Processes and apparatuses for formation, separation and pelletizing of gas hydrate

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Abstract
Despite the suggested applications for gas hydrate in transportation and storage of natural gas, desalination of water, etc., there has been no applied industrial application for it. There are several patents and papers on thermodynamically and kinetically promotion of gas hydrate formation and many concerning its related processes. In designing a process based on gas hydrate application in industry, one must include the following operations: formation, separation, pelletizing, storage, transportation and gasification. In this review, operations of each gas hydrate’s application are studied and processes for formation, separation and pelletizing of gas hydrate are widely discussed. Gas hydrates formation systems are classified based on contact type of gas and liquid. Autoclave, spray, bubble column, using micro bubbles, hydrate formation with emphasis on nucleation sites and gas ice process are discussed as hydrate formation systems. Separation of gas hydrate and unreacted water is a solid-liquid separation process which is done by operations based on density difference (using gravity force or centrifugal force) or mechanical separation such as filtration. Pelletizing of gas hydrate with more storage gas capacity and less decomposing rate has been accomplished by piston and cylinder or roller systems.

Keywords: Gas hydrate, Gas hydrate formation, separation, Natural gas transportation, Gas hydrate pelletizing
1. Introduction
Gas hydrates are solid crystals, trapping gas molecules in cages constructed by hydrogen bonds. Methane, ethane, propane, butane, carbon dioxide and hydrogen sulfide are some examples of hydrate former gases [1]. Earlier gas hydrate researches were focused on issues that hydrate formation caused in hydrocarbon transportation lines. The goal was to find ways to inhibit hydrate formation and solving safety and processing problems associated with that [2]. Studies showed 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 cooling systems [9]. Another application for gas hydrate is natural gas transportation and it’s been evaluated to be more economical than LNG [3, 10, 11]. Gas hydrate potential for industrial applications encourage researchers to find more practical production methods and therefore many patents have been granted in gas hydrate processes and apparatuses for formation, separation and pelletizing systems[12-30]. Several papers discussed thermodynamically and kinetically promotion of gas hydrate formation [31, 32] these papers tried to introduce and characterize promoters, which can make operational conditions for hydrate formation more desirable. We have to consider that critical factors in using gas hydrate are formation of gas hydrate with lowest energy consumption per kilogram of gas hydrate in continuous form with well thermodynamics and Kinetics conditions, 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 minimizing usage of mechanical systems such as agitators, and reciprocating cells. Designing a process based on gas hydrate according to its application can contain hydrate formation operations, hydrate separation, hydrate pelletizing, transportation, storage and gasification. Table 1 shows operations of each application for gas hydrate. This paper is a review on formation, separation and pelleting operations.

Table 1, gas hydrate application and their operations

<table>
<thead>
<tr>
<th>Application</th>
<th>Operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation of natural gas</td>
<td>hydrate formation → separation → pelletizing → shipping → gasification</td>
</tr>
<tr>
<td>Storage of natural gas</td>
<td>hydrate formation → separation → pelletizing → storage → gasification</td>
</tr>
<tr>
<td>Desalination of water</td>
<td>hydrate formation → separation → gasification</td>
</tr>
<tr>
<td>Concentration of solutions</td>
<td>hydrate formation → separation → gasification</td>
</tr>
</tbody>
</table>

2. Gas hydrate formation systems
Gas hydrate formation, as illustrated in equation (1), is mostly like crystallization of a solid from its super-saturated solution. Crystallization is carried out by lowering temperature in atmospheric pressure [33]. Generally any mass 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. 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. 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 that 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. Formation of hydrate in a stagnant system consists of three steps: 1) dissolving gas in water, 2) diffusion of gas molecules into hydrate surface (induction time) and 3) nucleation and growth of gas hydrate crystals. To increase the formation rate of gas hydrate time of every step should be reduced. Considering that rate could be expressed as: \( \text{rate} = \frac{\text{driving force}}{R_{\text{total}}} \), it’s possible to model the hydrate formation from mass or heat transfer 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 into it is more dependent on reaction nature and can’t be changed. Different gas hydrate device and processes are presented and compared based on their performance to obtain a better mass and heat transfer.

\[ \text{CH}_4 (aq) + 5.7 \text{H}_2\text{O} (l) \rightarrow \text{CH}_4 (5.7 \text{H}_2\text{O})(s) + \text{heat of reaction} \quad (1) \]

1.2. Autoclave (agitated vessel)
Autoclaves are pressurized vessel in which temperature is controlled via a thermal jacket. They can work as batch or continuous systems. 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. Agitation cause unwanted and excess water to trap in macroscopic crystals of hydrate then lowering reaction yield [34], they also have high maintenance and operational costs. For increasing the rate of dissolution of gas in water, a hollow shaft agitator can be used in these systems. 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 decrease 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 is preferable. Fig 2 shows an autoclave system.

