mid-sized volume transportation, where the large capital cost of LNG may seem uneconomical.

5.2 Recommendation

Some recommendation suggested to further improve the project:

1. A better cost estimation to increase the accuracy of the estimation.
   The estimation done for this project is preliminary, since there is limited data available. More data for costing could increase the accuracy of the estimation.

2. Use established process flow for transforming the natural gas into gas hydrate.
   Proposing a new process flow requires a lot more effort to understand the kinetics and thermodynamics behind the process, which could take longer time. An established process flow such as the Japanese can be used as the process flow for the process, thus eliminating the need to come up with a new one.

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APPENDIX A

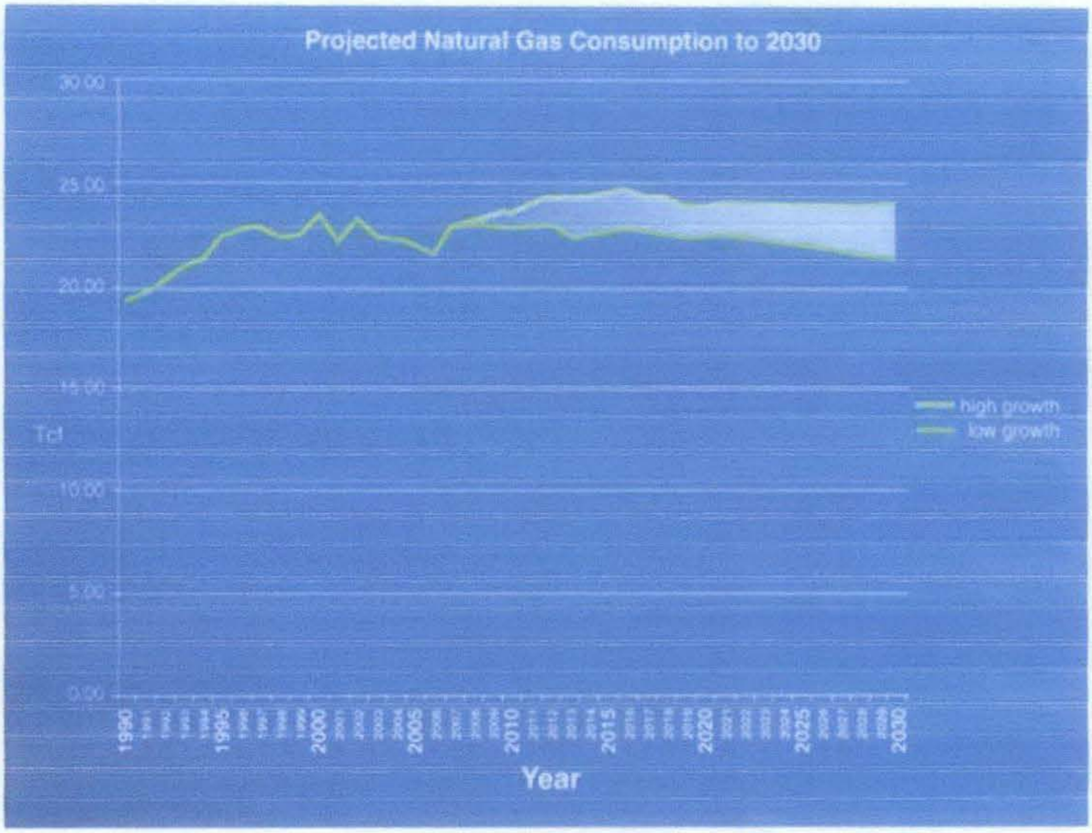


Fig A1 Graph of demand projection of natural gas

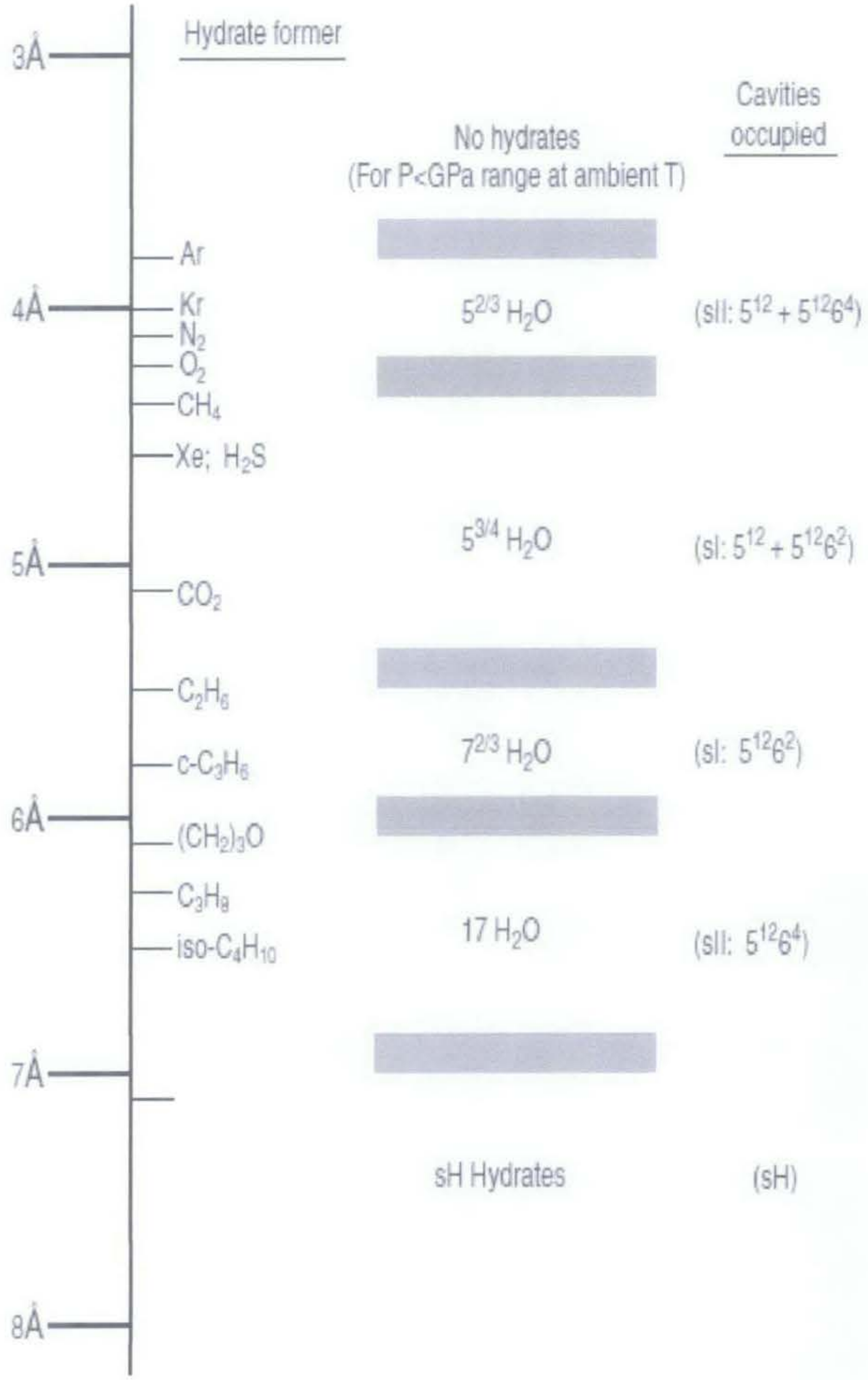
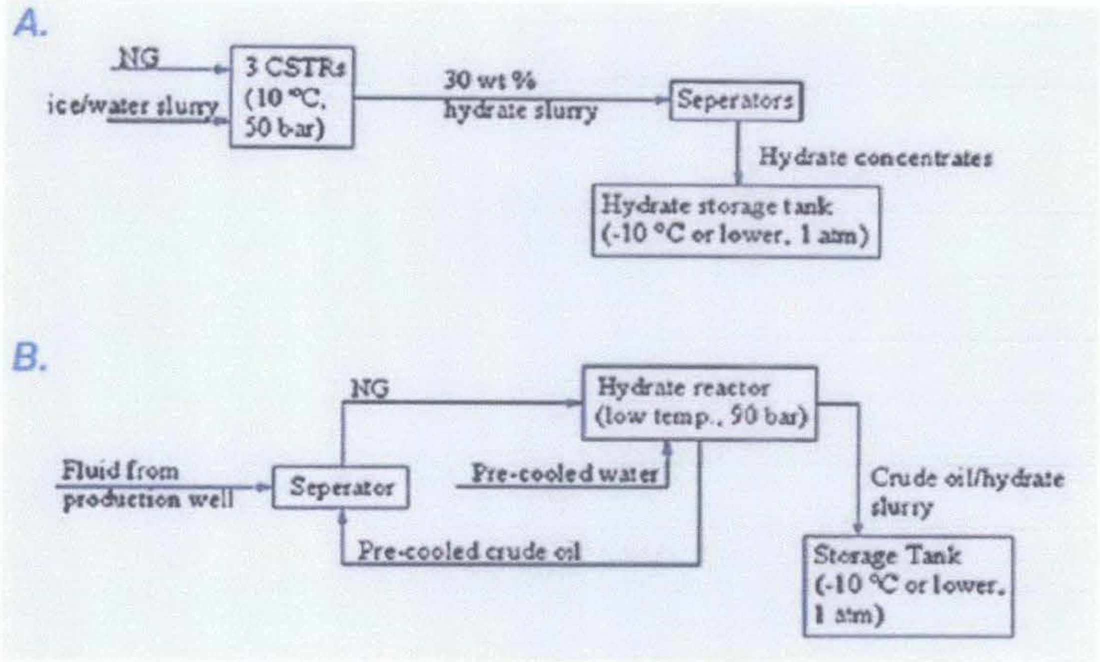
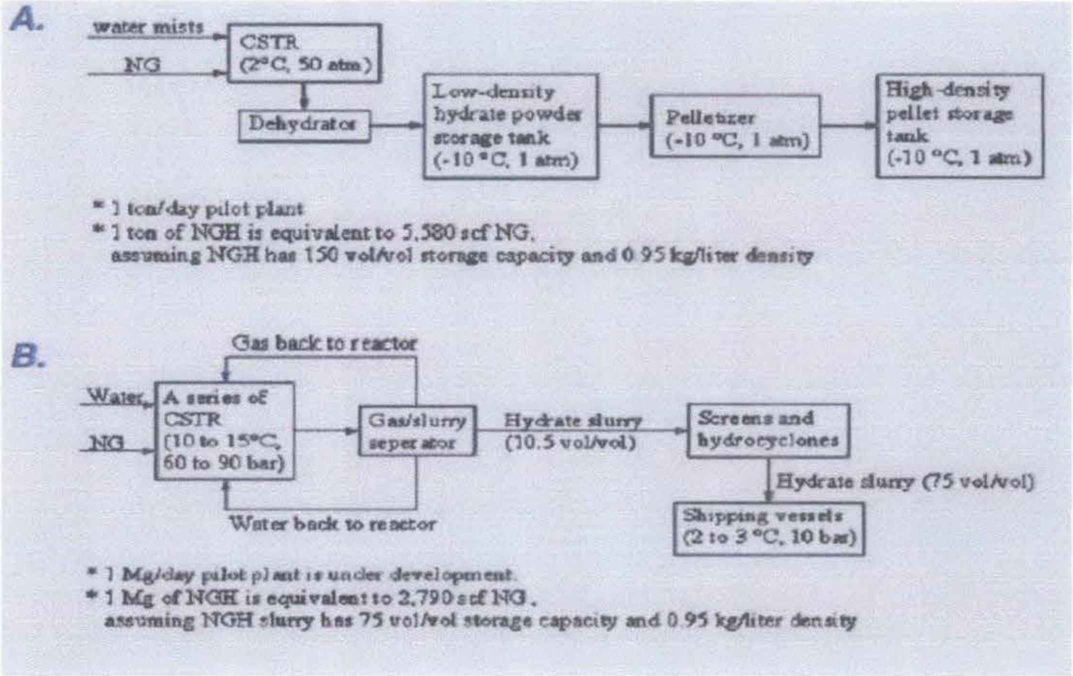


