

NATURAL GAS HYDRATE FORMATION AND GROWTH ON SUSPENDED WATER DROPLET

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ABSTRACT

The experimental formation of natural gas hydrate on pendant water droplet exposed to natural gas was conducted and visually observed under the pressures from 3.86MPa to 6.05MPa. The temperature was set at 274.75K and 273.35K. The diameter of the pendant water droplet was around 4mm. The nucleation and growth of hydrate film on the pendant water drop exhibited a generalized trend. The film initially generated at the boundary between the water drop and suspension tube, and afterwards grew laterally and longitudinally on the surface of the water drop. The phenomenon of the two layers of hydrate films growing on the pendant water drop distinguished from the experiments on the sessile water drop. The effect of the driving force that resulted from the overpressure from the three equilibrium pressure on the hydrate nucleation and growth was investigated. It was found that the elevation of the driving force reduced the nucleation time and shortened the process of the hydrate growth on the pendant water drop. The crystals on the hydrate shell became coarser with the increase of the driving force. The mechanism for the hydrate film formation and growth on static pendant water droplet included four stages, such as nucleation, generation of the hydrate film, growth of the hydrate film, and hydration below the hydrate shell.

Key words: gas hydrate, formation, crystallization, water droplet, morphology

NOMENCLATURE

INTRODUCTION

Gas hydrate is a sort of crystal compound consisting with host molecules and guest molecules. Host molecules form the cage structure to encapsulate guest molecules. Water molecules are the hosts in natural gas hydrate, which was

assembled by hydrogen bonds, and formed polyhedral cavities to accommodate the guest molecules like CH₄, C₂H₆, CO₂, etc. [1]. The knowledge on gas hydrates plays an important part in the fields of storage and transportation of natural gas in the form of hydrates [2, 3], exploration of natural gas hydrate under the seafloor and at the bottom of the permafrost,

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avoiding the plug in the oil and gas pipelines, and sequestration of carbon dioxide, etc.

Researches on the crystal morphology could provide valuable information on the mechanistic aspects of the hydrate crystal nucleation, growth, and dissociation. Servio and Englezos [4] conducted the morphology study of the structure-H hydrate formation on water droplets, which showed that elevated driving force resulted in smaller induction times than those obtained under a low driving force. Studies of the morphology of methane and carbon dioxide hydrates formed from water droplets were also conducted by Englezos [5]. It stated that under the high pressure water droplets quickly became jagged and exhibited many needlelike or hairlike crystals extruding from the droplets, whereas under the low pressure the surface of the water droplet was smooth.

Ohmura [6] described the visual observation of the formation and growth of structure-H hydrate crystals on a water drop that was partially exposed to methane and partially immersed in a pool of a LMGS. Hydrate crystals first formed on the surface of the water droplet, and then floated up to the apex of the drop. The crystals accumulated on the apex then formed a cap or shell covering the upper area of the drop. The shell exhibited a coarse polycrystalline surface texture.

Ju Dong Lee [7] performed the morphology study of gas hydrate formation and decomposition on water droplets by using 89.4% methane-10.6% ethane mixture, and 90.1% methane-9.9% propane mixture. All droplets nucleated simultaneously and the droplet size and shape had no visible effect on induction time and the morphology of crystal growth for the methane-ethane mixture. The surface of the hydrate crystals from methane-propane had a hairy-like appearance, and then changed to a smooth surface.

Enlightened by the water spray hydrate formation [8-10], we are paying our attention to the morphology of hydrate formation on single water droplet. According to our previous studies on

water spray hydrate formation [11-13], it was found that it is essential to explore the mechanism of nucleation and growth of gas hydrates on water droplets in the water spray reactor. However, in the above experiments water droplets were placed on a stage or platform, which could not provide sufficient evidences for the study of gas hydrates formation on falling water droplets in the water spray reactor. Therefore, in this paper an experimental apparatus for hydrate formation on pendant water droplet was presented, and the morphology of natural gas hydrate formation on the liquid droplet was investigated with the microscopic digital imaging system, in the hope of being able to discover the mechanism of nucleation and growth of gas hydrates on pendant water droplets, and provide some valuable information for the research on the water spray hydrate formation.

EXPERIMENTAL

Apparatus

Up to now, it is difficult to conduct the investigation of hydrate formation on falling water droplets, so an experimental apparatus to study the hydrate formation on the still pendant water droplet is designed and constructed, creating a preliminary surrounding for the research on the hydration behavior of the water droplets in the water spray reactor.

