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Research article

Methane hydrate combustion by using different granules composition

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ABSTRACT

Dissociations of methane gas hydrate during gas combustion were investigated. The anomalous behavior of a sample was revealed after termination of combustion and long stay of powder at the ice melting temperature ("secondary self-preservation of methane"). Increasing storage temperature and transport of natural gas hydrate are the important scientific and technical problems. The effect of combustion on decay of gas methane clathrate is considered using the important key parameters: powder layer height, external heat flux, granules composition. Existing methods of combustion modeling use a simplified one-dimensional case of kinetic combustion without taking into account the granule size and thickness of the hydrate layer. In the present research, the boundary dissociation conditions at non-stationary combustion were determined from the experiment data. The heat flux before combustion was constant and it was controlled by the ambient air temperature. During combustion, the heat flux increased by an order, and its value was determined experimentally. Currently, when simulating non-stationary combustion of CH_4 gas hydrate, constant flows of combustible gasses were used. In reality, magnitudes of mass gas flows vary by several orders in time. As a result, CH_4 combustion occurs under the non-stationary and non-isothermal regime in violation of stoichiometric ratio. The proposed model allowed us to connect the non-stationary gas flows with decomposition kinetics of gas clathrate. Thus, chemical reaction kinetics is controlled by means of the internal transfer processes. The existing predictions for describing the decomposition at negative temperatures did not take into account the structural parameters of particle surface as well. As a result, these simplified models incorrectly described the decomposition process. It is shown that non-uniform distribution of particle sizes and thick powder layer will result in unsteady dissociation and hydrate burning and this will lead to a decrease in combustion efficiency.

1. Introduction

Gas hydrates in the natural and in artificial conditions are generated at high ambient pressures or low temperatures, which ensure their equilibrium states. There are several main kinds of gas clathrate structures: cubic (sI); cubic (sII); and hexagonal (sH) [1]. The detected world deposits of gas hydrates contain huge natural gas reserves. Intensive gas extraction from the hydrate deposits will be started in the coming years [2]. The hydrate recovery from marine deposits was discussed in the paper of Li et al. [3]. Already today, gas hydrates cover both the global energy resources and the new effective technologies such as the CH_4 hydrate batteries [4]. Several energy efficient methods of gas hydrate recovery were compared in the paper of Wang et al. [5]. Effective technologies with brine injection, depressurization and thermal stimulation were compared in Refs. [6–8]. High-energy technologies, which use engine generators with CO_2 gas hydrate, were considered by Obara et al. [9]. The use of gas hydrates for biogas mixtures was discussed by Castellani et al. [10]. Great efforts are paid to the issue of storage and transportation of hydrate materials in large reservoirs [11], and security problems [2,12–19]. There is a lack of accurate physical models regarding CH_4 hydrate dissociation and the deficiency does not allow us to move forward more rapidly. It is necessary to reduce the transportation cost. The storage temperature of hydrate pellets is closely associated with the technology cost. The lowest rates of CH_4 hydrate decay were achieved at the temperature of about 263 K [20]. Furthermore, decomposition intensity of gas hydrates depends also on grain sizes, powder layer thickness, ice grains morphology and differences of temperatures and pressures. Experimental data on grain morphology are presented in Refs. [20–23]. The strong influence of hydrate layer thickness and particle diameter on decay intensity is shown by Falenty and Kuhs [22] and by Takeya et al. [24]. These key factors noticeably influence self-preservation mechanism [20–27]. It is important to indicate the different diffusion kinds at CH_4 hydrate formation and its disintegration. Intensity of gas hydrate formation and its further growth is considerably limited by thermal inertia of medium and gas diffusion flow within a solid granule and through a water film. The strong influence of external heat transfer on the decay character of CH_4 gas hydrate was demonstrated by Misyura [25] and by Kaneko et al. [28]. It was shown that at a change in heat transfer, both

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the quantitative decay character and qualitative dissociation nature are changed. The gas hydrate growth with consideration of diffusion was studied by Vlasov [29]. Gas hydrate decay on particle surface at positive temperatures (the transfer of gas hydrate to water and gas is implemented) depends on activation energy and internal kinetic constant [30]. In this case, there are no pores in the sample. Completely different kind of the hydrate behavior can be observed at negative temperatures. Porosity is formed during gas hydrate formation and its decomposition. The investigation of meso- and macro-pores formation on solid granule surface with the use of scanning electron microscopy was presented by Kuhs et al. [31,32]. It was illustrated that the pore sizes depend on the guest kind. The guest molecule is embedded into the host frame (water molecules). The kinetic behavior of the samples is controlled by porosity, and simulation should take porosity into account [33,34]. Natural gas hydrates, recovered from both the seafloor and continent, also have meso- and macro-pores [35–37]. The reaction rates between a gas and a solid porous particle depend on specific surface area [38–41]. The porosity regulates the dissociation rate of clathrate hydrate at self-preservation [42,43]. Filtration within the porous particle is a limiting factor for the decay behavior [44]. Chemical transformations at solid fuel combustion must also take porosity into account [45–51]. Gas hydrates burning covers not only the energy efficiency problem, but also the security issues. Critical concentration of combustible gas can lead to catastrophic consequences (spontaneous ignition of CH_4 and its explosion). Gas hydrate decay during combustion occurs with formation of a water film on the solid powder surface, ice and methane gas [28]. In this case, there is a heterogeneous system with gas hydrate-ice-water-methane. CH_4 hydrate combustion in the presence of the forced near-wall laminar flow was studied in Refs. [52–54]. Flame propagation velocities were changed from 6 mm/s to 1 m/s, when the sample temperature was varied from 193 K to 263 K [53]. This fact is connected with self-preservation. The average velocity of the CH_4 flow from a tank surface was varied from 0.2 mm/s to 18 mm/s [55]. The velocity of 0.2 mm/s corresponded to CH_4 hydrate dissociation without combustion and velocity of 18 mm/s was at combustion. In this case, there was high heat flux on the powder surface of 14,000 W/m^2. CH_4 combustion at free-convective flow was studied in Refs. [56–58].

