Experimental study of the combustion of artificial methane hydrate at different rates of external gas flow

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Abstract. The dissociation behavior of methane hydrate was experimentally investigated in the presence of a laminar air flow in a channel of constant height. The dissociation rate \( J \) increases with increasing air velocity \( U_a \) in the range of velocity values 0.5–0.7 m/s and decreases with increasing velocity. When simulating the combustion of methane hydrate, it is necessary to take into account the strong temperature irregularities on the surface of the powder layer. The area of maximum temperature and maximum rate of dissociation is located near the side walls of the tank.

1. Introduction

To date, open reserves of methane hydrate are many times greater than the reserves of methane mined by conventional methods. Much attention is paid to the phenomenon of self-preservation (abnormally low dissociation rates). Features of transportation and storage of the methane hydrate granules in the presence of self-preservation are considered in [1]. Dissociation of the double hydrate (methane-isopropanol) was considered in [2]. The dissociation rate of methane hydrate increases tenfold with a high heat flux and is quasi-constant with time [3, 4]. High rates of formation of gas hydrates are realized on the surface of gas bubbles [5-7]. The diameter of the granules [8, 9] and porosity [10] affect the rate of dissociation of methane hydrate. High heat fluxes lead to high hydrate growth rates and the high evaporation rate [11-15]. In this case, it is necessary to take into account the heat transfer coefficient not only for the hydrate, but also for the gaseous medium [16, 17]. When methane hydrate burns, steam is formed with water droplets. When describing the combustion of gas hydrates, it is necessary to simulate the evaporation of droplets, which was studied in [16-21]. With the close arrangement of water droplets in oil, spontaneous crystallization of gas hydrates occurs, which leads to gas-hydrate plugs and to the destruction of wells in the production of natural gas and oil [22]. Comparison of several options for the organization of combustion of methane hydrate is presented in [23-25].

Investigations of gas hydrates of natural gas concern four main areas: 1) improving the efficiency of natural gas production by drilling wells; 2) reducing the cost of transportation and storage of the extracted raw materials; 3) reducing the cost of production of artificial methane hydrate; 4) optimization of the conditions of combustion of methane hydrate. Experimental studies of this article concern the 4th area: increasing the efficiency of methane hydrate combustion.

The purpose of the research is to determine the experimental dependence of the dissociation rate of methane hydrate on the rate of external air flow. In existing studies, emphasis was placed on the study of the rate of movement of the flame edge. In the literature, there are very few data on the rate of gas
hydrate dissociation \( j = \frac{\Delta m}{\Delta t} \) (change in sample mass over time during dissociation). In this case, temperature measurement is carried out only at several points inside the layer. For correct modeling, however, data on temperature change for the entire powder surface are required.

2. Experimental data
A detailed description of the experimental setup is presented in [25]. During the experiment, the temperature of methane hydrate powder increased from the temperature of liquid nitrogen to 0 °C. The powder was heated from the environment. The external air-flow temperature was equal to room temperature (20 °C). Heating was realized from air through the upper surface of the powder and through the walls of the tank. The walls of the tank were made of 0.5 mm thick steel. The length \( L \) of the tank from the side of the external air-flow is 50 mm, width 50 mm, depth 15 mm. Around the tank is a heat-insulating material (thermal conductivity \( \lambda = 0.05 \text{ W} / (\text{m} \cdot \text{K}) \)), the wall thickness is 20 mm. The temperature of the upper powder surface was measured by the thermal imager (NEC-San Instruments). Hydrate dissociation occurs when there is an imbalance. The initial mass concentration of methane in the hydrate was 9-10%. The dissociation rate is measured using the gravimetric method. Combustion occurs in the channel with the continuous movement of air (laminar flow).

\[ U_a \]

Figure 1. Dynamic (1) and diffusion (2) boundary layer.