Fig A2 Chart of relation between molecule sizes with type of hydrate structure

I



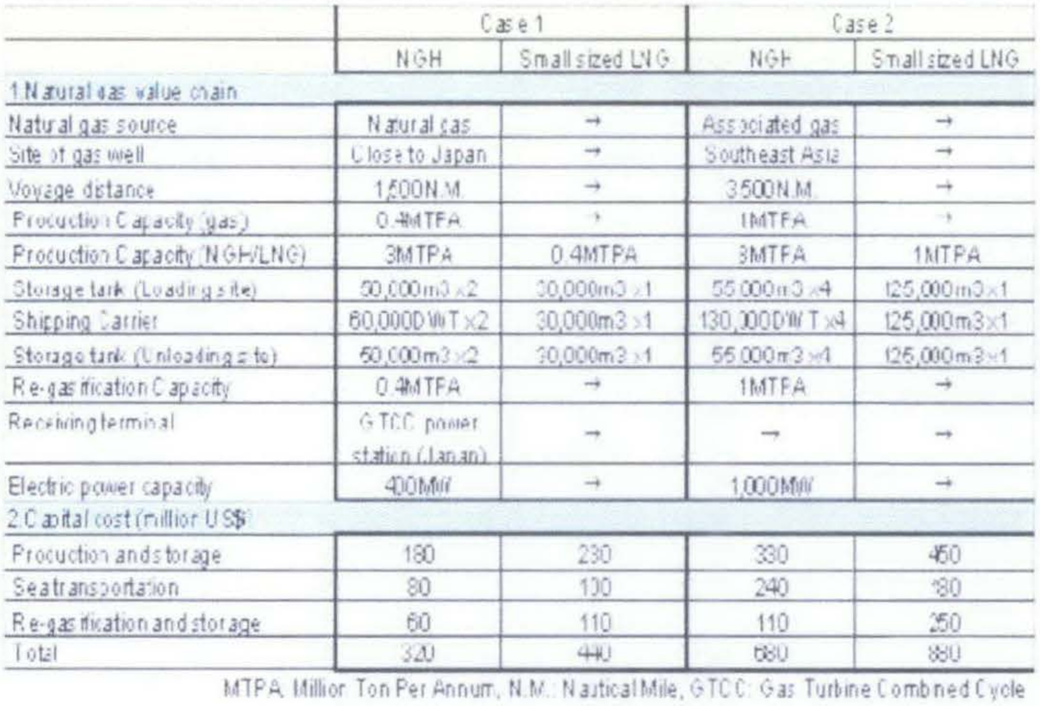
II



* 1 ton/day pilot plant
* 1 ton of NGH is equivalent to 5,580 scf NG,
assuming NGH has 150 vol/vol storage capacity and 0.95 kg/liter density

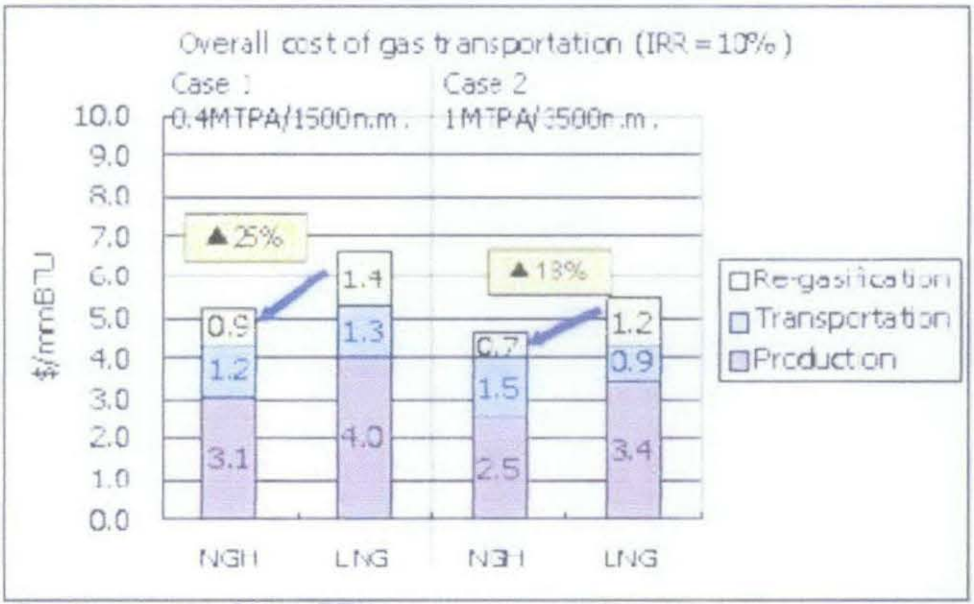
* 1 Mg/day pilot plant is under development.
* 1 Mg of NGH is equivalent to 2,790 scf NG,
assuming NGH slurry has 75 vol/vol storage capacity and 0.95 kg/liter density

