CSCanada
Energy Science and Technology
Vol. 4, No. 2, 2012, pp. 61-68
DOI:10.3968/j.est.1923847920120402.569

ISSN 1923-8460[PRINT]
ISSN 1923-8479[ONLINE]
www.cscanada.net
www.cscanada.org

Monetizing Gas: Focusing on Developments in Gas Hydrate as a Mode of Transportation

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Received 22 September 2012; accepted 14 November 2012

Abstract

Natural gas and energy resource management is a major challenge in the rapidly changing global and business environment. Increase in gas recoveries and gas production have led a major review in the ways of transporting natural gas energy. Monetizing gas has now become a high priority issue for many countries. Natural gas is a much cleaner fuel than oil and coal especially for electricity generation.

Interest in gas hydrate being used as a means of transporting natural gas has increased over the last decade. New technology development has been focusing on using gas hydrates as a way of converting gas to solids to transport to markets around the world. Gas hydrate may be a viable means of storing and transporting gas but more focus should be given to some critical considerations for this gas hydrate development.

This paper would discuss some of these issues as we move towards monetizing gas in the form of hydrate. These include energy balance in hydrate formation and re-gasification, storage of the hydrate, form of transporting the hydrate and distances to be transported. Other important factors are re-gasification technologies, economics compared to other gas transportation modes, environmental, climate and other issues.

Key words: Monetizing gas; Gas hydrate; Transporting natural gas

Rajnauth J., & Barrufet, M. (2012). Monetizing Gas: Focusing on Developments in Gas Hydrate as a Mode of Transportation. *Energy Science and Technology, 4*(2), 61-68. Available from http://www.cscanada.net/index.php/est/article/view/j.est.1923847920120402.569 DOI: http://dx.doi.org/10.3968/j.est.1923847920120402.569.

INTRODUCTION

For many years natural gas hydrates have been a nemesis to the petroleum industry causing blockages in pipes and equipments. Since then, there has been great interest to understand and avoid the formation of hydrate during the transportation of gas. Now, the gas hydrate concept can be used to capture, store and transport natural gas. Natural gas hydrates are ice-like crystalline solids formed from a mixture of water and natural gas subjected to high pressure and suitable low temperature conditions (1200-1500 psi and 2-10 ^oC). These conditions are found in the permafrost and under the ocean floor. Hydrates consist of geometric lattices of water molecules containing cavities occupied by lighter hydrocarbons or other type of gaseous components for e.g. nitrogen or carbon dioxide.

1. ENERGY DEMAND SCENARIO

Total world energy demand has increased by more than 5 fold over the last 50 years. With continued economic and population growth, the energy demand is expected to increase tremendously over the next 40 years. This will mean a greater dependence on natural gas and hence monetizing gas will be important to many countries.

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

2. WHY NATURAL GAS HYDRATES?

Researchers believe that gas hydrates formation provides an easier to produce, safer and cheaper to store method of capturing natural gas when compared to other transportation modes such as Compressed Natural Gas and Liquefied Natural Gas. This can therefore be a promising and attractive method of gas transportation. Some postulate based on studies of the kinetics that obtaining large volumes of solid hydrate may be expensive, energy consuming and long process (Makogon, 2002). The hydrate though has several attributes that have fostered further research around the world. These are now discussed.

Gas hydrate has a high gas to solid ratio. 1 m^3 of hydrate contains 150-180 m^3 of gas per m^3 of water. The storage capacity depends on the structure of the hydrate formed whether structure I, II or H. The formation of these structures is dependent on the natural gas composition and the additive used. Some factors that affect storage capacity include incomplete cage filling, impurities and incomplete packing of the hydrate.

Gas hydrate self preservation effect is quite good. Once formed the hydrate can be stored at atmospheric pressure and remain quite stable at -5 to -15 ^oC. Some dissociation may initially occur but a film of ice covers the hydrate surface and prevent further dissociation.

