Modeling of the combustion process of methane hydrate taking into account the kinetics of the decomposition process

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Abstract. This paper presents a mathematical model of the combustion process of methane gas hydrate in a closed volume, taking into account the kinetics of its decomposition. The system of basic equations, which includes the equations of conservation of mass (for the entire mixture of gases and each component separately), momentum and energy, is supplemented by the conditions for the balance of mass and heat at the boundary of the phase transition. In this case, the dominant factor determining the intensity of hydrate decomposition is the Arrhenius-type kinetics and conductive heat transfer. Based on the numerical solution of the obtained system of equations based on the method of large particles, the temperature and concentration fields of the system are obtained and analyzed. It is shown that at the initial moment of time, the rate of decomposition of the hydrate according to the model that takes into account the kinetics of the decomposition process is higher than that according to the model that does not take it into account.

1. Introduction

Gas hydrates are solid crystalline compounds of water and gas that form at specific pressures and temperatures. The main aspect of the study of hydrates is the huge reserves of natural gas accumulated in them [1]. Currently, gas hydrates are also considered as a reliable natural reservoir for the safe storage of greenhouse and industrial gases [2, 3]. It should be noted that mathematical models of the processes of decomposition of gas hydrates in porous media, as well as injection of CO₂ into methane hydrate formations, are presented, in particular, in [4 - 6].

Interest in the study of the combustion processes of gas hydrates is due to several factors: the high stability of the hydrate during transportation and its further use, the possibility of combustion at the development site and the use of this heat for the development of hydrate deposits [7]. Experimental works devoted to the study of the combustion of methane hydrate are presented, in particular, in works [8–10]. Flame propagation over methane hydrate was studied numerically in [11] and experimentally in [12, 13]. An analytical solution to the problem of the combustion of gas hydrate in the spherical-symmetric approximation, taking into account unsteady evaporation and diffusion of gas through the liquid layer, which appears during the dissociation of the hydrate, is presented in [14]. In this work, in contrast to [15], a mathematical model of the combustion of methane gas hydrate in a closed volume is presented, taking into account the kinetics of its decomposition.
2. Problem statement and basic equations

Consider a closed cylindrical volume of length $h$, in the end section ($0 < x < a$) of which there is a layer of methane gas hydrate, the initial thickness of which is equal to $a$. The rest of the section ($a < x < h$) is filled with a gas mixture including oxygen. In this case, in the region of thickness $L$ ($a < x < a + L$), directly adjacent to the gas hydrate, there is a mixture of air and methane, the content of which is sufficient to ignite the combustible gas mixture. The area ($a + L < x < h$) contains air. The entire gas mixture in the initial state is at a temperature $T_0$ and a pressure $p_0$. The initial state of the gas hydrate corresponds to the condition of its stability, i.e. $T_{h0} \leq T_S(p_0)$, where $T_S(p_0)$ is the equilibrium temperature of phase transitions corresponding to the pressure $p_0$.

Let the gas mixture ignite at the time $t = 0$ and the instantaneous combustion of methane in the region ($a < x < a + L$) with the formation of carbon dioxide and water according to the following chemical reaction scheme:

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + Q,$$

where $Q$ is the heat of oxidation reaction. Then, the thermal interaction of the hot gas mixture with the gas-hydrate layer begins across the boundary $x = a$. Due to this, the hydrate decomposes into water and methane. We will assume that the resulting water, due to contact with the hot gas mixture, instantly turns into steam. In this case, there will be diffusion mixing of the gas mixture consisting of methane released during the decomposition of gas hydrate, oxygen, carbon dioxide, nitrogen and water vapor. Moreover, this process will be accompanied by the combustion of methane hydrate.

We represent the mass concentration of the $i$-th component of the gas mixture as $C_i = r_i/r$ ($i = 1, 2, 3, 4, 5$). Here $\rho_i$ is the partial density of the $i$-th component; $\rho$ is the density of the gas mixture. Hereinafter, the subscripts $i = 1, 2, 3, 4, 5$ correspond to methane, oxygen, carbon dioxide, water vapor, and nitrogen. The pressure of the mixture in accordance with the Mendeleev-Clapeyron equation is written in the form:

$$p = \sum_{i} \frac{\rho_i}{\mu_i}RT,$$  \hspace{1cm} (1)

where $p$ and $T$ are the pressure and temperature of the gas mixture, respectively; $R$ is the universal gas constant; $\mu_i$ – molar masses of the mixture components.