![Fig 1, using hollow shaft to making better phase contact [35]](image)

### 2.2. Spray systems

Nozzles are used, to increase contact area in different operations such as combustion nozzles, spray dryer, gas coolers. One fluid and twin fluid are two different types of nozzles and both of them can be used in hydrate formation process. Nozzles are used for increasing the rate of dissolution and decreasing the mass transfer resistant which results in higher hydrate formation rate. In 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, so making separation easier. The most important parameter in decreasing mass transfer resistant is increasing the contact phase area. Fig 3 shows the relation between decreasing the bubble diameter and increasing special surface area.

**Table 2, surface and volume relation of droplets [36]**

<table>
<thead>
<tr>
<th>Droplet Diameter, μm</th>
<th>Surface Area of One Droplet, mm²</th>
<th>Volume of One Droplet, mm³</th>
<th>Total Droplet Count per Liter</th>
<th>Total Surface Area per Liter, m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,000</td>
<td>12.6</td>
<td>4.19</td>
<td>239,000</td>
<td>3</td>
</tr>
<tr>
<td>1,000</td>
<td>3.14</td>
<td>0.524</td>
<td>1,910,000</td>
<td>6</td>
</tr>
<tr>
<td>500</td>
<td>0.785</td>
<td>0.0655</td>
<td>15,300,000</td>
<td>12</td>
</tr>
<tr>
<td>250</td>
<td>0.196</td>
<td>0.00819</td>
<td>122,000,000</td>
<td>24</td>
</tr>
<tr>
<td>125</td>
<td>0.0491</td>
<td>0.00102</td>
<td>977,000,000</td>
<td>48</td>
</tr>
<tr>
<td>60</td>
<td>0.0113</td>
<td>0.000113</td>
<td>8,840,000,000</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>0.00283</td>
<td>0.0000141</td>
<td>70,700,000,000</td>
<td>200</td>
</tr>
<tr>
<td>15</td>
<td>0.000707</td>
<td>0.0000177</td>
<td>565,000,000,000</td>
<td>400</td>
</tr>
</tbody>
</table>

Twin fluid nozzle is showed in fig 3. In this nozzle, 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. Gas hydrate reaction chamber and formation of gas hydrates shown respectively in fig 4 and fig 5. Process flow diagram of gas hydrate formation by one fluid nozzles is shown in fig 6. In these systems gas is sprayed downward and water is
sprayed upward. Water and produced hydrate accumulate in the bottom of chamber and then is transport to the separation system.

Gas solubility in water normally increases with decreasing temperature, but in gas hydrate formation systems at forming temperature solubility shows different behavior with temperature changes. At temperatures, near hydrate formation condition, solubility of gas in water decreases as temperature drops [37, 38]. Gas hydrate formation rate increase in higher super saturations, pressure and temperature at nozzle inlet should be in a condition that joule-Thompson effect results in a temperature that provide 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.
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Fig 5, hydrate formation using twin nozzle

![Hydrate formation using twin nozzle](image)

Fig 6, hydrate formation process flow diagram with two nozzle for spraying water and gas respectively

![Hydrate formation process flow diagram](image)

2.3. **Bubble column**

These systems consist of one or more vertical column that are filled with water and cooled using thermal jacket. In the column gas is bubbled to the system and have specified residence time rising in water. Due to mass and heat transfer between gas and water, hydrate forms on bubble surface [39]. Formation of gas hydrate on the bubble surface increase both mass and heat transfer resistance which deteriorates hydrate growth [40,41]. One must find a way for surface renewal to solve this problem. Kinetic behavior of these systems has been modeled in papers [42]. To increase hydrate formation rate, bubbles should be small so providing more specific contact area. Fig 7 shows hydrate formation process in bubble columns. These hydrate formation systems systems recommended for gas mixture separation [43]. Fig 8 shows the gas hydrate formed on the bubbles. To enhance mass transfer in two phase systems the phase with higher resistance to mass transfer is usually dispersed. In hydrate formation the main residence is to dissolve hydrate former gas in water phase thus bubbling gas in column result in a better mass and heat transfer.
Microbubbles are another way dispersing gas in liquid. Their special properties, encourage industries to utilize them. macroscopic bubbles are hydrodinamical stable and have special rising speed and bursts at the liquid surface. On the contrary microbubble due to very high pressure difference between inside and out of bubble are very unstable and don’t make it to the liquid surface. They burst in the liquid which result in higher super saturation [44]. These bubbles are suitable for gas hydrate formation because of high internal pressure, high specific surface area and providing high gas solubility in liquid. Due to high internal pressure of microbubbles there is no need to bring the whole system’s condition to gas hydrate formation pressure. An aerator is used to produce microbubble [45-47]. There are two type of aerators: agitated and non-agitated. Fig 9 shows contact of gas and water using non-agitated aerator.
2.4. Reciprocating cells (rocking cell)
These type 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 don’t have any application in hydrate formation for transportation purpose [48].

