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Category

Research Article

Abstract

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Keywords

Methane hydrate, Decomposition, Dimensionless number, Damköhler number, Biot number

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Effects of dimensionless numbers on decomposition of methane hydrate

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Abstract

It is necessary to elucidate the decomposition and combustion of methane hydrate for fire safety during transportation and storage to utilize it for commercial practice. The amount of methane evolved during the decomposition of methane hydrates is affected by the conditions such as the initial temperature, initial density and ambient temperature. In the present study, the internal temperature of methane hydrate and the amount of methane evolved during its decomposition were investigated by a dimensionless numerical analysis using a transient one-dimensional conduction model from a symmetrical methane hydrate ball heated by ambient air. The numerically calculated central temperature and the mass of evolved methane were compared with corresponding experimental results, and good agreement was obtained. The Damköhler and the Biot numbers were identified as two important dimensionless parameters during the decomposition of methane hydrate; the time histories of the central temperature, the mass of evolved methane and the reaction rates were numerically investigated by changing these dimensionless numbers. Consequently, the effects of dimensionless numbers on the decomposition of methane hydrate were elucidated.

Keywords: Methane hydrate; Decomposition; Dimensionless number; Damköhler number; Biot number

Nomenclature

A	frequency factor	t	time
B_i	Biot number	Δt	time interval
c	specific heat	Y	mass fraction
d	diameter	θ	temperature
D_a	Damköhler number	λ	thermal conductivity
E	activation energy	ρ	density
h	heat transfer coefficient	ν	stoichiometric ratio
m	mass		
q	heat of decomposition	<i>Subscripts</i>	
r	radius	0	initial state
R	universal gas constant	∞	ambient state
RR	reaction rate		

Introduction

Methane hydrate is expected as a new alternative energy. It can include methane having equivalent volumes 170 times greater than the hydrate volume, but low-temperatures and high-pressures are neces-

sary for its stability. At atmospheric pressure, methane hydrate is stable at temperatures less than 193.15 K. However, it is generally considered that its storage may be possible at approximately 243.15-253.15 K under atmospheric pressure as a consequence of a characteristic peculiar to methane hydrate called the self-

preservation effect. By using this characteristic of the hydrate, the transportation of natural gas hydrates (NGH) may be expected to be an inexpensive mode of transportation in comparison with liquefied natural gas (LNG) transportation where the natural gas is liquefied by cooling to 111.15 K.

Methane hydrate has different combustion characteristics from common solid fuels because of peculiar characteristics such as the intense decomposition at room temperature or the so-called self-preservation effect. It is necessary to elucidate the decomposition and combustion of methane hydrate for fire safety during transportation and storage so it may be utilized in commercial practices [1–4].

Numerical analysis is a useful tool to examine the decomposition and combustion of methane hydrate. An accurate reaction rate equation is required because the decomposition reaction plays an important role in its decomposition and combustion; however, very few studies have examined these reactions. For example, Kim et al. [3] presented a reaction rate constant but it was for only a limited range of temperature between 274–283K under pressures between 0.17–6.97 MPa. In our study, the reaction rate constant that is effective for all temperature ranges up to 273.15 K was obtained by using a transient one-dimensional conduction analysis of a symmetrical methane hydrate ball heated by ambient air [4].

The amount of methane evolved during its decomposition and its internal temperature were investigated by using a dimensionless numerical analysis and the numerical calculations were compared with the corresponding experimental results. In addition, the effects of dimensionless numbers on the decomposition of methane hydrate were elucidated.

