Experimental study of the influence of the water level in the working volume on the gas hydrates formation the method of explosive boiling during decompression

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Abstract. Experiments on obtaining Freon 134a gas hydrate were carried out by a method based on explosive boiling of a liquefied gas layer in the water volume during decompression. It is shown that this method combines several factors leading to an intensification of the hydrate formation process, which leads to a rapid growth of gas hydrates. The influence of the ratio of the initial mass of the gas to the initial mass of water in the vessel on the fraction of the gas hydrate in the resulting sample was studied experimentally.

Introduction

Technological proposals for the storage and transportation of natural gas in the hydrated state appeared as early as in the beginning of the 20th century. This method has attracted the attention of experts for a long time because of the ability of gas hydrates to concentrate large volumes of gas at relatively low pressures. A promising way of transporting gas without a pipeline is converting it into a gas hydrate (solid) state and transporting at atmospheric pressure and low temperature (-10 ... -20 °C) [1]. The properties of gas hydrates, the main conditions and the features of their formation are described in [2-4] and some other works; the types of their crystallization, the mechanisms of formation and decomposition of gas hydrates are presented in [5-11].

A method for obtaining gas hydrates was proposed, which is based on the explosive boiling up of a liquefied gas-hydrate generation in the volume of water during decompression. This method is characterized by a large volume of the resulting gas hydrate in a short period of time. This is achieved by the fact that the heat released during the formation of the gas hydrate is absorbed by the intense boiling of the liquefied hydrate-forming gas, and the bubbles themselves constantly collide and deform, which leads to peeling off the hydrate shells from their surface, thereby constantly ensuring the contact of the hydrate-forming gas and water [12]. The research team continues searching for effective ways to intensify the formation of hydrates with the help of mechanical and thermal effects of gas-liquid media [13-16].
1. Experimental setup

The studies were carried out on a laboratory setup consisting of a high-pressure reactor up to 25 MPa. The reactor is made of stainless steel (diameter 100 mm, height 300 mm) with a water jacket for thermostating (Fig. 1).

![Figure 1. Schematic diagram of experimental setup: 1 – vessel; 2 – water jacket; 3 – lid; 4 – mixer; 5 – viewing windows; 6 – bottom tube; 7 – bottom valve; 8 – drive for working section lowering/lifting; 9 – mixer drive; 10 – cryostat.]

2. Method and results

The experiment was carried as follows. A different volume of water was supplied to the reactor: 100, 200, 400 and 600 ml (corresponding to a water level of 12, 23, 46, 68 mm). The water was cooled by a cryostat through the outer walls. Further, 200 g of Freon 134a entered the reactor, which was cooled and condensed, forming a layer below the surface of the water at the bottom of the vessel. After the temperature 2°C and pressure 0.42 MPa were established at the working site, decompression was performed at a rate of 70 l/min until the pressure was compared with the atmospheric pressure. Due to the strong decompression, the liquefied gas began to boil explosively, saturating the water layer with the bubbles of the hydrate-forming gas. Rising upwards in the volume of water, the bubbles fell into the area of hydrate formation and the hydrate film began to form on their surface. Due to the active mixing of the working volume as a result of boiling, constant bubble collisions occurred. This led to deformation and flaking of the film of the formed hydrate, as a result of which the contact of hydrate-forming gas-water was constantly maintained. The heat released during the formation of the
hydrate was compensated by the absorption of heat during boiling. Due to the superimposition of these factors, a rapid increase in the resulting gas hydrate occurred in a very short period of time.

After completion of the boiling process, the working section was filled with a mixture of the resulting gas hydrate, water and ice. To estimate the fraction of hydrate in this mixture, a method was used in which the resulting sample was heated and decomposed with evolution of gas. The gas released during the decomposition of the hydrate creates a pressure in the working volume, along which it is possible to estimate the mass of this released gas, and through it determine the mass of the resulting hydrate. Mass is further needed to determine the proportion of hydrate in the resulting sample \(K,\%\). Experimental studies have shown that with a decrease in the initial mass of water relative to the initial mass of the hydrate-forming gas \(m_g / m_w\) the proportion of gas hydrate in the hydrate mass increases. So with a mass of water 600 g and a modeling gas mass of 200 g the proportion of hydrate was 7.3\%, whereas with a water mass of 100 g the maximum hydrate content in the hydrated mixture was reached, namely 79.2\%.

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K, \%
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*Figure 2.* The influence of the ratio of the initial mass of the gas-hydrate-forming agent \(m_g\) to the initial mass of water \(m_w\) on the fraction of the gas hydrate in the resulting sample \(K\).

**Conclusion**

In this paper, an assessment was the influence of the ratio of the initial mass of the gas to the initial mass of water in the working volume fraction of the gas hydrate in the resulting sample in a method based on the explosive boiling of liquefied hydrate-forming gas in the volume of water due to decompression. It was shown that the maximum hydrate content in the resulting sample was obtained at an initial mass of water of 100 g and was 79.2\%.

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