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Derleme / Review

THE ROLE OF NATURAL GAS HYDRATE DURING NATURAL GAS TRANSPORTATION

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ABSTRACT

The dependence of industry on natural gas has increased a lot last decades so the transportation of natural gas has become one of the most important issue in natural gas industry. Although the formation of natural gas hydrate is a problem in natural gas pipelines, the transportation of natural gas as natural gas hydrates by ships or trucks is an advantage. Therefore, in this study, first, the studies related to the inhibition of natural gas hydrate in pipelines are reviewed because there are many gas pipeline projects so natural gas hydrate inhibition is an important issue in natural gas industry. Then, the studies related to the transportation of natural gas as natural gas hydrates are reviewed in this study because this is a new subject and for the future, if research and development in this transportation method could be done successfully, this method might be better alternative compared to LNG and CNG natural gas transportation methods.

Keywords: Gas hydrates, natural gas, hydrate inhibition, transportation

DOĞAL GAZ TAŞINMASI SIRASINDA DOĞAL GAZ HİDRATLARIN ROLÜ

ÖZ

Endüstrinin doğal gaza olan bağımlılığı son on yıllarda büyük oranda artmıştır bu yüzden doğal gaz endüstrisinde doğal gazın taşınması çok önemli konulardan birisi olmuştur. Doğal gaz hidrat oluşumu, doğal gaz boruları için bir problem oluşturmasına rağmen, doğal gazın doğal gaz hidratı olarak gemiler veya tırlar ile taşınması bir avantajdır. Bu yüzden, bu çalışmada ilk olarak boru hatlarında doğal gaz hidratlarının oluşmasının engellenmesi ile ilgili çalışmalar derlenmiştir çünkü bir çok gaz boru hattı projesi mevcuttur. Bu nedenle, doğal gaz endüstrisinde doğal gaz hidratlarının engellenmesi önemli bir konudur. Daha sonra, bu çalışmada doğal gazın doğal gaz hidratları olarak taşınması ile ilgili çalışmalar derlenmiştir çünkü bu yeni bir konudur. Gelecekte bu doğal gaz taşıma yöntemi ile ilgili araştırma ve geliştirme sonuçları başarılı bir şekilde tamamlandığında, bu metot LNG ve CNG doğal gaz taşıma metodlarına kıyasla daha iyi bir alternatif oluşturabilir.

Anahtar Kelimeler: Gaz hidratlar, doğal gaz, hidrat engellenmesi, taşınma

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1. INTRODUCTION

The number of gas hydrate studies has increased since last decades. These studies mainly focus on natural gas hydrate reservoirs (exploration, drilling, well completion and production), gas hydrate inhibition in pipelines, gas storage as gas hydrate, gas separation with gas hydrate formation, desalination with hydrate formation and refrigeration purposes [1-3]. The aim of this study is to review gas hydrate studies related to natural gas transportation. After first observation of hydrate by Sir Humphry Davy in 1810 [2], gas hydrates were considered as a problem during natural gas transportation via pipelines. However, with the development of technology and much more studies, it was observed that gas hydrates have several advantages in gas industry: high gas reserve potential in natural gas hydrates and natural gas hydrate transportation as natural gas hydrates [3]. Although there are many reviews related to natural gas hydrate reservoirs, the number of studies related to the importance of gas hydrates in the transportation of natural gas is less. Therefore, in this study, after short review of gas hydrates, it is aimed to review gas hydrate inhibition in gas pipelines and natural gas transportation as natural gas hydrates.

2. GENERAL INFORMATION ABOUT GAS HYDRATES

Gas hydrates or clathrate hydrates are solid compounds which their formation occur when gas and water come into contact at low temperatures and high pressures. Light hydrocarbon molecules such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and i-butane (i-C_4H_{10}) form their own hydrates at suitable temperature and pressure conditions with the presence of enough water in the system. Similarly carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2) and other gases form hydrate at their hydrate equilibrium conditions [1]. The first discovery of gas hydrate by Sir Humphry Davy was in 1810 [2] when he made an observation that there was a formation of solid due to a solution of chlorine gas (known as oxymetric gas) and water above the ice point [1]. The constitution of gas hydrate is roughly 85 v/v% of water but it contains different properties than ice such as mechanical strength, heat capacity, thermal conductivity etc. [3, 4].

There are three main types of gas hydrate crystal structure. Structure I (sI) subsumes two alterative cage types, a small pentagonal dodecahedral cage, implied 5^{12}(comprises 12 pentagonal faces on the cage), and a big tetrakaidecahedral cage, implied $5^{12}6^2$ (comprises 12 pentagonal and 2 hexagonal faces on the cage). Structure II (sII) also subsumes the small 5^{12} cage in addition to a big tetrakaidecahedral cage, implied $5^{12}6^4$ (comprises 12 pentagonal and 4 hexagonal faces on the cage). Structure H (sH) is constituted of the small 5^{12} cage, amid-sized $4^35^66^3$ cages (comprises 3 square, 6 pentagonal and 3 hexagonal faces on the cage and a big icosahedral cage, implied $5^{12}6^8$ (comprises 12 pentagonal and 8 hexagonal faces on the cage. The structure of formation is hinged mainly of the size of guest molecule [5]. If the formation of gas hydrates is succeeded only by one type of gas they are defined as pure or simple hydrates. Simple hydrates of CH_4, C_2H_6, CO_2, H_2S and Xe are named as sI type of gas hydrate. Furthermore, C_3H_8, i-C_4H_{10}, N_2 and O_2 compose sII type of gas hydrate. Apart from the sI and s II structures, for the formation of sH structure, a help gas like CH_4 is necessary with other components having larger diameters than i-C_4H_{10} such as i-C_5H_{10} [6]. sI and sII hydrates are common in nature worldwide, however sH hydrates are not common and there are only in few areas such as Gulf of Mexico, Cascadia and Caspian Sea [7]. Moreover, natural gas might be transported as natural gas hydrate [3]. Thus, the structure of pure gas hydrates and natural gas hydrate should be known. To comprehend the cause for the synthesis of alternative forms of gas hydrate structures with alternative gas molecules, Table 1 is frequently used. Table 1 presents the analogy between the molecular diameters and the cavity diameters. For example, the analogies for C_2H_6 in sI hydrate are 1.08 for small cages and 0.939 for big cages. For C_2H_6 in sII hydrate, the analogies are 1.10 for small cages and 0.826 for big cages. Hence, C_2H_6 form sI hydrate when temperature and pressure of the system are in C_2H_6 hydrate equilibrium curve because C_2H_6 fills big cages of sI hydrate better compared to big cages of sII hydrate.