Fig A3 Process diagram of gas hydrate synthesis developed by Japan, Norway and BG (I– Norway) (II – Japan (a) and BG (b))



	Case 1		Case 2	
	NGH	Small sized LNG	NGH	Small sized LNG
1.Natural gas value chain				
Natural gas source	Natural gas	→	Associated gas	→
Site of gas well	Close to Japan	→	Southeast Asia	→
Voyage distance	1,500N.M.	→	3500N.M.	→
Production Capacity (gas)	0.4MTPA	→	1MTPA	→
Production Capacity (NGH/LNG)	3MTPA	0.4MTPA	3MTPA	1MTPA
Storage tank (Loading site)	50,000m3 x2	30,000m3 x1	55,000m3 x4	125,000m3 x1
Shipping Carrier	60,000DWT x2	30,000m3 x1	130,000DWT x4	125,000m3 x1
Storage tank (Unloading site)	50,000m3 x2	30,000m3 x1	55,000m3 x4	125,000m3 x1
Re-gasification Capacity	0.4MTPA	→	1MTPA	→
Receiving terminal	GTCC power station (Japan)	→	→	→
Electric power capacity	400MW	→	1,000MW	→
2.Capital cost (million US$)				
Production and storage	180	230	330	450
Sea transportation	80	100	240	180
Re-gasification and storage	60	110	110	250
Total	320	440	680	880

MTPA: Million Ton Per Annum, N.M.: Nautical Mile, GTCC: Gas Turbine Combined Cycle



Feed gas cost = $1/mmBTU

IRR; Internal Rate of Return (after tax basis)