Hydrate can be used to capture flared gas, stranded and associated gas (Berner, 2003).

Once this method becomes viable it affords possibility for monetizing stranded gas and flared gas. It may well prove to be a cost effective transportation method of natural gas.

3. NATURAL GAS HYDRATE STRUCTURES

Gas hydrates are normally classified as structure SI, SII and H type gas hydrates. Structure I hydrates contain 46 water molecules per 8 gas molecules. The hydrate number is 5.75. The water molecules form two small dodecahedral voids and six large tetradecahedral voids. These voids can hold only small gas molecules (methane, ethane) with molecular diameters not exceeding 5.2 angstroms. Structure II hydrates contains 136 water molecules per 24 gas molecules. The hydrate number is 5.67. The water molecules form 16 small dodecahedral voids and 8 large hexakaidecahedral voids. They may contain gases with molecular dimensions from 5.9 to 6.9 angstroms, such as propane, a three-carbon hydrocarbon, and isobutene. Structure H hydrates contains 34 water molecules per 6 gas molecules. The hydrate number is 5.67. This structure is large enough to hold molecules like iso-pentane, a branched-chain hydrocarbon molecule with five carbon atoms (Sloan, 2000).

The fit of the molecules with in the cavities is important in determining the structure of the hydrate form. Therefore the composition of natural gas determines the type of gas hydrate structure formed. Generally, biogenic gas with small molecules forms the SI hydrate structure. Thermogenic gas with small amounts of propane and isobutane molecules tend to form SII type hydrate. What about combination of hydrate? It may be possible to have combination of hydrate types. This area should be further investigated.

4. HYDRATE FORMATION

Natural gas can be formed by mixing natural gas and water at certain temperatures and pressures. Mass production of gas hydrate is a present challenge now facing researchers in hydrate technology. While stirring and mixing water and natural gas in a reactor chamber at the required conditions and increases surface area have proven to be a viable process, the rate of formation of the hydrate is slow.

Some experiments have shown that using ammonium salts can increase the rate of hydrate formation. Tetra-Butyl Ammonium Bromide was used in a small scale experimental process and it believed that this compound changed the gas solubility and kinetic of hydrate formation (Masoudi, 2005). Other experiments on surfactants shows that hydrate formation and storage can be improved in the presence of promoters (Sun *et al*., 2003). Surfactants are hydrate formation promoters that can improve hydrate storage capacity and reduce the processing time costs of hydrate formation. Below is a summary of some of the promoters tested and the outcomes of those results (Table 1).

Table 1
Some Results from Hydrate Promoters Tested

Promoters tested	Results
Sodium Dodecyl Sulfate (SDS) anionic	Improve hydrate formation rate and storage capacity
Dodecyl Polysaccharide Glycoside (DPG) nonionic	Improve hydrate formation rate and storage capacity
Cyclopentane	Reduce time costs of hydrate formation and reduce the hydrate storage capacity
Tetra-Butyl Ammonium Bromide	Improve the rate of hydrate formation. Self preservation effect was significant at atmospheric pressure and low temperatures.

Further analysis can be done on the daily amount of surfactant required for plant operation and cost involved.

Other surfactants have been studied to test their ability to maximize the uptake of methane in the hydrate formation process (Link *et al*., 2003). This analysis was done at 1400 psi and -10 ^oC and the methane uptake was compared for the different surfactants. Sodium dodecyl sulfate give the highest uptake of methane. Below is a table which gives a summary of the results (Table 2).

Table 2
The Methane Uptake in the Different Surfactants

Surfactant	% Uptake
Dodecyl trimethyl ammonium chloride	13.9
Sodium dodecyl sulfate	97.3
Dodecylamine	9.9
Dodecylamine HCl	11.9
Sodium lauric acid	77.4
Sodium oleate	70.5
Superfloc	19.6

Studies have shown that gas hydrates can be produced in a dry or slurry state. The process for forming the hydrate slurry involves using excess water to form an unstable slurry hydrate which is then dehydrated to produce a more stable and concentrated slurry. Some problems associated with slurry method are the low production rate and the high pressure conditions for dehydration. These concerns make the process very expensive and raises shipping and storage cost. It is believed that biochemical additives may be useful in reducing storage pressure.