Numerical analysis

Analytical model

The analytical model is shown in Fig. 1. The methane

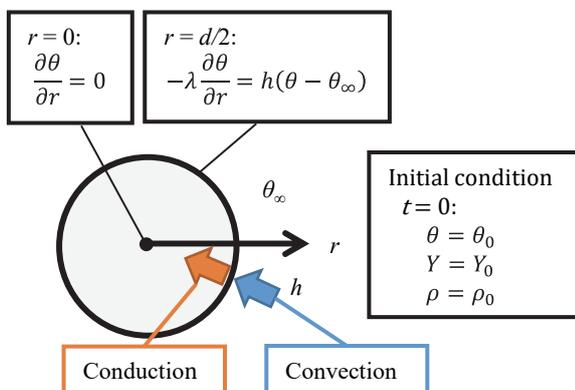
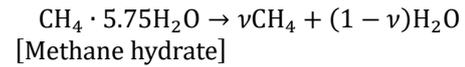


Fig. 1. Analytical model.

hydrate ball at temperature θ_0 and diameter d was heated by heat transfer due to convection from the ambient air at a temperature θ_∞ and the heat transfer coefficient h .

The global reaction shown below was assumed during the decomposition of the hydrate ball. The reaction rate was expressed by the Arrhenius approximation, as shown in Eq. (1), and the experimentally obtained chemical parameters [4] were applied for the frequency factor A and the activation energy E in Eq. (1).



$$RR = A\rho Y \exp\left(-\frac{E}{R\theta}\right) \quad (1)$$

The governing equations during decomposition included the conservation equations of mass, energy and species as shown in Eqs. (2)–(4), where ν is the mass-based stoichiometric ratio, and ρ, c, λ, Y and q are the density, specific heat, thermal conductivity, mass fraction of methane hydrate in the condensed phase and the heat of decomposition per unit mass, respectively. The heat of decomposition q is negative because the decomposition reaction is endothermic.

$$\frac{\partial \rho}{\partial t} = -\nu RR \quad (2)$$

$$\frac{\partial \rho c \theta}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(\lambda r^2 \frac{\partial \theta}{\partial r} \right) + q RR \quad (3)$$

$$\frac{\partial \rho Y}{\partial t} = -RR \quad (4)$$

Dimensionless form of equations

The governing equations were nondimensionalized by the following dimensionless expressions.

$$r' = \frac{r}{d}, \rho' = \frac{\rho}{\rho_0}, \theta' = \frac{\theta - \theta_0}{275.15 - \theta_0}, t' = \frac{t}{d^2 \left(\frac{c\rho_0}{\lambda} \right)},$$

$$q' = \frac{q + \nu\theta_0 c}{c(275.15 - \theta_0)}, Da = Ad^2 \left(\frac{c\rho_0}{\lambda} \right), Bi = \frac{hd}{\lambda}$$

Thereby, the dimensionless governing equations are shown in Eqs. (5)–(7).

$$\frac{\partial \rho'}{\partial t'} = -\nu RR' \quad (5)$$

$$\frac{\partial \rho' \theta'}{\partial t'} = \frac{1}{r'^2} \frac{\partial}{\partial r'} \left(r'^2 \frac{\partial \theta'}{\partial r'} \right) + q' RR' \quad (6)$$

$$\frac{\partial \rho' Y}{\partial t'} = -vRR' \tag{7}$$

where the dimensionless reaction rate RR' is expressed in Eq. (8).

$$RR' = D_a \rho' Y \exp\left(-\frac{E}{R\{\theta'(273.15 - \theta_0) + \theta_0\}}\right) \tag{8}$$

The dimensionless boundary conditions and the dimensionless initial conditions are shown as follows.

Boundary condition:

$$r' = 0 : \frac{\partial \theta'}{\partial r'} = 0 \quad r' = 0.5 : \frac{\partial \theta'}{\partial r'} = -B_i(\theta' - \theta'_\infty)$$

Initial condition:

$$t' = 0 : \theta'_0 = 0.0, \rho'_0 = 1.0, Y = Y_0$$

From these dimensionless expressions, it was determined that the dimensionless numbers to affect the temperature distribution of the methane hydrate ball were the Damköhler number D_a , the Biot number B_i , the dimensionless ambient temperature θ'_∞ and the initial mass fraction of methane hydrate Y_0 .