The dynamics of the gas mixture, taking into account combustion, is described by the equations of mass (for the entire mixture and each component), impulses and energy:

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} = 0, \quad \frac{\partial (\rho C_i)}{\partial t} + \frac{\partial (\rho C_i u)}{\partial x} = D \frac{\partial^2 (\rho C_i)}{\partial x^2} + n_i J,$$

$$\frac{\partial (\rho u)}{\partial t} + \frac{\partial (\rho u^2)}{\partial x} = \nu \frac{\partial^2 (\rho u)}{\partial x^2}, \quad \frac{\partial (\rho C_p T)}{\partial t} + \frac{\partial (\rho C_p Tu)}{\partial x} = \frac{\partial \lambda}{\partial x} \frac{\partial \rho^2 T}{\partial x^2} + LJ.$$  \hspace{1cm} (2)

Here $t$ – is time, $x$ – is a spatial coordinate; $u$ – is the speed of the mixture; $\nu$, $D$ and $\lambda$ – coefficients of viscosity, diffusion and thermal conductivity; $J$ – is the combustion rate, $L$ – is the specific heat of combustion of methane, $n_i$ are the stoichiometric coefficients: $n_1 = -1, n_2 = -2, n_3 = 1, n_4 = 2, n_5 = 0$. We represent the specific heat capacity $c_p$ of the gas mixture in the form $c_p = \sum_i c_{pi} \rho_i/\rho$, where $c_{pi}$ – specific heat capacity at constant pressure of the $i$-th component.

It should be noted that heat and mass transfer in the gas mixture during combustion is carried out due to turbulent mixing of the components. Therefore, these processes should be described by some turbulent transport models, such as "k-\omega" or "k-\omega" -models [16]. In this work, for a simplified analysis of heat transfer in a steady combustion process, the coefficients $\nu$ and $D$ are taken constant. In this case, the value of the thermal conductivity coefficient $\lambda$ of the gas mixture at each of its points is calculated.
through the thermal diffusivity coefficient $\kappa$, the value of which, like the values of $\nu$ and $D$, is taken constant:

$$\lambda = \kappa \cdot \rho c.$$ 

The combustion rate for the diffusion regime has the form [17]:

$$J = \frac{\rho \mu c_1}{\mu_1} - \frac{\rho \mu c_2}{\mu_2} \cdot k_r \exp \left( - \frac{E_a}{RT} \right).$$

Here $\mu_1$ and $\mu_2$ – are the molar masses of the fuel (methane) and oxidizer (oxygen); $\mu$ – is the molar mass of the mixture; $k_r$ – is the reaction constant; $E_a$ – activation energy.

The equation of thermal conductivity in the region of the gas hydrate layer has the form:

$$\rho_h c_h \frac{\partial T}{\partial t} = \lambda_h \frac{\partial^2 T}{\partial x^2},$$

where $\rho_h$, $c_h$, $\lambda_h$ are the density, heat capacity, and thermal conductivity of the gas hydrate.

The presented system of equations (1) - (4) must be supplemented with the conditions following from the conditions for the balance of mass and heat at the moving boundary of the phase transition $x = x(s)$, which separates the regions containing the gas hydrate and the gas mixture:

$$\rho(s) D \frac{\partial C_1}{\partial x} = \rho_h \left(G - C_{(s)}\right) \hat{x}(s),$$

$$\rho(s) D \frac{\partial C_2}{\partial x} = -\rho_h C_{(s)} \hat{x}(s),$$

$$\rho(s) D \frac{\partial C_3}{\partial x} = -\rho_h C_{(s)} \hat{x}(s).$$

Here $G$ – is the mass fraction of gas in the hydrate; $\hat{x}(s) = dx(s)/dt$ – the speed of movement of the boundary of phase transitions. The subscript $(s)$ corresponds to the values of the parameters at the moving boundary of phase transitions.

The heat balance equation at the boundary $x = x(s)$ has the form:

$$-\lambda_h \left( \frac{\partial T}{\partial x} \right)_{x = x(s)} + \lambda_h \left( \frac{\partial T}{\partial x} \right)_{x = x(s)} = \left( \rho_w L_w + (1 - G) \rho_n L_n \right) \hat{x}(s),$$

where $\rho_w$ – is the density of water; $\tilde{L}_w$ – reduced heat of decomposition of gas hydrate; $L_n$ – are the specific heats of decomposition of gas hydrate and evaporation of water, respectively. The signs “−” and “+” correspond to the values of the parameters at the boundary $x = x(s)$ from the side of the hydrate and the gas mixture. The temperature at this boundary will be considered continuous: $T_{(s)} = T_{(s)} = T(s)$.

