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MODELING OF NATURAL GAS HYDRATE FORMATION ON A SUSPENDED WATER DROPLET

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ABSTRACT

After reviewing the documents about the studies of hydrate formation kinetics in the world, this paper analyzed the process of hydrate formation on a suspended water droplet, which was based on the hydrate formation with water spay method, proposed a corresponding mathematical model, and solved it. Afterwards, the discussion about this model was presented. The results indicated that equilibrium time diminished with the decrease of the water droplet radius, and prolonged with the increase of sub-cooling degree, the reaction time for the second period reduced with the increase of subcooling degree, but was free from the effect of the variation of the water droplet size. The first period of the hydration on the water droplet was quite short, while the second period was considerably longer. Therefore, shortening the duration time of the second period of hydration was obviously able to accelerate the hydrate formation on the water droplet.

Keywords: water droplet; gas hydrate; formation kinetics; mathematical model

NOMENCLATURE

A Surface area [m^2]
c Specific heat capacity [kJ/kg•K^{-1}]
h_i Convection heat transfer coefficient [W/m^2•K]
ΔH Hydration heat per unit mass [kJ/kg]
M Molar mass [kg/mol]
n Molar number [mol]
Q The heat transferred to gas phase [kW]
Q_1 Hydration heat generated inside the hydrate film [kW]
Q_2 Hydration heat generated outside the hydrate film [kW]
r Radius of the water droplet covered by the hydrate film [m]
t Growth time of the hydrate [s]
T_{eq} The phase equilibrium temperature [K]
T The temperature of the water droplet [K]
ΔT Subcooling [K]
V_w The volume of the consumed water inside the hydrate film per unit time [m^3/s]
Z_V The volume expansion coefficient
ρ Hydrate density [kg/m^3]
λ Thermal conductivity [W/m•K]

Subscripts

$_w$ Water
$_H$ Gas hydrate

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$_i$ Inside of the gas hydrate

$_0$ Initial time

INTRODUCTION

Gas hydrates, also called clathrate hydrate is a sort of nonstoichiometric crystalline composed of water and gases with small-sized molecules [1], like CH_4, C_2H_6, CO_2, H_2S, etc. Currently, gas hydrate technology is being widely used in the fields of storage and transportation of natural gas, seawater desalination, carbon dioxide sequestration, and cold storage air-conditioning [2], etc., therefore, it is substantially important to perform studies on gas hydrate.

Kinetics research of gas hydrate started much later than the thermaldynamic research. The process of gas hydrates formation is quite complex, because it refers to heat and mass transfer among gas phase, liquid phase, and solid phase, meantime, a large amount of hydration heat is generated, and the whole process is influenced by many factors, so the kinetics research has progressed slowly. Recently, advanced observation and measuring methods have been adopted in the researches of hydrate formation kinetics worldwide. Sugaya and Mori [3] investigated the formation of refrigerant hydrate (CF_3CH_2 and $CClFCH_3$) with a high-speed photomicrography camera. Sun Chang-yu [4] et al. studied Freon-12 hydrate formation in a circulating flow loop system using light scattering technique, and Ma Chang-feng [5] et al. utilized a microscope camera to investigate the hydrate formation process of bubbles suspended in water. Ju Dong Lee [6] et al. conducted studies of gas hydrate formation and decomposition on water droplets using an 89.4% methane-10.6% ethane mixture, and a 90.1% methane-9.9% propane mixture. Ryo Ohmura [7] reported the visual observation of the formation and growth of structure-H hydrate crystals on a water drop partially exposed to methane gas and partially immersed in a pool of a liquid large molecule guest substance (LMGS). However, they did not present a mathematical model for the formation of gas hydrate on water drops, and quantitative descriptions of the process were absent. This paper analyzed hydrate formation process on a suspended water droplet on the basis of hydrate formation with water spay method, proposed a corresponding mathematical model, and presented the solution and discussion about the model, hoping to provide some valuable information for researchers in the circle of gas hydrates.

