INVESTIGATION ON A NOVEL REACTOR FOR GAS HYDRATE PRODUCTION

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ABSTRACT
Gas hydrates have a large capacity for the storage of gases and are an attractive method for gas filtration and transportation. However, hydrate formation is usually controlled by the rate of crystallization and thus it can be a slow process. A technology that will rapidly and continuously form hydrate is necessary for scale-up.

A novel reactor with an inner volume of 25 l has been designed, built and installed to form hydrates by injection of water through spray nozzles from the top of the methane-filled reactor. This method allows to maximize interfacial area between reactants and to minimize mass transfer barriers and thermal effects that negatively affect conversion of reactants into hydrate. A system was developed to remove heat released during hydrate formation, and to reach a good level of temperature control inside the reactor. A novel system for hydrate recovering and unloading was also designed. The objective of experimentation is to lower energetic costs of hydrate formation, also through surfactant promotion. Anionic surfactant sodium dodecyl sulphate, SDS, was tested. Results of a first set of experimental applications of the reactor for rapid methane hydrate formation are presented.

Keywords: methane hydrate, surfactant, scale-up, water spraying

NOMENCLATURE
n number of moles
P pressure [Pa]
R universal gas constant
SDS sodium dodecyl sulfate
t time [min]
T temperature [K]
V volume [l]
Z compressibility factor

INTRODUCTION.
Gas hydrates are crystalline compounds formed by the hydrogen-bonded water molecules in lattice structure that is stabilized by encapsulating a small guest molecule, such as methane or ethane [1]. Methane hydrates gives unique gas storage properties, as the hydrates can contain 150-180 V/V (standard temperature and pressure). Actually, after the discovery of hydrate self-preservation which allows hydrates to remain metastable at few degrees below the ice point at atmospheric pressure [2-3], scientists have become interested in studying the storage and transportation of gas in the form of hydrate. Research in this area started in the early 1990s by Gudmundsson and his group [3-4], and thereafter
several other researchers have reported results in this area [5-7]. The storage and transport of natural gas in methane hydrates does have some advantages over some of the conventional methods for methane storage. For instance two of the non-pipeline methods of methane storage consist in liquefying the natural gas (LNG) or in compressing it (CNG). Economic feasibility studies have been carried out especially by Japanese industrial researchers, and show how the cost of NGH is lower than that of LNG of the same scale, concluding that NGH is advantageous over LNG for gas transportation of amounts less than 1 million ton per annum [7]. Moreover, recent studies based on calculations of the total energy involved in the three technologies (NGH, LNG and CNG), from preparation of methane in its transportable form to its final use, show how LNG process is less energy demanding but by far more expensive when compared to storage and transport of gas hydrates, whereas CNG is comparable to the use of gas hydrates from energy and economical points of view, but the technology is nowadays developed only for small-scale systems [8]. The storage and transportation of gas as NGH is appealing for industrial utilization also because of its high safety.

Nevertheless, the feasibility of using clathrate hydrates for industrial purposes has long been an intriguing subject of engineering studies [9-10]. The main issues are the slow formation rates, unreacted interstitial water as a large percentage of the hydrate mass, reliability of hydrate storage capacity and economy of process scale-up. The lack of a technology that allows the production of hydrate in a continuous manner suitable for scale-up to industrial settings has hindered the utilization of gas hydrates in the above application, and also in others, such as, biogas refining, gas separation and capture, residential air conditioning, desalination of seawater. Hydrate formation is always the first process in any of these yet-to-be established technologies, and it may control the rate of the serial processes composing the technology. Thus, how to efficiently form hydrates is a technical task research of rather wide interest. If the guest substance is in a gaseous state and slightly soluble in liquid water, some means to enhance the mixing of the guest substance and water is necessary to realize hydrate formation at a rate high enough for industrial purposes.

Stirring is the most common method used to improve mass transfer and heat transfer in the methane hydration process: induction times was shortened, formation rates accelerated, and storage capacity was increased when stirring was applied [10-11]. Stirring reactors are widely used in laboratory settings to carry out fundamental studies on formation and dissociation of gas hydrates [10]. Anyway, as already established, there are several problems with stirring in an industrial-size process. Energy costs from stirring increase as slurry thickens. Thickening slurry of a stirred system may limit the hydrate mass in the water to as low as 5% [12] at which time filtering or clarification would be necessary. The separation of hydrates from the slurry requires additional work as does packing the hydrates in a storage vessel. Furthermore, hydrate particles entrain substantial amounts of interstitial water.