Numerical procedure

The dimensionless governing equations were solved numerically by the finite differential method. The second-ordered central difference scheme was applied for the diffusive terms, and the time advance was made by using Euler’s explicit method. The calculation domain was 0.5 in the r direction, the number of grid points 101, and the grids were taken with the same space interval. Also, the time interval was $\Delta t = 0.5 \times 10^{-2}$. The total amount m of methane evolved at time t is given in Eq. (9) by integrating the reaction rate of the methane hydrate over the whole ball for the time from 0 to t . In addition, the dimensionless expression of m is shown in Eq. (10).

$$m = \int_0^t \int_0^{d/2} vRR(4\pi r^2) dr dt \tag{9}$$

$$m' = \frac{\int_0^{t'} \int_0^{0.5} vRR'(4\pi r'^2) dr' dt'}{\frac{\pi}{6} v Y_0} \tag{10}$$

In the present study, the central temperature of methane hydrate, the mass of evolved methane and the reaction rate were investigated for a fixed dimensionless ambient temperature $\theta'_\infty = 1.27$ and a fixed mass fraction of methane hydrate $Y_0 = 1.0$ by changing the Damköhler number D_a and the Biot number B_i .

Experimental setup and method

Corresponding experiments were conducted to compare with the results of the numerical analysis. Schematics of experimental setup are shown in Fig. 2 and Fig. 3.

Methane hydrate used in the experiments was artificially produced in the laboratory by flowing high pressure methane and water into a closed stirred container while cooling. The produced methane hydrate was crushed finely, molded spherically and cooled to 193.15 K. The diameter of methane hydrate ball was 3.0×10^{-2} m; its density was calculated from the mass and volume of methane hydrate ball.

In experiments depicted by Fig. 2, the methane hydrate balls were placed on an insulation material and the change of mass was recorded every ten seconds to enable calculation of the mass of evolved methane; the decrease in mass of the methane hydrate ball was assumed to be equal to the mass of evolved methane. In the experiments of Fig. 3, the methane hydrate balls were placed on the same type of insulation and the central temperature of it was measured using a thermocouple every ten seconds.

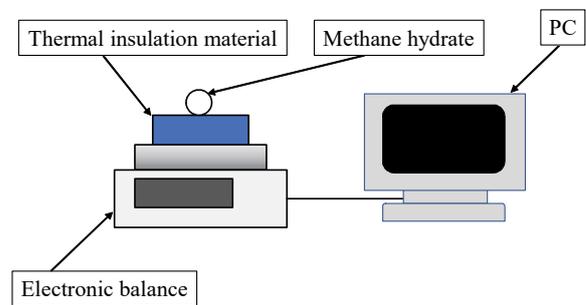


Fig. 2. Mass measurement experiment.

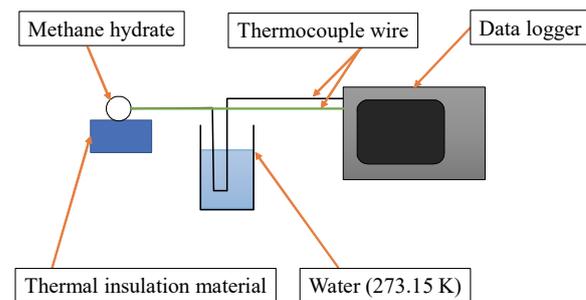


Fig. 3. Temperature measurement experiment.

Results and discussion

The calculated and the experimental results of the central temperature distribution of methane hydrate and the mass of evolved methane are shown in Fig. 4; the numerically calculated results are shown by the solid lines and the experimental results are plotted by the blue dots. The mass of evolved methane is shown by the thick line, and the central temperature of methane hydrate is shown by the thin line. The conditions used during the experiment were $\theta_0 = 202.75 \text{ K}$, $\rho_0 = 867.1 \text{ kg/m}^3$, $\theta_\infty = 292.15 \text{ K}$, $Y_0 = 0.443$ and $\lambda = 0.6 \text{ W/mK}$. Therefore, the Damköhler number was $D_a = 1.28 \times 10^{15}$ and the Biot number was $B_i = 0.75$. The Fig. 4 results show excellent agreement between simulation and experimentation for both the central temperature and the mass of evolved methane. As a consequence, the above listed experimental values of D_a and B_i were used as the standard values in the following numerical analysis.