2.5. Hydrate formation with emphasis on nucleation sites
Inspired by some ice making devices, in these type of systems, agitator is removed and a cooled nucleation sites is added to the reactor. Formation of hydrate on provided nucleation site eliminate need to separation of hydrate from unreacted water. After reaching to a specified diameter, gas hydrate leave the system by gravity or a vibrationg system. Fig 10 shows process flow diagram of these systems.

Fig 10, process flow diagram of hydrate formation with emphasis on nucleation site. 2) reaction chamber, 3) gas supply, 4) water supply
2.5. Gas in ice process
Gas hydrate formation in this method is carried out in an agitated vessels continuously. Pressure and temperature of hydrate formation is prepared in vessel. For example, 50 bar of pressure and 5°C are the conditions of the vessel, slurry of water and ice and gas are injected to the vessel, inside the vessel according to the conditions the ice melts by heat generated by the enthalpy of gas hydrate formation. The key point in these systems is producing of ice and water in another system. The advantage of this method is elimination of heat jacket from the vessel. According to the pressure of the vessel mechanical sealing of the shaft is not possible and should drive by electromagnetic forces that is expensive part of these systems. Fig 1 shows three part process of hydrate formation utilizing ice parts. Ice particles provide nucleation sites with suitable temperature thus enhance hydrate formation.

![Diagram of the process](image)

**Fig 11, three part process of hydrate formation utilizing ice parts**

3. Separation of gas hydrate and unreacted water
As mentioned earlier, gas hydrate formation is a crystallization process. Separation of gas hydrate and unreacted water is a solid-liquid separation. In crystallization processes the method is using density differences and or mechanical separation; both are usable in gas hydrate formation processes [49]. Density differences between hydrate and unreacted water is applied in two methods: gravity and centrifugal force. Gas hydrate density is less than water but the difference is very low and this cause a long residency time for separation by gravity force, e.g. methane hydrate is 0.9 grams per cubic centimeter. Fig 12 shows process of gas hydrate separation by gravity force. As shown in fig 12 gas hydrate is formed in agitated vessel and accumulated on the water surface, then water and gas hydrate transport to a settlement chamber. A method of separation by the means of centrifugal force is shown in fig 13, by the means of spinning of water and gas hydrate the less dense component which is gas hydrate moves into the center of the vessel and accumulate there.
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Fig 1, gas hydrate formation process and separation process by means of gravity force

Fig 12, gas hydrate formation process and separation process by means of gravity force

Fig 13, using centrifugal force for gas hydrate separation, hydrate is dischared from the center of chamber

4. Gas hydrate pelletizing systems
For transportaion and storage of natural gas using hydrate, possible methods are: 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 have 3 advantages, 1) more gas storage capacity 2) suitable fluidity and 3) better stability of gas hydrate. According to the exothermic dissociation of gas hydrate, decomposition of hydrate in a closed adiabatic system, cause pressure to increase and temperature to drop. These changes bring the system to a new thermodynamical equilibrium which leads decomposing to stop [50]. For better fluidity of gas hydrate pellets the suitable diameter is 100 mm. the purpose in pelletizing the gas hydrate is to have pellets with more stored gas and less decomposition rate [49].
4.1. Cylinder and Piston Systems

In these systems pellets are made by compressing the hydrate crystals. The less pressure drop at exit is a point for these systems, but according to reciprocating movement of system the operational life of system is not satisfying. Fig 14 and 15 shows two types of these systems. In Fig 15 the cylinder fills with gas hydrate and pressed between two piston by moving of the upper piston. Fig 17 is a simultaneously separation and pelleting of gas hydrate, in this systems unreacted water is separated by means of filter then pellets by pressure of piston. Fig 18 shows process flow diagram of separation and pelleting of gas hydrate by these systems.

Fig 14, pelleting by means of cylinder and piston, as shown gas hydrate enters to the cylinder and pistons press the gas hydrate then by moving of pistons pellet of gas hydrate exits the system.

Fig 15, gas hydrate pelleting with low pressure drop of reaction chamber A) gas hydrate valve to pelleting 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.
Fig 16, atmospheric separation of water and gas hydrate by means of filter and pelletizing by cylinder and piston systems

4.2. Rolling systems
In these systems slurry of gas hydrate is poured on two side by side roller and the gas hydrate pellets withdraw from the bottom of the rollers and discharge by means of a spiral. Fig 19,20 and 21 are three sample of these systems.
Fig 18, rolling pelletizer, rollers are cooled by internal fluids circulation

Fig 19, a rolling pelletizer system

Fig 20, a water separation system with rolling pelletizing system and withdrawn of gas hydrate without pressure drop by means of a well sealed spiral
References