Fig A4 Data and results for Mitsui Engineering's feasibility study

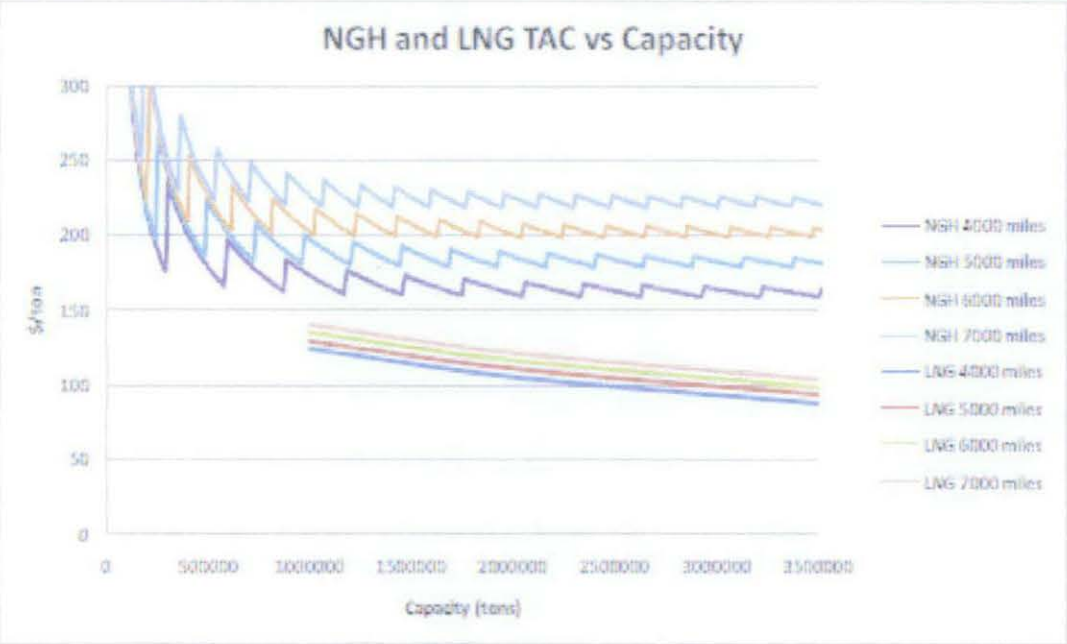


Fig A5 Graph of natural gas hydrates and liquefied natural gas TAC vs. capacity

Fig A6 Graph of natural gas hydrate and liquefied natural gas shipping capacity vs. ROI

