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Processes and apparatuses for formation, separation, pelletizing storage and re-gasification of gas hydrate

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ABSTRACT

In recent years, the feasibility of utilizing gas hydrates in industrial systems draws much attention as a subject of engineering studies. Despite the suggested applications for gas hydrate in transportation and storage of natural gas, desalination of water, etc., there have been few applied industrial experiences with gas hydrates. There are several patents and papers on promotion of gas hydrate formation thermodynamics and kinetics , but apparatuses and processes are rarely discussed. In designing a process based on gas hydrate for industrial application, one must include the following operations: formation, separation, pelletizing, storage, transportation and re-gasification. In this review article, different operations considering applications of gas hydrate are fully discussed. These operations are classified based on both contact of liquid and vapour phases and methods of conducting mass and heat transfer.

1. Introduction

Gas hydrates are a class of clathrates, composed of water and certain gas molecules such as methane, ethane, propane, and carbon dioxide. Due to hydrogen bounding, water molecules form a network of cavities. Under appropriate pressure and temperature (high pressures and low temperatures), gas (guest) molecules with favourable shapes and sizes can occupy this network. The structure of hydrate is thermodynamically stabilized through non-bonded interaction between the guest molecules and the water lattice [1]. Earlier gas hydrate researches were mainly focused on issues that hydrate formation caused in hydrocarbon transportation lines. The goal was to find ways to inhibit hydrate formation and to solve safety and processing problems associated with that [2]. On the other hand, studies show that gas hydrate has a high potential for storage of natural gas, water desalination, concentration of solutions and separation of gases [3-8]. Also according to considerably high crystallization enthalpy of hydrate formation, it can be used in refrigeration systems [9]. Another application for gas hydrate is natural gas transportation and it's been evaluated to be more economical than LNG in some cases [3, 10, and 11].

Gas hydrate potentials for industrial applications encourage researchers to find more practical formation methods and therefore many patents have been granted on gas hydrate processes and apparatuses for formation, separation and pelletizing systems [12-30]. Several papers discussed thermodynamic and kinetic promotion of gas hydrate formation [31, 32] these papers tried to introduce and characterize promoter chemicals, which can make operational conditions for hydrate formation more desirable. We have to consider that critical factors in using gas hydrate are continuous formation of gas hydrate with lowest energy consumption per kilogram of gas hydrate and also

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separation of crystals from water and pelletizing of hydrates as needed. According to the importance of energy consumption, the processes and apparatuses for hydrate formation should be most efficient and have the appropriate lifetime. In order to increase the energy efficiency and lifetime, design must be geared to minimized usage of mechanical systems such as agitators, and reciprocating cells.

Designing a process based on gas hydrate and desired application, can include hydrate formation, hydrate separation, hydrate pelletizing, transportation, storage and re-gasification. Table 1, shows operations required for each application.

In this review, different hydrate operations, processes and apparatuses are fully discussed and classified based on both contact of liquid and vapor phases and methods of conducting mass and heat transfer.

2. Gas hydrate formation systems

Gas hydrate formation, as illustrated in Eq. (1), is mostly like crystallization of a solid from its super-saturated solution. In Eq. (1), methane is an example of hydrate former gases. Crystallization processes are mostly carried out by lowering temperature in atmospheric pressure but this is not true for hydrate formation [33]. Gas hydrate is mostly formed in high pressure systems.

$$\mathrm{CH4\ (aq)} + 5.7\ \mathrm{H2O\ (l)} \rightarrow \mathrm{CH4\ (5.7\ H2O)(s)} + \text{heat of reaction} \quad (1)$$

Generally any mass or heat transfer phenomenon, at least in a definite range, can be kinetically expressed as: rate=constant*driving force. If we assume hydrate formation as simultaneous reaction and mass transfer of gas molecules to hydrate crystal, then we have temperature difference between bulk and equilibrium temperature of hydrate formation as driving force of the system. Also one must have in mind that equilibrium temperatures of hydrate formation is a function of pressure. Dependency of this equilibrium temperature makes the equation a function of both temperature and pressure. In order to increase driving force and rate of reaction one must decrease temperature while increasing pressure. By increasing driving force and lowering mass and heat transfer resistances, desirable formation rate is obtained.