DESCRIPTION OF THE HYDRATE FORMATION ON A WATER DROPLET

Gas hydrates might form on the surface of the water droplets which were in the direct contact with hydrate-forming gases at a certain temperature and pressure, and the formation process was able to be divided into three periods: (1) gases contacted water droplets directly, and then the hydrate film formed quickly on the surface of water droplets after partial dissolution of the gas into water phase, covering the entire surface of water droplets. (2) Gases permeated through the porous hydrate film to the interface between the hydrate film and water droplet, and continued to form hydrates. Because the volume of the formed hydrates was larger than that of consumed water, partial water molecules diffused to the outer surface of the hydrate film. (3) Hydration on the inner and outer surfaces of the hydrate film occurred simultaneously, and a large number of hydrates formed. The schematic of hydration process of a water droplet was presented in Figure 1.

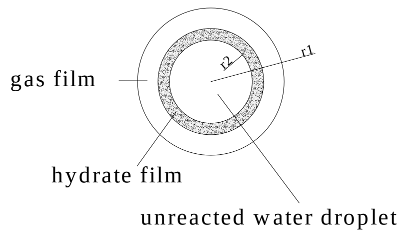


Figure 1 Schematic of hydration process of a water droplet

MODELING

If hydration heat released from the hydrate growth surface was removed very fast, the hydrate formation process would be controlled by the mass transfer rate of hydrate-forming gases onto the growth surface. Contrarily, the formation process would be controlled by heat transfer rate [8]. Since in the water spray reactor the sprayed water droplets were super fine, the hydrate film formed on a water droplet at the beginning was very thin and of a kind of porous medium, so the resistance of mass transfer was considerably low. Consequently, the mathematical model to describe hydrate formation on a suspended water droplet which was established under such condition was controlled by heat transfer rate.

First period of hydrate formation

Hydration heat released from the inner side of the hydrate film was totally transferred to the unreacted cooler water, so an equation based on the energy conversation law was formulated as

$$4\pi r_2^2 \frac{dr_2}{dt} \rho_H \Delta H = 4\pi r_2^2 h_i (T_{eq} - T_w) \qquad (1)$$

$$r_2 = r_0, \quad T_w = T_{w0}, \quad \text{at} \quad t = 0 \qquad (2)$$

$$r_2 = r_{2eq}, \quad T_w = T_{eq}, \quad \text{at} \quad t = t_{eq} \qquad (3)$$

Where, r_2 represents the radius of the water droplet covered by the hydrate film, t is the growth time of the hydrate, ρ_H is the density of the hydrate, ΔH is the hydration heat per unit mass, h_i is the convection heat transfer coefficient, T_{eq} is the phase equilibrium temperature of the hydrate under the experiment pressure, T_w is the temperature of the water droplet, and t_{eq} and r_{2eq} represent the elapsed time and the radius of the unreacted water droplet when the water droplet reached phase equilibrium temperature, respectively. Subscripts $_w$, $_H$, $_i$ and $_0$ represent water, gas hydrate, inside of gas hydrate, and initial time, respectively.

The temperature of the unreacted water droplet at any time was determined by the lumped parameter method, expressed as:

$$T_w = T_{eq} + (T_{w0} - T_{eq}) \exp\left(-\frac{h_i A_{w0}}{\rho_w c_w V_{w0}} t\right) \qquad (4)$$

Combining Eqs (1) and (4), equation (5) is formulated as

$$\frac{dr_2}{dt} \rho_H \Delta H = h_i (T_{eq} - T_{w0}) \exp\left(-\frac{h_i A_{w0}}{\rho_w c_w V_{w0}} t\right) \qquad (5)$$

Integrating Eq.(5) on the basis of Eqs.(2) and (3), so equation (6) is obtained.

$$r_2 = \left[1 - \exp\left(-\frac{h_i A}{\rho_w c_w V_{w0}} t\right)\right] \frac{\rho_w c_w V_{w0} \Delta T}{\rho_H \Delta H A_{w0}} + r_0 \qquad (6)$$

Therefore, the time for water droplets to reach the phase equilibrium temperature is deduced as:

$$t_{eq} = -\frac{\rho_w c_w V_{w0}}{h_i A} \ln\left[1 + (r_{2eq} - r_0) \frac{\rho_H \Delta H A_{w0}}{\rho_w c_w V_{w0} \Delta T}\right] \qquad (7)$$

When the temperature of the water droplet reached the phase equilibrium temperature, hydration heat generated on inner reaction front should be equivalent to the amount of heat which was absorbed by the water droplet to reach the phase equilibrium temperature, hence,

$$\left(\frac{4}{3}\pi \cdot r_0^3 - \frac{4}{3}\pi \cdot r_{2eq}^3\right) \rho_H \Delta H = \frac{4}{3}\pi r_{2eq}^3 \rho_w c_p (T_{eq} - T_{w0})$$