From the other side, C_3H_8 molecules form sII hydrate because these molecules are large enough not to fit into the cages of sI hydrate as seen in Table 1. As presented in the Table 1, C_3H_8 molecules only match into the large cages of the sII structure. In a simple hydrate of C_3H_8, 16 small cages of sII hydrate structure remain vacant. For this reason, C_3H_8 is not steady at higher temperature conditions due to empty cages. For C_3H_8 hydrate formation, firstly it is needed temperature more than 278 K (4.85^{o}C) and secondly high pressure values are also essential [8]. To comprehend the conduct of gas molecules in the cavities of simple hydrates and hydrates of gas mixtures, Table 1 is quite helpful.

Table 1. Analogies between Molecular Diameters and Cavity Diameters for Natural Gas Hydrate Formers with a Few Others [1] ^{a} Shows the cavity occupied by the simple hydrate former. ^{b} Shows that the simple hydrate is only formed at very high pressure

Molecular Diameter/Cavity Diameter for cavity type					
Gas Hydrate Former		**Structure I (sI)**		**Structure II (sII)**	
Molecule	**Diameter (A)**	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$
He	2.28	0.447	0.389	0.454^{ab}	0.32^{ab}
H_2	2.72	0.533	0.464	0.542^{ab}	0.408^{ab}
Ne	2.97	0.582	0.507	0.592^{ab}	0.446^{ab}
Ar	3.8	0.745	0.648	0.757^{a}	0.571^{a}
Kr	4.0	0.784	0.683	0.797^{a}	0.601^{a}
N_2	4.1	0.804	0.700	0.817^{a}	0.616^{a}
O_2	4.2	0.824	0.717	0.837^{a}	0.631^{a}
CH_4	4.36	0.855^{a}	0.744^{a}	0.868	0.655
Xe	4.58	0.898^{a}	0.782^{a}	0.912	0.687
H_2S	4.58	0.898^{a}	0.78^{2a}	0.912	0.687
CO_2	5.12	1.00^{a}	0.834^{a}	1.020	0.769
C_2H_6	5.5	1.08	0.939^{a}	1.100	0.826
c-C_3H_6	5.8	1.14	0.990	1.160	0.871^{a}
$(CH_2)_3O$	6.1	1.20	1.04^{a}	1.220	0.916^{a}
C_3H_8	6.28	1.23	1.07	1.250	0.943^{a}
i-C_4H_{10}	6.5	1.27	1.11	1.290	0.976^{a}
n-C_4H_{10}	7.1	1.39	1.21	1.410	1.07

3. GAS HYDRATES IN PIPELINES

Gas hydrates were not consulted to have any useful nexus until 1934, when Hammershmidt [9] discovered that instead of ice, gas hydrates were liable for blocking gas pipelines in Canada. Plugging can be avoided in pipelines by using different methods of inhibition, for example, by heating or insulating the critical pipeline expanses or by adding inhibiting chemicals such as methanol. All of those conventional methods of hydrate inhibition are not only very costly but also can pose hazards for the environment because most of inhibitors such as methanol are dangerous for environment and high weight percentage of these inhibitors should be added into the pipelines to avoid the plugging of pipelines with gas hydrates [10]. Many laboratories in the world are actively seeking the solution to the problem of natural gas transportation in pipelines [11]. Natural gas produced from natural gas reservoirs are transported to different locations (i.e. importers, house, industry etc.) mainly as in gaseous phase, solid phase or liquid [12]. Natural gas or stranded gas is transported in gaseous form by using pipelines, CNG (compressed natural gas), and LNG (liquefied natural gas). The transportation of natural gas (NG) is in solid phase only possible via natural gas hydrate (NGH) [13].

While selecting of NG transportation type from NG production site, the economy is quite important. Hence, the distance between NG production site and NG transportation place is quite important [13, 14]. Figure 1-a shows the economic comparison of natural gas transportation technologies. As shown in this figure, after approximately 2000 km, NG transportation via pipelines are not considered economical [15, 16]. Accordingly, after this distance, there are different alternatives to pipelines such as LNG, NGH and GTL (gas to liquids). Among these, if NG pipelines are not economical after certain transportation distance, currently the most common NG transportation is done via LNG. This is because with current technology, LNG is the most economical method in long transportation distances compared to other transportation methods [17, 18]. Mainly in LNG, produced NG is liquefied at gas liquefaction plants by decreasing temperature to -162^{o}C, then it is transported, mostly via giant ships and finally re-gasification occurs at the destination plants [19]. Qatar, Australia, Malaysia, Nigeria, Indonesia and Algeria are the top countries exporting NG as LNG in ships. Japan, South Korea, China, India, UK, Spain and Turkey are the top countries importing NG as LNG [18]. According to the cost of transportation, price of natural gas and technology, Figure 1-a might be updated. For example, different form of the comparison of CAPEX tendency among natural gas transportation media was shown in Figure 1-b. As stated in CAPEX tendency comparison among natural gas transportation media in Figure 1-b, the transportation of natural gas as NGH seems much more feasible than other methods when the transportation distance is between 1000 km and 6000 km. However, especially in short distances as seen in Figure 1, natural gas transmission with pipelines seems economical. Moreover, there are long natural gas transmission pipeline projects (such as West-East Gas Pipeline Project, TurkStream project) from Asia to Europe to provide natural gas needs of European countries [20, 21]. Consequently, the studies to prevent gas hydrate formation in natural gas transmission lines are necessary because there might be water even after gas-water separation and dehydration, so this might cause gas hydrate formation in pipelines. In this section, it is aimed to review the studies trying to avoid the plugging of gas pipelines due to gas hydrates.