$$\mathrm{Rate} = \frac{\text{driving force}}{\mathrm{R_{total}}} \quad (2)$$

On the other hand for crystallization first we need a saturated solution and the hydrate formation is result of both nucleation and growth. A well-designed gas hydrate formation system should work in a way which results in highest gas hydrate formation rate. Effective parameters on gas hydrate formation rate are: 1) higher super saturation of the solution 2) suitable nucleation sites 3) less mass transfer resistance and 4) less heat transfer resistance.

Table 1 gas hydrate application and their operations

Transportation of natural gas	hydrate formation →separation→pelletizing→shipping →re-gasification
Storage of natural gas	hydrate formation→separation→pelletizing→ storage→re-gasification
Desalination of water	hydrate formation →separation→re-gasification
Concentration of solutions	hydrate formation →separation→re-gasification

It’s possible to model the hydrate formation from mass, heat transfer or chemical affinity point of views. According to Fig. 1, and considering film theory, in both mass and heat transfer total resistance is sum of resistances in gas, liquid and crystal phases. It’s noteworthy that migration of gas molecules from crystal surface is more dependent on reaction nature and can’t be simply changed. Different gas hydrate device and processes are presented and compared based on their performance to obtain a better mass and heat transfer.

The timescale between establishment of thermodynamically suitable temperature and pressure and formation of first macroscopic hydrate crystal is called induction time. Models for induction time as a function diffusivity coefficient have been reported. In these models, the higher the diffusion coefficient, the lower the induction time [34]. In addition, there are reports concerning effect of ultrasound on diffusion coefficient which leads to possibility of ultrasonic ability to lower induction time of hydrate formation [35- 36].

2.1. Autoclave (agitated vessel)

Autoclaves are pressurized vessels in which

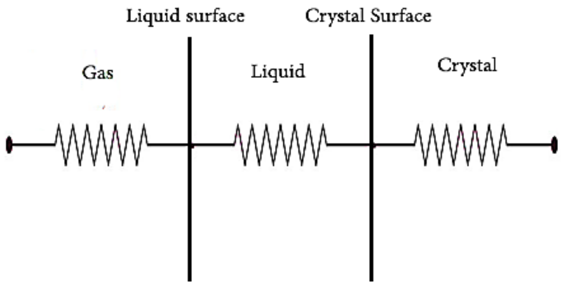

Figure 1. Hydrate formation mass/heat transfer resistances diagram

temperature is controlled via a thermal jacket and can operate batch or wise in continuous mode. Even though the gas hydrate formation rate in these systems can be high, but there are several operational difficulties. Formation of gas hydrate increases agitator power. More importantly agitation causes unwanted and excess water to trap in macroscopic crystals of hydrate thus, lowering reaction yield and also has high maintenance and operational costs [37]. For increasing the rate of dissolution of gas in water, a hollow shaft agitator can be used to obtain better dispersion of gas and liquid phases. The agitator is designed to disperse the gas into water, and high contact area that bubbles cause, decrease the mass transfer resistant. In these systems, the agitator task is to decreases the mass transfer resistant of dissolved gas molecules into gas hydrate crystal. In autoclave continuous phase is liquid and from heat transfer point of view, having a liquid as a continuous phase there is preferable. Fig 2, shows an autoclave designed for formation of gas hydrate.

2.2. Spray systems

Nozzles are utilized to increase contact area in different industrial operations such as combustion, spray dryers and gas coolers. Nozzles are used for increasing the rate of dissolution and decreasing the mass transfer resistance which results in higher hydrate formation rate. For twin fluid nozzles, since water is dispersed into gas phase, most of injected water is consumed and there is no need for any excess water in feed, which makes un-reacted water/hydrate separation easier. The most important parameter in decreasing mass transfer resistance is increasing the contact phase area. Table 2, shows the relationship between decreasing the bubble diameter and increasing special surface area.

