# Transportation and Storage of Natural Gas Hydrates

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## Abstract

Natural gas is a valuable fuel with increasing demand. Thus, natural gas must be transported from natural reserves to areas of high demand and stored for times when demand exceeds production. In this study, natural gas hydrates were considered as a possibility for the transportation and storage of natural gas. Several designs were considered for the production, shipping, and regasification of natural gas hydrates. Natural gas hydrates were found to be economically less favorable than LNG for the transportation of natural gas primarily due to the lower energy density of natural gas hydrates relative to LNG. However, natural gas hydrates were found to be economically viable for small capacity peak-shaving plants and natural gas storage due to the lower costs associated with natural gas hydrate synthesis.

# **Executive Summary**

- Natural gas is a mixture of small hydrocarbons commonly as a fuel and a chemical feedstock. Areas of high natural gas supply are generally far from areas of high natural gas demand, necessitating shipping.
- Natural gas hydrates are a solid phase of natural gas and water that forms a crystalline lattice. Hydrates condense the volume of natural gas, which is desirable for shipping and storage.
- Transportation of natural gas using hydrates requires three major stages.
  - 1. Production: The synthesis of hydrates from water and natural gas.
  - 2. Shipping: The transportation of hydrates from the production to the regasification plant.
  - 3. Regasification: The dissociation of hydrates to natural gas and water.
- Natural gas hydrates have a higher total annualized cost per ton of methane than LNG for the transportation of natural gas primrily because LNG has a higher energy density than natural gas hydrates. For a plant capacity of 2 mtpa and a transportation distance of 4,000 miles the total annualized cost for natural gas hydrates is \$160/ton compared to \$105/ton for LNG at an M&S index of 1000.
- Natural gas hydrates have a lower return on investment than LNG for the transportation of natural gas. For a plant capacity of 2 mtpa, a transportation distance of 4,000 miles, and revenues of \$120/ton of natural gas, the return on investment for natural gas hydrates is -5% and for LNG is 4.5% at an M&S index of 1000.
- Natural gas hydrates have a lower fixed capital investment per ton of methane than LNG for a peak-shaving process. For a plant capacity of 2 mtpa the fixed capital investment for natural gas hydrates is \$108/ton and for LNG is \$260/ton at an M&S index of 1000.
- Natural gas hydrates have a higher return on investment than LNG for a peak-shaving process. For a plant capacity of 2 mtpa and sales of \$120/ton the return on investment for natural gas hydrates is 35% and for LNG is 12% at an M&S index of 1000.
- Transportation of natural gas using hydrates is uneconomical when compared to LNG.
- Natural gas hydrates are economically favorable for peak-shaving compared to LNG.

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#### Introduction

The importance of natural gas to the proper functioning of a modern industrialized economy cannot be understated. As of 2006, natural gas accounted for 22.5% of the total energy consumption in the United States, making natural gas as important a fuel to the United States as coal. As natural gas is the cleanest burning fossil fuel, it would be expected that natural gas as a proportion of total fuel consumption will only increase as concerns over global CO<sub>2</sub> production become more of an issue. Moreover, natural gas has a myriad of uses as an industrial feedstock, such as its use in the production of methanol, ammonia, and hydrogen.

Natural gas is composed primarily of methane with small amounts of heavier hydrocarbons such as ethane, propane, and butane in addition to small amounts of inerts such as nitrogen. The hydrocarbons in natural gas can be burned in the presence of oxygen releasing water, carbon dioxide, and energy.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + energy$$
 Equation 1

The energy released from the burning of natural gas is commonly turned into electricity or used for heating. Natural gas is more environmentally friendly than heavier hydrocarbons or coal because more energy is released per CO<sub>2</sub> molecule produced. These properties of natural gas make it desirable in industrial and commercial processes.

Despite the usefulness and importance of natural gas, technical difficulties put a limit on the extent to which natural gas can be used. The primary producers of natural gas are located in the Middle East and Eurasia, many thousands of miles away from the primary consumers of natural gas in East Asia, North America, and Western Europe. Thus, most natural gas must be transported a considerable distance before it can be used. Compounding this transportation problem is the fact that natural gas is expensive to transport when compared to coal or oil. For a given distance, per BTU shipping costs for coal or oil can be 25% of the shipping costs of LNG due to greater economies of scale and greater competition amongst carriers. Moreover, coal and oil are both produced in a form that can be easily transported in bulk whereas natural gas must be compressed or liquefied for bulk transport.

Several methods are used to transport natural gas. The most common and most profitable method is using a pipeline to move the natural gas from one location to another. This method is not always practical, especially when it is desired to transport the natural gas between two locations separated by an ocean. Shipping natural gas over water is most commonly done by condensing the natural gas. This is done because the liquefied natural gas (LNG) has 570 times the density of natural gas at standard conditions making it easier to transport large quantities of natural gas. Other possible methods of transporting natural gas include compressed natural gas (CNG), gas to wire (GTW), gas to liquids (GTL), and natural gas hydrates (NGH).