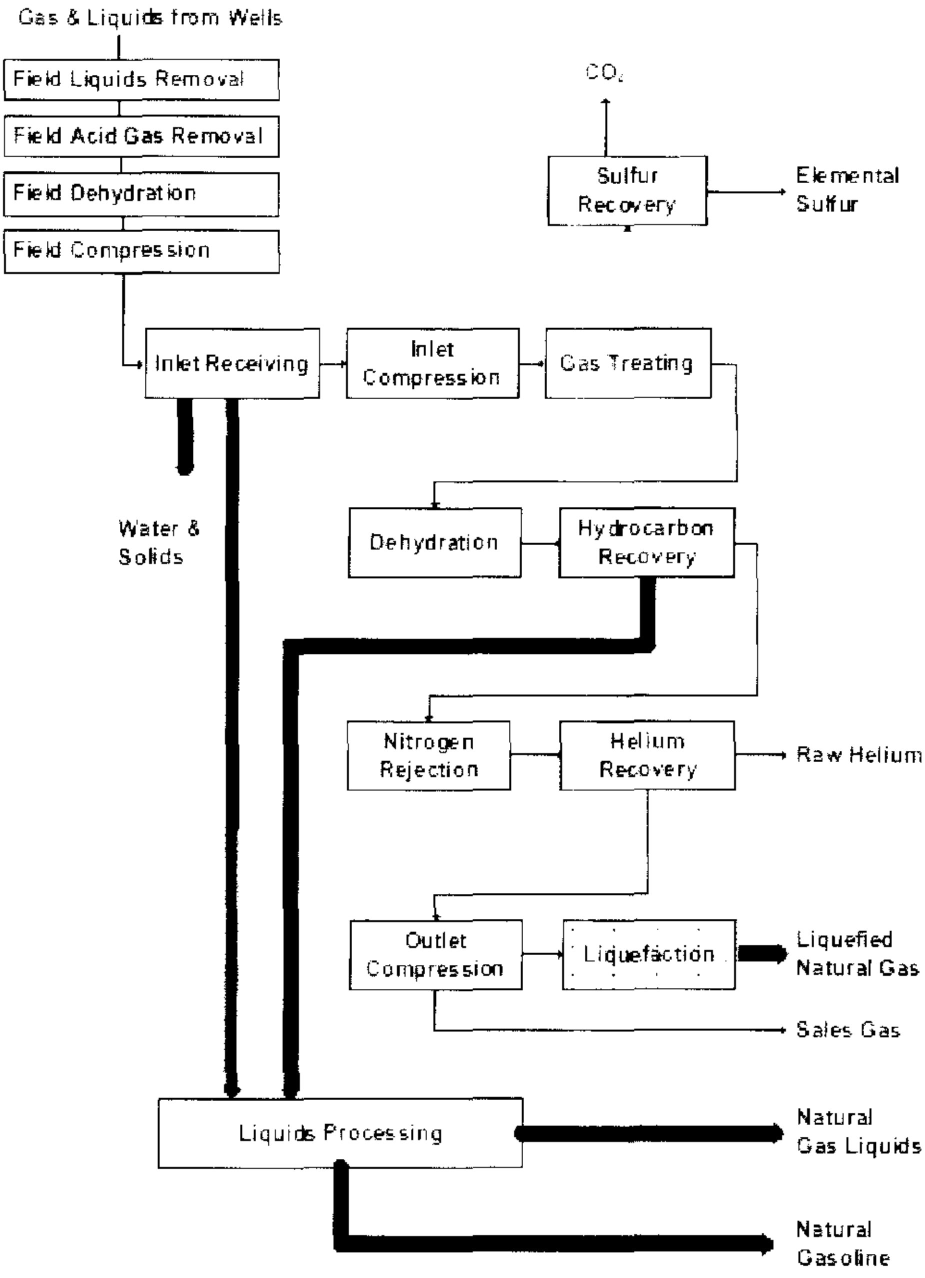


Fig A7 Common processing line for natural gas

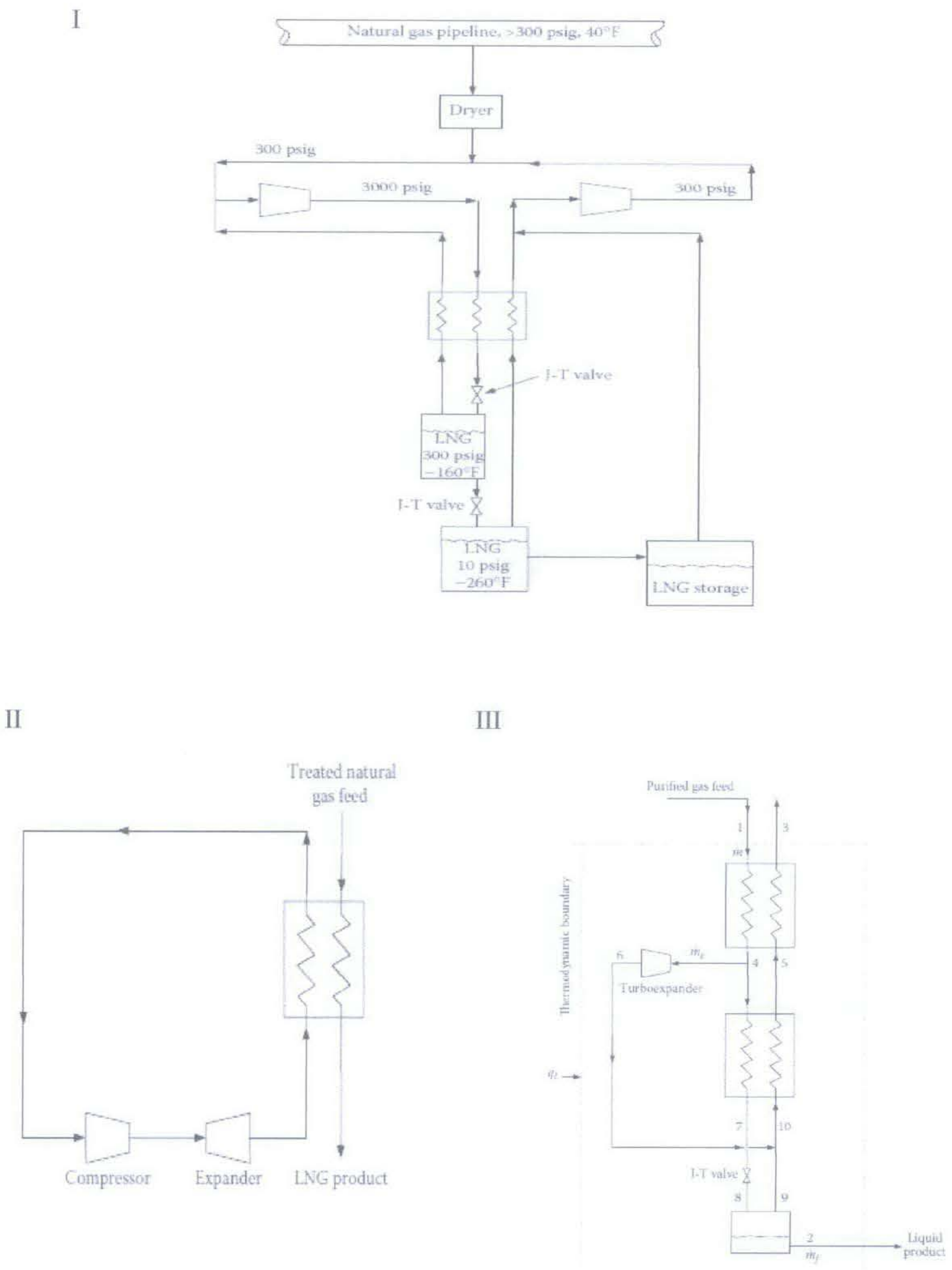


Fig A8 Liquefaction cycle for LNG (I – Joule-Thompson cycle, II – close expansion cycle, III – open expansion cycle)

