Hydrate Formation in Reactor with Cooling Spiral

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Abstract. This paper deals with methane hydrate formation from SDS solution of 0.1 wt% in reactor with cooling spiral. Intensity of methane hydrate formation process in a vertical and horizontal cylindrical reactor with a cooled spiral at three fixed volumes of a surfactant solution was compared. The dependence of the gas content of the obtained samples depending on volume of the liquid phase and on the position of the reactor was revealed. The hypotheses about influence of diffusion at the interface and capillary effect on the cooled element on the gas content were examined. Also the efficiency of gas supply mode was tested. The best result for gas consumption in single gas injection mode is 60.21 L•L⁻¹ achieved with a liquid volume of 300 ml in a vertical reactor. The best result for gas consumption in constant gas supply mode is 161.3 L•L⁻¹ achieved with a liquid volume of 500 ml in a horizontal reactor.

1. Introduction
Gas hydrates are clathrate compounds formed due to the inclusion in the cavity of the framework formed by water molecules (host) of hydrate-forming gas molecules (guest) [1]. The cavities are formed by water molecules due to hydrogen bonds, and small gas molecules (hydrogen, methane, carbon dioxide, nitrogen and hydrogen sulfide) are captured in the cavities due to van der Waals forces. Currently, four different hydrate structures are known: structure I (sI), structure II (sII), structure H (sH), and semi-clathrate hydrate (sc) [2-4]. Of greatest interest is methane hydrate (it forms the sI structure), since methane is the main component of natural gas, and significant accumulations of natural gas hydrates exist in the sediments of the seas and oceans, as well as in permafrost. According to various estimates, the world resources of hydrocarbon raw materials in the form of gas hydrates amount to 10¹⁴–10¹⁶ m³ [5]. In addition to a source for the extraction of natural gas from them, gas hydrates have the potential for practical application in the storage and transportation of natural gas [6, 7], separation of gas mixtures [8, 9], and water desalination [10, 11]. Method of storage and transportation of natural gas in a gas-hydrated state attracts a lot of attention. One volume of methane hydrate can store about 170 volumes (at standard temperature and pressure) of methane, so the storage of natural gas in this form is of great interest [12, 13]. In addition, the storage and transportation of natural gas based on hydrates has several advantages over other technologies such as compressed natural gas and liquefied natural gas, which usually require extreme pressure and temperature, respectively [14]. As a result, natural gas hydrate has gained attention over the past several decades, and there has been increasing focus on how to achieve rapid formation of natural gas hydrates along with high storage capacity, which is critical for industrial use. As a result, natural gas hydrate has gained attention over the past several decades, and there has been a growing focus on how to achieve rapid formation of natural gas hydrates along with high storage capacity, which is critical for industrial use in natural gas transportation and storage.
A huge number of works have been devoted to solving the problem of the rate and conditions for obtaining methane hydrate. In many studies, various solid additives are used as kinetic promoters: silicas [15-19], various nanoparticles (silicon dioxide, silver, activated carbon, metal oxides) [20-22]. Solutions of various surfactants are also used as kinetic promoters, which promote the formation of hydrates due to the presence of micelles or aggregates in solutions. Many researchers have used surfactants to intensify the formation of gas hydrates, and over the past two decades, various types of surfactants have been adopted, among which the greatest attention was paid to sodium dodecyl sulfate (SDS) [23–30] and its combined with nanoparticles [31-33]. Such additives significantly increase the rate of hydrate formation, but if we talk about their industrial application, their use significantly increases the cost of the process. Therefore, in this project aimed at industrial production of methane hydrate, we plan to use sodium dodecyl sulfate (SDS). SDS, in addition to a significant increase in the rate of hydrate formation, and has advantages such as low cost and availability. Most of the work is carried out with stirring, which allows high rates of hydrate formation to be achieved, but complex and expensive solutions will be required for use in industrial processes. The energy consumption for mixing increases as the slurry thickens [29]. Mechanical agitation problems increase equipment capital costs and maintenance costs. Therefore, on an enlarged scale of the process, strive for the rate of formation of a stirred system and economic advantages in the technological simplicity of an inactive system. Therefore, in [29] a system with internal cooling on a spiral is proposed, which allows obtaining hydrate formation rates similar to stirring.