Compressed natural gas is natural gas that is transported at very high pressures. The high pressures increase the amount of natural gas transported per unit volume. Gas to wire is the process of burning the natural gas to generate electricity then transmitting the electricity. Gas to liquids is the process of turning natural gas into longer chain hydrocarbons that are liquid at ambient conditions. Natural gas hydrates is the process of forming a solid phase of natural gas and water that can then be transported.

In addition to a transportation infrastructure, a natural gas storage infrastructure is required to account for varying seasonal natural gas consumption. In the United States, consumption of natural gas peaks in winter and summer due to increased heating demand and increased electrical power demand respectively. During these periods of peak usage, the rate of natural gas consumption in the United States can exceed the rate of natural gas production and importation. The problem of providing for peak natural gas consumption is further compounded by the difficulties associated with storing natural gas

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relative to other fossil fuels such as coal or oil. Similarly to the case of transportation, natural gas must be stored in a compressed or liquefied state, necessitating either large underground gas traps or large cryogenic storage facilities along with associated compression or liquefaction facilities if the gas supply is obtained from pipelines. In the United States, 57 of 113 active LNG facilities are devoted to storing natural gas against peak demand. With the demand for natural gas expected to increase over the next several decades, there is a need to analyze whether the currently implemented solutions to the problems associated with the use of natural gas can be improved through the application of new technologies such as the storage and transport of natural gas as a hydrate.

## **Natural Gas Hydrates**

Natural gas hydrates are a solid phase of natural gas and water that forms a crystalline lattice. Gas hydrates form between water and small gas molecules at high pressures and low temperatures (Koh & Sloan, 2007). The gas molecules become surrounded by a cage of water molecules trapping the gas in a solid phase. With no strong chemical bonds between the water molecules and the guest molecules, the hydrates are stabilized by van der Waals forces (Koh & Sloan, 2007). The water molecules and guest molecules can form three distinct structures based on guest molecule size as shown in Figure 1.



Figure 1: Polyhedral water cavities comprising sI, sII, and sH hydrates (Koh & Sloan, 2007).

With natural gas the most common guest molecules are methane, ethane, and propane. Methane and ethane will form an SI hydrate while propane will form an SII hydrate (Sloan, 2003). For methane, a volume of hydrate will contain 164 times its volume of natural gas at standard conditions (Koh & Sloan, 2007). The compact form of natural gas hydrates makes them a possible method for the transport of natural gas. For pure methane, the temperatures and pressures required for stable hydrates are shown below in Figure 2.



Figure 2: Pressure vs. temperature diagram for methane + water system (Ballard & Sloan, 2001).

Methane hydrates are stable at very moderate temperatures and pressures when compared to the conditions required for LNG. For natural gas not consisting of pure methane, the ternary phase diagrams for methane, ethane, and propane found in the appendix can be used (Ballard & Sloan, 2001). The ternary phase diagrams show that at constant temperature and composition, increasing the pressure will result in the formation of natural gas hydrates.

# **Natural Gas Transportation Using Hydrates**



The transportation of natural gas in the form of hydrates requires three major steps.

Figure 3: The process of shipping natural gas as hydrates.

The first step is the synthesis of hydrates from feed streams of natural gas and water. To synthesize the hydrates, the feed streams must be cooled and pressurized to conditions at which the hydrates will be stable. The feed streams must then be equilibrated in a reactor through mass transfer of the gas into the water before hydrate synthesis can take place.

The second step in the transport of natural gas hydrates is shipping. Due to the moderate temperatures at which hydrate are stable, modified bulk carriers can be used to ship the hydrate instead of purpose built vessels. Large bulk carriers allow for economies of scale that can reduce the shipping cost per ton of hydrate produced. When the ship reaches the final destination, the hydrates must be unloaded before regasification.

The third step in the process of transporting natural gas hydrates is the regasification of the hydrate. Regasification begins after the removal of the hydrates from the bulk carriers. The hydrates can then be dissociated into natural gas and water through the application of heat.

Equation 2

$$Hydrate + Heat \rightarrow H_2O + CH_4$$

After dissociation the natural gas must be dehydrated to remove any water vapor before being sent to the consumer.

In considering whether natural gas hydrates could be put to any economic use in the natural gas supply chain, the costs associated with the use of natural gas hydrates were broken down into two categories.

- The costs associated with the industrial synthesis and decomposition of natural gas hydrate.
- The costs associated with the transportation of natural gas hydrates by ship.