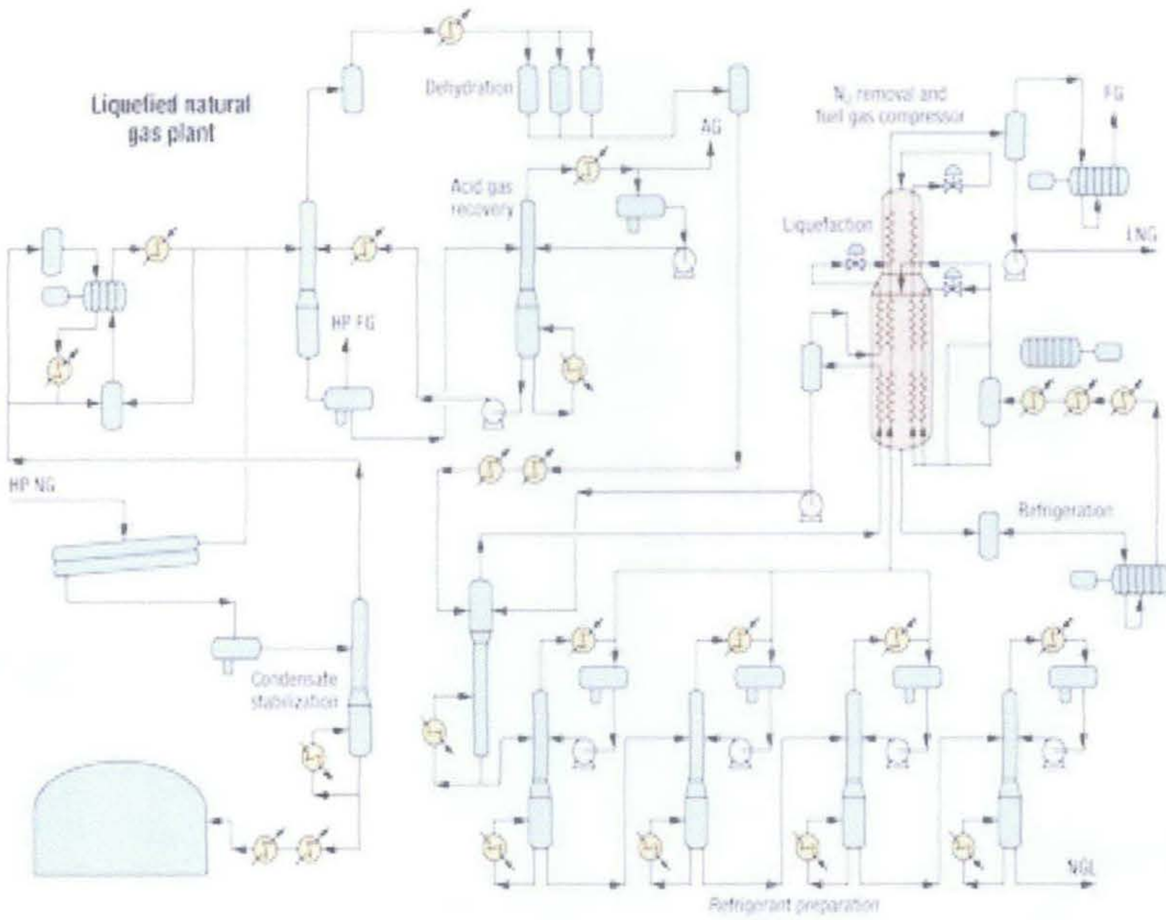


Fig A9 Process flow sheet for LNG