(8)

So $r_{2eq}^3 = \frac{\Delta H \rho_H}{\Delta H \rho_H + \Delta T \rho_w c_p} \cdot r_0^3$, the outer radius of the generated hydrates was $r_{1eq}^3 = [\frac{\Delta H \rho_H (1 - Z_V)}{\Delta H \rho_H + \Delta T \rho_w c_p} + Z_V] \cdot r_0^3$, where $\Delta T = T_{eq} - T_{w0}$, Z_V was the volume expansion coefficient, i.e. $Z_V = V_H / V_w$.

Second period of hydration formation

During this period, heat Q transferred to gas phase from the water droplet was the total hydration heat from inner and outer reaction fronts, i.e. $Q = Q_1 + Q_2$. According to the analysis with mass transfer theory, it was known that if the volume of the consumed water inside the hydrate film per unit time was V_w, the volume of the water diffused outside hydrate film would be $V_w (Z_V - 1)$. The relationship between the hydration heat generated inside and outside hydrate film was expressed as:

$$Q_2 = Q_1 (Z_V - 1) \tag{9}$$

$$Q_1 = \frac{4\pi\lambda_H (T_{eq} - T_1)}{\frac{1}{r_2} - \frac{1}{r_1}} \tag{10}$$

Concerning a suspended static water droplet, the heat transferred to ambient gas phase was formulated as

$$Q = 4\pi r_1^2 h_0 (T_1 - T_g) \tag{11}$$

And the heat transferred to gas phase from outer reaction front was the total hydration heat, so

$$Q = n_g M_H \Delta H \tag{12}$$

Equation (13) was obtained from the combination of equations (9) to (12).

$$n_g = \frac{4\pi h_0 Z_V \lambda_H \Delta T'}{M_H \Delta H} \frac{1}{h_0 (\frac{1}{r_2} - \frac{1}{r_1}) + Z_V \lambda_H \frac{1}{r_1^2}} \tag{13}$$

Because of $h_0 (\frac{1}{r_2} - \frac{1}{r_1}) << Z_V \lambda_H \frac{1}{r_1^2}$, $n_g = \frac{4\pi h_0 r_1^2 \Delta T'}{M_H \Delta H}$ was acquired, where $\Delta T' = T_{eq} - T_g$. Because the reaction between water droplets and gas occurred by stoichiometric coefficient *n*, equation (14) was formulated.

$$n \cdot n_g \cdot \frac{M_w}{\rho_w} = Z_V \cdot 4\pi r_2^2 \frac{dr_2}{dt} \tag{14}$$

$$r_2 = r_{2eq} \quad \text{at} \quad t = t_{eq} \tag{15}$$

Therefore, $\frac{dr_2}{dt} = \frac{n h_0 M_w \Delta T' \cdot r_{1eq}^2}{\rho_w M_H \Delta H Z_V r_2^2}$ was deduced, total hydration time for a water droplet was

$$t = \frac{\rho_w M_H \Delta H Z_V}{3 n h_0 M_w \Delta T' r_{1eq}^3} (r_{2eq}^3 - r_2^3) + t_{eq} \tag{16}$$

Therein, reaction time for second period of hydrate formation was

$$t_2 = \frac{\rho_w M_H \Delta H Z_V}{3 n h_0 M_w \Delta T' r_{1eq}^3}(r_{2eq}^3 - r_2^3)$$

$$(0 < r_2 < r_{2eq}) \qquad (17)$$

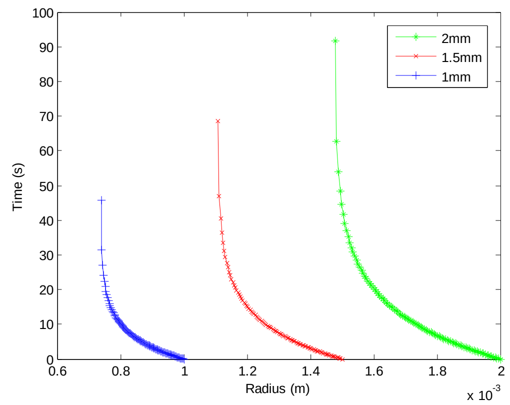
MODEL SOLVING AND DISCUSSION

Relation between the end time t_{eq} of first period and water droplet radius r_0