The schematic of the experimental apparatus is shown in Figure 1. The apparatus is composed of a stainless steel crystallizer with a cooling water jacket. The 25 vol% ethanol solution circulates continuously between the low constant temperature trough and the water jacket to cool the crystallizer chamber to a predetermined temperature. The crystallizer is a horizontal cylinder with an internal diameter of 45mm, a length of 150mm and a volume of 240ml, and the maximum allowed pressure is 10.0MPa. One side of the crystallizer is equipped with a piece of optical glass for the microscopic digital camera to

observe the water droplet. The optical glass is fixed on the crystallizer by a flange. The water droplet is squeezed into the chamber of the crystallizer by an injection pump. The dimension of the water droplet can be adjusted slightly by the injection pump, however, if the droplet exceeds its critical size it would drop onto the surface of the crystallizer. In order to observe the hydrate formation on water droplets with different size, the pipes to hang the water droplet come with three different diameters, which are 1.0mm, 1.5mm, and 2.0mm, respectively. In present study, only the pipe with inner diameter of 2.0mm has been used. Hydrate forming gas from the gas reservoir is supplied into the crystallizer after passing the pressure relief valve. The pressure in crystallizer is regulated and maintained by a pressure regulator at the outlet of the gas reservoir. The temperature in

the crystallizer is measured by a Pt100 thermal resistance (WPK-263s, Shanghai Automation Instrumentation Co., Ltd., Shanghai, China) with a measuring range of 223.15-283.15K, and a 0.2% accuracy, a pressure transducer (P45, Banna Electronics Inc., USA) which is used to report the pressure of the gas in the crystallizer with a range of 0-10.0MPa, and an accuracy of 0.5%. The microscopic digital imaging system consists of a CCD camera (1.3 mega pixel, Nikon digital camera), a monocular microscope (with a length of 168.0mm and a maximum working distance of 95.0mm) and the image acquisition software (Shanghai MicroImage Technology Ltd., Shanghai, China). A computer is used to record the output of the microscopic digital imaging system and monitor the experimental process.

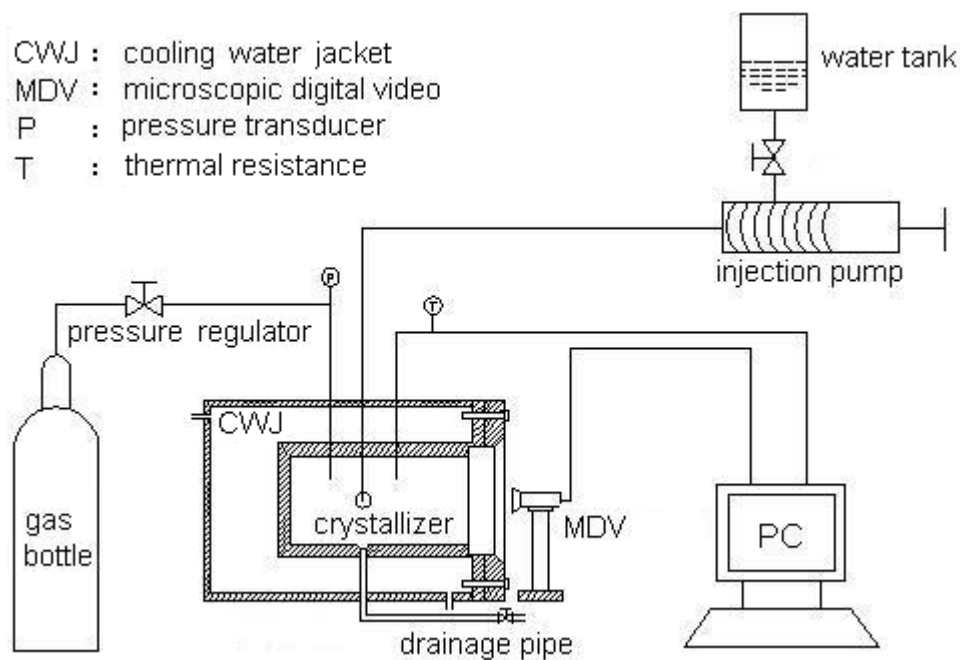


Figure 1 Schematic of experimental apparatus

Experimental procedure

The experimental procedure involves cleaning and drying the inside of crystallizer. The chamber of the crystallizer is flushed three times with natural gas at 1.5MPa, so as to remove any residual air in

the crystallizer, and then close the valves. Charge the chamber with natural gas to the experimental pressure after the crystallizer has been cooled to a predetermined temperature, squeeze a water droplet into the chamber, and keep it suspended at

the center of the crystallizer. Start to record the experimental time, observe the experimental process with the microscopic digital imaging system, continuously take pictures of the pendant water drop, and conduct data acquisition at the same time. In this work, the deionized and distilled water is used to produce water droplets, and natural gas from the western China is used as the hydrate forming gas, and its composition is listed in Table 1.