The purpose of this article is to study the factors affecting the efficiency of methane hydrate synthesis in a reactor with an internal cooling spiral.

2. Materials and methods

2.1. Materials
A steel cylindrical reactor with a volume of 960 ml equipped with a lid with a flange connection was used to obtain methane hydrate. The lid of the reactor was equipped with a reservoir for placing a thermocouple, gas supply line, a pressure sensor, and a spiral tube for refrigerant circulation. The spiral tube has been used as a cooling element on which the product of the target reaction is formed. The axis of the refrigerant circulation spiral is parallel to the axis of the cylindrical reactor.

The gas pressure in the reactor was measured by an AIR-10N pressure transducer with an accuracy of 0.01 bar. The pressure of the gas flowing from the cylinder to the reactor was regulated by a gas reducer. The temperature of the refrigerant circulating in the cooling element was controlled by a LOIP FT cryostat with an accuracy of 0.1 °C. The temperature of the medium inside the reactor was measured by a thermocouple with an accuracy of 0.5 °C. The gas volume was measured by a Ritter TG05 gas flow meter with an accuracy of 0.001 l. A Drexel bottle with an antifoam agent was installed between the flow meter and the reactor. The data received from the sensors was transmitted to the computer. Primary data processing was carried out using the OWEN Process Manager software. The purity of used methane was 99.6% (Moscow Gas Processing Plant). To intensify the hydrate formation process, solutions of sodium dodecyl sulfate (NaC12H25SO4) manufactured by PanReacApplyChem with a purity of 95% was used. In all experiments the same solution of 0.1 wt% of SDS was used.

2.2. Method
A schematic of the setup for producing and studying methane hydrate is shown in figure 1. The first mode assumes a one-time injection of methane into the reactor up to a given pressure. The second mode involved maintaining the pressure in the reactor at a constant level by supplying gas during the entire hydrate formation reaction.

The single gas injection mode is more suitable for research purposes, since it allows observing the methane consumption rate during hydrate formation by observing the pressure drop in the reactor. For this reason, the specified mode was used in this study to determine the optimal values of parameters of methane hydrate synthesis with the aim of further transferring them to a series of experiments in a constant gas supply mode.
The mode of constant supply of methane to the reactor makes it possible to achieve the highest gas consumption, since with continuous supply of methane, a larger amount of gas enters the reaction space, and also because there is no pressure drop due to gas consumption. This mode can be recommended for industrial production of methane hydrate.

The algorithm of synthesis describes below.

Loading the solution into the high pressure reactor. Injection of methane into the reactor through the gas supply line to flush it 3 times to remove air from the reaction volume. Leaks testing of the closed reactor for 2 hours temperature +20 °C. Then reactor was cooling down to –3.0 °C. The target cooling rate was 5 °C•min⁻¹. Methane supplied to the reactor. Stopping the gas supply upon reaching a pressure of 5.0 ± 0.1 MPa (single gas injection mode) or continuing the methane supply to the reactor to maintain the pressure at a level 5.0±0.1 MPa (constant gas supply mode). Observation on the experiment according to the readings of sensors data transmitted to the computer. Additional cooling of the sample to –20 °C in an hour to stabilize methane hydrate. Then, the unreacted gas was discharged and the hydrate was decomposed in order to determine gas consumption.

In the course of studying the process of methane hydrate formation in the presence of sodium dodecyl sulfate in reactor with cooling spiral, the goal was to clarify the significance of the contribution to the hydrate formation process of such factors as the capillary effect and diffusion at the interface. To achieve this goal, two series of experiments were carried out on the synthesis of methane hydrate for three given volumes of solution each.

3. Results and discussion

3.1. Comparison of the intensity of hydrate formation for vertical and horizontal reactor for single gas injection mode

The influence of the orientation of the reactor in space on the intensity of hydrate formation for three given volumes of liquid has been investigated. Consumption of methane was observed by measuring decrease in pressure due to the formation of gas hydrate. With no additional gas supply the amount of gas in the reaction volume is limited by amount of liquid placed in the reactor at the start of experiment.