The dry solid hydrate can be obtained from dewatering of the initial unstable slurry formed from mixing gas and water. A powder hydrate or pellets can be produced. This process has been tested successfully in laboratories and involves agitation, increasing surface area and a miscible hydrate former. Some researchers believe that the pellet form is very good in terms of storage, transportation and regasification (Masoudi, 2005).

Several methods of gas hydrate formation have been researched and include dry powder process, pelletization process, slurry process, combination slurry process and ice formation process. Summary of these processes are shown below in Table 3.

Table 3
Summary of Gas Hydrate Formation Methods

Process	Mixture	Requirement	Other	Adv/Disadv	Useful for
Dry	Water & Natural gas	Dewatering	Require screens, cyclones and centrifuge	Stored and shipped without freezing of free water	Non associated, stranded and flared gas
Pellet	Water & Natural gas	Dewatering & Pelletization	Require Pelletization equipment	Has been done by Japanese 600 kg/day	Non associated, stranded and flared gas
Slurry	Water & Natural gas	Partial Dewatering	Requires a coolant	Needs pressurized containers. Higher shipping cost	Associated gas
Combination slurry	Water, Ice & Natural gas	Ice maker		Ice removes some of the heat formed	Associated gas
Ice	Ice & Natural Gas	Ice maker		Minimize amount of water for shipping / acts as a coolant/ loss of heat that can be recovered	Associated gas

Additional focus should now be placed on gas hydrate plant sizes to produce the required daily amount of solid hydrate depending on the daily gas production available.

5. STORAGE OF THE GAS HYDRATE

This storage and transportation process is possible thanks to the metastability of gas hydrates. Provided that it is performed at higher temperature and lower pressure levels than those required for LNG and CNG, respectively, gas transportation using hydrates seems to be as viable as these proven processes.

Experimental work have shown that gas hydrate can be stored at atmospheric pressure once the temperature is subzero (-5 to -20 ^{o}C). This is particularly important in the design cost of storage containers. The storage containers could be cost effective if little or no pressurization is required in the design. The scale of storage in a refrigerated chamber can be small or large. Natural gas can be stored on a small scale or large scale before transporting it to markets. The storage can be done in an insulated container with design characteristics dependent on temperature and pressure required for the particular form of hydrate (slurry or solid). Technical and economic analysis can be done to obtain the most favorable storage option.

Over the years, several researchers have proposed different conditions for storing the hydrate (Gudmundsson *et al.*, 1994). A summary of this is shown in Table 4 below.

Table 4
Summary of Some Proposed Conditions for Storage

	Conditions for storage	Affect on design cost
1	-32 °C and 5 MPa	Very costly requiring insulation and pressurization
2	2-5 MPa using pipelines – for slurry storage	Expensive requiring pressurization
3	Submarine vessel for mobile storage	Very expensive requiring pressurization
4	Atmospheric pressure and -15 °C – stationary or mobile storage	Economical but still requiring additional insulation
5	Atmospheric pressure and - 5 °C to 2 °C – stationary or mobile storage	Refrigerated storage is very cost effective
6	Atmospheric pressure and 0 °C	As a result of metastability of hydrate

Some studies have shown that natural gas hydrate exhibit metastability at atmospheric pressure and regular cold storage temperatures and hence a possibility for cost effective storage and transportation.

Some comparisons of storage of the hydrate with Liquefied Natural Gas and Compressed Natural Gas are discussed below. The density of methane hydrate is 913 kg/m³. Therefore 1ft³ of hydrate contains 170 scf of gas. Then 1ft³ of hydrate weighs about 57.0 lb. By comparison, 1 m³ of liquid methane (at its boiling point -161.5 °C) contains 26.33 kmol, which converts to 622 m³ of gas at standard conditions. Alternatively, 1 m³ of compressed methane at 1015 psia and 27 °C contains 3.15 kmol or 74.4 sm³ of methane gas.