The costs associated with sequestering natural gas as a hydrate and later releasing the natural gas would be common to any application of natural gas hydrates, be it transportation or peak-shaving, and dependent only on capacity. The costs associated with transporting the hydrate would simply add an additional capacity and distance dependent cost to the cost of producing and decomposing the hydrate.

#### **Natural Gas Storage Using Hydrates**

Natural gas hydrates can also be used to store natural gas. The storage of natural gas would only require the synthesis of the hydrate and its regasification. This process can be beneficial since the density of natural gas hydrates reduces the space requirements for the storage of natural gas. Natural gas hydrates can be used for storage in peak-shaving applications to obtain a higher price for the natural gas and to provide for adequate natural gas supplies during periods of peak usage. Peak-shaving is accomplished through storing natural gas when natural gas demand is low, then selling the natural gas during periods of high demand.

# **Hydrate Synthesis**

Several designs of reactor were considered in determining the optimum method of synthesizing the hydrate. The reactors designs had a tank reactor plan in common, but the use of bubble diffusers with mechanical agitation as well as the use of gas transfer membranes were considered as means of equilibrating the feed streams in the reactor.





Figure 4: Bubble diffuser and membrane module.

The bubble diffuser design will have a higher operating cost due to the power requirements to agitate the natural gas and water. However, the membrane reactor will have a larger upfront investment due to the cost of the membranes. The product of the reactor will be a slurry of natural gas hydrate crystals suspended in the excess water fed to the reactor. This slurry can be prepared for transport through depressurization and cooling.



Figure 5: General reactor flowsheet.

The costs for the membrane reactor and the agitated reactor were calculated assuming that the composition of the natural gas feed is 100% methane in order to simplify calculations.

#### **Membrane Mass Transfer**

For the membrane reactor, the membrane was assumed to be made of 0.02 cm thick amorphous Teflon AF 2400 with a cost of \$250 per square meter. Values for the permeability of the Teflon membrane were taken from Pinnau and Toy (1996). Using the permeability and the feed conditions, the permeate flow rates per unit area were calculated using Fick's Law:

$$N_i = \frac{P_i}{z} \Delta P_i$$
 Equation 3

where  $N_i$  is the flux of methane through the membrane,  $p_i$  is the permeability of the membrane to methane,  $P_i$  is the partial pressure difference across the membrane for methane, and z is the thickness of the membrane.

It was assumed that hydrate formation occurred fast enough that the partial pressure on the water side of the membrane was negligible compared to the high pressure on the gas side of the membrane. If this assumption were incorrect, the required membrane area would increase.

Once the permeate flow rates per unit area were calculated, a total permeated gas flow rate was specified based on the total capacity of the plant. The number of moles per second of gas this capacity represented was calculated through the molar mass. Using the amount of gas that was permeated and the permeate flow rates per unit area, the required membrane area was calculated through simple division. Given a feed of 100% methane at a pressure of 5.17 MPa and a production rate of 1.5 million tons per annum (mtpa) of methane, the required membrane area is found to be 585,000 m<sup>2</sup>. By multiplying the membrane area by the cost of the membrane, the uninstalled incremental cost to the reactor of using the membrane can be calculated to be \$150 million.

#### **Reactor Design**

For determining the rate of hydrate formation in the reactor proper, the method described by Englezos 1987 was used. The rate of hydrate formation can be calculated using the following equation (Englezos, Kalogerakis, Dholabhai, & Bishnoi, 1987):

$${
m R}=4\pi {
m K}^*\mu_2({
m f}-{
m f}_{
m eq})$$
 Equation 4

where R is the rate of hydrate formation,  $K^*$  is the empirical kinetic parameter obtained from Englezos 1987,  $\mu_2$  is the second moment of the particle size distribution for the hydrate crystals in the reactor, f is the fugacity of the gas at reactor conditions, and  $f_{eq}$  is the fugacity of the gas at equilibrium pressure for the hydrate at reactor temperature. The fugacities required were calculated through the use of the CNGA equation of state which should be reasonably accurate for natural gas mixtures at the conditions used in the reactor:

$$Z = \frac{1}{1 + \frac{344400P10^{1.785SG}}{T^{3.825}}}$$
 Equation 5

where Z is the compressibility, P is the pressure in psig, SG the specific gravity of the gas relative to air, and T the temperature in °R. The value of the kinetic parameter for the hydration was determined by fitting a curve relating reactor temperature and the empirical kinetic parameter to the data provided in Englezos, 1987. The second moment of the particle size distribution was calculated using the following equations (Englezos, Kalogerakis, Dholabhai, & Bishnoi, 1987):

$$\mu_0=rac{3M(N-N_{eq})}{4\pi V
ho r^3}$$
 Equation 6

$$\mu_2 = 4r^2\mu_0$$
 Equation 7

where,  $\mu_n$  is the nth moment of the particle size distribution, M is the molecular mass of the hydrate, N is the number of moles of gas in solution at reactor conditions, N<sub>eq</sub> is the number of moles of gas in solution at the equilibrium pressure for the hydrate at reactor temperature, V is the volume of water for the above number of moles of gas,  $\rho$  is the density of the hydrate, and r is the mean particle radius for the hydrate crystals in the reactor. The number of moles of gas dissolved in the water can be calculated using Henry's Law for a gas of limited solubility in water such as methane.

$$C_i = K_{H,i}P_i$$
 Equation 8

where  $C_i$  is the concentration of methane in the water,  $K_{H,i}$  is the Henry's Law constant for methane at reactor conditions, and  $P_i$  is the partial pressure of methane.