Three laminar boundary layers arise over the powder surface: dynamic, diffusion and thermal. Figure 1 shows a dynamic boundary layer for air velocity (1) and a diffusion boundary layer (2) for a gas mixture: air-methane-water vapor. Methane and water vapor flows form upon dissociation of methane hydrate during combustion. The velocity \( U_a \) corresponds to the upper boundary of the dynamic boundary layer.

\[ \text{Figure 2. Change in the dissociation rate of methane hydrate during combustion and with a change in } U_a: \ 1 - 0 \text{ m/s}; \ 2 - 0.1 \text{ m/s}; \ 3 - 0.4 \text{ m/s}; \ 4 - 2.5 \text{ m/s}; \ 5 - 0.7 \text{ m/s} \]

(channel height \( H = 40 \text{ mm}, \) thickness of the powder layer is 15 mm).
Figure 2 shows the experimental data on the change in the dissociation rate \( J = \frac{\Delta m}{F \Delta t} \), where \( F \) is the area of the powder layer) at different air flow rates \( U_a \) and at a constant height of the air channel \( H = 40 \text{ mm} \). The origin \( (t = 0 \text{ s}) \) corresponds to the onset of combustion of methane hydrate. Combustion of the methane hydrate begins when the minimum limit concentration of methane with an oxidizing agent - oxygen in the air in the combustion area is reached. With increasing velocity, \( J \) first increases, reaches a maximum, and then decreases. There are two modes for the dissociation of the methane hydrate: 1) growth of \( J \) with increasing \( U_a \); 2) \( J \) drop after reaching \( J_{\text{max}} \). The dissociation rate of the methane hydrate depends on diffusion, heat transfer, and internal kinetics of the reaction. The heat flux from air to the powder increases with increasing velocity \( U_a \), since the Nusselt number \( (Nu) \) and the heat transfer coefficient \( (\alpha) \) are proportional to \( U_a \) \[26\] (for laminar flow \( Nu \sim Re^{0.5} Pr^{0.33} \), where \( Nu = \frac{\alpha l}{\lambda} \), Reynolds number \( Re = \frac{U_al}{\nu} \), Prandtl number \( Pr = \frac{\nu}{a} \)), where \( \nu \) is kinematic viscosity of gas, \( \lambda \) is thermal conductivity of gas, \( a \) is thermal diffusivity of gas). The dissociation rate \( J \) increases with increasing heat flux \( q \) \[3, 8\] \( (q = \alpha(T_0 - T_s) \), \( T_0 \) is air temperature, \( T_s \) is powder temperature that increases with time), \( J \sim q \), then \( J \sim (U_a)^n \). The extremum (maximum) of the dissociation rate is realized in the range \( U_a = 0.5-0.7 \text{ m/s} \). Further growth of \( U_a \) leads to the fact that the velocity profile strongly leans towards the wall. As a result, the stoichiometric ratio in the combustion region (the region of maximum combustion temperature) is strongly disturbed due to a substantial excess of oxidant. Strong violation the stoichiometric ratio and lowering the combustion temperature leads to a decrease in the dissociation rate. Thus, when modeling dissociation, several factors must be taken into account simultaneously: the heat flux from the external environment, the shape of the diffusion, thermal, and dynamic boundary layer, as well as the deviation from the stoichiometric ratio.

![Figure 3](image_url)

**Figure 3.** Change in the surface temperature (thermal measurement) of the methane hydrate before combustion (powder layer thickness of 15 mm).

Since dissociation depends on the degree of hydrate deviation from equilibrium, it is important to correctly model the temperature distribution over the entire surface of the powder layer. Figure 3 shows the temperature distribution of the powder on the surface of the layer before the start of combustion (thermal measurements). Measurements have shown that the temperature field both inside the powder and on its surface is extremely uneven, which lowers the burning efficiency and decreases the dissociation rate. The highest temperature of methane hydrate is near the side walls. Despite the fact that the insulation thickness is 20 mm, there is a significant heat flux on the walls. The highest dissociation rate will also be near the walls. An uneven thermal field is probably associated with highly uneven dissociation inside the layer. Earlier, when calculating the kinetics of combustion of methane hydrate, the temperature field was taken to be uniform. In fact, a strong temperature irregularity will lead to a change in the kinetics of combustion.

**Conclusions**

The dissociation rate \( J \) depends non-linearly on the air flow rate in the channel. \( J \) increases with increasing \( U_a \) from zero to 0.5-0.7 m/s and then decreases. When \( U_a \) is more than 2.5-3 m/s, combustion ceases due to a strong excess of oxidant over the fuel. The temperature in the area of
combustion becomes below the critical threshold, which is necessary to maintain combustion. When modeling the combustion of methane hydrate, it is necessary to take into account the strong temperature irregularity on the surface of the powder layer.

Acknowledgement
The measurements were carried out at the Kutateladze Institute of Thermophysics SB RAS and supported by the Russian Science Foundation (project number 15-19-10025).

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