Table 1 Composition of natural gas from the western China

Analyzed items	Volume percentage (%)
CH ₄	88.017
C ₂ H ₆	5.453
C ₃ H ₈	1.658
n-C ₄ H ₁₀	0.274
i-C ₄ H ₁₀	0.237
n-C ₅ H ₁₂	0.057
i-C ₅ H ₁₂	0.075
C ₆ H ₁₄	0.05
N ₂	2.796
CO ₂	1.382
H ₂ S	0.001

RESULTS AND DISCUSSION

The experiments that investigate the formation of

natural gas hydrates under various experimental conditions are listed in Table 2. Both the nucleation time and the opaque time are shown in Table 2. Nucleation time in this paper is defined as the time when the first crystal has been observed by the microscopic digital system since the experiment started, while the opaque time is defined as the time when the surface of the water droplet has appeared to be covered by the hydrate film since the crystals were observed by the microscopic digital system.

Experiments 1-2 were performed at 274.75K and 3.86MPa, and Experiments 3-11 were carried out at the temperature of 273.35K and the pressure between 4.78MPa and 6.05MPa. According to Sloan [14, 15], the formation conditions for natural gas hydrate are 1.2MPa at 274.75K and 1.01MPa at 273.35K. Therefore, the overpressure above the equilibrium hydrate formation pressure is 2.66MPa in Experiments 1-2, 3.77MPa in Experiments 3-5, 4.76MPa in Experiments 6-8, and 5.04MPa in Experiments 9-11, indicating that the driving force (deviation of experimental pressure from the three phase equilibrium pressure at a given temperature) increases with the elevation of the system pressure.

Table 2 Experiments with observed nucleation times

exp.	T (K)	P (MPa)	diameter (mm)	nucleation time (min)	opaque time (min)
1	274.75	3.86	3.6	184	^a
2	274.75	3.86	3.6	145	^a
3	273.35	4.78	4.1	167	63
4	273.35	4.78	4.1	185	71
5	273.35	4.78	4.0	136	54
6	273.35	5.77	4.0	141	47
7	273.35	5.77	4.0	160	55
8	273.35	5.77	3.9	162	49
9	273.35	6.05	3.9	147	31
10	273.35	6.05	4.0	158	46
11	273.35	6.05	4.0	133	27

^aThe water droplet didn't become opaque within 20 hours.

Morphology of hydrate formation on pendant water droplet

The morphological observation on the formation of natural gas hydrates was performed in each experiment, and photographs were taken to record the formation process and formation phenomenon. Figure 2 exhibited the process of Experiment 1. The pendant water droplet was 3.6mm in diameter, about 184 minutes after the beginning of the experiment, hydrate nuclei appeared randomly on the surface of the water droplet, see the scattered white spots in Figure 2 (a). It was observed that these tiny nuclei were sinking towards the bottom of the water droplet owing to the effect of the gravity. At the same time, they were unceasingly revolving around the central axis of the water droplet. It was analyzed that the heat convection between the gas phase and the water droplet forced the small crystal particles to revolve. The nuclei gradually accumulated at the bottom of the drop and grew. Over a short period of time, star-like crystals appeared on the edge of the steel pipe and at the bottom of the water droplet, as shown in

Figure 2 (b). With the advance of the experiment, these star-like crystals kept moving round the axis of the water droplet and growing, and new nuclei also appeared. Figure 2 (d) showed that a complete star-like crystal had eight branches, but most crystals were incomplete and continually growing. About 170 minutes after the initial formation of hydrate crystals, the star-like crystals had grown to a certain size that limited their movement. It was observed that some of these star-like crystals had not formed the shape with eight branches yet, seen in Figure 2 (e). As indicated in Figure 2 (f), 315 minutes after the initial formation of hydrate crystals, the growth of star-like crystals nearly ceased, and no new nuclei were generated either, crystals like snowflakes were sparsely distributed on the surface of the water droplet. The observation of the experiment process was carried out for 20 hours, but no progress was found 315 minutes after the initial formation of hydrate crystals. Therefore, 20 hours later we terminated Experiment 1.