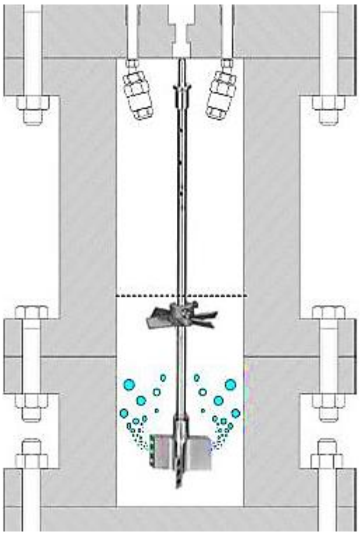

Figure 2. using hollow shaft for better phase contact [38]

Table 2 surface and volume relation of droplets [39]

Droplet Diameter, µm	Surface Area of One Droplet, mm^2	Volume of One Droplet, mm^3	Total Droplet Count per Liter	Total Surface Area per liter, m^2
2,000	12.6	4.19	239,000	3
1,000	3.14	0.524	1,910,000	6
500	0.785	0.0655	15,300,000	12
250	0.196	0.00819	122,000,000	24
125	0.0491	0.00102	977,000,000	48
60	0.0113	0.000113	8,840,000,000	100
30	0.00283	0.0000141	70,700,000,000	200
15	0.000707	0.00000177	565,000,000,000	400

A typical twin fluid nozzle is showed in Fig. 3. In these nozzles, gas and water are mixed and leave the nozzle in small droplets. Nozzle outlet enters the reaction chamber at suitable pressure and temperature for gas hydrate formation. Formation of gas hydrates is shown in Fig. 4. In single fluid nozzle systems gas is sprayed downward and water is sprayed upward. Water and produced hydrate accumulate in the bottom of chamber and then can be transported to a separation system.

Gases solubility in water normally increases with decreasing temperature, but for some hydrate former gases at certain temperatures and pressures solubility shows a different behavior. At temperatures, near hydrate formation conditions, solubility of gas in water decreases as temperature drops [40, 41]. In process design, pressure and temperature at nozzle inlet should be in a condition that Joule-Thompson effect results in a temperature that provides highest super saturation level. The continuous phase in these systems is gas and transferring the heat produced by hydrate formation enthalpy is a problematic parameter in designing of spray systems, thus making a continuous operation impossible. A proposed method for improvement of heat transfer is to use a metal-block surface, in front of the spray to remove the heat released by the hydrate formation. Two problems are recognized and reported in this method: a) the plugging of the spray nozzle, b) the growth of a hydrate layer on the metal-block surface [43].

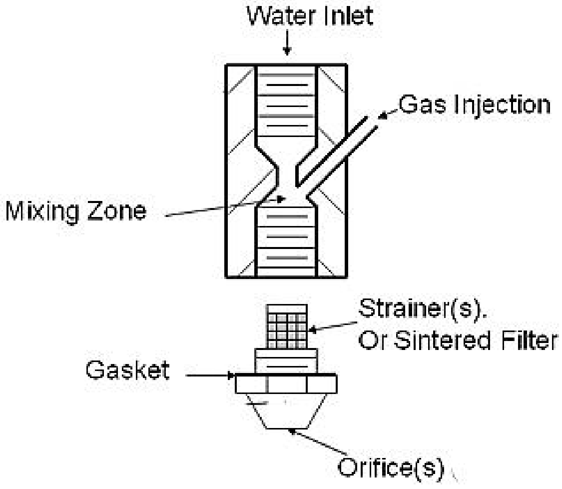

Figure 3. schematic of a two fluid nozzle [40]

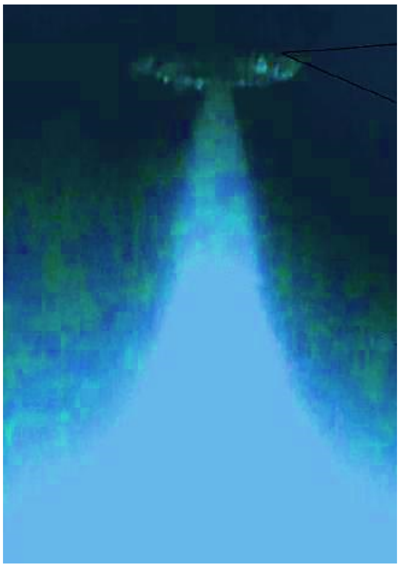

Figure 4. hydrate formation using twin nozzle [39]

hydrate layer on the metal-block surface [43]. Using a porous metal plate, which a coolant is seeping out of the plate instead of metal-block surface, is proved to be less problematic [44].