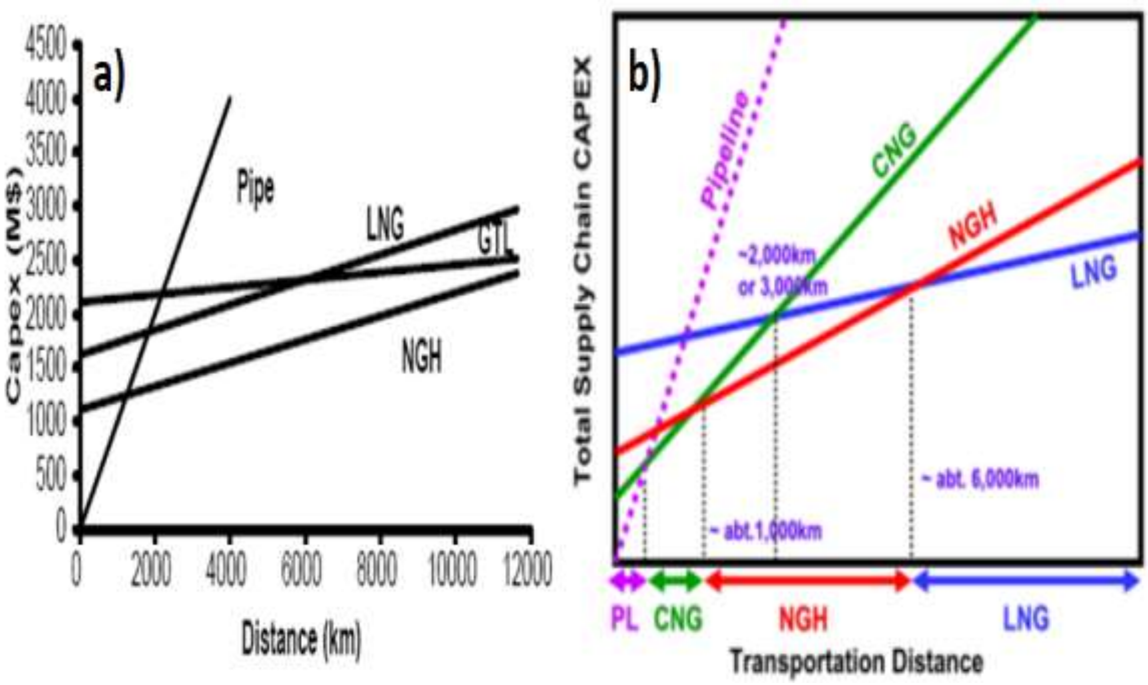

Figure 1. (a) Economic comparison of natural gas transportation technologies for the case of 400 MMscf/day, 3500 nautical mile supply chain [14, 15] (b) Comparison of CAPEX tendency among natural gas transportation media (for case: 1~1.5 million ton per annual) [16]

Figure 2. Plugging of natural gas pipelines with gas hydrates [28]

As well as gas hydrate plugging in gas pipelines, hydrates can also affect different types of natural gas pipeline's internal corrosion, which is a long-term trouble through physical and chemical procedures based on hydrate size, stage and contact period [22]. H_2S, CO_2 and Cl^- that are components of hydrate are acidic gases, which have been established to contribute to internal gas pipeline corrosion rate [23]. Methane (CH_4), the major component of natural gas, as a reducing agent also aids metal corrosion [24]. Water is another known corrosive agent [25]. Corrosion apart from the economic consequences will also create environmental and political corollaries and will guide to integrate substitution of the pipe-length at extra production rate [23].

Over the past decades, there have been crucial scientific and industrial concerns on clathrate gas hydrates [9, 26]. Formation of gas hydrates produces some specific problems such as in transportation through pipelines [27, 28] as seen in Figure 2, in well completion [29] and in oil and gas drilling in the wellbores [30]. For this reason, impeding the formation of gas hydrates is a crucial problem in oil and gas industry. There are two ways to solve this problem either hydrate avoidance (no entry in hydrate domain) or hydrate management (operate with risk in hydrate domain). The management of hydrate prevention includes activities that Figure 3 shows [31].

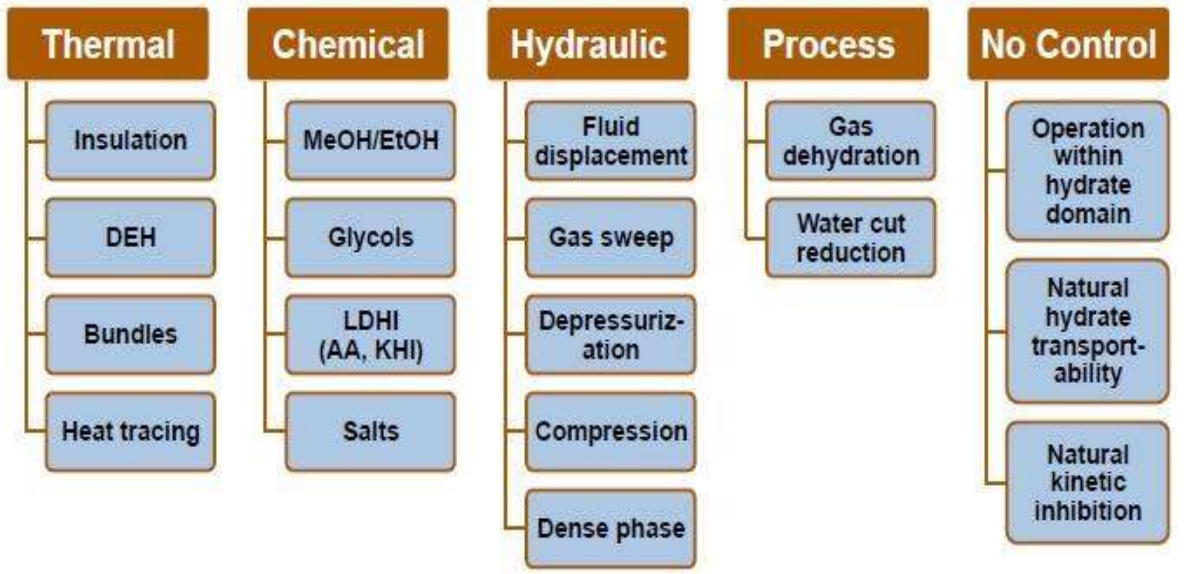

Figure 3. Hydrate Management Strategies [31]

Through any of these methods can be effective in preventing hydrates, some may not be attainable or covetable for deep-water operations. For example, dehydration is uneconomical for subsea wells or small platforms with limited space. Heating and insulation can be used independently or simultaneously; however, it may not be cost effective for longer flowlines to convey high GOR (gas/oil ratio) fluids. Chemical inhibition is by far the most commonly used method for avoiding the plugging due to hydrates [32]. Habitually, the impeding of hydrate formation has been succeeded in the addition of thermodynamic inhibitors (THIs) such as the organic compounds methanol, mono-ethylene glycol (MEG) and di-ethyl glycol (DEG) commonly referred to as glycol and triethylene glycol (TEG). Other thermodynamic inhibitors according to literature such as salts are sodium chloride (NaCl), chloride potassium (KCl), calcium chloride ($CaCl_2$), sodium bromide (NaBr), potassium bromide (KBr), calcium bromide ($CaBr_2$), potassium carbonate (K_2CO_3), magnesium chloride ($MgCl_2$) [33-37]. THIs are commonly used in large concentrations (e.g. 40-60 %vol) [38] and they work by changing the thermodynamic forming conditions of hydrates [39]. Apart from these large quantities, with large CAPEX needed in facilities to store and recycle them, the use of THIs is ecologically unsound [40].

