Efficiency of methane hydrate combustion for different types of oxidizer flow

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A B S T R A C T

Dissociation of natural methane hydrate was studied experimentally. Natural hydrate was mined from deep deposits. The granules of different sizes were obtained through crushing. Stable combustion is achieved at uniform diameter-distribution of granules and their average size of 0.5–0.8 mm, and at low height of the powder layer of 6 mm. At the layer height of 18 mm, an ice crust preventing gas hydrate decomposition was formed inside the granule layer. For the first time, the efficiency of gas hydrate combustion was studied experimentally for eight ways of the oxidizer flow, and a simple method to compare the efficiency of the dissociation rate was proposed. Kinetics of combustion is correlated with the methane hydrate dissociation kinetics. Experimental data show that the most stable combustion with the maximal reaction rate occurs for uniform composition of small granules, low layer height, and at the joint flow of the oxidant in the outer flow and inside the powder layer. An oxidizer flow inside the powder layer led to methane combustion inside this layer and excluded partial self-preservation. The maximal dissociation rate was achieved in the presence of the external incident airflow (velocity is 1.0–1.5 m/s) and with the oxidizer flow inside the powder layer. At that, combustion inside the granule layer allows a significant increase in the layer height. The extreme of combustion rate is observed in a wide range of velocities. The extreme position depends on the injection parameter, length of dissociation region, ratio of velocities, and prehistory of the external incident airflow. To model the combustion, it is necessary to take into account the repulsion of the dynamic boundary layer from the wall and velocity and temperature distribution above the powder surface.

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1. Introduction

1.1. Reserves of natural gas hydrates, their production and storage

There are three main structures of gas hydrates: (sI), (sII) cubic structure and (sH) hexagonal structure [1]. Most natural gas hydrates have the cubic structure. Huge interest in gas hydrates is caused not only by exhaustion of the typical sources of natural raw materials, but also by the rapid development of new technologies. For example, it is the development of hydrate batteries [2], use of gas hydrates for biogas mixtures [3], and storage of hydrogen in the form of gas hydrates [4–8]. The current state of hydrogen storage and future development are presented in Ref. [4]. The structural transformation from *tert*-butylamine hydrate (sVI) to *tert*-butylamine + H$_2$ double hydrate (sII) was clearly observed under

hydrogen pressures [6]. The hydrogen storage capacity in this system was about 0.7H$_2$ wt %. Phase equilibria of H$_2$ + tetrahydrofuran mixed gas hydrate system have been measured in Ref. [7] for various concentrations of tetrahydrofuran aqueous solutions. The Raman spectra of H$_2$ and tetrahydrofuran for H$_2$+tetrahydrofuran mixed gas hydrate do not change with variation of tetrahydrofuran mole fraction from 0.010 to 0.130 in the aqueous solution. Equilibrium phase relations for the H$_2$–THF–H$_2$O system as a function of aqueous THF (tetrahydrofuran) concentration are reported in Ref. [8]. Gas hydrate deposits contain huge reserves of natural gas, and their intensive development will be started in the next decade. Today, the deterrent to an increase in the volume of methane hydrate production is the high cost of artificial methane hydrate synthesis and extraction of natural raw materials. The problems and prospects of mining the alternative energy sources are considered in Refs. [9–11]. A review of natural gas hydrates as an energy source is presented in Ref. [9]. The global review of recent research in molecular structural kinetic studies of gas hydrates, and