2.3. Hydrate formation in bubble column

Bubble column consists of one or more vertical columns that are filled with water and cooled using thermal jacket or coils. In the column, gas is bubbled to the system and has specified residence time rising in water. Due to mass and heat transfer between gas and water, hydrate forms on bubble surface [42]. Formation of gas hydrate on the bubble surface increases both mass and heat transfer resistance which deteriorates hydrate growth [45, 46]. For improving hydrate formation rate, one must find a way for surface renewal to solve this problem to increase hydrate formation rate, bubbles should be small so providing more specific contact area. [47]. If a gas mixture is introduced into column, the hydrate former gas is trapped and other constituents of gas would leave the column which suggests that hydrate formation in bubble column can be used for gas mixture separation [48]. Fig. 5, shows gas hydrate formed on a single bubble.

Microbubbles are another way of dispersing gas in liquid. Their special properties encourage industries to utilize them. Macroscopic bubbles are hydrodynamically stable and have special rising speed and bursts at the liquid surface. On the contrary, micro-bubble due to very high pressure difference between inside and outside of bubble is very unstable. They burst in the liquid which result in higher super saturation [49].

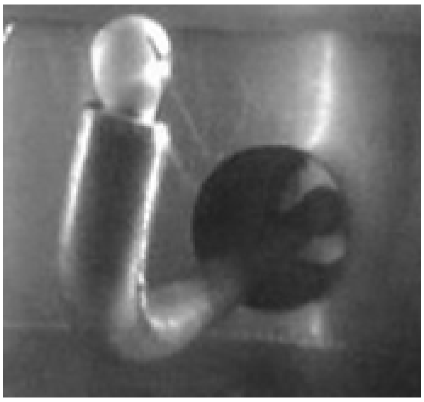

Figure 5. hydrate formed on methane bubble [39]

These bubbles are suitable for gas hydrate formation because of high internal pressure, high specific surface area and providing high gas solubility in liquid. Also due to high internal pressure of microbubbles there is no need to bring the whole system's conditions to gas hydrate formation pressure. An aerator is used to produce microbubbles [50-52]. There are two types of aerators: agitated and non-agitated. Fig. 6, shows contact of gas and water using non-agitated aerator.

2.4. Reciprocating cells (rocking cell)

These types of cells are designed for simulation of hydrodynamic and geometric of hydrocarbon transportation pipelines and investigation on hydrate formation in these pipelines and because of their high energy consumption they are not appropriate for application of hydrate in industrial processes [53].

2.5. Hydrate formation on sub-cooled tubes

Inspired by some ice making devices, in proposed system, agitator is removed, sub-cooled tubes as a nucleation site are added to the reactor. Prior to injection of reactants in reactor, hydrate former gas is dissolved in water to make a hydrate former solution. In the reactor, this liquid film passes over the sub-cooled jacket also hydrate forms on the tube. Formation of hydrate on a provided tube (nucleation site) eliminates need for separation of hydrate from unreacted water. After hydrate formed on the tube reaches a specified diameter, gas hydrate can be detached by sudden temperature change or a vibration mechanism.

