Experimental study of dissociation of double gas hydrate at various combustion methods

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Abstract. The dissociation during combustion of a propane-methane gas hydrate double powder is experimentally investigated. Gas hydrate combustion is implemented in four ways: 1) induction heating; 2) radiation and convective heating in a muffle furnace; 3) combustion without forced gas flow; and 4) combustion in the presence of forced air convection \( u_a \). The maximum \( J \) is achieved by burning granules of gas hydrate powder on a metal surface with induction heating, where \( J \) is the specific dissociation rate. The minimum of \( J \) corresponds to the combustion of a layer of gas hydrate powder in the absence of forced air flow. With an increase in the velocity air convection \( u_a \) from 0 to 1.2 m/s the \( J \) increases and reaches a maximum. A further increase in \( u_a \) leads to a decrease in \( J \). For \( u_a > 3.5 \) m/s combustion does not occur.

1. Introduction

Currently, the open reserves of methane gas hydrates significantly exceed the reserves of gas fields associated with conventional mining methods [1, 2]. The successful development of technologies for the extraction of natural methane hydrate, the production of artificial gas hydrate, storage and combustion technology is associated with the creation of models that should take into account the kinetics of growth and dissociation. An increase in the diameter of gas hydrate particles leads to a decrease in the dissociation rate [3]. Using a monolithic sample is more cost-effective than providing an increase in diameter by pressing small granules [4]. The temperature, external pressure, and porosity of the sample affect the dissociation rate of gas hydrates [3-6]. The strength of the ice shell on the surface of hydrated granules depends on dendritic structures which are also observed on the surface of aqueous hydrates of salts [7-12]. The data on the kinetics of dissociation of mixed gas hydrates are given in [13]. During the combustion of methane hydrate high heat fluxes and high dissociation rates are realized [14]. Different dissociation rates result in different reaction rates due to changes in the concentration of fuel and oxidizer. The unevenness of the temperature field on the surface and inside the layer of gas hydrate powder, as well as a change in the rate of the incoming external air flow, affect the nature of combustion [15-17]. The flame propagation rate in the laminar boundary layer is studied in [18]. The vapor concentration released during the combustion of a gas hydrate reduces the temperature in the combustion region by 200-250 K [19]. In this case, it is necessary to take into account the heat transfer coefficient for a gaseous medium [20-22]. Combustion of different diameters of the spheres of methane hydrate obtained by pressing from small particles is considered in [23, 24]. The formation of an aqueous film on the surface of the sphere of methane hydrate during combustion promotes the appearance of gas bubbles.
which leads to flame instability [24]. When burning gas hydrates, it is necessary to take into account the evaporation rate of water [25-28].

This experimental work relates to increasing the combustion efficiency of a double gas hydrate. The main objectives of this study are to compare the dissociation of a double hydrate (propane-methane) with various combustion methods: 1) induction heating; 2) radiation and convective heating in a muffle furnace; 3) combustion without forced gas flow; 4) combustion in the presence of free and forced convection of air. Currently, the data on the comparison of the combustion efficiency of double gas hydrates for different methods is very scarce.

2. Experimental data
A sample of methane-propane double gas hydrate powder was produced in a high pressure reactor [4]. The created sample was crushed and sieved using sieves. Using chromatographic data, the ratio of the volume concentration of propane to the volume concentration of methane was determined as 60% to 40%. The initial mass concentration of gas hydrate $C = 11\%$. The unit cell of the resulting double hydrate had the structure $\text{siI}$. The formula of the elementary cell was $16\text{D} \cdot 8\text{H} \cdot 136\text{H}_2\text{O}$ or $16(\text{SiD}) + 8(\text{SiD}^6)$. Double gas hydrate samples were stored in liquid nitrogen. Fig. 1 (a) shows a scheme of an experimental setup for the combustion of a propane-methane double gas hydrate in a muffle furnace. Before each experiment, the sample of gas hydrate 1 was weighed on the electronic balance (Vibra AJH 4200 CE) and then placed in a reservoir (cone-shaped metal mesh with small cells, cone height of 6.5 mm, and base radius of 6.5 mm). During the combustion of gas hydrate, water was removed through the mesh. The initial mass of gas hydrate was $m_0 = 0.15$ g. The final mass $m$ of the powder after cessation of combustion was about 5–8% of $m_0$ (defined as the product of the remaining volume of powder and its bulk density). The dissociation rate $j$ during propane-methane hydrate combustion was determined as $j = \Delta m / \Delta t \approx 0.11 m_0 / \Delta t$, with $\Delta t$ being the time corresponding to the duration of combustion). Using an automatic coordinate device 3, the sample was delivered to the center of the muffle furnace 2. The temperature in the muffle furnace was 780 °C. The temperature gradient in the center of the furnace at a distance of several centimeters was about 5 °C. The process of the beginning and end of combustion of gas hydrate was recorded through the inspection window of the muffle using a video camera 4 (Phantom v4). Ambient temperature was 23 °C, and pressure was 1 atm.

Fig. 1 (b) shows a diagram of conductive heating of the gas hydrate. Granules of gas hydrate powder with a diameter of 0.7 - 1 mm making up one layer of powder were placed on a heated cylindrical horizontal steel metal surface 1 with a diameter of 20 mm and a height of 30 mm in length. The surface was heated using an induction heater 2. The surface temperature before placing the powder was measured using a pyrometer 3. The surface temperature of the metal cylinder was 780 °C. The dissociation rate was determined as $j = \Delta m / \Delta t = 0.11 \Delta V \rho N / \Delta t$ ($\Delta V$ – difference between the initial and final powder volume, $\rho$ – density of powder, and $N$ – number of powder granules located on a heated surface).