Given a feed stream of pure methane at 5.17 MPa and 273 K, the rate of reaction can be calculated to be 1.29 (mol/m<sup>3</sup> s) using the above equations. Given the rate of hydrate production and the plant production capacity the required volume of a CSTR can be found:

where V is the volume of the reactor, Q is the flow rate of gas into the reactor, and R is the rate of hydrate formation. For a plant capacity of 1.5 mtpa the required reactor volume is calculated to be 2400 m<sup>3</sup>. The process will use multiple reactors each with a volume of 76 m<sup>3</sup>. For the above production capacity, the process will use 32 reactors for a total cost of \$1,760,000 including agitation equipment and bubble diffusers.

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

Agitator power requirements for the agitated reactor were calculated using the following equation with the agitator assumed to be 10 m in diameter, rotating at 45 RPM, and with a power number of 4(Perry & Green, 1997):

$$P = N_P \rho N^3 \frac{D^5}{gc}$$
 Equation 10

where P is the agitator power, N<sub>p</sub> is the dimensionless power number, ρ is the density of the fluid being agitated, N is the rotations of agitator in a given time period, D is the agitator diameter, and gc is the gravitational dimensional constant. Agitator power demand is very much dependent on reactor and agitator geometry. Thus, agitator power demand can change significantly for differing agitation setups. However, with the specified assumptions the required power for 1.5 mtpa production capacity amounts to only 1,400,000 kWhr/year, which amounts to \$100,000/year at an electricity rate of \$0.07 per kilowatt hour.

#### **Ancillary Equipment**

Power requirements for all required compressors were calculated by simulation in Pro/II for a given capacity then linearly related to all other capacities analyzed. Efficiencies for all compressors were assumed to be 60% and the compressors were assumed to be running off of electrical power for the purposes of calculating operating costs.



Figure 6: Pro/II compressor simulation

All heat exchangers were seized using the heat duties as predicted from the specific heats of water and natural gas hydrate, the heat of dissociation of methane hydrate, and the heat of fusion of ice(Rueff, Sloan, & Yesavage, 1988). The heat exchangers could then be sized by PRO/II simulation similarly to the compressors. Feed pump power requirements were calculated using the following equation with an efficiency assumed to be 74% and the head requirement assumed to be 150 feet (Perry & Green, 1997):

$$P = \frac{HQ\eta}{3960}$$
 Equation 11

where, P is the power in HP, H is the head in ft, Q is the capacity in gal/min, and  $\eta$  is the pump efficiency.

Once the required equipment design parameters were determined, the prices for each of the pieces of equipment used were estimated using power law cost relations to capacity (Perry & Green, 1997). All of the equipment cost power law relations obtained assumed an M&S index of 1000. From the equipment costs, the total fixed capital investment for the reactors was estimated through the use of the Lang factors (Perry & Green, 1997). To determine the annualized cost of each of the reactors, it was assumed that the fixed capital investment for each of the reactors was depreciated linearly over 20 years and that 5% of the uninstalled cost of each reactor would be required in maintenance each year. It

was further assumed that water would be available out of a suitable body of water for no cost other

than the power required to pump the water.

### **Summary**

All of the equipment required in a 1.5 mtpa production facility are summarized in Table 1.

Membrane Area Required (m2)	590000	
Minimum Reactor Volume (m3)	2400	
Total Initial Cooling Duty (BTU / s)	73000	
Initial Cooling Heat Transfer Area (ft2)	35000	
Initial Cooling Power Demand (kWhrs / yr)	17000000	
Recycle Compressor Power Demand (kWhr / yr)	4000000	
Intake Compressor Power Demand (kWhr / yr)	1500000	
Feed Pump Power Demand (kWhr / yr)	1000000	
Agitator Power Demand (KWhr / yr)	1400000	
Post Cooling Duty (BTU / s)	34000	
Post Cooling Power Demand (kWhrs / yr)	7900000	

Table 1: Major Pieces of Equipment in Production Facility

The costs associated with a production capacity of 1.5 mtpa are given in Table 2.