2.6. Gas in ice process

Gas hydrate formation in this method is carried out in multiple agitated vessels continuously. Temperature and pressure are controlled in a manner that favors hydrate formation and ice

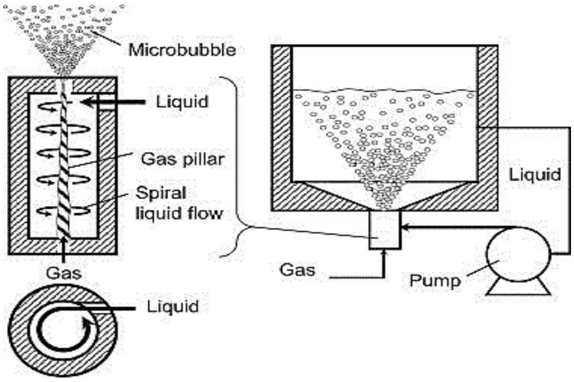

Figure 6. process flow diagram and internal structure of microbubble aerator [51]

decomposition (e.g. for methane hydrate 50 bar and 5°C). Slurry of water and ice and gas are injected to the vessel. Inside the vessel, the ice melts by heat generated by hydrate formation enthalpy. The advantage of this method is elimination of heat jacket from the vessel; also ice particles provide nucleation sites with suitable temperature thus enhance hydrate formation.

2.7. Diffusion of hydrate former gas in solid crystal

While hydrate formation is mostly achieved in gas/liquid/hydrate systems, it can also be formed in gas/ice/ hydrate systems. If we have ice and a hydrate former gas but thermodynamic conditions favor gas hydrate formation, gas diffuses through ice. Due to low mass transfer rate in solid ice particles this method is inherently slow and high ice particle surface area is needed for high absorption rate of hydrate former gas. The advantage of this method is that because of the low operating temperatures (e.g. -20), equilibrium pressure of hydrate formation can be very near to atmospheric conditions.one proposed way for generation of fine ice particle is to use ultrasonic mist generator and conversion of mist to ice particles(average diameter of 0.5 µm) [53]. Consequential formation of CO_2 hydrate from CH4 hydrate is another example of diffusion of gas in crystal processes.

3. Separation of gas hydrate and unreacted water

As mentioned earlier, gas hydrate formation is a crystallization process thus; separation of gas hydrate from unreacted water is a solid-liquid separation. In crystallization processes density differences and/or mechanical separation (filtering) are common choice of separation [55]. Both gravitational and centrifugal separations are possible but as density difference is very low, gravitational method needs long residence time (e.g. methane hydrate density is 0.9 grams per cubic centimeter). Fig. 7, shows process of gas hydrate separation by gravity force. As shown in Fig. 7, gas hydrate is formed in agitated vessel and accumulated on the water surface, and then water and gas hydrate are transported to settlement vessel. A method of separation by means of centrifugal force is shown in Fig. 8, as gas hydrate is the less dense component, it moves into the center and accumulates there.

4. Gas hydrate pelletizing systems

There are four possible physical forms for transportation and storage of gas hydrate: 1) powder of gas hydrate 2) slurry of gas hydrate in water phase 3) slurry of gas hydrate in oil phase and 4) pellets of gas hydrate. Pelletizing of gas hydrate has three important advantages, 1) more gas storage capacity 2) suitable fluidity and 3) better stability of gas hydrate. According to the endothermic dissociation of gas hydrate, decomposition of hydrate in a closed adiabatic system, causes increase in pressure and decrease in temperature. These changes bring the system to a

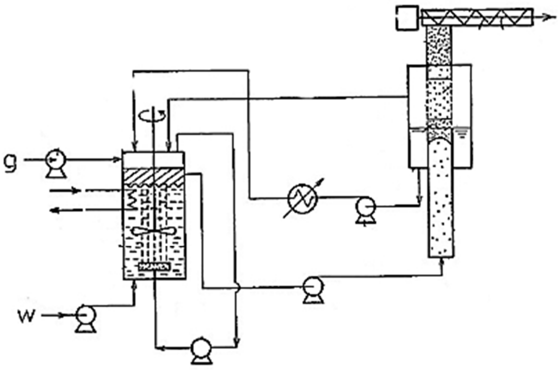

Figure 7. gas hydrate separation process by gravity force [25]

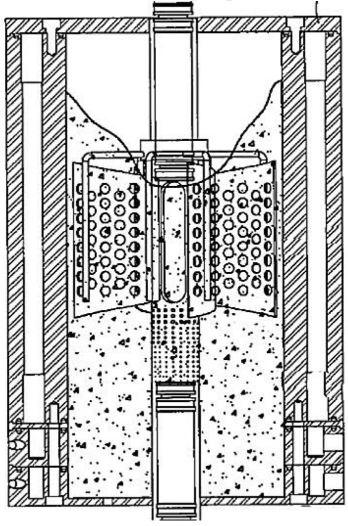

Figure 8. using centrifugal force for gas hydrate separation, hydrate is dischared from the center of chamber [22]

new thermodynamic equilibrium which stops hydrate decomposition [54, 55].

