

Development of Natural Gas Hydrate (NGH) Supply Chain

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What is NGH?

Natural Gas Hydrate (NGH), often referred to as “Fiery Ice,” is a chemical compound where natural gas molecule (guest molecule) is being trapped within a cage composed of water molecule (host molecule). This configuration is known as clathrate (Figure 1). Methane, Butane, Propane, Carbon Dioxide, Nitrogen, Hydrogen Sulfide, etc., can make such clathrate as the guest molecule although the conditions of clathrate formation vary depending on its guest molecule inside. When the guest molecule is mixed gas, it is referred to as NGH. When NGH is discussed, it can be often confused with or referred to as methane hydrates, existing naturally and discovered under ocean beds and in permafrost regions around the world. Although chemical structure of Methane hydrates is the same as that of NGH, however, NGH is different from methane hydrates in the sense of being produced artificially. NGH can contain about 160-170 times of natural gas in volume whereas LNG can contain about 600 times of natural gas (Table 1). When the hydrate dissociates, the trapped natural gas inside is released, and dissociated water remains. NGH has a unique feature, so called, “Self Preservation Effect,” which enables it to be stabilized around minus 20 degrees Celsius under atmospheric pressure, not requiring cryogenic conditions like LNG. This enhances its easy-handling as a transportation medium.

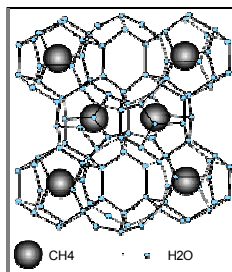


Figure 1: Chemical structure of methane hydrate

	Natural Gas Hydrate (NGH)	Liquefied Natural Gas (LNG)
Physical State	Solid	Liquid
Energy Density	165 Nm ³ /m ³ (+0.87m ³ Water)	600Nm ³ /m ³
Temperature	-20 deg C	-162 deg C
Pressure	Atmospheric Pressure	Atmospheric Pressure

Table 1: Comparison of characteristics of NGH and LNG

NGH Technological Development by MES and Key Feature of NGH

Mitsui Engineering & Shipbuilding Co., Ltd. (MES) has been continuously investing in research and development of all the segments of NGH supply chain: production, transportation, storage and re-gasification (Figure 2) since late 1990s.