Table 2: Costs Associated with Production Plant		
Membrane Cost (Uninstalled)	\$150,000,000	
Reactor Cost (Uninstalled, No Agitator)	\$300,000	
Reactor Cost (Uninstalled, With Agitator)	\$1,760,000	
Initial Cooling Heat Exchanger Cost (Uninstalled)	\$240,000	
Initial Cooling Annual Power Cost (Assuming \$0.07 / kWhr)	\$11,800,000	
Recycle Compressor Cost (\$ / yr) (Assuming \$0.07 / kWhr)	\$2,800,000	
Intake Compressor Cost (\$ / yr) (Assuming \$0.07 / kWhr)	\$1,000,000	
Feed Pump Power Cost (\$ / yr) (Assuming \$0.07 / kWhr)	\$730,000	
Agitator Power Cost (\$ / yr) (Assuming \$0.07 / kWhr)	\$100,000	
Post Cooling Annual Power Cost (Assuming \$0.07 / kWhr)	\$5,500,000	
Post Cooling Heat Exchanger Cost (Uninstalled)	\$110,000	
Recycle Compressor Cost (Uninstalled)	\$2,200,000	
Intake Compressor Cost (Uninstalled)	\$870,000	
Feed Pump Cost (Uninstalled)	\$690,000	
Membrane Reactor Equipment Cost (Uninstalled)	\$150,000,000	
Agitated Reactor Equipment Cost (Uninstalled)	\$5,860,000	
Membrane Reactor Equipment Cost (Installed)	\$220,000,000	
Agitated Reactor Equipment Cost (Installed)	\$8,550,000	
Membrane Reactor FCI	\$600,000,000	
Agitated Reactor FCI	\$23,000,000	
Membrane Reactor Annualized Cost	\$210,000,000	
Agitated Reactor Annualized Cost	\$29,000,000	

Overall, two orders of magnitude improvement in either membrane permeability or membrane price would be necessary before the membrane reactor would be competitive with the stirred tank reactor.

# **Hydrate Transportation**

The following options were considered for hydrate transportation.

- The transport conditions could vary between 1 atmosphere of pressure at 241 K or 85 atmospheres of pressure at 285 K.
- The hydrate could be handled as a fluid suspension of hydrate crystals in water or as a solid suspension of hydrate crystals in ice.

• The hold of the hydrate transport vessel could be refrigerated in order to prevent all hydrate dissociation or the vessel could be built to handle some production of methane from hydrate dissociation.

The measurements for each vessel were taken from the measurements of the *MV Vogebulker*, a reasonably average Capesize bulk carrier of 18 meters in draught, 45 meters in beam, and 290 meters in length(H. Vogemann, 2008).

#### **Atmospheric Pressure**

The losses of natural gas hydrate in the absence of any cooling were calculated using Fourier's Law by assuming ambient water and air temperatures of 293 K and 300 K respectively:

$$\mathbf{Q} = \mathbf{U}\mathbf{A}\Delta\mathbf{T}$$
 Equation 12

where Q is the amount of heat transferred, U is the overall heat transfer coefficient, A is the surface area of the ship, and  $\Delta T$  is the temperature difference between the inside and outside of the ship.

It was assumed that the only source of heat being introduced into the hydrate storage compartment was conduction through the walls of the cargo compartment. The walls of the cargo compartment were taken to be insulated with 10 cm of polyurethane (with a conductivity of 0.021 W / m-K) in addition to the 2.5 cm of steel of the hull plating and the thickness of steel required for containing the pressure in the cargo compartment (with a conductivity of 46 W / m-K). It was further assumed that radiant heat flux and convection were both sufficient to maintain uniform surface temperatures at ambient conditions over the whole of the cargo carrying portion of the vessel. Lastly, the vessel was assumed to be rectangular in cross section giving a surface area of 46,000 m<sup>2</sup>. The rate of heat transfer to the cargo was then calculated to be 5,400 W. The values for the heat of dissociation of the hydrate and the specific heat of the hydrate were taken to be 430 (kJ/kg) and 2.16 (kJ/kg K) respectively, (Rueff, Sloan, & Yesavage, 1988). The heat transferred is divided by the heat of dissociation

of the hydrate to give the rate of hydrate loss, 1,080 kg/day. While the actual hydrate carried in the vessel will not be pure methane hydrate, the hydrate will be 88+% methane so the error introduced through this assumption will be minimal. As these assumptions do not precisely describe the actual heat transfer conditions faced by the vessel, it is likely that the actual hydrate losses will be somewhat higher than the losses predicted here. However, in the absence of detailed information as to the geometry of the ship and the precise location where the ship will be traveling, any more precise methods of determining the heat transferred to the hydrate would likely introduce just as much error as the assumptions made due to the lack of precise specifications.