The experimental setup for studying the dissociation of gas hydrate by the gravimetric method is shown in Fig. 1 (c). A sample of gas hydrate is placed in the working section 1 (length of 50 mm, width of 38, and height of 20 mm). The walls of the working section 2 are made of heat-insulating material TZMK-10 with a thickness of 20 mm. The powder is heated due to ambient air (the temperature of the powder varies from the temperature of liquid nitrogen to the temperature of the onset of combustion). The surface temperature of the sample is measured using a thermal imager 3 (NEC R500EX-Pro). When the surface temperature of the powder exceeds the equilibrium temperature ($T_s > -40 ^\circ\text{C}$), ignition is carried out using a pilot burner. The decrease in the mass of the sample upon dissociation of the gas hydrate is measured by weights 4. The dissociation rate $j$ of the double gas hydrate is determined experimentally as $j = \Delta m / \Delta t$ (where $m$ is the mass of the sample, and $t$ is the time of dissociation). The measurement error $j$ does not exceed 10%. When burning above the surface of the working section with the sample dynamic, thermal and diffusion boundary layers are realized.
Figure 1. (a) Combustion of propane-methane double gas hydrate in a muffle furnace: 1 – tank with gas hydrate, 2 – muffle furnace, 3 – coordinate device, 4 – video camera, 5 – PC; (b) Scheme of the experimental setup for conductive heating: 1 – working surface, 2 – induction heater, 3 – pyrometer, 4 – video camera (Phantom v4); (c) The experimental setup for the combustion of methane-propane hydrate in a forced air flow $u_a$ with a constant rate: 1 – working section, 2 – thermal insulation, 3 – thermal imager, 4 – electronic scales, 5 – PC, 6 – video camera.

Figure 2 shows photographs of the flame during double gas hydrate combustion in the presence of free and forced air convection $u_a$. At the entrance to the test section, there is a standard laminar boundary layer with about 1 mm thickness. At the outlet, in the area of gas mixing, the boundary layer thickness is more than 7 mm. The air flow rate is measured using a WindLiner ATS-40 anemometer. When $u_a$ becomes higher than 1.8 m/s (Fig. 2 (b)), the flame inclines toward the wall and part of the combustion region is realized outside the surface of the powder.

![Figure 2](image-url)

Figure 2. Flame shape: a) $u_a = 0$ m/s; b) $u_a = 2.7$ m/s.

Table 1 shows experimental data on the comparison of specific dissociation rate $J$ of gas hydrates for various combustion methods ($J = j/F$, where $F$ is the surface area of the powder)). For induction
heating this is the surface area of all granules. For combustion in a muffle furnace the surface area of the cone is taken. For variants with combustion without \( u_a \) and in the presence of \( u_a \) the area does not change in time (rectangle surface area). As seen from the table the maximum rate of dissociation is achieved by combustion of the particles on the metal surface by induction heating. The minimum dissociation rate corresponds to combustion of a thick layer of powder in the absence of \( u_a \).

Table 1. Comparisons of the dissociation rate of gas hydrates with various combustion methods.

|                  | Induction heating | Muffle furnace | Rectangular work area \((u_a=0 \text{ m/s})\) | Rectangular work area \((u_a=1.2 \text{ m/s})\) |
|------------------|-------------------|----------------|---------------------------------------------|---------------------------------------------|
| \( F \cdot 10^4 \), m\(^2\) | 160               | 254            | 1900                                       | 1900                                       |
| \( j \cdot 10^6 \), kg/s   | 4.80              | 3.3            | 3.42                                       | 5.89                                       |
| \( J \), kg/(s·m\(^2\))  | 0.030             | 0.013          | 0.0018                                     | 0.0031                                     |

Figure 3 shows experimental data on the effect of the rate of \( u_a \) on the \( J \) (kg/(s·m\(^2\))) during gas hydrate combustion on rectangular work area.

![Figure 3](image-url)

Figure 3. The dissociation rate \( J \) of the propane-methane double gas hydrate versus the velocity \( u_a \) during combustion.

Three modes of dissociation are realized. For the first regime with an increase in the velocity \( u_a \) the \( J \) increases and reaches its maximum value \((u_a = 1.2 \text{ m/s})\). For the second regime \((1.2 < u_a < 3.0 \text{ m/s})\) the \( J \) decreases with increasing velocity \( u_a \). For \( u_a > 3.5 \text{ m/s} \) combustion does not occur. The stoichiometric ratio is violated (the ratio of concentrations of oxidizing agent (oxygen) to fuel (propane-methane) due to a significant excess of fuel over the oxidizing agent in the combustion area. As a result the dissociation rate and combustion temperature are reduced. A decrease in temperature leads to cessation of combustion and loss of fuel.

Conclusions
As a result of the experiments data have been obtained on different dissociation rates of propane-methane double hydrate (with a volume concentration of propane to methane of 60% to 40%) at combustion for different heating methods: induction, radiation and convective heating in a muffle furnace, without forced gas flow, in the presence of forced air convection. The maximum \( J \) was realized by burning granules of gas hydrate powder with a diameter of 0.7 - 1 mm with induction heating. The minimum \( J \) corresponded to the burning of a thick layer of powder in the absence of air flow over a horizontal surface. \( J \) increased and reached a maximum at a velocity \( u_a = 1.2 \text{ m/s} \) with an
increase in the velocity of the air convection $u_a$. A further increase in $u_a$ led to a decrease in $J$ by 8-12%. At $u_a > 3.5$ m/s combustion was not observed. The conducted research data is important for the development of existing gas hydrate combustion technologies.

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