Development of a Method for Producing Molded Hydrates of Natural Gas

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Abstract. The article proposes a method for producing natural gas hydrates in the form of cylindrical pellets with a continuous production cycle. The method involves the formation of hydrates in a natural gas atmosphere at pressures from 5 to 8 MPa and a constant temperature equal to +5 °C, in the form of a hydrate slurry formed by stirring a hydrate-forming liquid in an environment of a hydrate-forming gas. The resulting gas hydrate slurry is collected in a perforated sleeve equipped with a filter and pressed into cylindrical pellets using a hydraulic plunger. The main feature of the developed method is to simplify the technology for obtaining the finished product in the form of cylindrical pellets of natural gas hydrates by placing all production processes within a single sealed tank.

1. Introduction

Gas hydrates are crystalline solid compounds that are formed under certain thermodynamic conditions from water and various gases including natural origin such as natural gas. These substances are characterized by the unique property to contain a vast amount of the initial gas without any losing its quality during their further dissociation [1, 2]. This ability of gas hydrates is estimated by such a parameter as the specific gas content, which depends on the molecular weight of the hydrate-former gas, the structure and composition of the hydrate, as well as the degree of filling of the hydrate cavities and the presence of inclusion compounds and crystal lattice defects [3, 4]. For example, with 100% filling of the hydrate structure with methane molecules (CH₄·5.75H₂O), its specific gas content is 164 m³/m³ [2].

A review of the application of technologies for the transportation and storage of natural gas in the form of gas hydrates (in solid state) are given in [5, 6].

Nowadays the regions where the use of gas hydrate technologies is most promising are the regions of the Russian Arctic, rich in hydrocarbon resources and characterized by the absence of a developed transport infrastructure. It is assumed [7] that in the cold regions of Russia it is possible to compensate for the heat of phase transitions during hydrate formation and maintaining a low temperature in the process of their accumulation by using natural air low temperatures. Also, at low temperatures, a very important property of hydrocarbon gas hydrates is manifested - the effect of self-preservation, i.e. their decomposition delay at atmospheric pressure and negative temperatures [8, 9].
According to a number of authors, the optimal form for the transportation and storage of hydrocarbon gases in gas hydrate form are large agglomerates with the shape of tablets or pellets, molded from finely dispersed gas hydrate raw materials [10-13]. However, the production cycle of gas hydrate pellets consists of several stages, which leads to its complicated execution and, as a consequence, to an increase in the price of the final product.

Currently, there are prerequisites for the development of continuous methods of gas hydrate synthesis with a simultaneous reduction in energy costs in the technological cycle of their production [14, 15]. But they also imply multi-stage production of the final product. Therefore, the problem of continuous production of gas hydrate product directly in a synthesis reactor itself still remains unresolved [16].

Thus, in this work we show a new method for the continuous production of pellets of hydrocarbon gas hydrates directly in a sealed reactor tank.

2. Experimental
Distilled water was used as a hydrate-former liquid medium. Natural gas of the Srednevilyuysky gas condensate field was used as a hydrate-former gas, the composition of which is given in Table 1.

| Components | CH₄ | C₂H₆ | C₃H₈ | i-C₄H₁₀ | n-C₄H₁₀ | N₂     | CO₂   |
|------------|-----|-------|-------|---------|---------|--------|-------|
| Content, vol.% | 93.9 | 4.44  | 1.10  | 0.087   | 0.108   | 0.33   | 0.035 |

3. Discussion
Our method provides production of the gas hydrate product in the form of pellets into two operation steps directly inside the sealed reactor vessel. Firstly (the first step): the synthesis of gas hydrate slurry, and secondly (the second one): its dehumidification and molding into a final product.

The experimental setup is shown in Figure 1.