Kinetic inhibitors (KHIs) are low dosage inhibitors (LDHs) that are added at low concentrations (<1 weight %) and do not affect the thermodynamics of hydrate formation [41]. However, these kinetic inhibitors disperse hydrate particles as they form such as special surfactants or some of them inhibit hydrate formation for a long period of time by extending the induction time for hydrate formation such as kinetic hydrate inhibitors (KHI) [11, 42]. The time to the formation of the first hydrate crystals is called induction time [43]. KHIs allow you to transport hydrate-forming fluids for a certain period before hydrates start to form. There are three main categories of KHIs developed for field applications, all of which are polymeric compounds. These are [44]:

1) Poly (N-vinyllactam) polymers containing a variety of copolymers and grafted polymers. Some examples are polyvinypyrrolidine (PVP), polyvinylpiperidone (PVPip), polyvinylcaprolactam (PVCap) and polyvinylazacyclooctanone (POVACO)
2) Hyper-branched poly (esteramide)s. It is feasible to modify the tips on its molecular structure to make the polymer more or less hydrophilic
3) N-Isopropylmethacrylamide (IPMA) polymers and copolymers. KHIs which have also been tested are: maleic polymers, polymaleimides, polyaspartamides, alkylamides and polyalkyloxazolines.

Anti-agglomerants are low dosage inhibitor (LDHI's) confers to researchers and companies an additional tool for checking hydrates in their systems. On the contrary to kinetic and thermodynamic inhibitors, anti agglomerants LDSH's inhibit hydrate plugging rather than hydrate formation. Anti- agglomerants permit hydrates to form but retain the particles small and well dissipated. In other words, AAs have a hydrophilic head and hydrophobic tail [45]. According to Koh et al. [46], AAs are described as emulsifying agents, which suspend hydrate crystals in condensate (light weight liquid hydrocarbon) because the ends of AA molecules have qualities attractive to both hydrates and oil including dissolved gas. The amount of AA demanded for hydrate blockage impeding is almost only a fraction of the THI dosage and therefore AA does not appreciably shift the hydrate thermodynamic equilibrium curve of system. Due to the mechanisms by which AA works, its felicitous application requests the presence of hydrocarbons [47]. AAs as chemicals are polymers and surfactants which are also added at low concentrations (<1 weight % of AA).

Apart from the three main classes of inhibitors (THIs, KHIs, AAs) there is one more which can be named dual function thermo-kinetic inhibitors and are inhibitors that are capable of not only shifting the Hydrate Liquid Vapour Equilibria (HLVE) curve but also slow down the nucleation and/or growth rate. In this category belongs imidazolium based- ionic liquids. Ionic liquids are organic salts with strong electrostatic charges, their anions and cations can be selected to form hydrogen bonding with water and they are environmentally friendly solvents due to their stability [48, 49]. The outcomes as far as it concerns the cation type of ionic liquid on shifting the HLVE curve is regarded inconclusive while the anion does not seem to influence the performance of ionic liquid in HLVE curve. On the contrary, the results of anions and cations on induction time were better. Tetrafluoroborate's performance was better than other ionic liquids and even better than PVP. The performance on induction time of EMIM-BF_4 was preferable compared to Luvicap and pure PVCap. It should be noticed that an ionic liquid concentration larger than 1% wt does not give better outcomes in the hydrate formation [50].

The main points in order to avoid the plugging of pipelines due to gas hydrate formation are:
- The selected gas hydrate inhibition type should be feasible.
- The chemicals should be used in low concentration.
- The chemicals should have minimum risks for health, environment and safety

Due to the reasons explained above, there is a tendency to change inhibitor type from thermodynamic inhibitors to kinetic hydrate inhibitors, anti-agglomerants and thermo-kinetic inhibitors to avoid the plugging of natural gas pipelines due to hydrate formation.

4. NATURAL GAS TRANSPORTATION AS NATURAL GAS HYDRATES

Figure 1 shows the main natural gas transportation methods, which are mainly pipelines, liquefied natural gas (LNG), compressed natural gas (CNG), natural gas hydrate (NGH) and gas to liquid (GTL) [14-16]. Although for short distances, gas pipelines are preferred, especially for long distances, LNG is commonly preferred as natural gas (NG) transportation method nowadays. However, there are many risks of LNG transportation with both ships and road trucks:
- Ship or truck accidents might cause the explosion of LNG. That is why LNG is regarded as extremely dangerous with container ships called floating bombs [51].
- If there are leaks in the storage tanks of LNG, some of LNG might return to gaseous state and at certain concentration, there is a risk of flammability and explosion [52].
- LNG is stored at approximately -162^{o}C and it should be kept at this temperature during transportation. If there are problems related to keep temperature constant at this extreme condition, it might cause explosions [52].
- Liquefied gases are non-toxic and insoluble in water so compared other oil spills, there are minimum risks of it for the environment but extremely dangerous for people since it is toxic and explosive [53].

The transportation of natural gas (NG) as natural gas hydrate (NGH) is considered as an alternative to LNG because as explained, there are many risks of LNG transportation and compared to other transportation method, NGH transportation is much safer [54-57]. Table 2 lists some physical properties of NGH, LNG and CNG transportation methods [16, 54, 58, 59, 60]. At atmospheric pressure conditions and nearly -20^{o}C, it is possible to store nearly 170 standard m^3 of NG inside 1 m^3 of NGH (in solid form) as shown in Table 2. Compared to LNG and CNG, the risks of NGH transportation method is low because it is stored near atmospheric pressure so it is not explosive.

Table 2. Physical Property Data for NGH and LNG [16, 54, 58, 59, 60]

	Natural Gas Hydrate (NGH)	**Liquefied Natural Gas (LNG)**	**Compressed Natural Gas (CNG)**
Phase	Solid	Liquid	Gas
Temperature, ^{o}C	~ -15 to -20	~ -162	~ 25
Pressure	Atmospheric	Atmospheric	20 MPa
Gravity	0.85-0.95	0.42-0.47	~ 0.55
Contains in 1 m^3	Natural Gas: 150 to 180 (~ 170) standard m^3 Water: ~ 0.8 m^3	Natural Gas: 600 to 620 standard m^3	220 standard m^3
Risks	Low	High	High
Natural gas purification requirement before production	Low	High	High
Storage tank	Common adiabatic atmospheric storage tank	Cryogenic storage tank using double layer metal structure	Seamless pressure storage tank

This method is safest, cleanest and might be the most feasible one if necessary development in this technology is completed [58, 61-63]. Hence, many experimental studies are necessary to provide optimum gas hydrate formation, storage and dissociation methods. Natural gas transportation as NGH includes three stages: production (gas hydrate formation), transportation and regasification [16, 61-68]. In NGH transportation method, first gas hydrate is formed by mixing water and natural gas (NG), then gas hydrates form at certain preparations conditions (0-20^{o}C and 2-6 MPa). Then, free water is separated from gas hydrates. The temperature of the system is lowered up to -20^{o}C to store gas hydrate at atmospheric pressure mostly as dry hydrates, hydrate slurries and pellet hydrates in ships (mostly) or trucks. When gas hydrate is transported to the destination point via NGH transportation method, gas hydrate is dissociated by increasing temperature of the system [16, 69]. This procedure is briefly summarized in Figure 4. In NGH transportation, the most important part is the hydrate formation part because it determines the cost of NGH transportation. If hydrate formation rate and gas storage capacity in hydrate are high, the cost of NGH transportation is reduced further [70].