The time histories of the temperature at the center of the methane hydrate ball, the mass of evolved methane and the reaction rate for different D_a numbers and different B_i numbers are shown in Figs. 5–7, (a) and (b), respectively. The values of D_a were changed between the standard value, and 1/10, 1/5, 1/2, 2, 5 and 10 times of the standard value for fixed standard B_i and the values of B_i were changed between the standard value, 1/10, 1/5, 1/2, 2, 5 and 10 times of the standard value for fixed standard D_a . The calculated results by using the standard value is shown by the thick line in the figures, and the results for other changed values are shown by the thin lines.

The central temperature increased consistently until near $t' = 0.18$ and $\theta' = 0.6$ for the different D_a numbers. Then the temperature rise rate was slowed

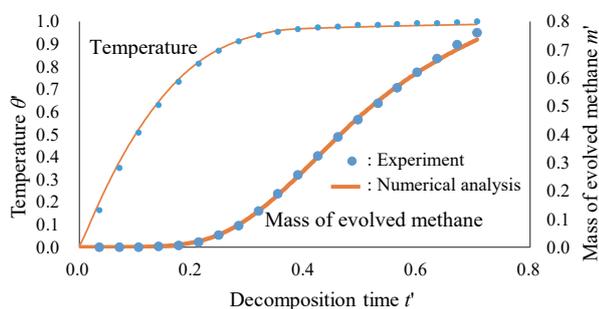


Fig. 4. Comparison between the calculated and the experimental results for the transient central temperature and the transient mass of evolved methane.

since endothermic reactions began to predominate. As D_a was increased, the rise rate in the temperature further slowed.

On the other hand, the temperature increased rapidly with an increase in B_i , and the mass of evolved methane also increased rapidly with increases in D_a and B_i . At maximum values of reaction rates the reactions rapidly proceeded to termination as D_a was increased. Although the reaction rate increased with increases in B_i , it did not change as much compared to when D_a was increased.

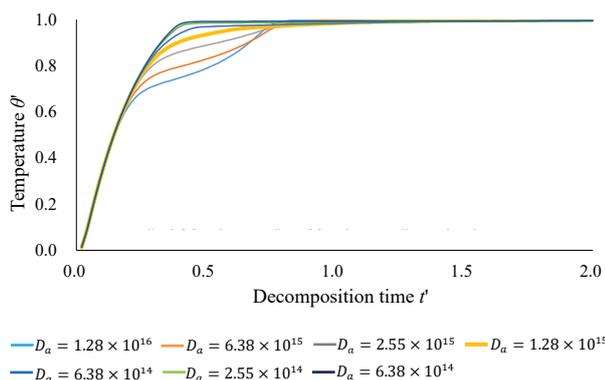
Conclusions

Both dimensionless numerical calculations and experimentally-acquired central temperatures and the masses of evolved methane from laboratory synthesized methane hydrate samples were in good agreement. The results were also in agreement as values of D_a or B_i numbers were changed, thereby elucidating the effects of dimensionless numbers on the decomposition of methane hydrates.

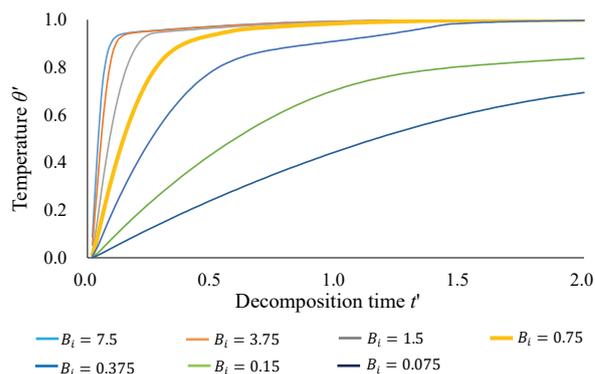
The central temperature of the methane hydrate samples changed uniformly for different D_a numbers, and the reaction rates became large as D_a was increased. At high reaction rates, the effects of endothermic reactions caused these increases to weaken. On the other hand, the temperature and the reaction rates increased rapidly with increases in B_i such that the maximum reaction rates were approximately equal for different D_a numbers. The mass of evolved methane also increased rapidly with increases in D_a and B_i .