Therefore to store 25,000 m³ (0.88 MMSCF) of methane requires about 150 m³ (5300 ft³) of hydrates. This compares with 40 m³ (1400 ft³) of liquefied methane or 335 m³ (11,900 ft³) of compressed methane.

6. THERMAL CONSIDERATIONS

The formation of hydrate is an exothermic reaction with heat being produced during the hydrate formation. The heat of formation is approximately 410 kJ/kg. The produced heat must be removed from the reaction chamber. This heat can be used in dissociation of other hydrates that has been temporarily stored.

Analysis of the volumes have shown that gas hydrate have tremendous potential for capturing and transporting natural gas. However, a more effective analysis involves studying the specific energy content. The specific energy content should include the energy used in gas hydrate formation, transportation and dissociation at the market. Some researchers have suggested that the specific energy content of methane hydrate is 12 times lower than LNG.

It has been shown that the process of formation and dissociation of gas hydrate absorbs about 13-15% of the energy of the transported gas (Makogon, 2002). Therefore by looking at the kinetic data, large scale production of gas hydrates may pose a challenge. However detailed economic analysis together with other considerations may still show the viability of natural gas hydrate for stranded and flared gas. This is one area where more focus and detailed analysis is required.

7. HYDRATE TRANSPORTATION

Gas hydrate can be transported to markets using special carriers that are either modification to existing carriers or new carriers. These carriers would be designed to ship the slurry form, dry hydrate form or postulated form of the hydrate. The dry solid could be transported at atmospheric pressure and -5 to -10 °C and therefore no refrigeration is required in the insulated carrier. The metastability factor could further enhance the economic for transportation of the hydrate especially at atmospheric pressure and zero degrees Celsius.

For the slurry hydrate, transportation is possible at 10 bars and 2 °C, however the barges would require pressurized containers to store the hydrate. Several types of carriers have been proposed. These include bulk carriers, towed barges, LPG ships, detachable barges and truck transportation. Below in Table 5 is summary of some of the proposed transportation modes for gas hydrates.

Table 5
Summary of Transportation Modes for Gas Hydrate

Type of carrier	Operations	Hydrate form	Distances	Modifications
Truck	Land Non Associated & Flared Gas	Dry	Anywhere on land	Insulation
Truck	Land Associated Gas	Slurry	Anywhere on land	Insulation and Pressurization
Bulk Carriers	Offshore Non Associated & Flared Gas	Dry	Large distances	Insulation
Bulk Carriers	Offshore Associated Gas	Slurry	Large distances	Pressurized vessels
Bulk Carriers	Offshore Associated Gas	Crude Oil & Slurry hydrate	Large distances	Insulated pressurized pipe on deck of carrier

To be continued

Continued

Type of carrier	Operations	Hydrate form	Distances	Modifications
Towed Barges	Offshore Non Associated & Flared Gas	Dry	Short distances	Insulation
Detachable Barges (New)	Offshore	Dry & Slurry	Large Distances	Several Modifications. Attached to Processing Plant
Carrier with removable storage container (New)	Offshore & Land	Dry	Short Distances	Storage container could be removed by crane at markets

8. TRANSPORTATION DISTANCES

In the literature, there have been diverse views on the possible distances that gas hydrate could be transported once commercialized. Some have indicated that gas hydrate should only be transported to markets with short distances while others believe in transportation anywhere.