Figure 1. Scheme of the reactor for gas hydrate synthesis: 1.1. the housing of hydraulic press, 1.2. the plunger of hydraulic press, 1.3. the lid of hydraulic press; 1.4. hydraulic port; 2.1. sealed reactor vessel, 2.2. screw pump, 2.3. electric motor, 2.4. fluid flow channel, 2.5. hydrate-former medium supply port, 2.6. hydrate-former gas supply port, 2.7. perforated sleeve with filter, 2.8. cutting knife, 2.9. receiver for removing excess liquid formed during hydrate molding, 2.10. the zone of saturated hydrate formation, 2.11. hydrate plug separating the zone of saturated hydrate formation from the hydrate storage container; 3. hydrate storage container, 3.1. molded cylindrical hydrate samples.
The experimental setup consists of three main elements:

- A sealed reactor vessel (2.1), equipped with a screw pump (2.2), a zone of saturated hydrate formation (2.10), a receiver for removing excess liquid formed during hydrate molding (2.9) and a channel for its overflow (2.4);
- A hydraulic press, consisting of a high-strength housing (1.1), a plunger (1.2) and a press lid (1.3);
- A storage container for hydrate prepared (3).

A distinctive feature of the described method and experimental setup is the production of hydrate slurry by continuous mixing of the hydrate-former medium and its aeration with a hydrate-former gas during liquid circulation inside the reactor. And also in the creation of a hydrate plug, in the process of pressing the hydrate, which separates the high-pressure zone in the reactor from the storage container with the final product under a low overpressure of the hydrate-former gas, maintained to prevent a decrease in the consumer properties of the resulting product, due to the dissociation of the gas hydrate.

The process of gas hydrate production is as follows: inside the sealed reactor vessel (2.1), in which the temperature is maintained at +5 °C, through the port (2.5) a hydrate-former medium - distilled water is supplied to a certain level. Also, surfactant solutions, saline solutions, etc. can act as a hydrate-former medium. Through port (2.6), a hydrate-former gas is fed into the reactor until a pressure of 5 or 8 MPa is reached (Figure 2 (1)).

Further, the screw pump (2.2) creates a circulation of water through the filter element (2.7), where the gas hydrate slurry formed during the interaction of natural gas with water is accumulated (Figure 2 (2)). Then, with the accumulation of the critical mass of hydrate pulp, pressure is exerted on it by moving the plunger (1.2) of the hydraulic press.

Thus, the hydrate slurry is exposed to dehumidification from excess water and compacted, thereby forming a gas hydrate plug (2.11), which separates the reactor (2.1) from the storage container (3) (Figure 2 (3)).

The operations described above are repeated until a sufficient amount of hydrate is pushed from the reactor into the storage container to form a pellet, which is cut off with a knife (2.8), thereby giving the final cylindrical shape to the product (Figure 3). Further, the molded hydrate matures in storage container at a temperature of +5 °C and an excess pressure of the hydrate-forming gas equal to 2 MPa (Figure 2 (4)).

**Figure 2.** Operation steps in the reactor for gas hydrate synthesis: (1) Scheme of circulation of the hydrate formation medium in the reactor, (2) gas hydrate formation, (3) hydrate sample molding, (4) cutting of molded gas hydrate sample by special knife.

Thus, the developed scheme implements the principle of continuity of production of ready-to-sell pellets from gas hydrates in a sealed reactor tank.
Samples of natural gas hydrate pellets obtained by molding are shown in Figure 3. The optimization of the method requires additional research, the results of which will be published further.

![Figure 3. Molded gas hydrate samples.](image)

4. Conclusion
The technical result obtained by the implementation of the described method is achieved by continuous production of hydrate samples in the reactor itself due to the constant circulation of the gas-saturated hydrate-former liquid and the capture of the hydrate slurry in a special zone for further molding / pressing by means of a hydraulic plunger built into the reactor vessel. The technological scheme for the production of hydrates can find application in the separation / purification and storage / transportation of natural gas in solid hydrated form in small and medium-sized oil and gas fields due to the simplicity and mobility of this technology. The main feature of the developed method is to simplify the technology for producing natural gas hydrates and reduce production costs through the use of a molding device in the reactor vessel.

5. References
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