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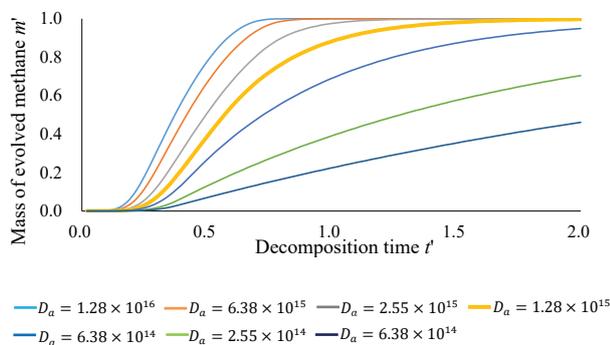


(a) Effects of D_a ($B_i = 0.75$).

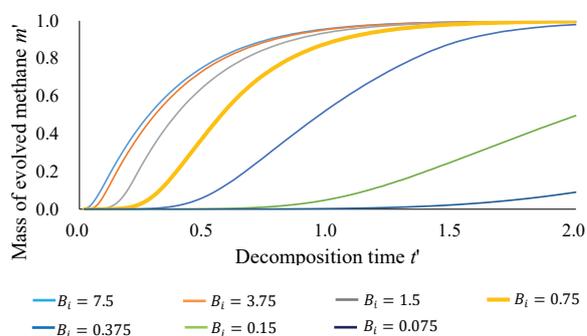


(b) Effects of B_i ($D_a = 1.28 \times 10^{15}$).

Fig. 5. Effects of D_a and B_i numbers on the transient central temperature.

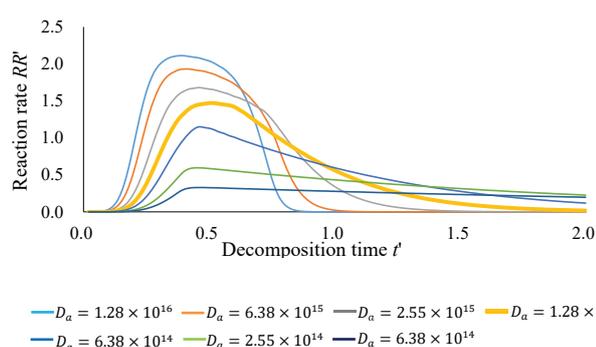


(a) Effects of D_a ($B_i = 0.75$).

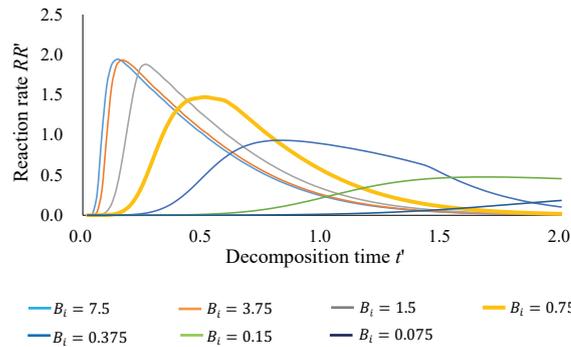


(b) Effects of B_i ($D_a = 1.28 \times 10^{15}$).

Fig. 6. Effects of D_a and B_i numbers on the transient evolved methane.



(a) Effects of D_a ($B_i = 0.75$).



(b) Effects of B_i ($D_a = 1.28 \times 10^{15}$).

Fig. 7. Effects of D_a and B_i numbers on the transient reaction rate.