Experimental Study on the Methane Hydrate Formation from Ice Powders

Weiguo Liu, Lijun Wang, Mingjun Yang*, Yongchen Song**, Liang Zhang, Qianqian Li, Yunfei Chen

Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, School of Energy and Power Engineering, Dalian University of Technology, Dalian 116024, P. R. China

Abstract

An experiment with methane hydrate formation from ice powders was conducted through the gas consumption method (PVT system) to corroborate the existing phenomenological multistage kinetic model. The influence of temperature, pressure and ice grain size on hydrate formation was experimented and analyzed. Lower temperature can enhance the hydrate formation. At the temperature up to nearly the melting point of ice, the excess pressure dominantly influenced the rate of methane hydrate formation. The smaller grain size of the ice powder can promote the methane hydrate formation. The lower rate of pressurization has good effect on the pressure drop process.

1. Introduction

Methane hydrate is a nonstoichiometric compound that trap guest molecules CH₄ in the cavity of cages composed of hydrogen bonded water host molecules under appropriate temperature and pressure [1]. It is attracting increasing focus since it is found and researched to apply in the storage and transportation [2]. Methane hydrate formation in laboratory from ice powders is one of the primary means to have comprehensive understanding of hydrate formation kinetics. Up to now, a series of experiments and models are performed to research the kinetic of hydrate formation [3, 4]. A phenomenological model about the kinetics of the gas hydrate formation from ice powders was presented by Staykova et al. [5]. Afterwards, Claudio and Paulo conducted a review to summary the modelling of hydrate formation kinetics in detail, and to indicate the future development directions [6]. Chen et al. studied the influence of pressurization and ethanol on methane hydrate synthesis from ice [7]. Kuhs et al. did some experiments to study the kinetics of CO₂-Hydrate formation from ice powders and compared with CH₄-Hydrate [8]. In order to achieve optimality condition of methane hydrate formation from ice powders, the objective of this paper is to study the influence of temperature, pressure and grain size.

* Corresponding author. Tel.: +86-411-8470-9093. Fax: +86-411-8470-8015. E-mail: yangmj@dlut.edu.cn
** Corresponding author. Tel.: +86-411-8470-6608. Fax: +86-411-8470-8015. E-mail: songyc@dlut.edu.cn
2. Experimental Section

2.1. Experimental apparatus

In this research, a PVT system based on gas consumption during the hydrate formation reaction in a closed ice-gas system was used. The sketch of the experimental system is shown in Fig. 1. Further details of the experimental apparatus can be found in the previous publications of our research team [9]. The high-pressure reactor was a cylindrical pressure cell with the effective volume of 460 ml. The maximum pressure that the reactor can bear was 30MPa. The pressure was measured by a pressure sensor with an accuracy of ±0.01MPa. In addition, 5 equidistant (35 mm) interfaces of thermocouples were opened along the reactor to measure the temperature. The estimated error of the thermocouple was ±0.1°C. The cold storage provided low environment temperature and the thermostatic bath control system of ethylene glycol was used to control the temperature precisely with stability ±0.1°C.

Fig 1. Scheme of the methane hydrate formation apparatus
1- high pressure reactor; 2- thermocouple; 3- glycol-water bath; 4- pressure sensor; 5- cold storage; 6- A/D module; 7- computer; 8- vacuum pump; 9- needle valve; 10- relief valve; 11- reducing valve; 12- waste bag; 13- N2 cylinder; 14- CH4 cylinder; 15- flowmeter; 16- check valve;

2.2. Specimen preparation and experimental procedure

Methane hydrate was formed from pure methane (purity: 99.99%) and ice powders. Ice powders were manufactured by freezing deionized water. The standard 20, 40 and 80-mesh sieves were used to obtain the particles with mean diameters of 380μm and 180μm respectively. The batch of ice powders used in each experiment had substantially identical mass of 150±5 g.