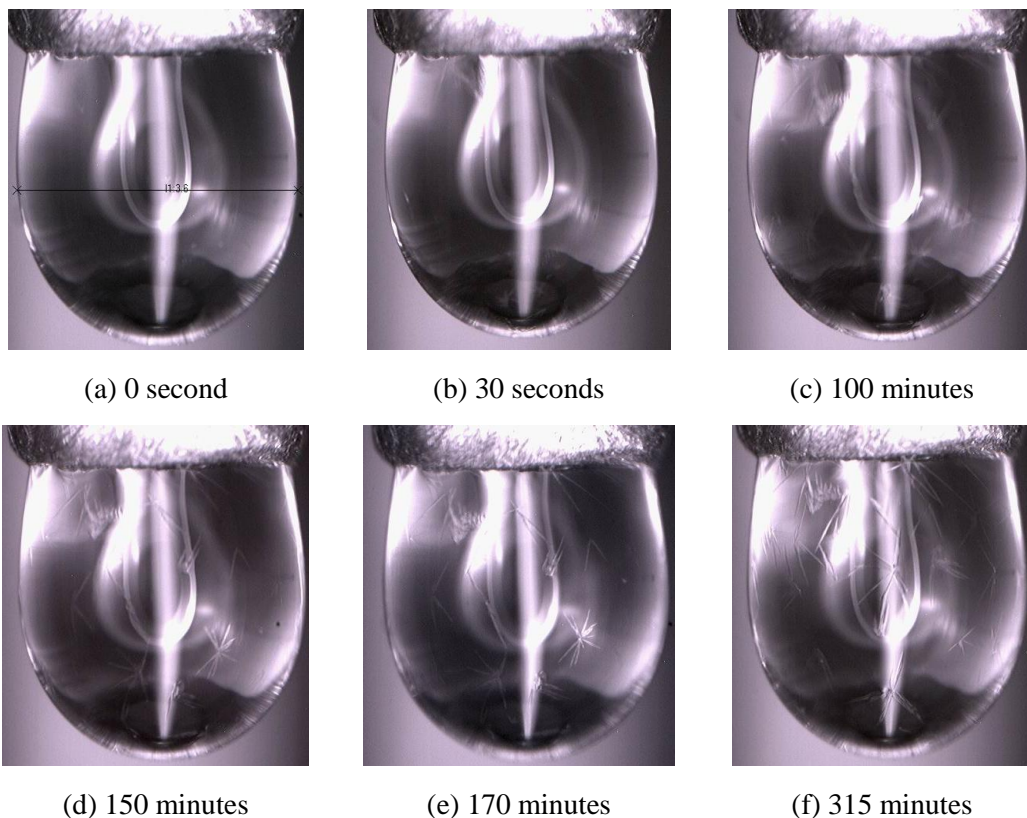
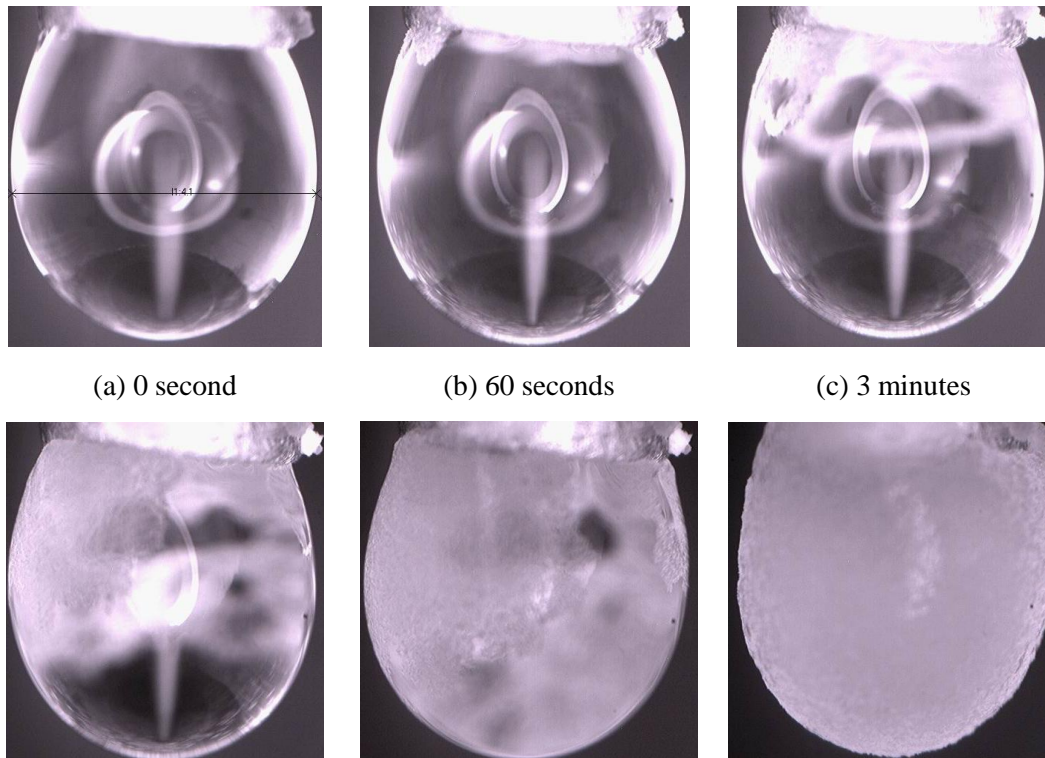