The cost of the refrigeration equipment necessary to prevent all dissociation of hydrate in the storage compartment was calculated using the rate of heating calculated in the determination of the rate of hydrate loss and a power law cost relation (Perry & Green, 1997). The power demand associated with running this refrigeration equipment was calculated by assuming an efficiency of 8 BTU/hr of cooling per W-hr of electrical power. It was assumed that the cost of electrical power generation onboard the ship was \$0.07 per kWhr.

The required total capital investment for a shipping distance of 4,000 miles, six ships, was found to be \$1,100,000,000. The cost to add a refrigeration unit to prevent hydrate dissociation is \$6,000 per ship with electrical costs of \$3,000 per year for each ship.

#### **Ambient Temperature**

The amount of steel necessary to construct the hydrate storage compartment was determined using the Faupel formula for determining the bursting pressure of a pressure vessel assuming 1020 carbon steel was used in the construction of the vessel:

$$P_{B,min} = \frac{2}{\sqrt{3}} \sigma_s \ln(k)$$
 Equation 13

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where  $P_{B,min}$  is the minimum bursting pressure of the pressure vessel,  $\sigma_s$  is the yield strength of the material being used in constructing the pressure vessel, k is the outer radius of the vessel divided by the inner radius of the vessel.

Once the required thickness of steel was determined, the cost of steel can be determined by applying the density of the steel and the cost per ton of the steel (assumed to be \$833 per ton). The cost of 10 cm of polyurethane foam at \$2974 per ton was added to the cost of steel in order to obtain the cost of the raw materials necessary to add a storage compartment to the hydrate transport vessel. A margin of 20% was added onto this estimate of raw materials cost to account for the equipment necessary to mount the pressure vessel in the ship. In addition, 46% of the cost of the raw materials was added onto the cost of the ship overall to account for the labor associated with installing the storage compartment (Perry & Green, 1997).

Shipping a distance of 4,000 miles at elevated pressure requires twelve ships with a total capital investment of two billion dollars. The increased number of ships required is due to the weight taken up by the steel, reducing the capacity of the ship.

#### **Operating Costs**

Fuel consumption will vary substantially between ships based on hull geometry, engine age, and the state of repair of the engine. A value of 54 tons per day of heavy fuel oil was assumed for the fuel consumption of the ship based on the information in Stopford, 1997. This fuel consumption is based on a speed of 18 knots, the average speed of an LNG vessel.

The time spent unloading the hydrate was calculated based on a crane being able to lift 40 tons 50 times per hour. It was further assumed that given 290 meters of length, two cranes would be able to access the hydrate simultaneously.

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The labor necessary to run each ship was assumed to be a constant \$900000 per year based on a crew of 20 with an average salary of \$45000 per year. The cost of maintenance and other ancillary costs were assumed to be a constant 5% of the value of the ship per year.

The total annualized costs for transporting the hydrate at atmospheric pressure and ambient temperature 4,000 miles was found to be \$150,000,000 per year and \$300,000,000 per year respectively.

#### **Shipping Summary**

The hydrate slurry produced by the reactor could be shipped at high pressures and ambient temperatures or at atmospheric pressure and low temperatures. Shipping the hydrate at high pressure was found to be more costly because the storage containers would have to have thicker walls increasing the cost of the ship and decreasing the weight of hydrate which could be carried. Unlike with compressed gases, shipping gas hydrates at elevated pressures provides no increase in capacity due to the incompressibility of the hydrates. Also, polyurethane insulation is far more efficient in terms of weight at reducing hydrate losses due to dissociation than increasing the pressure rating of the storage vessel in order to allow hydrate transport at elevated temperature. However, at atmospheric pressure the stable temperature for hydrates is below the freezing point of water which would cause the hydrate slurry to freeze solid in the ship's hold. Thus, in order to handle the hydrate as a fluid, the hydrate slurry would have to have ethanol added to depress the freezing point of the water. Alternatively, the hydrate slurry mixture could also be frozen into manageable blocks onshore and loaded onto the ship by crane. The ethanol-water-hydrate slurry would be more easily loaded and unloaded from ships by the use of pumps, which would reduce the amount of time each ship spent in port from approximately 36 hours to approximately 16 hours. However, additional equipment would be necessary to separate the ethanol vapor that would result from regasifying the hydrate-water-ethanol mixture from the natural gas. Also,

the ethanol displaced natural gas hydrate, reducing the effective capacity of each ship by 4% - 5% for a slurry of 3% - 4% water. Thus, shipping the hydrate in slurry form was only viable for shorter transportation distances of 2500 miles or less where loading and unloading times were a significant portion of total trip time. For distances of 3500 miles or more, shipping the hydrate as blocks proved to be more profitable.

## Regasification

In determining the economically optimum method of regasifying the natural gas hydrate, two methods of regasification were analyzed.