During the formation of gas hydrates (CH_4 hydrate, natural gas hydrate etc.) in reactors, the rotation speed is quite important because it determines gas hydrate formation time. Similar to the rotation speed, as agitation speed increases, induction time decreases [71].

Reactor design is crucial for gas hydrate formation. Turbulence inside the reactor is necessary for fast hydrate formation so during the design of reactors, the mechanical approaches mainly stirring, bubbling, spraying are the most important parts of gas hydrate formation reactors [27, 56, 72-74]. In the study of Jiang et al. [71], special experimental set-up (i.e. gas-inducing agitated reactor with a volume of 300 mL) was designed to increase the amount of gas stored in a unit of gas hydrate. Mainly, the induction time of CO_2 hydrate formation decreased from 261 to 24 minutes when the rotation speed increased from 0 to 800 rpm (with 200 rpm increment) respectively. As expected, pressure and temperature affect gas hydrate formation. As temperature decreases and pressure increases, gas hydrate is much more stable. In the study of Kim et al. [56], the effect of subcooling temperature (difference between experimental temperature and equilibrium temperature) was investigated on CH_4 formation rate. CH_4 hydrate formed faster when subcooling 8 K or greater. Additionally, it was observed that water injection into gas in the reactor is better for gas hydrate formation compared to gas injection method or the usage of magnetic stirrer.

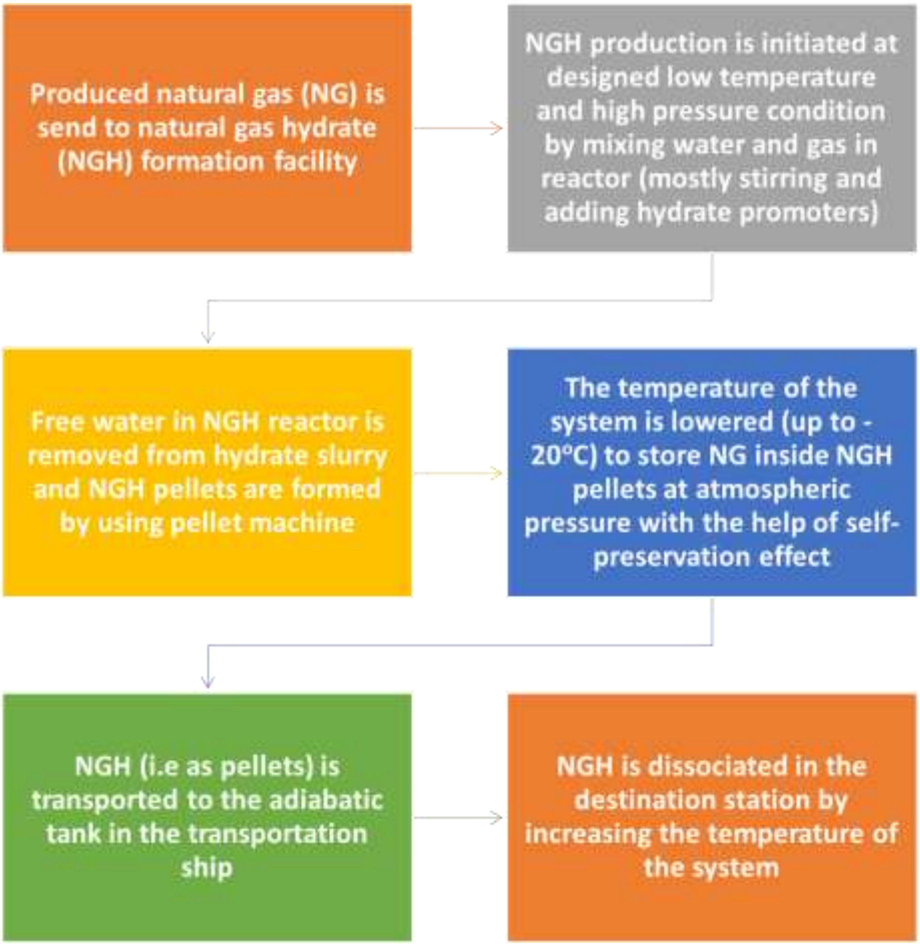

Figure 4. Transportation of NG as NGH

For transportation purposes of gas hydrates, there is a tendency to speed up hydrate formation by increasing gas-water contact. This can be done by adding some chemicals to promote hydrate formation mainly by changing the surface tension in the system [75-77]. Nonetheless, it is important to remind that these chemicals are mostly environmentally harmful so necessary precautions should be taken. There are different gas hydrate promoters which lower gas hydrate formation pressure such as 1,3-dimethylcyclohexane, polyvinylpyrrolidone (PVP), calcium hypochlorite, tetrahydrofuran (THF), acetone, octyl, decyl or dodecyl sulfates, cyclopentane, tetra-butyl ammonium bromide and dodecyl polysaccharide glycoside (DPG) nonionic [27, 57, 78] because mostly, in NGH transportation technology, the aim is to transport NGH nearly atmospheric pressure conditions [64]. Among these hydrate promoters, THF is commonly used [79]. THF is used to speed up hydrate formation. In the study of Veluswamy et al. [80], for the first time, it was observed that rapid mixed methane/THF hydrate formation kinetics at 293.2 K in presence of just 100 ppm sodium dodecyl sulfate surfactant with methane gas uptake of 3.45 (±0.17) kmol/m^3 of water in 1 hour. Furthermore, decomposition of methane/THF hydrates were performed by simple thermal stimulation demonstrated that it is possible to recover 97.9 (±0.98) % of the stored methane gas at 293.2 K. Consequently, THF increases gas hydrate storage capacity in gas hydrates and also its dissociation percentage is still high [80].

Compared to sI hydrate, much more gas might be stored in sH gas hydrates. sH hydrate forms from heavy hydrocarbon molecule than i-butane such as i-pentane, neohexane and the help gas such as CH_4. In the study of Khokhar [81], CH_4 and neohexane were used to form sH hydrate. According to the experimental results, it was found that CH_4 filled 3 small cages and 2 medium cages but the one large cage was filled with neohexane. Hence, compared to pure CH_4 hydrate, much more gas (up to 200 times volume) might be stored in sH hydrates [81].

The formation of gas hydrate is one of the most important part of NGH transportation technology [62]. The fast formation of gas hydrates and its storage are necessary because the induction time of gas hydrate formation is high and the kinetic of gas hydrate formation is slow [56, 82]. In the study of Veluswamy et al. [83], as kinetic promoter, amino acid (leucine) was suggested to speed up hydrate formation without stirring or with stirring. Fast hydrate formation was observed when hybrid method was applied. In the hybrid method, hydrate formation is a simple combination of stirred and unstirred reactor configurations wherein during the first 30 seconds of hydrate formation, the reactor is in stirred reactor configuration mode after which the stirrer was switched off resorting to an unstirred/quiescent reactor configuration mode. Hence, with this method, less energy is consumed compared to complete stirring but higher hydrate formation was observed in the hybrid method in the study of Veluswamy et al. [83].