Figure 2 Gas hydrates formation on a suspended water droplet exposed to natural gas. Times given below each picture are the time from the appearance of hydrate nuclei. (Experiment 1, $T=274.75\text{K}$, $P=3.86\text{MPa}$).

Photographs that exhibited the process of Experiment 3 were presented in Figure 3. It should be noted that Experiment 3 was carried out at 273.35K and 4.78MPa , and the diameter of the suspended water droplet was 4.1mm , as marked with the solid line in Figure 3 (a). At the 167 minutes of the experiment, the transparency of the water droplet waned, the surface of the water droplet became foggy (Figure 3 (a)). 60 seconds later, hydrate crystals were spotted at the interface of the water droplet and the steel tube, as indicated in Figure 3 (b). And then, the crystals grew towards the bottom of the water droplet from the edge of the suspension tube, and the area that was covered by hydrate crystals turned to be opaque, referred to Figure 3 (c). In Figure 3 (e), it exhibited a phenomenon that was different from the previous observation on sessile water drop presented by other researchers. A cloudy hydrate film of 0.02mm spread quickly to cover the surface of the water droplet in 16 seconds, the surface of this

film was super smooth. Subsequently, coarse crystals that originally formed at the interface between the water droplet and tube edge covered the cloudy film, with the thickness of 0.08mm . In the end, the surface of water droplet was enclosed by hydrate crystals from upside to downside, and hydration continued inside the water droplet, but, it was observed that the surface remained smooth without any change, shown in Figure 3 (f).

It was analyzed that the stainless steel suspension tube directly passed through the cooling water jacket, so the heat transfer on it was much faster than the heat convection between the reactor wall and the gas phase. Therefore, it was believed that the top of the water droplet that was in contact with the suspension tube was slightly cooler than the lower portion. In addition, the interface between the water droplet and the tube was not as smooth as the surface of the water droplet, so the crystallization first occurred at the boundary between the water droplet and the suspension tube.



(d) 10 minutes

(e) 20 minutes

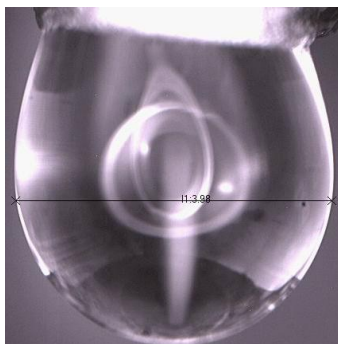
(f) 70 minutes

Figure 3 Sequential photographs of hydrates formation on a suspended water droplet exposed to natural gas. Times given below each picture are the time from the appearance of hydrate nuclei. (Experiment 3, $T=273.35\text{K}$, $P=4.78\text{MPa}$).

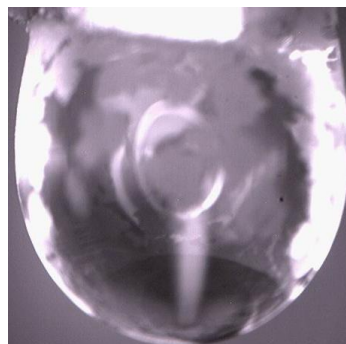
Figure 4 recorded the process of Experiment 6 that was performed at the temperature of 273.35K and the pressure of 5.77MPa . As measured in Figure 4 (a), the initial diameter of the water droplet was 3.98mm . About 141 minutes after the start of the experiment, nucleation occurred at the surface of the water droplet, and the transparent surface of the water droplet turned to be foggy, see the central zone of the water drop in Figure 4 (a). 60 seconds later, laminar hydrate crystals appeared in the area near the edge of the tube, which was floating on the upper surface of the water droplet (Figure 4 (b)). Figure 4 (c) showed that clearances among hydrate plates disappeared, and the dispersed hydrate plates had grown into a complete film cap covering the upper water droplet. 20 minutes later, the whole surface of the water droplet was wrapped by the hydrate film. It was indicated that the laminar hydrates not only grew towards the bottom of the water droplet, but also grew laterally, which was consistent with the result presented by Servio [5]. Figure 4 (d) exhibited a clear boundary between the films located on the upper and lower part of the water droplet. The upper hydrate film of 0.2mm was ice-like and coarse, but the lower one was cloudy and thin, with the thickness of 0.04mm . As interpreted in

Figure 3 (e), it was the phenomenon of the growth of two layers of hydrate films distinguished from observations on sessile water drops by other researchers. About 47 minutes later, the hydrate film on the entire surface of the water droplet turned to be identical, but it was not smooth any more. Embryos of hydrate were observed to project from the surface of the hydrate shell, as indicated in Figure 4 (e).