The bubble tower reactor is a traditional industrial reactor type suitable for gas-liquid reactant system, and it was tested for hydrate formation. So far, results from use of this type of reactor are not encouraging in terms of hydrate formation rate, and hydrate shells formed are not easy to be broken [10, 13].

Spraying reactor is another type of reactor for gas-liquid reactant system. Application of water spraying into a gas phase to form methane hydrates has been studied by Mori and co-workers, who designed and modified spraying reactors [14-15]. We believe this technique is worthy of further development for applications to scaled-up systems. In this work we report and discuss the design and development of a new scaled-up spraying reactor, with inner volume of 25 l, with 6 nozzles. It was designed to be suitable for practical engineering use, for rapid and in continuo production of hydrates. So far, it has been tested as batch reactor, as will be shown in detail in the next section. The objective of experimentation is to lower energetic costs of hydrate formation, also through surfactant promotion. We tried to decrease the overall time, both induction time and hydrate-formation time: in fact, time is an important factor to be taken into account so that some authors use the expression “time cost” [16]. At this regards, the use of surfactants in hydrate-forming systems provides an intriguing subject of research. Previous studies reported that addition of surfactant to liquid water causes a drastic promotion on the rate of formation and occupancy of gas hydrates, and decreases the induction time [9, 16-21]. In our work we used anionic surfactant sodium dodecyl sulphate, SDS, which seems one of the best commercially
available surfactant to be used for enhancement of methane hydrate formation [17-19].

**REACTOR DESIGN**

A novel apparatus of internal volume of 25 l has been designed and built to carry out studies on the scale-up of gas hydrate formation. A schematic diagram of it is shown in Figure 1.

![Schematic diagram of the experimental apparatus.](image)

The reactor has been designed to maximize interfacial area between reactants, thus minimizing mass transfer barriers and thermal effects that negatively affect conversion of reactants into hydrate. Hydrates, in fact, are formed in the reactor by injecting water through spray nozzles from the top of the methane-filled reactor. It consists of a high-pressure cylindrical AISI 304 stainless steel vessel with internal diameter of 200 mm, an internal length of 800 mm and a total internal volume of 25 l. It has been designed for pressure values up to 120 bar and provided with a safety valve. A system was developed to remove reaction heat and to ensure a rather constant temperature inside the reaction vessel. The reactor is provided with a screw conveyor. Thread depth increases from flanges toward the center of the vessel and is tangent to a finely-perforated metal sheet. This system is designed to allow conveyance of the solid hydrates to the unloading flange, with a first separation of liquid water from solid products. Two AISI 304 stainless steel flanges are used to seal the reactor. One flange has appropriate ports for access to the interior. The four ports are used for inserting 2 temperature sensors and for supplying methane and the pressurized aqueous solution. The temperature sensors are mineral insulated type T thermocouples (accuracy class 1) and measure the temperature inside the vessel in the lower part and in the upper part, near spray nozzles (see scheme 1). The methane inlet line is equipped with a pressure sensor, that is a digital piezo-resistive manometer (accuracy class 0.5). Gas is supplied directly by gas bottles through a pressure-reducing valve, that provides adjustment of the pressure to the methane injection line. Water-supply system comprises the device for water pressurization and cooling and the manifold for its injection. The aqueous solution is flowed by a circulation pump to a high-pressure vessel, placed in a cylindrical water thermostatic bath. The bath was equipped with an immersion type cooler. The cooling medium is ethylene glycol – water solution. The aqueous solution is pressurized inside the vessel through injection of nitrogen and sent to the manifold, equipped with pressure gauge for the measure of water pressure before nozzles. In the internal part of the manifold, water is atomized by six hydraulic nozzles. Such devices for water spraying allow control of dimensions of water droplets and water flow. The temperatures of the thermostatic bath was measured by a thermocouple inside of the bath, and the temperature of the injected aqueous solution was measured by another thermocouple placed on the inlet pipe. Voltage signals from pressure transducers and temperature sensors are collected by a software for data acquisition on a personal computer. The installation of the system is shown in Figure 2. The reactor is in the foreground. Seen in the background there are gas bottles, the pressurized water vessel, and liquid nitrogen cylinder. Nitrogen (99.999 % purity) and methane (99% purity) were supplied by Air Liquide Italia Service. Distilled water was used to prepare solutions.
APPLICATION OF THE REACTOR FOR METHANE HYDRATE FORMATION WITH SURFACTANT PROMOTION

We used the reactor described to produce methane hydrates, but it can be used for other types of hydrates (natural gas for instance). It was designed to produce hydrates in a rapid manner, with hydrate formation times below 1 hour. The experimental procedure includes the preparation of the system and the carrying out of the experiment itself. Hydrate formation is carried out through the injection of atomized aqueous solution into the methane-filled reactor.