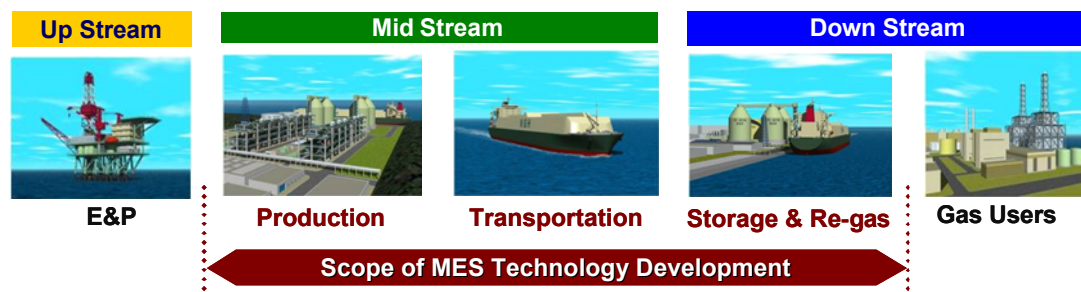


Figure 2: NGH supply chain by means of NGH pellets

MES first came up with a concept of transporting the NGH in a pellet form (Figure 3) for easy and high efficient transportation of natural gas. The basic concept of such supply chain, as shown in the Figure 2, is that the NGH pellets are produced at a production plant, and then carried by NGH carriers. Those NGH pellets are unloaded to onshore storage tanks and re-gasified back to natural gas for use. For the first commercial project, MES is targeting a marine transportation supply chain with production of 6000 ton-per-day per train and is currently under development of relevant technologies which cover the entire NGH marine transportation supply chain. MES assumes NGH can be a solution for monetizing of small to medium gas fields by establishing economical marine transportation of natural gas by means of NGH. NGH does not require cryogenic conditions like LNG in production, storage and re-gasification, however, NGH supply chain needs more carriers than that of LNG due to its smaller density of natural gas in the same volume, which inevitably results in higher cost in transportation segment. Even so, surplus costs of transportation would be offset by reduced cost in production, storage and re-gasification segments due to its milder stable temperature, and this makes the overall life cycle cost of the NGH supply chain lower than that of LNG by about 20% in case of production of 1 to 1.5 million-ton per annum between about 1000km and 6000km transportation distance. Moreover, Figure 4 is a conceptual chart which shows a relation of total supply chain CAPEX and transportation distance of NGH, Pipeline, CNG and LNG. The figure indicates that NGH is the most suitable for small to medium production in short to mid-range distance transportation.



Figure 3: NGH pellets under atmospheric pressure

Relation of Total Supply Chain CAPEX and Transportation Distance of each Natural Gas Transportation Medium (case: 1~1.5 million ton per annual)

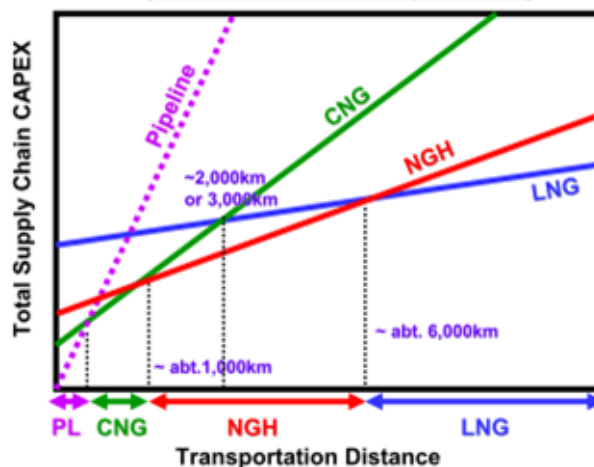


Figure 4: Comparison of CAPEX tendency among natural gas transportation media (Source: NGH Japan Co., Ltd)

Regarding the technological milestone, MES's first attempt to produce NGH pellets artificially was in 2003. MES constructed a testing unit in Chiba, Japan with a capacity of 600 kg-per-day, called Process Development Unit (PDU) (Figure 5). PDU successfully produced high purity NGH pellets at continuous high speed, and those pellets were re-gasified. Further, in 2005, as the second-stage of production process development, another NGH production experimental unit, called, Bench Scale Unit (BSU) was constructed in Chiba Works (Figure 6). The BSU succeeded in producing

NGH pellets from mixed gas, which had been considered challenging at that time, and became a technological breakthrough.



Figure 5: PDU plant in MES Chiba Works



Figure 6: BSU plant in MES Chiba Works

Since then, MES has increased research and development activities through the operations of both PDU and BSU, conducting a series of operations under different operational conditions. MES has accumulated a wide range of engineering data for stable production of high quality NGH pellets. Over the course of recent years, the BSU has been upgraded with newer process equipment, and a variety of tests are ongoing for scale-up process development.

The World's First NGH Land Transportation Demo Project

In 2006, MES obtained an opportunity to advance their technological development further. That was a NGH Land transportation demonstration project subsidized by a Japanese national institution, New Energy and Industrial Technology Development Organization (NEDO), which ended in 2009. MES, pairing with The Chugoku Electric Power Co., Inc. (CEP), constructed a NGH production plant with a capacity of 5 ton-per-day in the Yanai LNG-based Power Station of CEP, located in west side of Japan (Figure 7).



Figure 7: NGH production plant with 5 ton-per-day capacity built in Yanai LNG-based Power Station of CEP

This demonstration project was called “Y Project” after the name of the city, Yanai-city, Yamaguchi Pref., where the demonstration plant was constructed. Produced NGH pellets were actually transported by purpose-built tank trucks to natural gas consumers approx. 100km away from the demonstration plant and re-gasified/utilized in industrial setting and as city gas.