In the reactor of the considered design, the coolant circulation loop is a spiral tube welded to the lid. The cooled tube is located in the reaction volume with a small gap from the bottom and walls. Methane hydrate forms due to the capillary effect on the part of the spiral above the liquid level. If the solution touches the cooled element, a liquid volume of more than 100 ml can be reached. In theory, the cooled element surface above liquid to gas interface is expected to be available for hydrate formation by capillary action.

Figure 1. Schematic of the tank reactor setup for hydrate formation and decomposition. Schematic of the tank reactor setup for hydrate formation. 1 — gas cylinder, 2 — pressure regulator, 3 — cooling spiral, 4 — reactor, 5 — cryostat, 6 — gas flow meter, 7 — computer.
In addition, it can be assumed that part of the methane hydrate is formed due to the diffusion of gas into the solution through the interface. The interface is a cross-section of the cylindrical volume of the internal space of the reactor by a horizontal plane at the liquid level. The design of a cylindrical reactor with a spiral refrigerant circuit allows the reactor to be placed horizontally or vertically. Thus, the area of the diffusion surface depends on the orientation of the reactor and the volume of liquid with a horizontal arrangement of the reactor.

After determining the parameters that are affected by the volume of liquid in the reactor, a number of experiments were carried out on the synthesis of methane hydrate from solutions with volumes of 300, 500, and 800 ml in order to find out the optimal volume of liquid to achieve the highest efficiency of the process.

In the first series of experiments, the cylindrical reactor was placed vertically, in the second — horizontally.

![Figure 2. Dependence of the amount of methane in the hydrated form, on the time in the process of obtaining methane hydrate. Reactor orientation: (a) — vertical, (b) — horizontal. Solution volumes: 1 — 800 ml, 2 — 500 ml, 3 — 300 ml.](image)

Figure 2 shows graphical dependences of the amount of methane substance consumed for the formation of gas hydrate on the reaction time. Despite the differences in quantitative indicators for the investigated value, the qualitative indicators of the two obtained graphs are quite similar. Analysis of the curves shows that with an increase in the volume of the solution, the amount of absorbed methane decreases. In both cases, the best results were achieved with a liquid volume of 300 ml: an average of 0.70 mol for the horizontal and 0.81 mol for the vertical orientation of the reactor. The worst results are observed for reactions in 800 ml of solution - on average 0.20 mol and in one and in the other case.

The synthesis efficiency of a 300 ml solution exceeds the synthesis efficiency of 800 ml by 3.6 times for a horizontally located reactor and 4.1 times for a vertical.

It should be noted that the drop in the efficiency of hydrate formation as a function of the volume of liquid, regardless of the orientation of the reactor, is not linear. The observed deviation from linearity for a volume of 500 ml is 27% for a vertical reactor and 21% for a horizontally located one, relative to the expected value.

In case of vertical reactor, the liquid phase occupies a cylindrical volume in the lower part of the reactor and does not touch the lid. In this case, the diffusion of methane into the solution (and further into the formed ice) occurs through the upper base of the cylindrical liquid column — a circle with a diameter that coincides with the inner diameter of the reactor, from the area of which the cross sections of the tubes of the cooled coil and the thermocouple reservoir are excluded. The upper part of the cooled circuit remains in the gas volume. Methane hydrate is formed in this part due to the diffusion of methane into the previously formed ice. The latter is formed due to the capillary effect.

In case of horizontal reactor, the liquid phase is distributed over a segment of the cylindrical volume of the internal space of the reactor. Part of the cooling circuit remains in the gas volume. The proportion
of methane hydrate formed due to the capillary effect on the spiral segment, which appears on top with the horizontal arrangement of the reactor, differs from that obtained with the vertical arrangement of the reactor for geometric reasons.

3.2. Identification of factors affecting the gas consumption of methane hydrate at different orientations and filling of the reactor

Comparison of the gas consumption of the samples obtained with the vertical and horizontal orientations of the reactor of the design under consideration makes it possible to judge the efficiency of the synthesis process with different ratios of the area theoretically available for hydrate formation by diffusion into the frozen solution and hydrate formation due to the capillary effect.