Once it is feasible and competitive with other transportation means, it could be useful for gas transportation. Whether short or long distances to be transported, there are markets for natural gas. For small volume applications, there are small tourist islands around the world that are ideally located to stranded gas areas. For example, stranded gas in Trinidad could be converted to gas hydrates and transported to the islands of the Caribbean. See map below which gives an indication of the distances from Trinidad to the other islands in the Caribbean (Figure 1).

www.maps.com

Figure 1
Island Chain in Caribbean

9. RE-GASIFICATION PROCESS

This involves using heat to dissociate the hydrate. Once the heat energy is available the process is simple. Re-gasification plants could be in close proximity to power plants. In this case the distance to the markets is small and the option of using waste heat from the power plants to drive the dissociation process. For the solid hydrate, the dissociation process involves converting the hydrate into slurry by addition of water and then using heat to transform the slurry to gas.

Dissociation of the hydrate can be obtained by mechanical, depressurization, chemical and thermal methods.

Focus on a large scale dissociation plant pilot project can be very useful in the technological advancement of natural gas hydrate. Funding of this could come from gas hydrate interested parties and governments.

10. ECONOMIC CONSIDERATIONS

Economic evaluation of the entire hydrate supply chain is important in the total evaluation of gas to solids becoming commercial. Comparison with other methods of gas transportation is key for economic analysis.

Many researchers believe that gas to solid is a cheaper and cost effective form of gas transportation. Once commerciality is achieved, a better economic evaluation can be done with the methods of gas transportation. It may be difficult at times to compare already proven technology with proposed technology. However, it is still a useful guide to determining investment needed and income generated from the sale of gas at the markets.

Some comparison with LNG done by a researcher showed the following economic evaluation (Gudmundsson *et al*., 1998) in Table 6.

Table 6
Cost Comparison with LNG

Cost	Gas hydrate comparison
Transportation	25% less than LNG
Production Process	3% less than LNG
Re-gasification Process	9% less than LNG

There is also tremendous potential for gas hydrate in smaller applications and shipped to small markets like tourist island chains around the world like the Caribbean and Mediterranean islands.

11. ENVIRONMENTAL CONSIDERATIONS

It is expected that during transportation of the hydrate some small amount of gas would be released. This can be captured and used as fuel for the vessel.

Natural gas in the hydrate form is generally safer than the other forms of capturing natural gas. Some of the reasons for this include: low toxicity, moderate storage conditions, low combustibility and reduced opportunity for damage of containment vessels.

Gas is ideal for use in combined cycle power plants. Natural gas produces less than half the carbon dioxide emissions per unit of electricity generated compared to conventional fuels. Gas is now considered the best fuel for electricity generation.

12. SOME MAJOR STUDIES DONE

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

A summary of some major studied done on gas hydrate is listed below in Table 7. Other studied have been carried out around the world including US and Australia.

The main studies on transporting gas as a hydrate include:

• UK (1996) by Advantica (Fitzgerald & Taylor, 2001)

• Norway (1990) by NTNU (Norwegian University of Science and Technology) (Gudmundsson *et al*., 1994)

• Japan (2001) by Mitsui Engineering (Taylor & Dawe, 2003)

There were also several small scale laboratory studies.

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

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

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

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

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

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

(vi) Most of the previous studies focused on simple gases such as methane and ethane (Table 7). Most natural gas has much more components than just methane and ethane and hence the composition can have significant impact on hydrate formation.

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

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

Table 7
Summary of Some Major Studies Done in Gas Hydrate

Country		Natural gas sample used in study	Deductions
UK	Advantica (Since 1996)	Methane	Hydrates are simple and intrinsically safe Technology appropriate for associated and flared gas
Norway	NTNU (Since 1990)	Methane sample and Mix sample of 92% methane, 5% ethane and 3% propane	NGH is attractive and favorable compared to other methods Long and short transportation possible
Japan	Mitsui Engineering (Since 2001)	Methane	Produced pellets – 600 kg/day NGH – 20-30% less than cost associated with LNG

13. WAY FORWARD

Further future studies should include the following.

Creation of a model that would incorporate all aspects of gas hydrates including kinetics, economics, field size etc. Figure 2 below shows a depiction of this model. The evaluation using this model would focus on the many short coming of previous studies.