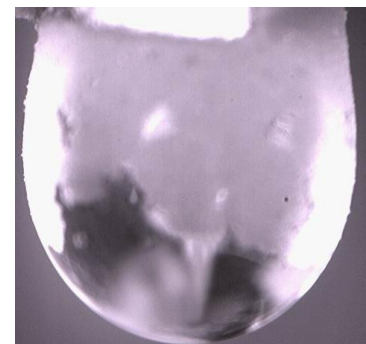
It was believed that natural gas permeated through the porous hydrate crystals to the interior interface between the hydrate film and the water droplet, and continued to form hydrates. The capillarity-driven water molecules [16] went out of the porous hydrate layer to the outer surface of the hydrate film and formed hydrates. Figure 4 (f) presented that small hydrate embryos had grown into branches, the volume of the water drop shrank, and the surface near the large branches depressed, indicating that the transport of the water molecules to the gas/hydrate interface developed and the hydration at the hydrate/water interface continued. The appearance of such branches generated under a high driving force was different from the needlelike crystals extruding from the droplets at high pressure [5, 7].



(a) 0 second



(b) 60 seconds



(c) 3 minutes

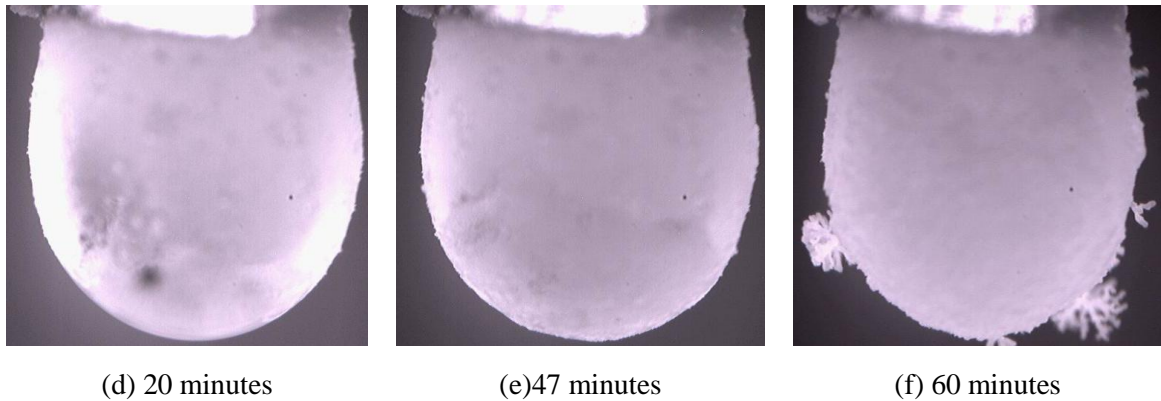


Figure 4 Photographs of hydrates formation on a suspended water droplet exposed to natural gas. Times given below each picture are the time from the appearance of hydrate nuclei. (Experiment 6, $T=273.35\text{K}$, $P=5.77\text{MPa}$).

Figure 5 exhibited the crystal formation in Experiment 9 which was conducted at the temperature of 273.35K and the pressure of 6.05MPa . The solid line in Figure 5 (a) indicated that the diameter of the water droplet was 3.9mm . About 147 minutes after the beginning of the experiment, tiny hydrate nuclei were observed at the interface between the water droplet and the edge of the suspension tube, as shown in the top right corner in Figure 5 (a). Meanwhile, the transparent surface turned to be cloudy, small hydrate particles were floating on the surface as well. 60 seconds later, hydrate film extended from the top of the water droplet to the lower point, as shown in Figure 5 (b). Compared to Figure 4 (b), it was found that the crystal growth in this experimental round was much faster, for nearly half of the water droplet was covered by the hydrate film in 60 seconds, rather than sparse crystals floated on the surface of the water droplet in Figure 4 (b). Figure 5 (c) also showed the