It is obvious that intensity of gas emission at combustion is associated with non-stationary decay of CH_4 gas hydrate. Thus, it is impossible to simulate accurately the non-stationary hydrate combustion excluding the tasks of CH_4 hydrates dissociation because the boundary conditions of the task are conjugated by the thermal and mass flows. Thus, the studies of CH_4 hydrate combustion combined with dissociation of gas hydrate are of a particular interest. It is necessary to conduct additional studies on conjugate effect of key factors (heat exchange, powder homogeneity, powder layer height, hydrate dissociation rate) on non-stationary hydrate combustion.

2. Experimental data and analysis

2.1. The effect of powder uniformity and layer thickness on hydrate dissociation and combustion stability

The measurement scheme for studying gas hydrate dissociation is shown in Fig. 1. The experimental setup with powder and scales was covered by a shell, to control the given temperature and pressure. An excessive pressure in the shell was thrown off by an automatic valve and the external temperature was kept constant. The thermocouples were placed inside the tank (1) (Fig. 1) and platinum thermocouples were placed above the powder surface. Before experiments, air in the shell was dewatered by sorbent. The thermal measurements of powder surface were carried out by the thermal imager (4). Relative measurement error of the thermocouple was within 1.5 K. The difference between the temperatures measured by the thermal imager and the thermocouple did not exceed 2.0%. Relative measurements error of the thermal imager (4) (without combustion) was within 2.5%. The tank diameter was 60 mm, and the tank height was 30 mm. Thermocouples were inside the hydrate powder (2). Thermocouples were located at the tank axis near the right and the left lateral walls. A change in mass of the powder vs. time was determined with the help of the scales (3).

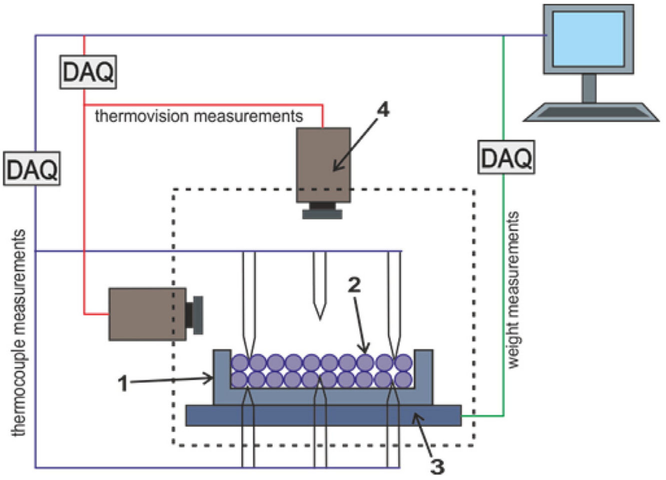

Fig. 1. The measurement scheme: 1 – the tank for methane hydrate powder; 2 – methane hydrate powder; 3 – scale; 4 – thermal imager.

To produce the methane hydrate granules, the ice powder was located in the cooled autoclave, then the methane pressure of about 6 MPa was set in the autoclave. The autoclave was maintained at the temperature of + 274 K for a long time (until the pressure drop). Hereupon, the powder was taken, ground and put into the autoclave again. Regranulation of hydrate particles was performed to increase the specific surface of powder and rate of hydrate formation. The hydrated particles with the diameter of up to 2 mm were produced by the long stay in the reactor. The pellets with the size of 0.6 mm and 1.7 mm were obtained by sieving. Deviation of particle size from the sphere diameter was within 20–30%. The large particles of 6-mm diameter were made by pressing the particles in the spherical moulds under the equilibrium conditions, excluding gas hydrate decay at its production. These spheres were obtained from the gas hydrated particles with the diameter of 0.1–0.3 mm. The porosity of these spheres was 31 ± 1%. The resulting samples were stored in the closed containers at the temperature of liquid nitrogen. At that, the storage conditions excluded granule sticking to each other. The total mass of extracted methane from the powder corresponded to initial methane concentration. The measurement of total extracted methane mass by the weight method at methane hydrate decay had shown that the initial mass concentration of methane in the powder varied within 11.5–12.2%. The elementary cell formula was $2D^*6T^*46H_2O$ $(2(5^{12}) + 6(5^{12}6^2))$ with consideration of crystal edges and faces. The methane hydrate corresponded to structure sI. Before the experiments, the samples were removed from the container with liquid nitrogen and put into the storage tank 1 of the experimental setup (Fig. 1). Then the sample temperature was increased to initial testing temperature. The initial sample temperature was close to the equilibrium temperature of 188 K (the external gas was air). The external gas pressure was constant (P = 0.1 MPa) during all experiments. Then, the air over the powder was heated, which led to an increase in the powder temperature. This heating occurred at automatic keeping the constant temperature difference $\Delta T = 7–9$ °C. ΔT is the temperature difference between powder (2) (the average temperature of entire powder was determined by several thermocouples mounted along the height and diameter of the sample layer) and air above gas hydrate. Methane hydrate decay started, when its temperature exceeded the equilibrium temperature. The powder temperature increased with time, as the warmer outside air heated the sample. Difference ΔT was constant (preset) and this simplified dissociation modeling. It is