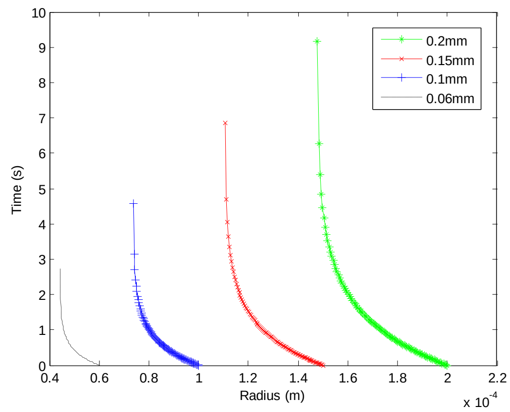
Figure 2(a) and Figure 2(b) indicated that t_{eq} diminished with the decrease of water droplet radius r_0 at the same sub-cooling degree. It was showed in Figure 2(a) that when r_0 was at the value of 2.0mm, 1.5mm and 1.0mm, t_{eq} was at 90.0s, 70.0s and 45.0s, respectively; in Figure 2(b) when r_0 was at the value of 0.2mm, 0.15mm, 0.1mm and 0.06mm, t_{eq} was at 9.2s, 7s, 4.6s and 2.8s, respectively. Therefore, it should be noted that the smaller the water droplet, the shorter the first stage lasts. In addition, it was shown in Figure 2 that despite of the size of the water droplet, hydrate film formed on the water droplet stopped at the same relative position by the end of the first period, that is, the thickness of the hydrate film was about 0.261r_0 at the end of the first stage. Accordingly, it was indicated that in water spray devices hydrate film would quickly formed on water droplets as soon as water droplets with the diameter of micron grade left the nozzle, which was one of the advantages of producing hydrate with water spray method.

Relation between the end time t_{eq} of the first stage and the subcooling degree ΔT

As illustrated in Figure 3, t_{eq} has increased with the rise of subcooling degree ΔT when the initial water droplet radius was set at a fixed value. When the initial radius r_0 of the water droplet was at the value of 2.0mm, t_{eq} was 73.0s, 82.0s, 90.0s and 121.0s corresponding to the subcooling degree ΔT of 1.0℃, 2.0℃, 4.0℃ and 6.0℃, respectively. Besides, by the end of the first period the thickness of the formed hydrate film has varied from the subcooling degree ΔT, for example, the thickness of the hydrate film formed on the water droplet was 0.13mm, 0.26mm, 0.52mm and 0.78mm corresponding to the subcooling degree ΔT of 1.0℃, 2.0℃, 4.0℃ and 6.0℃, respectively. Therefore, the reaction time went up with the increase of subcooling degree ΔT, i.e. t_{eq} has increased.



(a)



(b)

Figure 2 Diagram of the relation between t_{eq} and water droplet radius r_0 (ΔT= 4℃)

Relation between the end time t_2 of the second period and the subcooling degree ΔT

When the initial radius r_0 of the water droplet was at the value of 0.2mm, 0.15mm and 0.1mm, respectively, by the end of the first period the radius of the unreacted water droplet had been calculated with Eq.(7), i.e. r_2=0.833 r_0, as shown in Fig. 4. Seen from the diagram, t_2 did not change with the variation of the radius of the water droplet under the condition of the same subcooling degree, it was evidently indicated that t_2 was at a fixed value. t_2 turned out to be 6800s when ΔT was at the value of 4.0℃. It concluded that blindly decreasing the radius of water droplets could not be able to obtain a desirable effect on hydration formation in water spray reactors.

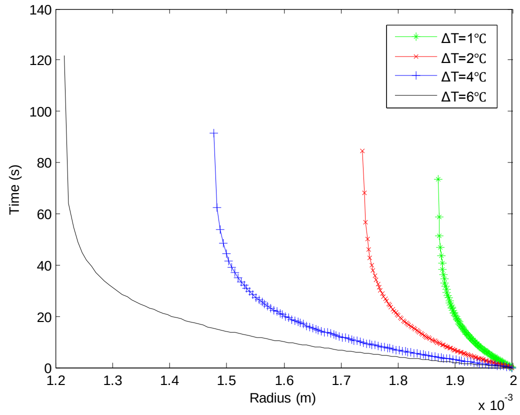


Figure 3 Diagram of the relation between t_{eq} and subcooling degree ΔT (r_0=2mm)