producing energy from arctic and oceanic hydrated deposits is done in Ref. [10]. The ability to simulate the behavior of geologic hydrate reservoirs has been improved substantially over the past 5—10 years. Currently, there are several numerical modes that can simulate the behavior in hydrate-bearing geologic media [11]. A survey of gas hydrate development in the marine field is presented in Ref. [12], global distribution of methane hydrate in ocean sediments is given in Ref. [13]. The calculated range of methane volumes in oceanic gas hydrates is 26.4—139.1 $\times$ 10^{15} m^3, with the most likely value on the lower end of this range [14]. While the role of salts as thermodynamic inhibitors is well-known, the presence of salts significantly affects kinetics of hydrate formation, resulting in a 6-time reduction in conversion and significant reduction in the rate of hydrate formation [15]. Evaluation of gas production from methane hydrate sediments with heat transfer considered in Ref. [16]. The production of hydrocarbons from sediments with gas hydrates was studied in Ref. [17]. A counter-current heat-exchange reactor for hydrate-bearing sediments was studied in the paper of Schicks et al. [18]. Energy efficiency is compared by three methods: single well depressurization, inverted five-spot water flooding method in cubic hydrate simulator [19] and combination of these two methods [20]. Behaviors and heat transfer characteristics of methane hydrate dissociation by depressurization with warm water stimulation in horizontal wells were studied in Ref. [21]. The study of technological processes using CO_2 hydrate presented in Refs. [22—24]. The kinetic model was constructed to describe the replacement process, which considers not only the kinetic reaction of CH_4—CO_2 replacement but also the reaction between CO_2 and free water [23]. Hydrate dissociation experiments by thermal stimulation and combination of depressurization and thermal stimulation were carried out for complete recovery of hydrated gas [24]. A driving force of 23 K was found to be sufficient to recover all the hydrated gas within 1 h and silica sand can be an effective porous media for separation of CO_2 from fuel gas when compared to silica gel. Much attention is paid to the problems, related to transportation and storage of raw materials in large containers [25]. The tankers carry liquefied natural gas at the temperatures below 110 K. Pelleted methane hydrate can be stored for a long time due to the phenomenon of self-preservation at the temperatures of 253 K. An increase in the temperature allows saving of about 40% of energy. Obviously, transportation of fuel raw materials in such tankers requires increased security requirements, and it is necessary to develop the risk assessment methodologies for spontaneous ignition and explosion of natural gas in order to prevent catastrophic consequences. The problems of transportation, storage and possible risks are considered in Refs. [26—33]. Without doubt, an increase in the temperature of methane hydrate pellets during their transportation by a tanker reduces significantly the cost of technology. However, the question regarding the comparison of economic benefits for different alternative technologies of natural gas transportation (pelleted methane hydrate, pipeline, LNG (liquefied natural gas), CNG (compressed natural gas)) remains open. The analysis of capital investment and operational costs of technologies with a wide set of production rates from 20 to 800 $\times$ 10^3 Nm^3 ·h^{-1} and transport distances from 200 to 10,000 km are considered in Ref. [26]. In contrast to the previous studies, model calculations in this study reveal a weak economic benefit of methane hydrate transportation versus competing technologies. Comparison for capital cost of NGH (natural gas hydrate) and LNG technologies for natural gas transport is considered in Ref. [28]. The effects of different operational conditions such as seawater temperature and hydrate storage temperature have been investigated in Ref. [29]. These economic evaluations were made for various gas markets of Spain, Belgium, Japan, Korea, India, China, Turkey et al. The nozzles for spraying water in the form of droplets into the natural gas

dramatically reduce the time of hydrate formation and increase its solubility [30]. The mass fractions of NGH were larger than 70% after 3 months of storage [31]. These results demonstrate the excellent characteristics of NGH pellets produced by continuous production, improving their suitability for the use as the natural gas storage media. To increase the efficiency of gas hydrate storage and transportation, it is necessary to develop the technologies, which will allow the maximal approach to the temperature of 267 K.

1.2. Key parameters of dissociation and self-preservation

It is known that the lowest dissociation rate of methane hydrate is achieved at the temperatures of 265—267 K [34]. In this temperature range, a region of anomalously low dissociation rate is formed, when methane in the state of hydrate can be successfully stored for several months. This annealing temperature region was called "self-preservation". One of the fast developing avenues is production of large granules and pellets with stable properties. Safety and economic analysis of a natural gas hydrate pellet carrier were presented in Refs. [35,36]. Transportation in the form of solid methane hydrate considerably reduces the risk of ignition or accident on the tanker in comparison with LNG [37]. A significant increase in the security of solid gas hydrate storage creates great prospects for the development of this technology. The importance of the phenomenon of self-preservation for the sea carriers is indicated in Ref. [38]. Guidelines for the construction and equipment of ships carrying natural gas hydrate pellets are presented in Ref. [39]. Anomalous preservation of NG (natural gas) hydrate pellet under thermodynamically unstable conditions at 253 K and atmospheric pressure was observed during three weeks [40]. Pelleting occurs by sintering and pressing the small granules. These pellets are convenient for transportation and require separate studies on the strength of the shell and resistance to dissociation. It is necessary to study the influence of heat and mass transfer, structural parameters of pellets in terms of gas hydrate collapse. It is important to note that the safe storage of natural gas hydrates and development of combustion technology are the different tasks with common physical properties. In the problems of storage and transportation, there is a trend to exclude dissociation of gas hydrates and improve the efficiency of self-preservation. In the tasks of combustion, self-preservation leads to flame blowout and unstable combustion; this negative factor must be overcome. Since the technologies of gas hydrates storage and methane hydrate combustion are faced with self-preservation, it is necessary to pay special attention to this issue. Dissociation and mechanism of gas hydrate self-preservation were studied in papers [40—53]. Scanning electron microscopy showed that the formed outer ice layer contained many pores while the internal microstructure of NG hydrate pellet was without pores [40]. The phenomenon of self-preservation was discovered and studied as one of the first ones by Yakushev and Istomin [41]. The presence of electrolyte crystals increases the mobility of water molecules and this promotes the formation of a contiguous ice layer that acts as an obstacle to diffusion of methane [42]. It was revealed that the dissociation rate of methane hydrate containing sodium chloride was faster than that of pure methane hydrate. In addition, the smaller particles of methane hydrate exhibited a higher effect of sodium chloride on dissociation [43]. Ultra-stability of natural gas sII hydrates was maintained during 256 h. At that, only 0.04% of the original gas underwent disintegration [44]. The dependence of anomalous preservation of CH_4 hydrate on the ice morphology is demonstrated in Ref. [45]. Data obtained by means of the X-ray imaging techniques, X-ray interferometric imaging and diffraction enhanced imaging show that the thickness of the ice layer under anomalous preservation is inhomogeneous, with an average thickness of about