Natural Gas Conversion Method into the Solid Hydrate Form Using Low Ambient Temperatures

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Abstract. The article describes a method of natural gas hydrate synthesis in a closed type reactor with the possibility of using low ambient temperatures of the Russia’s cold regions. The advantages of the hydrate synthesis method in closed reactors and the possibility of their use on an industrial scale for the gas hydrate production are noted. Special closed-type reactors with different internal volumes were developed, as well as a thermal cycling technique to accelerate hydrate formation, and a concept of hydrate production technology using natural cold-air was proposed. New experimental data on the production of massive samples of natural gas hydrates with high gas saturation (130-150 cm³/g) from ice as feed in the constructed reactors are presented. A comparison of the proposed conceptual technology operations with the existing industrial technology of natural gas hydrate synthesis was made. It is shown that in closed-type reactors, from the large ice fractions during thermal cycling of the system, it is possible to synthesize natural gas hydrates in the form of massive pieces with high natural gas content (up to 90%).

1. Introduction
The development of brand new and efficient technologies for the storage and transportation of hydrocarbon raw materials is one of the key issues of oil and gas field exploitation on the Russian Arctic coast. The solution of this problem will make it possible to start commercial development of small and remote oil and gas fields, which nowadays exploitation is unprofitable due to weak transport infrastructure [1, 2].

Today the most promising alternative, in addition to the classical method of storage and transportation of natural gas and its components, are techniques designed on the basis of gas hydrate technologies [3-5]. Such technologies are based on the ability of natural gas and its components to concentrate in the form of gas hydrates.

Natural gas hydrates are solid crystalline substances formed by natural gas and water molecules under certain temperature and pressure conditions via entrapment of gas molecules into cavities, which resemble ice-like skeleton constructions made of hydrogen-bonded water molecules [6].

In many countries, research and development of the technologies for the production, storage and transportation of natural gas hydrates are implemented by national special-purpose projects, taking into account the advantages of introducing these technologies into current oil and gas industry [4, 7].
Natural gas hydrate production methods [8] and development of up-scale technologies, storage and transportation of natural gas hydrates [9].

The most well-developed gas hydrate technologies are gathered in Japan - a country keenly interested in ensuring its energy security and independence in energy supplies [7-9]. The main element of this technology is presented by a multistage flow type reactor, in which at the initial stage the suspension of NGH is formed and further undergoes a multistage dewatering process with final formation of hydrates in the form of pellets (figure 1).

![Figure 1. Pellets of natural gas hydrates.](image)

This reactor is an integral part of the plant for the regasification of liquefied natural gas (RLNG), which cryogenic potential makes above-described production unit cooled. Thanks to this cheap source of cold and raw materials, the production of natural gas hydrates can be profitable. However, a significant disadvantage of flow type reactors is their multistage configuration, which leads to significant energy waste and the necessity in a complex chain of additional devices linked with a decrease in reliability and production safety.

Consequently, the relevance of design of the single-stage production reactor for synthesis of natural gas hydrates with sufficiently large and dense forms suitable for further transportation and storage is increasing. In addition, cold climatic conditions and the presence of permafrost are favorable factors for the implementation of natural gas transportation projects in the form of gas hydrates in the Arctic. Thus, we suggest a simplified method of natural gas hydrate synthesis from ice in a closed-type reactor under static conditions which operate with usage of low temperatures of ambient air and the permafrost zone [10]. The advantages of gas hydrate synthesis from ice are described in [11-22].

### 2. Objects and methods

Synthetic natural gas hydrates were obtained from ice and processed natural gas (the Srednevilyuiskiy gas condensate field GCF (table 1)) in the closed-type reactors. The composition of natural gas used was determined by gas adsorption chromatography on a GC-2010 Plus (Shimadzu, Japan).

| Component | CH₄ | C₂H₆ | C₃H₈ | i-C₄H₁₀ | n-C₄H₁₀ | N₂ | CO₂ |
|-----------|-----|------|------|---------|---------|----|-----|
| Content, vol.% | 92,9 | 5,25 | 1,2  | 0,1     | 0,12    | 0,38 | 0,05 |

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Table 1. Composition of used natural gas (Srednevilyuiskiy GCF).
Based on the gas composition (table 1), the equilibrium conditions for the gas hydrate formation were calculated (figure 2).

![Equilibrium conditions of hydrate formation of the Srednevilyuiskiy gas (calculated using CSMHYD software [6]).](image)

**Figure 2.** Equilibrium conditions of hydrate formation of the Srednevilyuiskiy gas (calculated using CSMHYD software [6]).

The synthesis of gas hydrates was carried out by lowering the temperature inside the reactor chamber so that throughout the entire process the P, T conditions were higher than the calculated equilibrium curve in the region of hydrate formation (figure 2).

![Steel closed-type high pressure reactors: a) with a volume of 1.1 dm$^3$; b) with a volume of 3.6 dm$^3$.](image)

**Figure 3.** Steel closed-type high pressure reactors: a) with a volume of 1.1 dm$^3$; b) with a volume of 3.6 dm$^3$.

High pressure reactors were developed by the team of the Technogenic Gas Hydrates Laboratory of the Institute of Oil and Gas Problems, SB RAS (figure 3). They consist of a cylindrical chamber and a cover-flange on which a pressure gauge and a filling valve are mounted.