(2) Continued research funding in gas hydrates studies because most new technological processes began with major challenges, but as time goes by there has been considerable improvements. Some commercialized processes might have an initial start up of 50% or more efficiency but has tremendous improvement in the future.

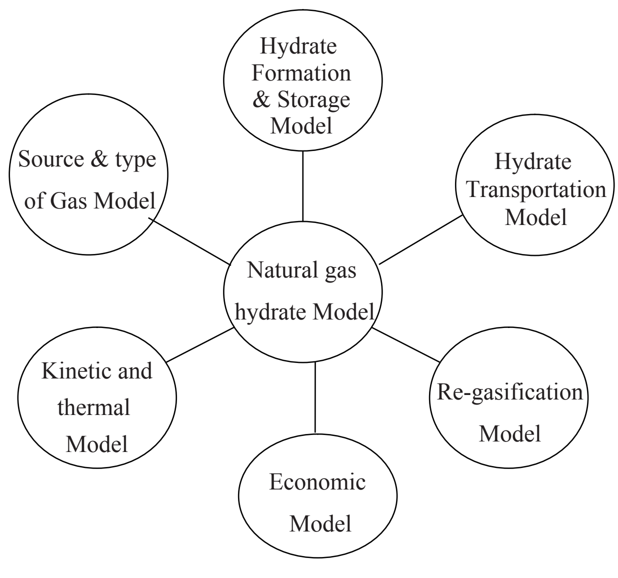

Figure 2
Gas Hydrate Model

(3) A very detailed feasibility study in the natural gas hydrate supply chain should be done incorporating all interested parties and governments. Creation of gas hydrate world task force would be useful. The feasibility study should compare the different natural gas transportation modes.

(4) Other possible uses of hydrates can also be investigated. Some of these include: temporary gas storage, gas separation, desalination and water treatment, carbon dioxide disposal and volatile organic compound (VOC) recovery,

14. PROPOSAL

The author proposes new work in evaluation natural gas transportation of small amount of gas from the well to the gas market and focus on all aspects of the gas hydrate model. The main components in producing natural gas hydrate (whether for gas storage or for transportation), are water and natural gas, at low temperatures and high pressures. Each variable has a significant effect on the formation of gas hydrate. It is therefore critical to analyze the effect of each variable on hydrate formation to ascertain the best conditions required for a successful gas hydrate formation process

In doing this, the follow are the proposed analysis

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

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

Since future work will evaluate gas transportation of gas volumes 5 MMscf/d or less it is therefore proposed that the same vessel used to form the hydrate be also used for storage and transport to its delivery point. The “one vessel” concept is very useful to avoid moving the solid hydrate from vessel to vessel for storage and transportation, reduce costs, since no additional facility is needed for dissociation at the final destination, and allow water re-cycling.

The results of this analysis would be highlighted in another technical paper. The analysis would only evaluate transportation of gas by hydrates and not exploiting naturally occurring hydrates.

CONCLUSIONS

Natural gas hydrates has the potential to contribute to the growth of the safe and eco-friendly natural gas usage all over the world.

Because these hydrates are not understood yet, there are still many scientific and engineering problems to solve.

Future work will pre-design a system for transporting natural gas in hydrate form to islands in the Caribbean.

The natural gas hydrate model shown in Figure 2 can be useful in evaluating natural gas hydrate supply chain.

Heat required for the dissociation can be obtained from waste heat from industrial plants that are in close proximity. Geothermal energy may also be a possibility but more analysis is needed.

Stranded gas, associated gas and some unconventional gas have great potential of being captured by a cost effective gas hydrate system.

Using one vessel for formation, storage, transportation and dissociation of the hydrates gives operational flexibility for temporary storage and transportation gas hydrate system.

NOMENCLATURE

CNG = Compressed Natural Gas
LNG = Liquefied Natural Gas
NGH = Natural Gas Hydrate

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