This demo project has become the world's first NGH land transportation demonstration project in verifying 5 ton-per-day capacity and confirming viability of natural gas land transportation by means of NGH.

Background of Y Project

To cope with global climate changes, natural gas has gained tremendous attention as a “clean energy” source of reducing amount of greenhouse gases in the world and the Japanese government has been encouraging the use of natural gas as its Basic Energy Plan and has been trying to spread the use around the country.

Although Japan currently has about 40 working LNG receiving terminals, the nation itself is not thoroughly covered by pipeline network like the United States or European countries. Therefore, for large natural gas consumers in the non-pipeline areas, LNG trucks have been playing a major role of transporting natural gas from those LNG receiving terminals. On the other hand, relatively small but potential natural gas users who are not able to afford LNG receiving facility and its maintenance have been kept abandoned. The Japanese government's incentive for Y Project, therefore, was to verify a safe and cost-effective transportation method of natural gas for those potential users in non-pipeline areas in the country. In this context, MES saw an opportunity there to verify a larger scale of production of NGH since NGH can be a good solution to deliver natural gas to such potential users.

Outline of Project

One of the other objectives of Y Project was to effectively utilize surplus LNG and cold heat from LNG at the terminal for NGH production. The cold heat from the LNG was used for a coolant of the production facility, and LNG, which is Methane rich multi-component gas, was used as feed gas of NGH production. Produced NGH pellets were delivered by NGH purpose-built tank trucks to a 280kW gas engine generator and re-gasified to generate electricity by the engine. Smaller amount of NGH pellets around 0.4-ton were carried in NGH containers by a small truck to a testing facility equipped with home appliances as simulated household user for city gas use (Figure 8).

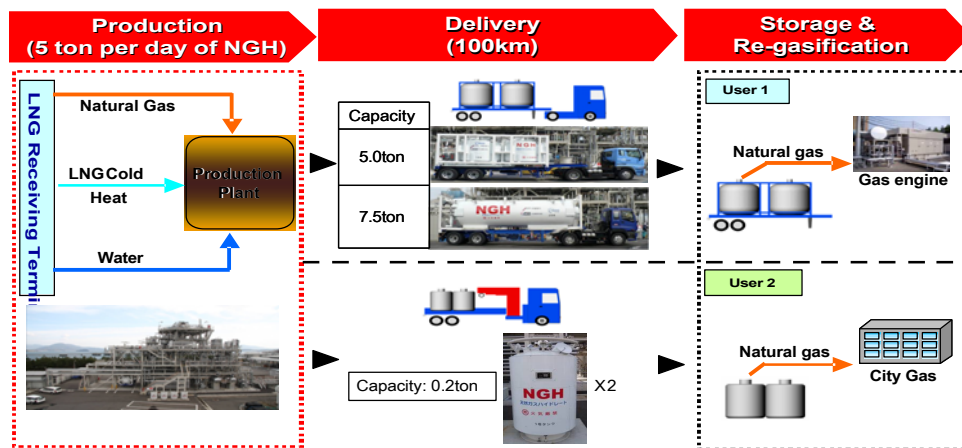


Figure 8: Outline of the Y Project

NGH Production

This production plant was constructed based on the same production process as used in BSU, which had been developed and operated at MES Chiba R&D Center with solid proven track records. The NGH production has 5 main production processes consisting of NGH formation, de-watering, pelletizing, cooling and de-pressurizing. Key features of each process will be described hereafter.

(1) NGH formation

Natural gas comes in contact with water in NGH reactor whose agitator stirs and mixes natural gas and water at around 5 degrees Celsius under 5.3MPaG of high pressure conditions. Then, the NGH slurry is produced continuously under high pressure conditions. At the same time, the water is circulated in outer heat exchanger refrigerated by cold heat from LNG via a medium of propane. The slurry of 10% NGH is produced in the reactor (Figure 9) and is carried off to the de-watering process.

