Experimental study of the dissociation of a double gas hydrate with a change in the initial height of the layer

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Abstract. In this work, experimental studies of the dissociation of methane-ethane hydrate with and without combustion are carried out with a change in the initial height of the layer. Gas hydrate powder with an initial height of 3 and 15 mm was used. In the samples, the initial concentration of methane is 64% and ethane is 36%. An increase in the initial height of the powder layer led to a 1.3-fold increase in the flame front velocity. Due to the increase in the initial height of the layer, the dissociation rate decreases by 7.2 times before combustion and by 4.1 times during combustion.

1. Introduction
An increase in the world's population leads to an increase in energy consumption. In addition, due to climate change on the planet, the demand for environmentally friendly energy is increasing [1]. Due to the low emission of harmful gases during combustion, the use of methane gas hydrate is considered as the best option to replace fossil fuels [2]. Particular attention in the world is paid to the development of technologies for the extraction of natural methane hydrate, transportation, storage, combustion and manufacturing of artificial gas hydrates. The study of various factors affecting the synthesis of artificial gas hydrates was considered in [3-5]. Mathematical modeling of natural gas production from gas hydrate deposits is presented in [6-7]. The efficiency of gas hydrate combustion technology depends on the powder dissociation rate. The dissociation rate of gas hydrates is affected by external pressure, temperature, structure and size of granules, and powder porosity [8-9]. Methane gas hydrates have a cubic structure (sI), the unit cell formula is 2D·6T·46H₂O [8, 10]. At a temperature of 230–268 K, an ice shell forms on the surface of gas hydrate granules, which leads to an anomalous low dissociation rate (self-preservation phenomenon) [11-12]. The growth rate and strength of the shell depends on the surface structures. Structures in the form of dendrites can form both on the surface of gas hydrates and during the crystallization of salt solutions [13-17]. During the combustion of gas hydrates, an inhomogeneous porosity is formed inside the layer, which leads to an uneven release of gas from the surface of the powder and unstable combustion [9]. Different dissociation rates lead to a change in the concentrations of fuel and oxidizer in the combustion region. An excess of fuel can lead both to a decrease in the combustion temperature of the gas hydrate and to an increase in the combustion rate and flame height [18]. For a mixture of gas hydrate and quartz sand, the duration of combustion is shorter in time than for pure hydrate [19]. The effect of heat transfer on the rate of dissociation of methane hydrate during combustion was considered in [20-21]. When modeling dissociation and evaporation, it is necessary to take into account external air convection [22-25].
Features of the combustion of methane hydrate with a change in the air flow rate are considered in [22]. The motion of the flame leading edge over the surface of methane hydrate was studied in [26]. During the dissociation of the powder during combustion, a thin film of water and droplets is formed on the surface of the gas hydrate. The resulting water vapor during evaporation reduces the temperature of the flame. Droplet evaporation was studied in [27-29]. A decrease in the vapor concentration in the combustion zone can be achieved by removing water from the surface of the gas hydrate [30]. Non-contact temperature measurements during ignition are shown in [31].

The purpose of this experimental work is to study the combustion of mixed methane-ethane hydrate at different layer heights.

2. Materials and methods

Samples of gas hydrates were synthesized in the high pressure chamber. A detailed description of the synthesis is shown in [9]. The resulting samples of gas hydrates were sifted through a sieve in liquid nitrogen to obtain an average powder particle size of 0.3–0.45 mm. Using chromatographic analysis, the ratio of the concentration of methane to ethane was determined as 64% to 36%. Mass concentration of gas in the powder is 11%. Methane-ethane hydrate has a cubic structure (sII), unit cell formula 16D1·8H·136H2O [8, 10]. The resulting powder of gas hydrates was stored in the Dewar vessel (SDS-6M, volume 6 l) with liquid nitrogen.

The scheme of the experimental setup for studying the dissociation of methane-ethane hydrate during combustion is shown in figure 1. The resulting gas hydrate powder was removed from the Dewar vessel and placed in a metal tank with thin stainless steel walls (wall thickness 0.4 mm). Tank size: length 50 mm, width 40 mm, height corresponded to \( H_1 = 3 \) mm and \( H_2 = 15 \) mm. The heat insulator (TZMK-10, fibrous material based on amorphous quartz fiber) with a thermal conductivity coefficient of 0.05 W/(mK) and a porosity of 90–95% was placed on the side walls and bottom of the tank. The walls thickness of the heat insulator is 15 mm.