In the preparation, the reactor is filled with methane from gas bottles until the internal pressure equals the experimental pressure and then cooled by liquid nitrogen. The temperature is controlled in order to achieve relatively uniform values inside the reactor. Water (aqueous surfactant solution) is injected into the pressurization vessel with a circulation pump and cooled in the thermostatic bath. Then, it is pressurized with nitrogen from gas bottles, until the correct value of differential pressure on nozzles is reached.

When the experimental conditions are reached, aqueous solution is flowed through the nozzles. Since the flow rate of aqueous solution through the nozzles depends on the differential pressure on nozzles themselves, the water spraying is continued for several minutes until the established total amount of aqueous solution is injected. During the experiment pressure and temperature data are collected every 5 seconds. Figure 3 represents typical profiles of values of pressure and temperature vs time; data reported in this figure are for experimental run 2 in Table 1. The pressure is the total pressure inside the reactor, and the temperature values are three, because two values are monitored inside the reactor in two different positions (see Figure 1) and one value is relating to the temperature of sprayed water.

As regards the temperature values, our efforts in the reactor design were devoted to obtain an high level of temperature control. Dealing with temperature control is one of the important factors deciding the performance of the hydrate formation for at least two reasons: subcooling and heat removal. In fact, under the experimental condition of a pressure of 8 MPa, the equilibrium temperature of methane hydrate is 287.0 K [1]. However, subcooling is generally required for hydrate formation so that it is often considered a driving force for the process. Under certain limits, formation rate increases with increasing subcooling [21]. In our work the experiments were carried out at initial temperature values of ca. 3-4 °C, with a relatively high subcooling. Furthermore, during the hydrate formation the temperature increases as a result of the exothermic process, and it is of no help in hydrate formation, so that an efficient system for reaction heat removal is necessary. Moreover, in a scaled-up system there is the further problem of temperature uniformity inside the volume of the reactor. In Figure 3 we can see how we were able to attain constant experimental values of temperature and pressure in the first minute (no water is present inside the reactor).
reactor in the first minute). After this time had elapsed, water spraying started, and continued for 15 minutes. Temperature profiles reported in Figure 3 show how our system for temperature control was able to maintain a relatively constant and uniform values of temperature in the reactor during hydrate formation, with variations within 3°C.

As regards variation of pressure with time, one would expect a pressure increase during water spraying due to the decrease of available volume. In Figure 3 it can be clearly noted that the pressure increase tends to be linear at the beginning, in the first 4-5 minutes. Afterwards, the pressure variation tends to be smoother, and then it levels off. This can be ascribed to gas consumption due to hydrate formation. For clarity in Figure 4 pressure values during water spraying are reported for experiments carried out with and without SDS surfactant, i.e. runs 1 and 2 in Table 1.

Despite that, the apparatus is designed for collecting gas hydrates through the activation of the rotating screw. Therefore, at the end of the experiment, gas was vented out from the methane injection port through a three-way valve. Visual observations was possible opening the flange, and interesting images were taken.

In this first set of experimental applications of the reactor we chose to work in batch conditions, to open the reactor and have a visual analysis of the situation, and to take hydrate samples out from the reactor for characterization in terms of gas content.

Figure 5 shows the picture of the hydrate formed in run 2, after 15 minutes reaction time. It can be clearly seen how there is no liquid water left. The hydrate formed mainly on metal surfaces, such as the lower part of the inner surface of reactor, the outer surface of the screw conveyor, the upper part of the finely-perforated metal sheet. This phenomenon is consistent with those observed by different authors, who reported that hydrate form on the metal surfaces [17, 21-22]. Several samples were taken directly out from the reactor since the flange is open. Hydrate storage capacity was determined putting hydrate samples inside a custom built dissociation vessel, shown in Figure 6. It is a cylindrical AISI 304 stainless steel vessel with a volume of 1.4 lt. It was designed and built to carry out the dissociation of samples of gas hydrate formed.