Comparing the data obtained on the gas consumption of the samples with the area of the interface, no correlation is observed (table 1). Then, as if hydrate formation predominantly proceeded by a diffuse mechanism, we would observe a significant increase in the gas content of the samples obtained with the horizontal arrangement of the reactor in comparison with the samples obtained with the vertical orientation.

Moreover, if the diffusion process made a significant contribution, we would observe the maximum gas consumption in the horizontal orientation of the reactor with a liquid volume of 500 ml, i.e. under conditions of maximum diffusion surface area. However, the most methane containing sample of the hydrate was obtained with a liquid volume of 300 ml in the vertical orientation of the reactor.

Table 1. Parameters of the performed syntheses of methane hydrate with a single injection of a fixed volume of methane to the reactor.

| Specifications                      | Orientation of the reactor |
|-------------------------------------|----------------------------|
| Liquid phase volume, \( V_l \), ml  | Horizontal     Vertical     |
|                                     | 800           500          300   800 500 300 |
| Gas consumption, \( V_{CH_4} \cdot V_l^{-1}, L\cdot L^{-1} \) | 5.49        26.46     52.22 5.51 28.02 60.21 |
| Interface area, \( S_{\beta+} \), dm² | 1.76          2.03     1.94  0.31 0.31 0.31 |
| Surface area of the cooling element above the solution, \( S_{L+} \), dm² | 0.89        2.01      2.96  0.84 2.14 3.01 |

At the same time, with an increase in the surface area, on which in theory methane hydrate can be formed due to the capillary effect, we observe a proportional increase in the gas content for all samples. As you can see, in fact, with the vertical orientation of the reactor, these areas exceed the areas corresponding to the same volumes of liquid for the horizontal orientation. A similar increase is observed in the values of the gas content of methane hydrate samples.

3.3. Comparison of the intensity of hydrate formation for a vertical and horizontal reactor for a constant gas supply mode

In this series of experiments, the methane content in the resulting hydrate was compared with solution volumes of 300, 500, and 800±1 ml, constant pressure 5.0±0.1 MPa, horizontal and vertical orientations of the reactor.

The difference between the lowest and highest gas content of the samples in a vertically located reactor is 89.2 L·L⁻¹ for a sample of 500 ml of solution (table 2). The area of the interface for all three volumes of the solution in this case is the same and is 0.31 dm². The difference in the interface area for a horizontally located reactor between samples in 300 and 500 ml of solution is 0.03 dm², the difference in gas content is 9.1 L·L⁻¹. Similar indicators for samples of 300 and 800 ml of solution — 0.18 dm² and 109.4 L·L⁻¹.

The results obtained make it possible to say that there is no linear relationship between the surface area of the interface and the gas consumption of methane hydrate. The obtained data do not allow completely rejecting the assumption about the contribution of diffusion to the process of hydrate formation, however, at least, they show the presence of other more significant factors affecting the studied value.
Table 2. Parameters of the syntheses of methane hydrate while maintaining a constant pressure throughout the reaction.

| Specifications                  | Orientation of the reactor |
|---------------------------------|----------------------------|
|                                 | Horizontal | Vertical |
| Liquid phase volume, \( V_l \), ml |          |          |
| Gas consumption, \( V_{CH4} \cdot V_l^{-1}, L\cdot L^{-1} \) | 42,77     | 161,3    |
|                                 | 152,2      | 135,9    |
|                                 | 42,73      | 131,9    |
| Interface area, \( S_{g-l} \), dm² | 1,76       | 2,03     |
|                                 | 1,94       | 0,31     |
|                                 | 0,31       | 0,31     |
| Surface area of the cooling element above the solution, \( S_{s-l} \), dm² | 0,89 | 2,01 |
|                                 | 2,96       | 0,84     |
|                                 | 2,14       | 3,01     |

Comparison of the surface area of the cooled element and the gas consumption of the samples shows no apparent correlation. The highest value of the considered parameter (3.01 dm²) corresponds to the sample with not the highest gas consumption (131.9 L•L⁻¹). The sample with the highest gas consumption (161.3 L•L⁻¹) corresponds to the surface area by almost a third less (2.01) than in the previous case. The lowest gas consumption of two samples from 800 ml of solution is most likely explained by the lack of gas entering the reactor, as in the case with a single gas injection. In the latter case, the smallest value of the area of the cooled element is more likely a consequence of the small volume of space above the solution.