The tank with gas hydrate was placed on the electronic balance (ViBRA AJ-6200CE, with a resolution of 0.01 g). The digital scales recorded the change in the mass of the gas hydrate sample over time (gas hydrate dissociation). The average surface temperature of the powder \( T_S \) was measured using the thermal imager (NEC R500, measurement accuracy ±1°C). Ignition was carried out using a pilot burner. The combustion process was recorded with the high-speed video camera (Phantom-v4, Vision

![Figure 1. Scheme for studying the dissociation of methane-ethane hydrate during combustion (a); Thermal imaging measurements before combustion for heights \( H_1 = 3 \) mm and \( H_2 = 15 \) mm (b).](image-url)
Research). All experiments were carried out at atmospheric pressure, air temperature 20 °C, humidity 38%.

3. Results and Discussion
High-speed photographs of the flame front movement at different heights are shown in figure 2. In the process of dissociation, methane and ethane are released from the powder, which fell into the region of mixing with the oxidizing agent (oxygen in the air). When $T_s = -40 °C$ was reached, ignition was performed. The flame front moved from the right edge of the working area to the left. The results of processing high-speed photographs are shown in figure 3.

![Figure 2](image1.png)

**Figure 2.** Frames of the flame front movement on the surface of the methane-ethane hydrate powder over time: (a) $H_1 = 3$ mm, (b) $H_2 = 15$ mm.

![Figure 3](image2.png)

**Figure 3.** Movement of the flame front ($L$) on the powder surface over time: 1 – $H_1 = 3$ mm, 2 – $H_2 = 15$ mm.

Curves for heights of 3 and 15 mm are quasi-linear. Let us determine the front velocity $U = \Delta L/\Delta t$. Flame front velocity $U_1 = 0.89$ m/s (for $H_1 = 3$ mm) and $U_2 = 1.19$ m/s (for $H_2 = 15$ mm). For a height
$H_2 = 15 \text{ mm}$, the velocity of the flame front is 1.3 times higher than for $H_1 = 3 \text{ mm} \ (U_2/U_1 = 1.3)$. This ratio in the velocity of the flame front can be associated with the temperature over the volume and the temperature inhomogeneity over the surface of the gas hydrate powder before combustion. The dissociation rate of the powder will depend on the temperatures, which will lead to a change in the concentration of the fuel (gas) and oxidizer (oxygen) in the mixing region before the start of combustion.

The change in powder mass over time is shown in figure 4. With an increase in the height of the powder layer, the duration of complete dissociation increases due to the slower heating of the layer. For two different heights, there are characteristic areas of mass change: I - no combustion, II - there is combustion.

![Figure 4. Change in powder mass ($m$) over time during the dissociation of methane-ethane hydrate (region I - no combustion, II - combustion, dotted lines separate these regions): 1 - $H_1 = 3 \text{ mm}$, 2 - $H_2 = 15 \text{ mm}$..](image)

After the start of combustion, the slope of the curves increases (region II, figure 4) due to an increase in the convective heat flux from the combustion zone to the powder surface. The curves for different heights for regions I and II are quasi-linear. Dissociation rate $j = \Delta m/(m_0 \Delta t)$ (1/s). Dividing by the initial mass $m_0$ eliminates the influence of different masses for different heights of the powder layer. The results for the dissociation rate are shown in table 1.

| Layer height $H$, mm | $j \cdot 10^5$, 1/s (without combustion) | $j \cdot 10^5$, 1/s (with combustion) |
|----------------------|----------------------------------------|--------------------------------------|
| 3                    | 55.7                                   | 281.9                                |
| 15                   | 7.7                                    | 68.9                                 |

As can be seen from table 1, with an increase in the layer height, the dissociation rate before combustion drops by 7.2 times, and during combustion by 4.1 times.

**4. Conclusion**

The dissociation with and without combustion of methane-ethane hydrate at different initial layer heights was studied experimentally.

The velocity of the flame front above the powder surface increased by a factor of 1.3 when the height changed from 3 to 15 mm. An increase in the flame front velocity can be associated with the temperature over the volume of the powder and the temperature inhomogeneity of the hydrate surface before combustion.

Using the gravimetric method, data were obtained on the change in the dissociation rate. An increase in the layer height led to a decrease in the dissociation rate before combustion by 7.2 times, and during combustion by 4.1 times.

The experimental data obtained can be applicable for gas hydrate combustion technologies.
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