(2) De-watering

The slurry goes into the de-watering tower from the bottom, and the screen set inside the tower dewater the water. Then, as the slurry bed is gradually raised, further dewatering is caused by the gravity. Figure 10 shows a rough image of de-watering system.



Figure 9: NGH reactor and slurry generated inside

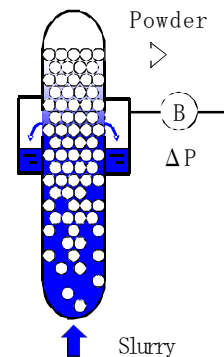


Figure 10: De-watering system

(3) Pelletizing

Further de-watering takes place in a pelletizing process. From experimental and operational results from BSU, MES has revealed that pelletizing and squeezing out additional water enhances production of higher-quality NGH pellets. A high-speed briquette machine is equipped for molding pellets.

(4) Cooling and De-pressurizing

The NGH pellets are refrigerated down to minus 20 degrees Celsius in the cooling drum via cooling gas circulated inside where its Self Preservation Effect manifests itself (Figure 11). After the pellets are cooled down, de-pressuring operation is carried out to reduce the pressure from 5.3MPaG to atmospheric pressure by using a batch process in the thin vessel equipped inlet and outlet ball valves for the passage of NGH pellets.



Figure 11: NGH Pellets in cooling drum

(5) Conveying and Shipping

After the pellets are de-pressurized, they are carried by vertical and horizontal

conveyors to loading point and are automatically loaded by a distributing machine to the trucks or containers for shipping. This conveying system verified easy-handing of natural gas in pellet form.

NGH Transportation

The NGH pellets are transported to a gas engine power generator (User 1) as a demo of industrial use and a testing facility simulating household users (User 2) as a demo of city gas use. Both sites are located about 100 kilometers away from the demonstration plant in Yanai. The developed containers function for the double roles: storage and re-gasification. Table 2 shows main specifications of containers for each user. Figure 12 and 13 are photos of a developed purpose-built tank truck and a container for each type of consumer, respectively.

A combination of a glass wool felt in vacuum packing and ordinary hard urethane foam is applied as insulating material of outside containers against heat release and input. The pellet container for User 1 is a 20 feet truck. The trucks can be detached from a tractor head at the consumer site so that the tractor head can come back to the demo plant for another delivery. On the other hand, small containers for city gas use for User 2 are delivered on a truck and unloaded at the testing facility (User 2). During the 2 hour-transportation, it was revealed the temperature of gas phase in the container increased only slightly, which indicates that dissociation rate of produced NGH pellets were low.

	User 1	User 2
Consumer	GE Power Generator	Testing Facility equipped with home appliance
Amount of Pellets	5-7.5 ton	0.4ton / 2 containers
Amount of Gas	650Nm ³	50Nm ³
Design Pressure	0.8MPaG	0.8MPaG
Normal Use Pressure	0.5MPaG	0.5-0.7MPaG

Table 2: Specifications of NGH pellet containers



Figure 12: 7.5 capacity purpose-built tank truck equipped with re-gasification device



Figure 13: Pellet container for User 2

NGH Re-gasification and Utilization

After the NGH trucks arrive at the re-gasification sites (users' sites), they are connected to its gas supply and utilization system by a flexible hose. Re-gasification takes place by circulating warm water in the bottom of containers and NGH pellets submerged at the bottom are dissociated and generate natural gas. As the NGH pellets in the bottom of the containers dissociate, NGH pellets stored upper part of the container gradually slide down by gravity and start to dissociate accordingly. Further, the amount of gas generated was assumed equivalent to the amount of dissociated gas from NGH pellets. The speed and amount of the re-gasification were controlled by the amount of circulation water into the containers.