- The hydrate could be heated in an atmospheric pressure vessel with the resulting gas being pressurized from atmospheric to pipeline pressure with a compressor.
- The hydrate could be heated in a pressure vessel rated for the pipeline pressure with the dissociation of the hydrate providing the pressure.

With the atmospheric pressure option, the hydrates can be dissociated at lower temperatures, but the natural gas would then have to be compressed by a compressor to pipeline pressure. Alternatively, the hydrate could be heated in a pressure vessel along the hydrate equilibrium curve to pipeline pressure. The resulting dissociated natural gas would then be at pipeline pressure, eliminating the need for a compressor. The fixed capital investment for a 1.5 mtpa regasification plant using pressure vessels was found to be \$140,000,000 and the total annualized costs were found to be \$85,000,000 per year. A 1.5 mtpa regasification plant using a compressor would have a fixed capital investment of over \$250,000,000 and a total annualized cost of \$125,000,000 per year. Thus, it would be preferable to use hydrate dissociation in a pressure vessel rather than hydrate dissociation at atmospheric pressure.



Figure 8: Hydrate dissociation flow diagram

## **Economics**

The total annualized cost per ton of methane, fixed capital investment per ton of methane, and return on investment were calculated for natural gas hydrates and for LNG both at a M&S index of 1000. These economic factors were found for shipping distances between zero and ten thousand miles. The economics at zero miles represent the total annualized cost, fixed capital investment, and return on investment for the production and regasification facilities alone with no transportation, as would be found at a peak-shaving plant. These three economic factors were then compared to determine the relative merits of transporting natural gas as either hydrates or LNG.

The fixed capital investment for natural gas hydrates is the sum of the fixed capital investments for the production facility, the shipping, and the regasification facility. The total fixed capital investment is 1.25 billion dollars for a total production rate of 1.5 mtpa and a transportation distance of 4,000 miles. The total annualized cost is found by summing the total annualized cost of synthesizing, shipping, and dissociating the methane hydrates. The total annualized cost is \$260,000,000 per year for the above production rate and shipping distance. Dividing either the fixed capital investment or the total annualized cost by the production rate gives the FCI and TAC in dollars per ton of methane. The fixed capital investment per ton of methane and total annualized cost per ton of methane are \$840/ton and \$172/ton respectively. The return on investment is then calculated assuming that sales per ton of methane are between \$0 and \$200. The return on investment is calculated using the below equation.

$$ROI = \left[\frac{(sales/ton) - (TAC/ton)}{(FCI/ton)}\right] (100) (0.85)$$
 Equation 14

The return on investment assuming sales of \$100 per ton of methane is found to be -7.3%.

For LNG the fixed capital investment and total annualized costs are estimated as an average of different LNG plants. For a plant capacity of 1 mtpa the fixed capital investment is \$350/ton and the total annualized cost is \$410/ton. The return on investment for LNG is found the same way as for methane hydrates. The return on investment with sales of \$100/ton and a transportation distance of 4,000 miles is -5.8%.



Figure 9: TAC vs. Capacity for NGH and LNG distances of 4000-7000 miles.

The total annualized cost per ton of natural gas for both natural gas hydrates and for LNG increases as the transportation distance increases. This trend occurs because at larger transportation distances more ships are required resulting in increased costs. This trend is also observed for the fixed capital investment per ton of methane and for the return on investment. The total annualized cost per ton of methane for LNG is lower than the total annualized cost per ton of methane for natural gas hydrates primarily due to lower shipping costs made possible by the greater energy density of LNG. The return on investment is shown below at different transportation distances with revenues per ton of natural gas varied between \$0 and \$200 per ton for natural gas hydrates, Figure 10, and for LNG, Figure 11.



Figure 10: ROI for natural gas hydrate transportation distance of 3000 miles.



Figure 11: ROI for LNG transportation distance of 3000 miles.

As would be expected, the calculated return on investment increases as the revenues per ton of natural gas increase. Overall, LNG has a better return on investment than natural gas hydrates as seen in Figure 10 and Figure 11. The total annualized cost per ton of natural gas and the return on investment show LNG as the better economic option for the transport of natural gas.

LNG is better economically due to the fact that the shipping costs for natural gas hydrates are much higher than the shipping costs for LNG. The costs for shipping natural gas hydrates are high because 6.5 tons of water, which generates no revenue, is shipped for every ton of natural gas shipped. In comparison, all of the weight shipped as LNG generates revenue. The total annualized cost per ton of methane for shipping natural gas hydrates, (i.e. free production and regasification of natural gas hydrates) compared to the total annualized cost for the total LNG process can be seen below, Figure 12.



Figure 12: TAC/ton for LNG vs. NGH Shipping

At low transportation distances and low production capacities the costs for shipping natural gas hydrates are lower than the costs for the entire LNG process. However, as transportation distance increases and capacity increases, LNG becomes a better economic option than natural gas hydrates even with free hydrate production and regasification.