Thus, we can say that the capillary effect does not make a significant contribution to the efficiency of hydrate formation with constant gas supply to the reactor.

3.4. Comparison of the efficiency of gas supply modes

Analysis of the data presented in Table 1 and Table 2 confirms the hypothesis that the highest gas consumption is achieved by methane hydrate synthesis with continuous gas supply. The difference in the maximum gas consumption of the samples was 101.9 L•L⁻¹.

In addition, as shown above, in the mode of single gas injection into the reactor, such a parameter as the area of the cooled surface above the liquid level is essential. Whereas the efficiency of hydrate formation with constant gas supply to the reactor is affected only by the ratio of the gas and liquid phases.

4. Conclusion

Analysis of the data obtained shows that in this configuration of the setup for producing methane hydrate with a single injection of gas into the reaction space, the vertical orientation of the reactor is preferable, since for all three investigated volumes of liquid it allows to obtain samples with the highest gas consumption index relative to samples obtained in a horizontally located reactor. The most indicative is the result for 300 ml of solution. The difference in the gas content of the samples obtained in a vertical and in a horizontal reactor for a given volume of liquid is 7.99 L•L⁻¹.

However, with a constant gas supply to the reactor, the best gas consumption results were obtained for the horizontal orientation of the reactor.

In addition, according to the data obtained, the gas consumption of the samples decreases with an increase in the volume of the solution in the mode of a single gas injection. The synthesis efficiency in a 300 ml solution exceeds the synthesis efficiency in 800 ml by 3.6 times for a horizontal reactor and 4.1 times for a vertical one. This effect is explained by the fact that the amount of hydrate-forming gas in this experiment is limited by to the volume of the liquid. Accordingly, with an increase in the volume of the solution, the lack of gas also increases.
A similar effect is observed for the constant gas supply mode. But in the latter case, the best results were achieved for 500 ml, and not for 300. Apparently, it is the ratio of the gas and liquid phases, close to 1:1, that makes it possible to achieve the greatest completeness of the reaction. Whereas for 300 ml under the same conditions, the limitation of the lack of the liquid phase slows down the reaction rate.

Comparison of the surface area of the interface and the gas content of the samples showed the absence of any visible correlation between the factors under consideration. However, the data obtained do not allow refusing or confirming the presence of a nonlinear correlation between these factors for the constant gas supply mode. Possibly, this question requires additional research.

The hypothesis about the contribution of the capillary effect to the hydrate formation process is tested. Comparison of the surface area of the cooled element above the liquid level and the gas consumption of the samples showed the presence of a correlation between these values for the mode of a single gas injection into the reactor. The best result is achieved with a liquid volume of 300 ml in a vertical reactor: \( V_{\text{CH}_4} \cdot V_l^{-1} = 60.21 \text{ L} \cdot \text{L}^{-1} \) with \( S_{\text{sl}} = 3.01 \text{ dm}^2 \). The worst result is achieved for a liquid volume of 800 ml in a horizontal reactor: \( V_{\text{CH}_4} \cdot V_l^{-1} = 5.49 \text{ L} \cdot \text{L}^{-1} \) with \( S_{\text{sl}} = 0.89 \text{ dm}^2 \). However, such a correlation is not observed in the constant gas supply mode.

Summarizing the data obtained, we can conclude that when designing setup for the synthesis of methane hydrate, involving a single injection of gas, it is preferable to maximize the area of cooled element above the liquid level. However, the synthesis of methane hydrate in the constant gas supply mode is more efficient. The gas content of the samples obtained in this mode depends less on the geometric parameters of the reactor and the cooled element and is regulated by the liquid level in the reactor.

5. References
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