After sealing the vessel, the dissociation starts and gas methane pressure and temperature after dissociation are measured. To calculate number of methane moles the following equation was used:

$$P \times V = Z \times n \times R \times T$$

(1)
where \( P \) is the methane partial pressure in the vessel at the end of dissociation, \( V \) is the volume of gas in the vessel, \( n \) is number of the gas methane moles, \( T \) is the temperature in K at the end of dissociation, \( R \) is the universal gas constant, and \( Z \) is the compressibility factor, which can be calculated using Benedict-Webb-Rubin equation of state.

Figure 6: The dissociation vessel.

As the number of gas moles is calculated, hydrate storage capacity, measured in % of weight, can be determined, because sealed vessel had been weighted right after closure. The maximum value of methane storage capacity in methane hydrate of structure-I is 13.4 in weight %.

In Table 1 we report the results of our first set of experimental applications of the reactor for rapid methane hydrate formation. As initial temperature we indicate the mean value between values measured in the upper and lower part of the reactor before starting water spraying. In the formation of gas hydrate by adding SDS, the decision of the ideal concentration of SDS is primarily required. Several investigations reported in the literature indicate different optimal SDS concentrations, in different conditions and reactors [9, 16-17]. Anyway a concentration in the range of 250-500 ppm seems the best choice: as a starting concentration for a first set of experiments we chose 300 ppm. We also carried out an experiment in the absence of SDS for the sake of comparison. First of all, it is clear, as already outlined from profiles in Figure 4, that without SDS the gas content in the hydrate is very small.

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial T, °C</th>
<th>SDS, ppm</th>
<th>Water, ml</th>
<th>Water spraying time, min</th>
<th>%CH₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>-</td>
<td>5070</td>
<td>15</td>
<td>&lt;1 (1)</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>300</td>
<td>5070</td>
<td>15</td>
<td>4 (6)</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>300</td>
<td>2500</td>
<td>15</td>
<td>4 (8)</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>300</td>
<td>6000</td>
<td>25</td>
<td>6 (8)</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>300</td>
<td>6000</td>
<td>25</td>
<td>2 (4)</td>
</tr>
</tbody>
</table>

⁺ weight %; mean value among several samples; maximum value in parentheses.

Table 1: Summary of the results of the experimental application of the novel reactor for methane hydrate production.

In presence of SDS, in general, we have to say that the amount of methane stored in the hydrates is not high compared to literature values, which refer to laboratory scale reactors. It was expected, because the scale-up effects studied so far indicate that the hydrate formation rate, the moles of gas consumed per unit mass of water and time decreased rapidly with increasing the mass of water loaded in the reactor [10, 22]. Our result confirms this general trend, but it is necessary to point out that our reaction time is quite short, even compared to laboratory scale experiments where times of hundreds of minutes are used and our water volumes are significantly greater than the amounts used in the laboratory scale, that are few hundred ml or less [9-21]. We also have to point out that we never found liquid water left in our experiments. Due to the fact that large scale industrial applications can not face long reaction times, we tried to improve the performance changing conditions but without lengthening so much the time. A decrease in the water amount from ca 5 l to ca. 2.5 l did not change so much the situation (runs 2-3). We tried to leave time to the system for hydrate formation to occur after finished water spraying, but almost nothing happened after water spraying had finished (data not shown in table 1). On the other hand, the methane storage increased if the spraying time was lengthened from 15 to 25 minutes, even with a greater amount of water (runs 2-4). A modification in the reactor, with momentary elimination of the screw conveyor, gave a worse performance, and it can be related to a decrease in the metallic surface available (runs 4-5).
In conclusion, a novel reactor, with a volume of 25 l, for the production of methane hydrates was designed, constructed and tested for its application to rapid hydrate formation, with the word rapid meaning a reaction time of some tens minutes, instead of the hundreds minutes used in the literature also in the laboratory scale. Results of a first set of applications indicate that we could obtain an high level of temperature control in the reactor during hydrate formation, and we could obtain methane hydrates, without water left, in some tens minutes only with SDS surfactant promotion. The amount of water loaded was up to 6 l. Changing some experimental conditions we improved the gas content in the hydrate, that is not generally high: the best value we have obtained is ca. half the maximum. On the basis of these results, our application of the reactor is continuing. Other variations in the conditions are planned, and slight variations in the reactor design, via interchangeable pieces, are under development in order to obtain an higher level of gas content in the rapidly formed methane hydrates.

REFERENCES