First of all, the reactor was washed three times by deionized water, and made it dried with nitrogen and methane alternately. Then, precise checks of set-ups for possible leaks were made to ensure the reacted system completely closed. Next, the reactor was pre-cooled in thermostatic bath for a few minutes before the ice sample was put into it. After that, the high-pressure lines and the reactor were flashed by nitrogen purging. A vacuum pump was used to discharge the gas in the vessel. When the temperature in the reactor reached stability, methane gas was applied with different rate to get the gas pressure from 3.0 to 10MPa. Finally, the temperature of the bath was adjusted to the chosen value. The data acquisition system was used to record the temperature and pressure history. Repeat above operations within each experiment.
3. Results and Discussion

3.1. Effect of temperature and pressure on methane hydrate formation

Research the effect of temperature on hydrate generated from ice is of crucial importance. The surface temperature of ice powders inside the reactor will have a slight rise after a large amount of hydrate generated due to the exothermic reaction. But the rise trend cannot be observed obviously owing to the influence of thermostatic bath. Three groups of the pressure drop and temperature history curves starting with the maximum pressure value after inflating are shown in Fig 2. This trend is in accordance with the research of Li et al. [10]. The results show that the lower temperature can enhance the hydrate formation.

Pressure is the main driving force for hydrate formation in the previous research. Four experimental runs in PVT system at the mean grain size of 380μm and the temperature of -4 and -8°C with different initial pressures were conducted respectively. The typical pressure drop curves were obtained for the hydrate formation in Fig 3. The quasi-liquid layer plays an important role in the nucleation of clathrate hydrates from ice. At the melting point of ice, it’s relatively easy to form the quasi-liquid layer. And so the different of initial pressure clearly influence the rate of pressure drop in the experimental process.

3.2. Effect of the grain size and pressurization rate on methane hydrate formation

The grain size of ice powder is the main factor that affects the hydrate formation. Three experiments of methane hydrate formation with the mean grain size of 380μm and 180μm under the condition of different initial pressure were performed. The curves of pressure drop with time are shown in Fig 4. The pressure drop rates are higher for the sample with smaller grains in accordance with theoretical predictions [5]. The smaller the grain size of ice powder, the bigger the specific surface area, and so the more likely it is to form the crystallization center. For the same grain size, the rate of hydrate formation is relatively faster with the higher initial pressure, even if the initial pressure difference is 0.5MPa.

The rate of pressurization is the speed of gas was pumped into the reactor. Three different rate of pressurization experiments were performed at the mean grain size of 180μm and the temperature of -3°C with similar initial pressures. Three kinds of pressure drop curves obtained for the hydrate formation in Fig 5. The results show that the slower of aeration, the relatively faster of pressure drop. Chen et al. [7] obtained the similar conclusion. But the calculate data indicate that its influence on the total amount of hydrate formation yields is not very obvious.
Fig 5. (a) Pressure dependence of methane hydrate formation process at temperature of -3°C and the average particle size of ice powder of 180 μm. (b) Detail with enlarged scale of the pressurization until the temperature reached stabilization.

4. Conclusion

According to the research and discussion above, the major results can be summarized as follows. (1) The trend of temperature rise substantially may not be observed in the experiment process due to the effect of pressurization and the bath system. However, it is confirmed that a certain degree of low temperature is helpful to methane hydrate formation. (2) At the lower temperature (far below the ice melting point), the pressure difference has a minor role on it. (3) The smaller grain size of the ice powder can promote the methane hydrate formation. (4) The lower rate of pressurization has good effect on the pressure drop. While its influence on the total amount of hydrate formation yields is not very obvious.

Acknowledgements

This work was supported by the Natural Science Foundation of China (Grant No.51276028).

References

Biography

Weiguo Liu was born in Shandong, China and completed his PhD at Dalian University of Technology. He is currently Associate Professor at Dalian University of Technology and his interesting fields are focus on the methane hydrate formation kinetics and the mechanical properties of hydrate-bearing sediments.