First, taking into account the geometrical parameters of the reactors used, the maximum amount of ice needed to bind a given volume of natural gas in hydrate form was calculated (table 2).

| Reactor volume, dm$^3$ | $P_{load}$, MPa | $T_{load}$, K | Ice sample mass, g | $V(gas)_{load}$, cm$^3$ |
|------------------------|-----------------|---------------|-------------------|-------------------------|
| 1.1                    | 5               | 263           | 150               | >30000                  |
| 3.6                    | 8               | 263           | 1500              | >300000                 |

By freezing distilled water, hemispherical ice samples were obtained (figure 4). 10-15 of ice samples with a mass of 10 g and a diameter of 4 cm each were obtained.
The gas hydrate synthesis began with loading the calculated amount of ice into the pre-cooled reactor. After that, the reactor chamber was evacuated and filled with natural gas to a pressure of 5 or 8 MPa. The reactor filled with reagents was placed in a refrigerator and preliminarily kept at a temperature of 263 K to check its tightness. Synthesis of hydrates was carried out by cyclically varying the temperature of the refrigerator in the range from 268 to 278K for 96 hours, according to [23-25].

At the end of gas hydrate synthesis, the reactor was opened immediately in the freezer. The morphology of the obtained crystalline hydrates was recorded using Pentax K200D digital camera.

Determination of the hydrate gas saturation was carried out by measuring the volume of gas evolved during the decomposition of ~ 50 g of the hydrate sample. The method used for hydrate decomposition is described in detail in [10]. The specific gas content of the hydrates obtained (α, cm³/g) was calculated as the ratio of measured volume of the released gas to the mass of the synthetic hydrate sample [10].

3. Results and discussion

Comprehensive studies were carried out on NGH synthesis in closed-type reactors with volumes of 1.1 and 3.6 dm³ under static conditions from ice samples with diameters of 4 cm.

Due to thermal cycling [23-25] of hydrate-forming system in the temperature range from 268 to 278 K and the selection of the optimal heating / cooling rates, it was possible to convert whole ice sample into massive natural gas hydrate (figure 5) with high gas saturation (table 3).

| Reactor volume, dm³ | Ice sample mass, g | P<sub>load</sub>, MPa | Synthesis duration, hours | α, cm³/g |
|---------------------|-------------------|-------------------|-------------------------|---------|
| 1.1                 | 150               | 5                 | 96                      | 147±7.3 |
| 3.6                 | 1500              | 8                 | 96                      | 136±9.5 |
Thus, it was established that the most promising way to produce gas hydrate in closed-type reactors is to synthesize them from ice by thermal cycling with cyclically lowering and increasing temperature with passing through the freezing point of water or ice melting.

**Table 4.** Comparison of technological operations of NGH synthesis in flow and closed-type reactors.

| Flow reactor [7] | Closed-type reactor [10] |
|------------------|--------------------------|
| **1. Water / ice and gas preparation** | **1. Water / ice and gas preparation** |
| • Gas obtained from the regasification of liquefied natural gas (LNG); | • Separated gas from the gas transmission network or field; |
| • Purified industrial water | • Ice production during natural cool down. |
| **2. Formation of NGH** | **2. Formation of NGH** |
| • Continuous line for natural gas supply (bubbling); | • Single loading of ice and natural gas into the reactor; |
| • Constant stirring of the reaction mixture; | • Thermal cycling reactor; |
| • Low temperature maintenance in the reactor due to LNG regasification. | • Cooling due to natural cool down. |
| **3. Removal of excess water from 10% NGH suspension** | **3. Freezing of NGH (gas saturation 80-90%) and depressurization** |
| • Dewatering; | • Freezing due to naturally low temperatures; |
| • Creation of additional natural gas pressure difference. | • Depressurization; |
| 4. Pelletting of NGH (gas saturation 40%) | 4. Shipment of NGH |
| • Removal of residual water; | • Discharge of NGH from the reactor. |
| • Pelletting in natural gas environment; | • Shipment of NGH in storage containers or in vehicles. |
| **5. Freezing of NGH (gas saturation 75-90%)** | |
| Freezing of NGH tablets due to cold from regasification | |
| **6. Depressurization and NGH Shipment** | |
| • Depressurization; | |
| • Shipment of NGH in storage containers or in vehicles. | |

**Figure 5.** Samples of the synthesized natural gas hydrates: a) sample obtained in the reactor with a volume of 1.1 dm$^3$; b) sample obtained in a 3.6 dm$^3$ reactor.
At the same time, we propose a technological solution in the process of thermal cycling in the form of using available naturally low ambient temperatures.

Taking into account the results obtained, as well as the well-known theoretical and experimental data, and knowledge of the conditions and features of the NGH formation/dissociation and the natural climatic features of the northern Russia, a flow chart of NGH production was proposed [10].

The proposed method of gas hydrate production from ice can be used for development of gas hydrates from foreign analogues in its energy efficiency. The obtained experimental data can be used to determine the effectiveness of NGH production, which uses the natural cold of the Russian Arctic regions, may differ favorably on foreign analogues in its energy efficiency. The obtained experimental data can be used to simulate of NGH synthesis technology.

4. Conclusions

It was found that in closed reactors from relatively large fractions of ice (5 ÷ 40 mm) during thermal cycling of the system, it is possible to synthesize natural gas hydrates in the form of dense solid agglomerates with a high content of natural gas (up to 90%). Consequently, the proposed technology of NGH production, which uses the natural cold of the Russian Arctic regions, may differ favorably from foreign analogues in its energy efficiency. The obtained experimental data can be used to simulate of NGH synthesis technology.

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