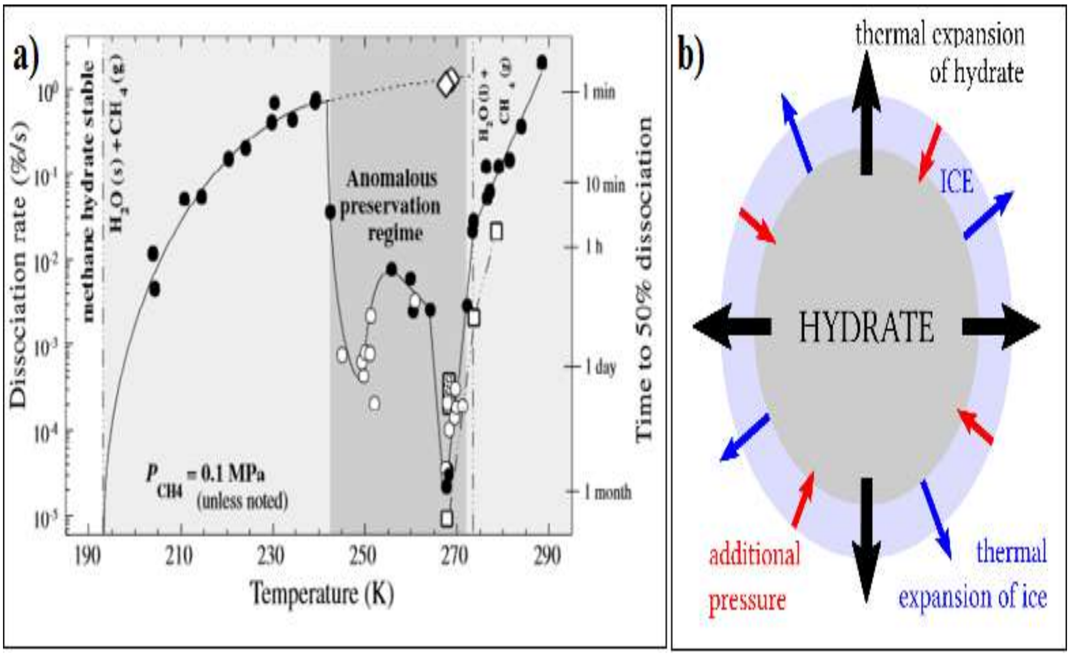

Figure 5. (a) Average rates of CH_4 hydrate dissociation calculated by its half-life time after pressure drops to 0.1 MPa at various temperatures [84] (b) Illustration of the Self-Preservation Effect [85]

During the production stage or gas hydrate formation stage of NGH transportation technology, self-preservation effect of gas hydrates is quite beneficial for NGH transportation [84, 85]. Self-preservation of gas hydrate is defined as a very slow decomposition of gas hydrates when the external pressure drops below a three-phase equilibrium pressure of the gas-ice hydrate system at sub-zero temperature (below -3 ^oC or -2^oC) as a result of thin ice film emergence on gas hydrate surface [86] as seen in Figure 5-b. The self-preservation phenomena in gas hydrates occurs between 242 K (-31.15^oC) and 271 K (-2.15^oC) as shown Figure 5-a. This mechanism is very important for natural gas transportation at ambient pressure conditions as gas hydrates [87-89]. Generally, NGH at ambient pressure and nearly -20^oC are converted to hydrate pellets [90]. Figure 6 shows hydrate pellets formed in the study of Mimachi et al. [91]. Masoudi and Tohidi [92] tested the self-preservation effect on natural gas hydrate and CO_2 hydrate at atmospheric pressure and temperature of -10 ^oC to -15^oC. NGH was formed by using hydrate promoter; tetra butyl ammonium bromide (TBAB). The self-preservation of NGH at atmospheric pressure was quite good (even after 100s hours) but it was not good for CO_2 hydrate. Therefore, it was suggested that the self-preservation effect is suggested for NGH but not for CO_2 hydrate in the study of Masoudi and Tohidi [92]. In the study of Mimachi et al. [91], the pellets of natural gas composed of 91.5% CH_4, 6.7% C_2H_6, and 1.8% C_3H_8 were formed by following these steps: slurry formation, dewatering, molding, cooling, and depressurization. These pellets were stored at 253 K and atmospheric pressure for 3 months and were scanned with X ray CT. It was observed that rapid increases in temperature might cause cracks on the ice shield around hydrate pellets. Similar to this, in the experimental study of Falenty et al. [93], it was proposed that after hydrate pellet production, these pellets should be kept at a temperature of approximately 250 K to avoid any micro fracture on hydrate pellets because gas might escape from the pellets if necessary temperature conditions are not satisfied. Thus, hydrate pellet machine design is quite important. The new hydrate pellet machine was developed by Murayama et al. [94] with more than 90% NGH ratio and less than 0.1% dissociation rate. NGH pellets are transported near atmospheric pressures when the temperature inside truck or ship is -20°C. Due to mainly self-preservation effect of gas hydrates in Figure 5, the dissociation rate of NGH pellets is small but the measures should be taken in case of explosion risks, etc. [89]. It is known that when CH_4 concentration in air is above 5 v/v% there is a risk of explosion (lower explosion limit of CH_4 is 5 v/v %). Hence, there is a risk of explosion inside trucks or ships including NGH pellets and air if little of NGH pellets dissociate but this risk is low compared to LNG or CNG. The dissociation of NGH pellets should be kept minimum as soon as possible to reduce the risk of explosion.