4.1. Piston and cylinder systems

In piston cylinder systems, pellets are made by compressing hydrate particles. Fig. 9 and Fig. 10 show two types of these systems.

4.2. Rolling systems

In these systems slurry of gas hydrate is poured on two side by side rollers and the gas hydrate pellets withdraw from the bottom of the rollers and discharge by means of a spiral. Fig. 11, Fig. 12 and Fig. 13, are three examples of these systems.

5. Storage and shipping

As a general concept, produced hydrate must be transported using pipes or conveyors to storage drums in carriers [57]. Carriers' design is most importantly affected by hydrate physical form, (i.e. slurry or dry). Some proposed storage conditions are summarized in Table 3. In the same way, Table 4 classifies transportation modes for gas hydrate.

Tank carriers are mostly made of stainless with combination of glass wool and hard urethane foam for insulating [57]. Temperature and pressure of -20 and 1 atm are recommended for storage in tank carriers [59, 60] while 2 and 10 bars for transportation of slurry hydrate [58]. Insulated bulk carriers do not need to be refrigerated and hydrate can be preserved adiabatically [59, 61].

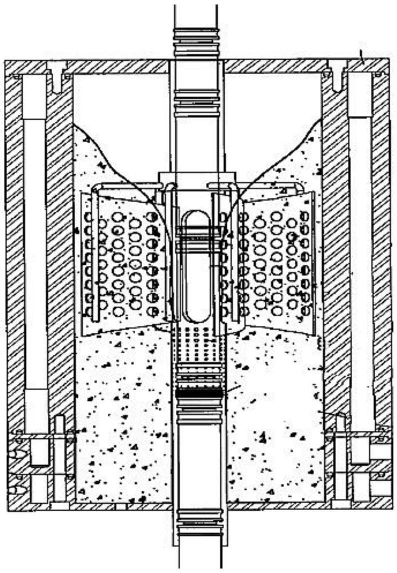

Figure 9. pelletizing by means of cylinder and piston, as shown gas hydrate enters to the cylinder and piston presses the gas hydrate

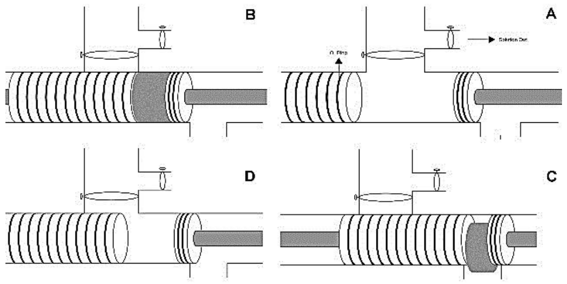

Figure 10. gas hydrate pelletizing concept with low pressure drop of reaction chamber. A) gas hydrate valve to pelletizing system is closed B) the right shaft is stable and the left one presses the gas hydrate C) both shafts move to right and withdraw the pellet D) returning to the first position

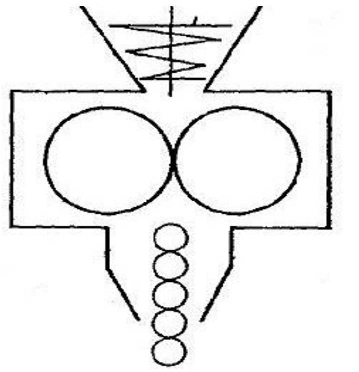

Figure 11. rolling pelletizer, rollers are cooled by internal fluids circulation[57]