phenomenon of the growth of two layers of hydrate film. As measured, the thickness of the cloudy film and the coarse hydrate film was 0.04mm and 0.24mm , respectively. About 30 minutes later, the entire surface of the water drop was wrapped by the coarse hydrate film (Figure 5 (d)), and it was observed that crystals of the hydrate shell was not as fine as that in Figure 3 and Figure 4, the drop was 4.4mm in diameter. With the development of the hydration, the volume of the droplet diminished (Figure 5 (e)), the diameter reduced to 4.2mm , and hydrate branches were observed extruding to the gas phase from the surface of the hydrate film. A clear collapse of the surface at the bottom of the droplet was observed as well. Figure 5 (f) presented the further growth of the hydrate branches towards the gas phase, which grew up like trees covering the surface of the droplet, and the collapse was more clear than that in Figure 5 (e).

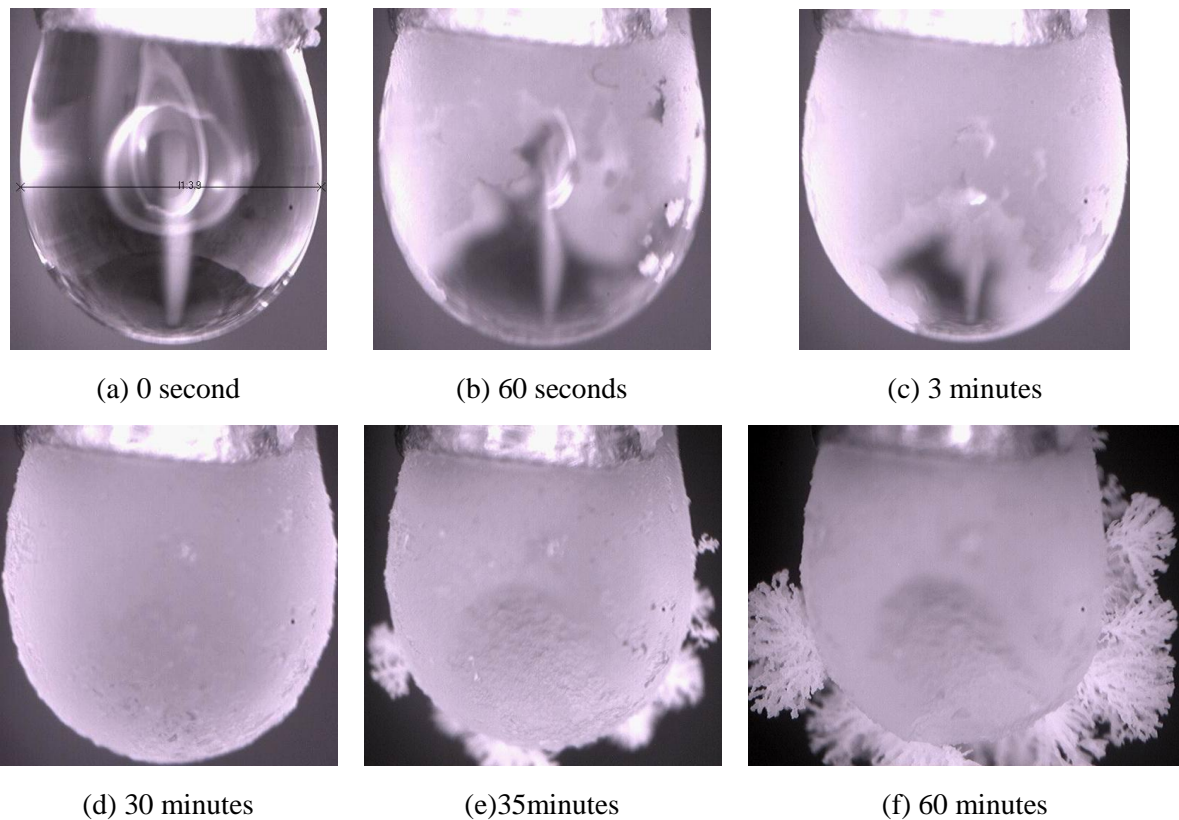


Figure 5 Photographs of hydrates formation on a suspended water droplet exposed to natural gas. Times given below each picture are the time from the appearance of hydrate nuclei. (Experiment 9, $T=273.35\text{K}$, $P=6.05\text{MPa}$).

