Decomposition of methane hydrate on a solid substrate (glass) and water surface

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Abstract. Studies on the decomposition of gas hydrate on a solid base (glass) and water surface were carried out at the Kutateladze Institute of Thermophysics. The purpose of these studies was to determine the rate of dissociation of gas hydrate. The data obtained can help with the introduction of gas hydrate as boiler fuel.

1. Introduction
Under natural conditions, the existence of methane gas hydrate requires certain thermobaric conditions, namely high pressure, ambient temperature close to 273 K, the presence of free water and free or dissolved gas in contact with it. In most natural accumulations of natural gas hydrates, the hydrate-forming gas is 98 ... 99% methane, the rest is a mixture of ethane, propane, butane, hydrogen sulfide, nitrogen, carbon dioxide and other gases in various ratios. According to recent estimates, methane reserves in the hydrated state are estimated at 2 · 1016 m3, which significantly exceeds all currently known gas, oil and coal reserves combined. This fact poses the problem of studying gas hydrates and methods of their extraction at one of the priority places. Accumulations of gas hydrates in natural conditions are in a relatively stable state, but they can decompose rapidly or mechanically or thermally, with the release of large volumes of gas [1-5].

A variety of inclusions of gas hydrates are found in the earth's crust, from tens of centimeters for monolithic layers to small lenses, as well as small inclusions in the form of “hydrated cement” existing at temperatures above 0 °C. The city of Norilsk has for many years been supplied with natural gas produced from gas hydrate at the Masonic gas field. This field is located in permafrost and is the only field in the world where ordinary natural gas is extracted from gas hydrate [6-8]. Economic studies have shown that transporting natural gas in a hydrated state can be the most cost-effective way of transporting natural gas by sea. The transportation of natural gas in the form of a hydrate can bring an additional economic effect, since the decomposition of the hydrate produces not only gas, but also fresh water. This fresh water can be sold along with gas. The use of gas hydrate as a boiler fuel has significant advantages over many fossil fuels. The decomposition products of gas hydrate are natural gas and pure water. When gas hydrate is burned, no ash or ash remains. In recent years, a fairly large number of new methods for the synthesis of gas hydrates have been developed in the world. [11-14].

2. Experimental setup and methods
Fig. 1 shows a schematic diagram of a laboratory setup designed to monitor the dynamics of the redecomposition of methane hydrate artificially produced in a laboratory environment, which is a granular powder. Decomposition was carried out on a solid and liquid surface with an initial temperature of + 20 °C. The mass of hydrated powder used in the experiments ranged from 1.2 to 4 g.
Using the X-ray method, the relative mass concentration of methane hydrate in the hydrate mass was determined, which was about 50%. The change in the mass of methane hydrate during the experiment was measured using an Ohaus Explorer analytical balance with an accuracy of 0.01 g. The value of the measured values were recorded in real time on a stationary computer connected to the balance [9-10].

In preparation for the experiments, experiments were conducted on the evaporation of distilled water at various temperatures. These experiments made it possible to take into account the background values of the rate of water evaporation during the main experiments. During research, thermal imaging was carried out with a NEC TH 7100 thermal imager. The thermal imager is equipped with an uncooled matrix[15-17]. Thermal imaging made it possible to see the temperature field of the surface of the gas hydrate during research. During the experiment, the weight method of the empty, dry installation was taken into account in advance by the weight method. This is necessary for the correct calculation of the change in the weight of the hydrated mass during the experiment.

During the experimental studies, a certain sequence of actions was followed.

- The temperature indicators of the entire installation and the environment were brought to the required value (20 °C).
- The measured values of the mass of methane hydrate were recorded in an automatic mode.
- The surface temperature on which the decomposition of methane hydrate was carried out was measured using a thermocouple.
- The required amount of methane hydrate was extracted from the tank with liquid nitrogen. Methane hydrate was kept outdoors for some time. This was done to remove residual liquid nitrogen that could remain inside the sample.
- A sample of methane hydrate was placed on the bottom of the glass cup, and its initial temperature t0 was recorded using a thermocouple. At the same time, the balance fixed the initial mass m0.
- As the methane hydrate sample decomposes, its current temperature t and mass m are determined.
- The experiment on the decomposition of a sample of methane hydrate was considered completed when the rate of decomposition of the hydrate became equal to the rate of background evaporation of water at the same temperature.
Figure 2. Change in the relative mass of methane hydrate samples under adiabatic decomposition conditions on a solid surface (glass) with an initial temperature $t_0 = +20^\circ\text{C}$. ◊ – Background change in mass upon evaporation of water. Δ – Change in the relative mass of a sample of methane hydrate in the form of a cylinder. □ – Changes the relative mass of the free-form methane hydrate sample. x – Change in the relative mass of a sample of methane hydrate in the form of a powder with particle sizes from 0.1 mm to 1.5 mm.

The decomposition of methane hydrate samples on the surface of distilled water was carried out according to the same scenario. The initial water temperature was $t_0 = 20^\circ\text{C}$. A sample of methane hydrate was placed on the surface of the distilled water layer; the thickness of the distilled water layer did not exceed 4 mm; the total volume of water was -16 cm$^3$.

Figure 3. Change in the relative mass of methane hydrate samples under adiabatic decomposition conditions on the surface of distilled water with an initial temperature $t_0 = +20^\circ\text{C}$. ◊ – Background change in mass upon evaporation of water. Δ – Change in the relative mass of a sample of methane hydrate in the form of a cylinder. □ – Changes the relative mass of the free-form methane hydrate sample. x – Change in the relative mass of a sample of methane hydrate in the form of a powder with particle sizes from 0.1 mm to 1.5 mm.

In the course of the research, a thermal imaging survey of the decomposition of gas hydrate was carried out, which made it possible to see the thermal fields.
Figure 4. Thermograms of the decomposition of a methane hydrate sample on the surface of the water at an initial temperature of $t_0 = 20 \, ^\circ\text{C}$.

Conclusions
Studies have shown that gas hydrates can in some cases successfully compete with or complement traditional boiler fuels. The obtained dependencies will help in the use of gas hydrates as boiler fuel.

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