(1) Gas Engine Power Generator (User 1)

The purpose-built tank trucks are equipped with a re-gasification device so that there is no need for users to set up a re-gasification facility on site, which reduces a burden of cost on the users.

The re-gasified gas was supplied to the gas engine at Energia Economic and Technical Research Institute of CEP. The re-gasified gas was sent at the maximum rate 65Nm³/hr, the maximum 280kW of electric power was generated at the gas engine. The heat source for re-gasifying NGH pellets was obtained by a heat exchanges between gas engine exhaust



Figure 14: Gas Engine Power Generator Site (User 1)

heat and the circulation water. The dissociated water, which is around 6-7 degrees Celsius, was sent back to the cooling tower of the engine as a coolant for recycling. Gas supply system composed of water circulation system, a gas buffer tank, other related machinery and pipes, and a NGH pellet container and the operation, all of these were controlled and monitored by a control panel. In this site, the gas engine operates daytime, what is called, Daily Start & Stop. In this test, MES successfully achieved a stable re-gasification from NGH pellets and verified one of the industrial applications of NGH (Figure 14).

(2) Testing Facility equipped with home appliances (User 2)

This testing facility (User 2) was located at Technology Research Institute of Hiroshima Gas Co., Ltd (Figure 15) and was designed to simulate household, therefore, it was set to meet 24-hour continuous & automatic operation. The re-gasified gas at the rate of 0.5-6.0 Nm³/hour was supplied to the facility. Re-gasification takes place in the bottom of the panel filled with NGH pellets by circulating warm water heated by a heat pump. Since the cylindrical tank stands vertical to the grand, the pellets fall in the warm water. Because the area of the heat transfer between pellets and water is fixed approximately, it is possible to control the generation of the gas by the quantity or the temperature of circulation water. Controllability of amount and speed of re-gasification were tested to see if the re-gasification could keep up with gas demand simulating a housing complex of about 10 households. Moreover, gas quality was examined to meet local city gas regulation such as moisture, odor level and wobble index. The gas re-gasified from NGH was also applied to home gas burners and gas heaters were to confirm applicability and safety of NGH as city gas use.



Figure 15: Testing facility equipped with home appliance (User 2)

Outcomes

In the sense of NGH technological advancement toward its commercialization, achieving 5-ton per day production of NGH is a great step toward to commercialization of the technology, because up to the Y Project, MES succeeded in the NGH production only with bench-scale units, although a land transportation project is not the business that MES is targeting at as the final goal of commercialization. What is also important for MES is that it could accumulate process design data and operational know-hows and conditions for commercially adoptable technology development.



Figure 16: NGH purpose-built tank truck delivering NGH to non-pipeline area

Y Project also has a significant meaning itself and a great impact on future possibility of land transportation of natural gas because it has verified the entire land transportation supply chain by means of NGH including production, transportation, storage and re-gasification. Through the supply chain, MES confirmed a possibility of both industrial and city gas applications of NGH. This new medium of transporting natural gas would broaden a range of possibility of distributing natural gas to non-pipeline areas in Japan or inland areas of other countries where it is geologically difficult to lay out the pipeline network (Figure 16). Although the NGH supply chain like Y Project using LNG as a feed gas was the particular condition to this demonstration project, land transportation of NGH to inland potential users isolated from the current natural gas distribution network could be realizable, if the NGH pellets transhipped from an NGH ship to tank trucks at the receiving terminal. Such kind of operation could be an advantageous utilization method of NGH and it may be an incentive for the potential users to introduce NGH. Finally, we have to emphasize that what is additionally important in this specific demonstration project was not only we could examine robustness of the NGH production process with multi-component natural gas in a certain scale but also we could demonstrate an effective way of utilizing untapped cold heat generated in LNG receiving terminals.

Toward Commercialization of NGH marine supply chain

In parallel with Y Project mentioned above, MES has been developing such new commercial production process on target at high speed and compact process design, which remains to be proven, however, the development is now nearly completed with experiences and operational know-hows in Y Project reflected on the development.