The return on investment for shipping natural gas hydrates is also compared to the return on investment for the overall process of transporting LNG, Figure 13. The trends observed are the same as for the total annualized cost per ton for LNG compared to the shipping of natural gas hydrates.



Figure 13: ROI for LNG vs. NGH Shipping assuming sales of \$100/ton.

Overall, shipping natural gas as LNG is better economically than shipping natural gas as a hydrate. Even though the shipping of natural gas hydrates becomes competitive with the total LNG process at short distances and low capacities, the cost of the production and regasification plants would eliminate any benefits.

# **Peak Shaving**

Peak shaving the cost of natural gas is done by storing natural gas when prices and demand are low and selling the natural gas when prices and demand are high, Figure 14.



Figure 14: Seasonal surpluses and deficits that can be peak shaved.

The peak shaving production and regasification facilities are designed in the same way as the production and regasification facilities for the transportation of natural gas hydrates, Figure 7 and Figure 8. The economics for a peak shaving plant are calculated in the same way as for the transportation of natural gas hydrates except that there are no shipping costs associated with a peak shaving plant. The fixed capital investment and total annualized cost for a LNG and natural gas peak-shaving process are shown in Figure 15.



Figure 15: Peak-shaving TAC/ton and FCI/ton for NGH and LNG.

At higher capacities, the total annualized cost per ton of methane is similar for hydrates and for LNG. However, at lower production capacities that would be more characteristic of a peak-shaving plant, the total annualized cost per ton of natural gas is higher for LNG than for natural gas hydrates. The fixed capital investment per ton of methane is also much lower for a natural gas hydrate plant than for a LNG plant. The return on investment for natural gas hydrates and LNG peak-shaving plants assuming sales of \$100/ton can be seen below, Figure 16.



Figure 16: Peak-shaving ROI for NGH and LNG.

At lower capacities, the return on investment for natural gas hydrates is better than for LNG. Thus, natural gas hydrates seem the better economic option than LNG for low capacity peak-shaving plants.

LNG is a better option economically than natural gas hydrates for the transportation of natural gas. Both the total annualized cost per ton of natural gas and the return on investment are lower for transport by natural gas hydrates than for transport by LNG. However, in a peak-shaving plant where transportation costs are not a concern, natural gas hydrates are economically superior to LNG at low production capacities.

## Recommendations

The transport of natural gas as LNG is a well developed and proven technology that works on a large scale both economically and physically. Natural gas hydrates are in a research and development stage with no large scale production plants. The possibilities of natural gas hydrates have not been

proven and the use of natural gas hydrates in the development of a natural gas field would entail more risk than the use of LNG. LNG has less uncertainty and risk associated with it than natural gas hydrates.

Moreover, LNG is a better economic option for the transport of natural gas than natural gas hydrates. The main cost associated with the transportation of natural gas hydrates is the cost associated with the purchase and operation of ships. Natural gas hydrates contain 6.5 tons of water for each ton of natural gas, while LNG contains only natural gas. The additional weight associated with natural gas hydrates requires both larger ships and more fuel costs when compared to LNG. Natural gas hydrate ships must transport 7.5 times the weight that LNG ships must transport for the same revenue. Thus, the increased weight of transporting natural gas hydrates makes it economically unfavorable when compared to LNG.

Peak-shaving plants, however, do not require any ships since they are designed for the temporary storage of natural gas. Production and regasification of natural gas hydrates is cheaper than LNG. The production of LNG requires very low temperatures which are achieved with expensive refrigeration cycles. Natural gas hydrates are produced at moderate temperatures which can be achieved with small less expensive refrigeration cycles. The moderate production conditions of natural gas hydrates makes it economically more favorable than LNG for the temporary storage of natural gas.

Natural gas hydrates should not be used to transport natural gas at this time because LNG is better economically. Natural gas hydrates could be considered as a means of transporting natural gas if the price of shipping natural gas hydrates decreases, or the cost of producing and shipping LNG increases significantly. Peak-shaving using natural gas hydrates is better economically than LNG. Low capacity peak-shaving plants could see significant improvements in profitability through the use of natural gas hydrates instead of LNG.

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# Appendices Phase Diagrams



Figure 17: Pressure vs. temperature diagram for ethane + water system (Ballard & Sloan, 2001).



Figure 18: Pressure vs. temperature diagram for propane + water system (Ballard & Sloan, 2001).



Figure 19: Pseudo-ternary diagram for methane + ethane + propane + water system at 277:6 K and 10 atm (Ballard & Sloan, 2001).



Figure 20: Pseudo-ternary diagram for methane + ethane + propane + water system at 277:6 K and 45 atm(Ballard & Sloan, 2001).

# **Economic Graphs**





































