Effects of driving force on nucleation time

It should be noted that each experiment in Table 2 experienced crystal nucleation. For example, in Experiments 1-2, the average value of nucleation time was 164.5 minutes. Under the condition of 273.35K and 4.78MPa the nucleation time was 162.7 minutes, which is an average value of Experiments 3-5. The average nucleation time was 154.3 minutes for Experiments 6-8 and 146 minutes for Experiments 9-11. It was found that under the same experimental conditions the nucleation time was a bit different (Table 2), which indicated that the nucleation of hydrates has a stochastic factor [7]. However, although the amount of the nucleation time in different experiment groups (Experiments 3-5, Experiments 6-8, and Experiments 9-11) varied from 133 minutes to 185 minutes, the average nucleation time in each experiment group

exhibited a trend that the nucleation time decreased under a higher driving force.

Effects of driving force on the formation of hydrate film

According to the above description on the morphology of crystallization in different experiments, it was discovered that the driving force played an important role in the formation of gas hydrate on the pendant water drop. Among the four experiment groups, the driving force in Experiment 1 was lowest, and in Experiment 9 was highest. From the morphologies of all experiments, it can be seen that with the elevation of the driving force the crystallization became faster, and the crystals of the hydrate film became coarser. For example, seen from Table 2, the time for the hydrate film to cover the entire water drop (i.e., opaque time) in Experiment 3, 6, and 9 was 63min,

47min, and 31min, respectively. It was proved that the crystallization accelerated under the high driving force. It should be noted that in Experiment 1 the surface of the water drop wasn't wrapped by the hydrate film, which was ascribed to the termination of the mass transfer under the low driving force. In addition, in Experiments 3-11 the hydrate film on the water drop thickened with the rise in the experiment pressure, for instance, the thickness of the coarse hydrate film in Experiment 3, 6 and 9 was 0.08mm, 0.2mm, and 0.24mm, respectively. It should be noted that these thickness values were almost obtained over 20min since the nucleation appeared. Therefore, it was indicated that the elevation of the driving force promoted the formation of the hydrate film on the pendant water drop.

Mechanism of hydrate formation on static pendant water droplet

Through the observations and analysis of hydrate formation on the static pendant water drop under different experiment conditions, the mechanism of hydrate formation on static pendant water droplet was acquired. As long as the formation condition for the hydrate film was satisfied, such as the Experiments 3-11 in this paper, the crystals formation and growth on the pendant water drop would undergo four stages. In the first stage, hydrate nuclei appeared randomly on the surface of the water drop and the surface became cloudy (the time equals the nucleation time); in the second stage, hydrate crystals initially appeared at the boundary of water drop and suspension tube, in this paper the time was in the range of 20 seconds to 60 seconds after the nucleation. In the third stage, two hydrate films that generated at the boundary between the water drop and the suspension tube grew laterally and longitudinally on the surface of the water drop. At first, the foggy hydrate film with the thickness of about 0.04mm quickly covered the water drop in 16 seconds or so. Then the coarse hydrate film covered the thin

hydrate film and enclosed the water drop completely in about 1 minute. The thickness of the coarse hydrate film increased with the elevation of the driving force. In present work, it varied from 0.08mm to 0.24mm. In the fourth stage, hydrate formation continued below the hydrate layer, which lasted till the end of the experiment. The appearance of the hydrate layer exhibited differently according to the degree of the driving force. For instance, in Experiment 3 (T=273.35K, P=4.78MPa) the surface of the hydrate layer was smooth, while in Experiment 6 (T=273.35K, P=5.77MPa) and Experiment 9 (T=273.35K, P=6.05MPa) hydrate branches extruded from the surface of the hydrate layer to the gas phase.

Recommendation for hydrate formation relevant to industrial system

As the hydration formation on pendant water droplet were only investigated at different pressures in this work, recommendations for the industrial formation were proposed based on this study. A higher driving force (i.e., a higher system pressure) is favorable to the industrial application, as the experiment results in this paper proved that a higher driving force could avoid the termination of the hydrate film formation on the pendant water droplet, and could shorten the process of the hydrate formation. It is very useful to the industrial water spray formation of gas hydrates in the future. The studies of the effects of other parameters (subcooling degree, the size of the water drop, etc.) on the hydrate formation on pendant water droplet are underway.

CONCLUSION

The observations of natural gas hydrate formation on pendant water droplet were carried out at different pressures ranging from 3.86MPa to 6.05MPa. The experiment temperature was set at 274.75K and 273.35K. It was found that the driving force had an important effect on the hydrate nucleation and growth, and the crystal

morphology on the pendant water droplet. The process of the hydrate nucleation and growth was shortened under a higher driving force, and the hydrate layer on the pendant water drop became coarser under a higher driving force. The mechanism for the hydrate formation on static pendant water droplet was discovered based on the realization of the hydrate film formation. It included four stages, i.e. nucleation, generation of the hydrate film, growth of the hydrate film, and hydration below the hydrate shell.

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