Figure 17: NGH carrier under basic design

In addition to the production process development, MES has devoted itself to the development of NGH carrier, whose concept is based on existing bulk carriers (Figure 17). The safety guideline of the carrier was submitted to the International Maritime Organization (IMO) and its provisional safety guideline was enacted in May, 2010. Furthermore, storage tanks and re-gasification technology are also being under development toward commercialization. MES is now under planning of a 100 ton-per-day class pilot project, in cooperation with Mitsui & Co. Ltd. (Mitsui) as the final stage of technical verification which is the indispensable step for moving on to the 1st commercial project. In the pilot project, we will confirm the viability of all the technologies

necessary for the commercialization, including the currently-developing production process and the technologies relevant to the other segment such as a storage silo, a tank simulating a cargo hold of NGH carrier, loading/unloading facility and re-gasification system in 100 ton-per-day scale. The 1st commercial project will be assumed to be an onshore-base project. After successful completion of land-based project, we seek its FPSO application, targeting monetization of offshore natural gas fields including flare gas and associated gas (Figure 18).

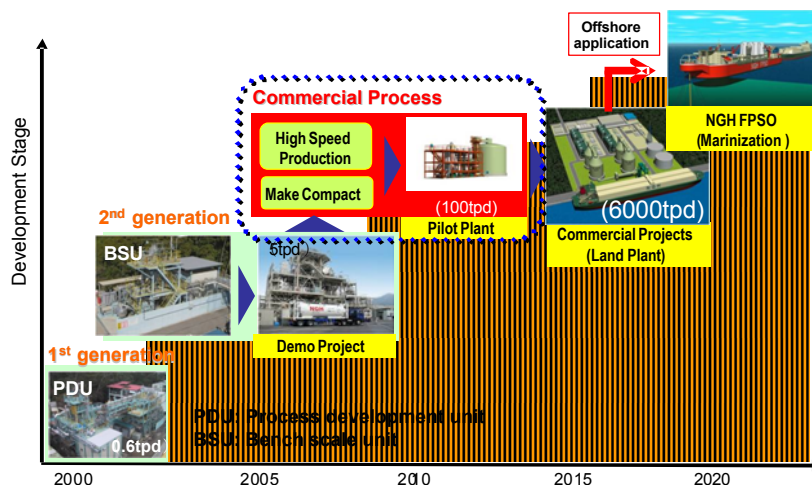


Figure 18: Roadmap toward commercialization

Conclusions

Amid expectations that the NGH technology could play an important role as a new transportation and storage medium of natural gas, MES has completed the world's first land transportation demonstration project of natural gas using NGH in conjunction with CEP with financial assistance of NEDO. The completion of Y project has increased a potential of land transportation of NGH in near future and made R&D stage of MES step forward from bench-scale to a certain industrial scale. The supply chain in Y Project is different from a marine transportation supply chain, which MES aims at, however, the Y project has a significant meaning in terms of being able to verify the entire transportation supply chain of natural gas by means of NGH, and to confirm the 5 ton-per-day capacity of NGH production. Technologies for monetization of the small and medium gas field have become the center of attention in the gas business over the past years, however, not a technology, including Small-Scale LNG and CNG, has yet to be successfully commercialized up to now. NGH has its unique strengths and aims at niche markets suitable where current LNG technology may not see an opportunity. For NGH, it is important to become ready for the market entry by realizing the pilot project as early as possible. Finally, the hydrate technology can be not only a promising technology to unlock small to medium gas fields around the world, but also has other potentials of applications in the future. For example, hydrate formation technology, using mechanism of gas molecule being hydrate can be applied for carbon dioxide separation from other gases. In particular, MES has been also devote itself to research and development on carbon dioxide separation by hydrate method to be applied to IGCC (Integrated coal Gasification Combined Cycle) or monetizing high carbon dioxide content gas fields. NGH is a technology carving out a new future with natural gas. A quest for NGH commercialization by MES will continue unabated.



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