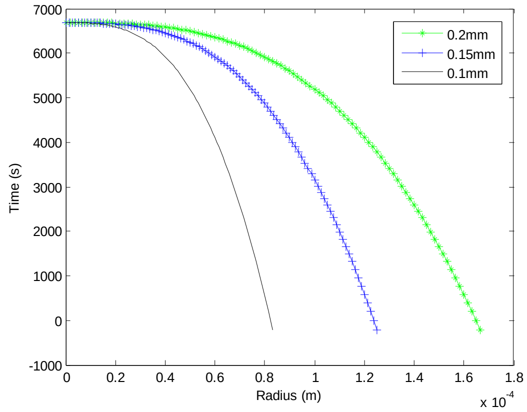


Figure 4 Diagram of the relation between t_2 and radius of the water droplet (ΔT=4℃)

Relation between the end time t_2 of the second stage and the subcooling degree ΔT

It was observed that t_2 had reduced with the increase of the subcooling degree ΔT, as shown in Figure 5. When the initial radius r_0 of the water droplet was at the value of 2.0mm, t_2 was 40000s, 17500s, 6800s and 4000s corresponding to the subcooling degree ΔT of 1.0℃, 2.0℃, 4.0℃ and 6.0℃, respectively. It was indicated that increasing the subcooling degree could be able to shorten the process of complete hydration of the water droplet. Actually, subcooling degree could not be lifted infinitely, because the requirements for the insulation of the experimental equipment and the performance of refrigeration system would be much higher, and tiny water droplets might have freeze into ice particles before hydration occurred owing to the huge subcooling degree, which has exceeded the research scope of this paper. Consequently, it should be noted that under a specific situation a proper subcooling degree has to be set in the research of hydration on water droplets.

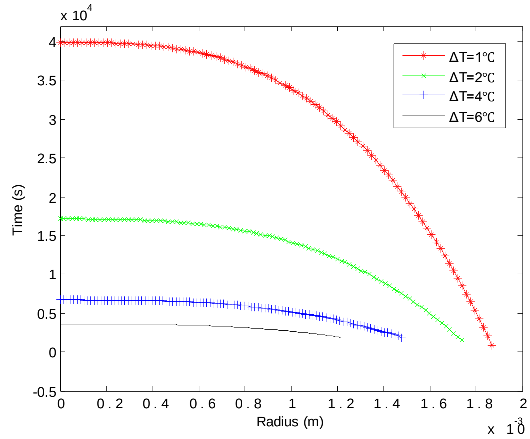


Figure 5 Diagram of the relation between t_2 and subcooling degree ΔT (r_0=2mm)

Complete hydration time *t* of the water droplet

Eq.(16) indicated that the total hydration time t of a suspended water droplet consisted of the end time t_{eq} of the first period and the end time t_2 of the second period. Through solving the above mathematical model we have found that the duration time of the first period was considerably short, varying from 1.0s to more than 100.0s, but the duration time of the second period was much longer, changing from 1.0 hour to more than 10.0 hours. As a result, in order to reduce the complete hydration time of a water droplet, it is proposed to focus on lowering the duration time of the second period, like increasing the subcooling degree, etc., so as to accelerate the process of gas hydrate formation.

CONCLUSION

The process of hydrate formation on a suspended water droplet was analyzed based on the hydrate formation with water spay method, and a corresponding mathematical model to describe this process was proposed in this paper. The process of the hydrate formation was divided into two periods, in the first period hydration heat generated on the inner side of the hydrate film was totally transferred to the unreacted cooler water; and in the second stage, hydration heat released from the inner and outer reaction fronts on the water droplet was completely transferred to the ambient gas phase. Through the model solving and the discussion of the calculated results, it was found that the end time t_{eq} of the first period had diminished with the decrease of water droplet radius r_0, and had increased with the rise of the subcooling degree ΔT; the end time t_2 of the second period had reduced with the increase of the subcooling degree ΔT, but was free of the influence of the variation of the water droplet. In addition, the duration time of the first period was pretty short, but the duration time of the second period was much longer. Thereby, in order to accelerate the hydration of the water droplet, shortening the duration time of the second period was substantially necessary and important.

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