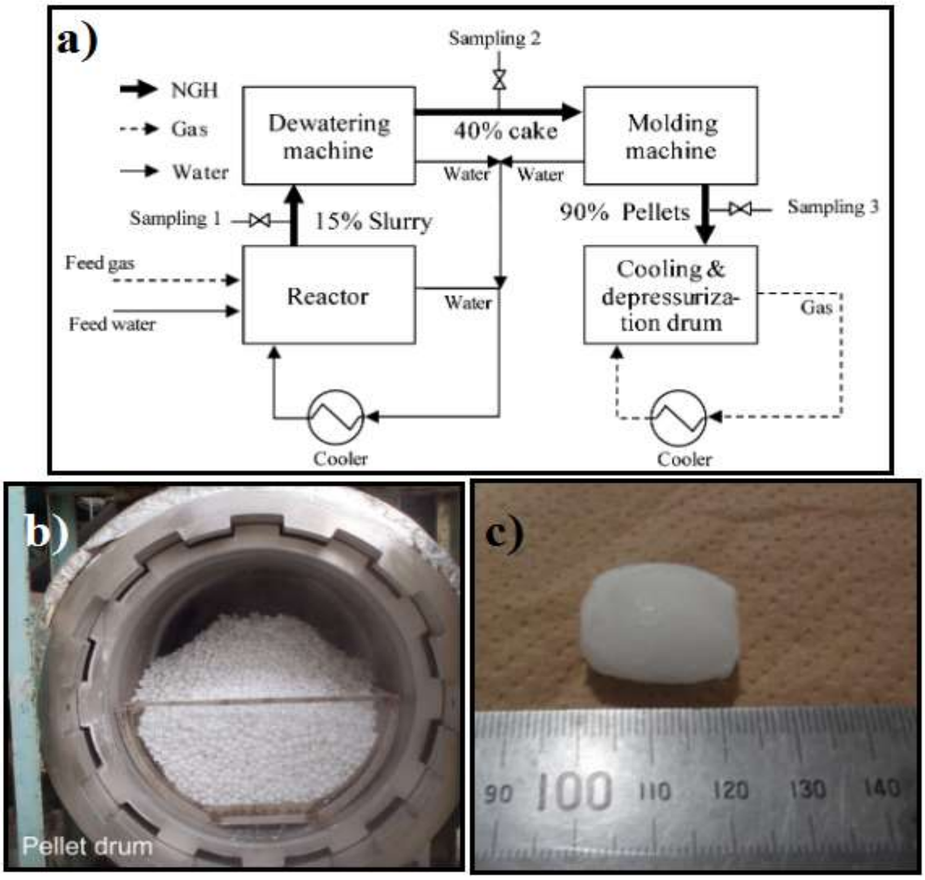

Figure 6. (a) Production scheme of NGH pellets (b) Pellet drum (c) Pellet [91]

Similar to the study of Mimachi et al. [91], the pilot project (Mitsui Engineering & Shipbuilding (MES) Y-Project) was held in Japan for the transportation of natural gas as natural gas hydrate [16]. As previously explained in Figure 4, NGH transportation technology includes three main parts: NGH production (NGH formation, de-watering, pelletizing, cooling and depressurizing), NGH transportation, NGH re-gasification and utilization. In Y Project of MES [16], firstly, natural gas and water are mixed with agitator stirrers at approximately 5°C and 5.3 MPa to form natural gas hydrate slurry in the reactor (Figure 7-a). Then, free water is removed from natural gas hydrate slurry by using de-watering system (Figure 7-b). Natural gas hydrate slurry is sent to pelletizer by squeezing. NGH pellets are cooled to -20°C by using cooling drum (Figure 6-c) in order to take the advantage of self-preservation effect in Figure 5. When NGH pellets are cooled, the system is depressurized and then loaded to ships, trucks or pellet container (Figure 7-d). The selection and design of the transportation mode for moving NGH pellets to the destination place are also important [57].

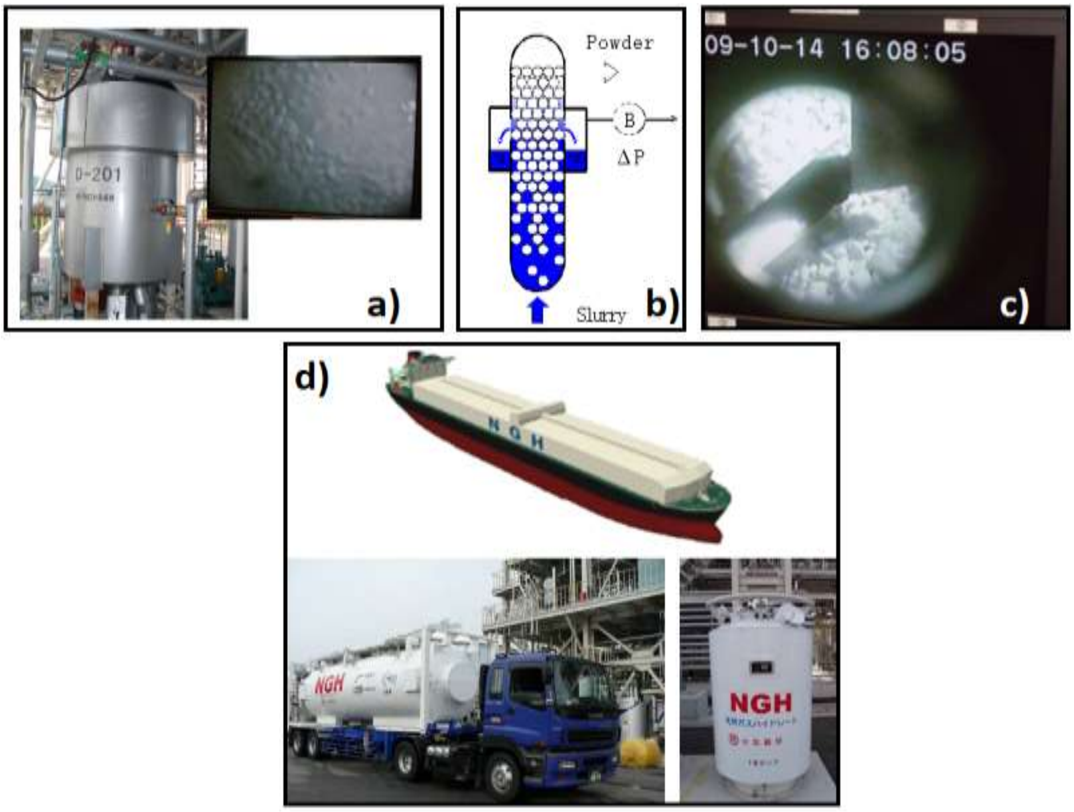

Figure 7. (a) NGH reactor and slurry generator inside (b) De-watering system (c) NGH pellets in cooling drum (d) Transportation [16]

MES aims to commercialize NGH transportation technology as soon as possible. As seen in Figure 8, between 2000 and 2005, necessary preparation and studies were conducted for demo project. The first commercial project is aimed to be conducted at land plant and then marinization project until 2020. These studies are mostly conducted in Japan because Japan is the top natural gas importer in the world [18]. Accordingly, they plan to reduce the cost and risks of natural gas transportation.

Figure 1 shows the cost of transportation of natural gas with different methods. Natural gas transportation as natural gas hydrate (NGH) is almost new subject compared other methods such as LNG, CNG, etc. Therefore, many scientific and economical studies are necessary to make NGH transportation technology applicable in natural gas industry. Recently, there are some economical comparison of NGH transportation method with other transportation methods but these should be updated often because the price of gas and the advanced of technology might change these cost estimations.