6. Re-gasification

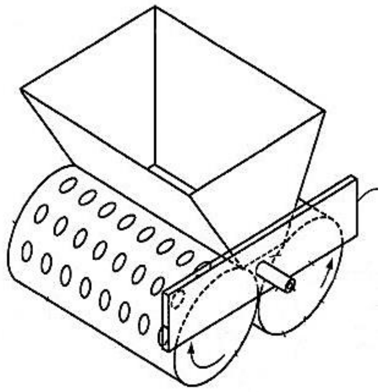

Figure 12. Schematic of a rolling pelletizer [19]

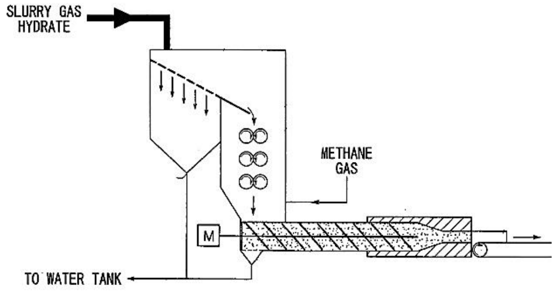

Figure 13. a water separation and rolling pelletizing system. Withdrawn of gas hydrate without pressure drop by means of a well-sealed spiral is achieved [21]

In application of gas hydrate for transportation or storage of natural gas one of the key operations is to re-gasify hydrate [57]. Decomposition of hydrate is highly endothermic and high heat transfer rate is the key in regasification of gas hydrate. For this purpose warm water can be pumped into the cargo tank or re-gasifier [61]. Re-gasification of hydrate pellets needs pellet crashing prior to further treatments to accelerate heat transfer and hydrate decomposing rate. Separated gas has to be dried in a dehydration unit and compressed. Pellets also can be decomposed by in-water stirring method, water spraying method, and immersing method. Table 5, summarizes and compares these methods [28]. Among these methods packed bed re-gasifier has been proofed to be more efficient in heat transfer than re-gasifier with stirring and crusher.

Table 3 summary of some proposed conditions for hydrate storage

	Condition for storage	Effect on design cost
1	-32°C and 5 MPa	Very costly, requires insulation and pressurization.
2	2-5 MPa using pipelines- for slurry storage	Expensive, requires pressurization.
3	Submarine vessel for mobile storage	Very expensive, requiring pressurization
4	Atmospheric pressure and 15°C - stationary or mobile storage	Economic 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 meta-stability of hydrate

Table 4 msummary of transportation modes for gas hydrate [58]

Type of carrier	Hydrate form	Distances	Modification
Truck	Dry	Anywhere on land	Insulation
Truck	Slurry	Anywhere on land	Several Modification Attached to Processing Plant
Bulk Carriers	Dry	Large distances	Insulation
Bulk Carriers	Slurry	Large distances	Pressurized vessels
Bulk Carriers	Crude Oil & Slurry hydrate	Large distances	Insulated pressurized pipe on deck of carrier
Towed Barges	Dry	Short distances	Insulation
Detachable Barges	Dry & Slurry	Large distances	Several Modifications. Attached to Processing Plant
Carrier with removable storage container	Dry	Short distances	Storage container could be removed by crane at market

Table 5 comparison of different re-gasifying methods [28]

Method	**Advantages**	**Problems**
In-water stirring	Increase the contact efficiency between pellet and water	high power consumption large re-gasifier size
Water spraying	Enables the storage-transportation and re-gasification of the pellet to take place in same apparatus	Difficult to achieve stable gas supply Cannot be stopped the decomposition when stopped the spraying
Immersing	Better water content control	Bridge phenomenon

7. Conclusions

The choice of hydrate formation process is manly dependent on which application we need hydrate to be formed. For gas separation processes, which mass transfer resistance is in the gas phase, dispersing gas bubbles in continuous liquid phase (bubble column) is the best choice. For desalination and concentration of solutions purposes hydrate formation methods are preferred that assist hydrate/water, separation which makes hydrate formation on sub-cooled tubes a preferable choice. For transportation and storage of natural gas two fluid nozzles are preferred because they lower induction time of hydrate formation.

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