According to some cost estimations [60, 66, 95], the transportation cost of NGH transportation is expected to be 18–24% lower than with liquefied transportation (LNG). Besides, it is proposed that 14 % of total energy is consumed for the NGH transportation (25.31 % Pretreatment, 17.34% hydrate formation, 1.88% refrigeration, 54.49% transportation, 0.95% hydrate dissociation) [61, 68]. Based on the results of conceptual designs of Ota et al. [89], the costs of transportation and concluded that NGHP carriers could economically competitive to LNG carriers if the distance of transportation was less than 3000 nautical miles (5556 km). Figure 9 indicates the comparison of life cycle cost of LNG, NGH and CNG in the study of Nogami et al. [67]. According to this comparison, it is obviously seen that for the case of Nogami et al. [67], NGH transportation method is the most feasible one. Moreover, 26%, 32%, 36% and 6% of NGH transportation cost are for process plant, import terminal, carrier and export terminal respectively as seen in Figure 9 [67]. According to Shi et al. [60], NGH transportation might be cheaper than LNG transportation. Additionally, 44.4%, 33% and 22.6% of NGH transportation cost are for pretreatment, transportation and regasification respectively. In these three different estimations, the technology designs used for NGH transportation were different. Moreover, other parameters in the calculations might be different so there are small variations among these three estimations.

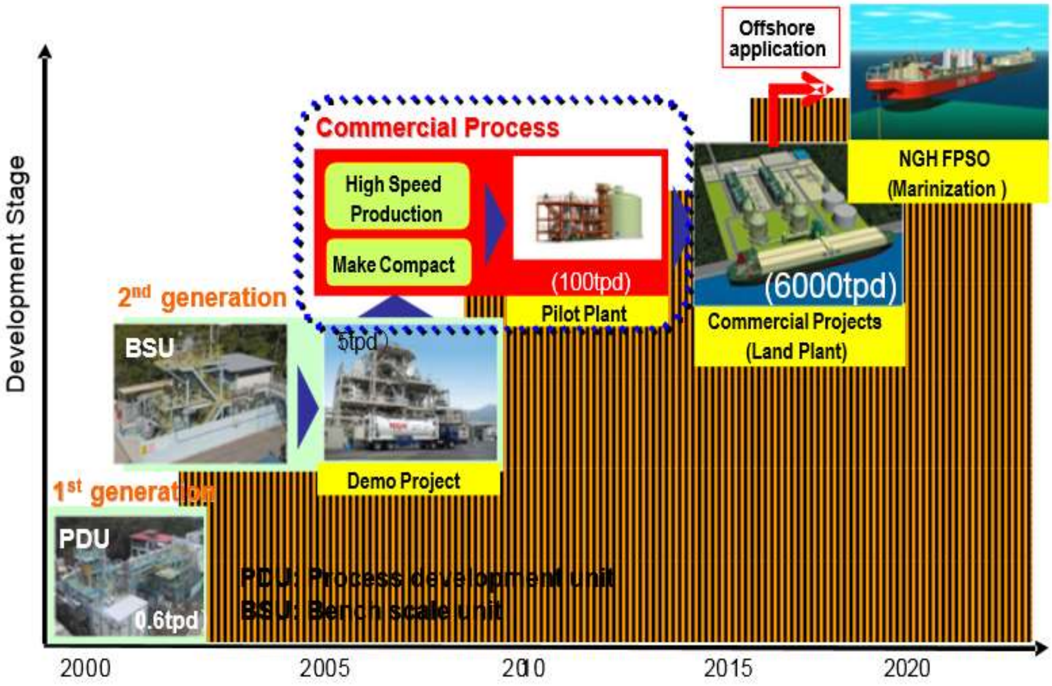

Figure 8. Roadmap toward commercialization [16]

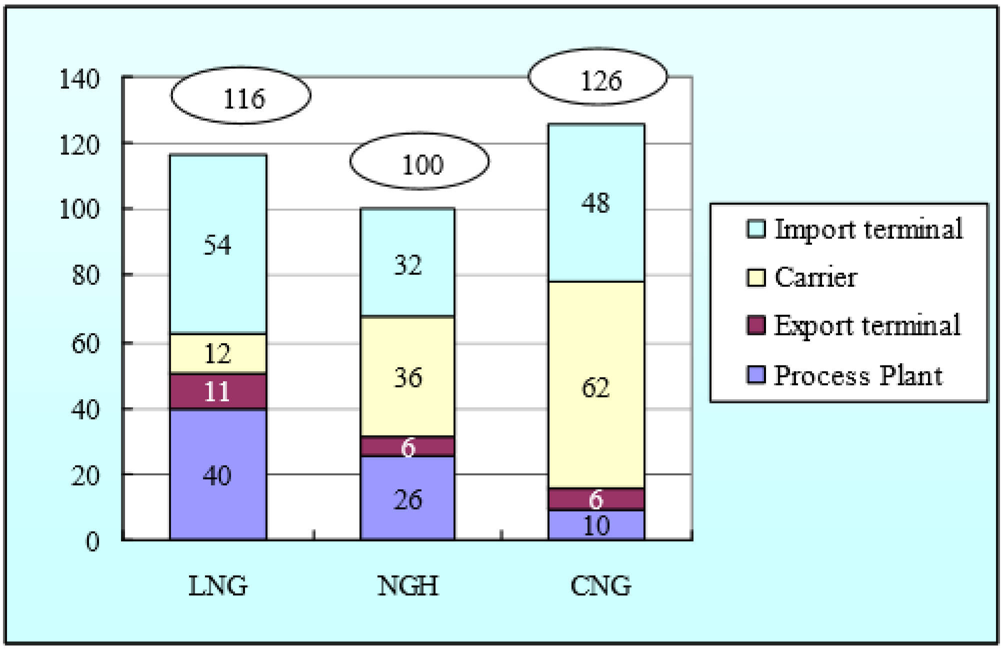

Figure 9. Comparison of Life Cycle Cost (LCC) [67]

5. CONCLUSIONS

After the first discoveries of hydrates in the end of 19th century, first natural gas hydrates were considered as a problem in natural gas transmission with pipelines in 1930s. Most of hydrate studies focused to prevent natural gas hydrate plugging in pipelines. Especially with the decline of conventional natural gas reservoirs, the number of natural gas hydrate studies related to natural gas hydrate reservoirs has increased sharply last decade. Currently, natural gas consumption in industry is quite high so the transportation of natural gas has become important in terms of economy, health, safety and environment (HSE). With the increase of LNG transportation with ships, the risks related to HSE has increased as well. Therefore, alternative natural gas transportation method is required in long transportation distance. Natural gas transportation as NGH might be a good alternative if necessary investments are done for research and development in this area. In this study, it is aimed to show the importance of natural gas hydrates in natural gas transportation industry by reviewing the studies in this area. The number of studies related to this area should increase as in natural gas hydrate reservoirs.

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