In contrast to the traditional Stefan problems, we will assume that the temperature $T(s)$ at the frontal boundary of phase transitions is an unknown variable parameter. By analogy with the well-known Hertz-Knudsen theory for nonequilibrium evaporation of liquids [18], for the decomposition intensity per unit area of the phase transition front, we can write:

$$j = -\rho_h \hat{x}(s) = -k_h \left(T_{(s)} - T_s(p)\right).$$

Here $T_s(p)$ is the equilibrium temperature of phase transitions corresponding to pressure $p$ and determined from the expression:

$$T_s(p) = T_{s0} + T_s \ln \left( \frac{p}{p_0} \right),$$

where $T_{s0}$ is the reference temperature.
where \( T_{s0} \) – is the equilibrium temperature of the hydrate corresponding to the pressure \( p_{s0} \); \( T_{s*} \) – is an empirical parameter. The dependence of the proportionality coefficient \( k_0 \) on temperature is taken according to the Arrhenius law:

\[
k_0 = k_{s0} \exp\left(-\frac{E_s}{RT_s}\right).
\]

Expressions (7) adopted for the intensity of the decomposition process, taking into account (8), are a certain generalization of the kinetics of tomochemical reactions [19].

We take the reduced heat of decomposition taking into account the overheating of the hydrate at the decomposition front with respect to the equilibrium temperature of phase transitions for the pressure \( p \):

\[
L_s = L_{s0} - c_s \left(T_{s0} - T_s(p)\right),
\]

where \( L_{s0} \) – is the specific heat of decomposition corresponding to the equilibrium regime at the pressure \( p \).

In addition, we assume that the partial pressure of water vapor at the boundary \( x = x_{i(0)} \), \( p_{s(i)} \) is determined by the Clapeyron - Clausius equation:

\[
p_{s(i)} = p_* \exp\left(-\frac{T_*}{T_{s(i)}}\right),
\]

where \( p_* \), \( T_* \) – are empirical parameters.

The conditions on the outer boundaries of the cylindrical volume \( (x = 0 \) and \( x = h \) are presented in the form:

\[
t > 0: \frac{\partial T}{\partial x}\bigg|_{x=0} = 0, \quad \frac{\partial T}{\partial x}\bigg|_{x=h} = 0, \quad \frac{\partial p}{\partial x}\bigg|_{x=h} = 0, \quad \frac{\partial C_v}{\partial x}\bigg|_{x=h} = 0. \quad (i = 1, \ldots, 5)
\]

The initial conditions are as follows:

\[
t = 0: T = T_{s0} \quad (0 \leq x \leq a); \quad T = T_0, \quad C_v = C_{v0} \quad (a < x \leq h). \quad (i = 1, \ldots, 5)
\]

The system of equations (1) - (10) with initial-boundary conditions (11) and (12) is closed; its solution is carried out by the method of large particles [20].

For the hydrate to ignite, some heat must be generated near the hydrate's surface. As a heat source, as noted earlier, you can use a layer of a gas mixture with a thickness \( L (a < x < a + L) \) containing gaseous methane. The initial mass concentration of methane in this area is selected in the range of molecular values of the transfer coefficients are taken. However, during combustion, a convective gas flow is activated due to the temperature and pressure difference between the flame area and the surrounding gas area. This is followed by the formation of turbulent eddies. Turbulent transport models assume that the values of the variable coefficients of mass transfer, momentum, and heat are approximately equal to \( D = \nu = \lambda/\rho c \). This corresponds to the Lewis number and Prandtl number \( Le = Pr = 1 \). In this work, the simulation was carried out at different values of the transport coefficients corresponding to both molecular and turbulent transport. This allows the evolution of turbulent transport to be analyzed without complex turbulence modeling.

For the parameters characterizing the system, the following values are taken: \( \mu_1 = 0.016 \text{ kg/mol}, \mu_2 = 0.032 \text{ kg/mol}, \mu_3 = 0.044 \text{ kg/mol}, \mu_4 = 0.018 \text{ kg/mol}, \mu_5 = 0.028 \text{ kg/mol}, \quad c_1 = 2483 \text{ J/(kg} \cdot \text{K}),\quad c_2 = 913 \text{ J/(kg} \cdot \text{K}), \quad c_3 = 837 \text{ J/(kg} \cdot \text{K}), \quad c_4 = 2020 \text{ J/(kg} \cdot \text{K}), \quad c_5 = 1051 \text{ J/(kg} \cdot \text{K}), \quad \lambda_0 = 0.45 \text{ W/(m} \cdot \text{K}), \quad \lambda = 1.0 \text{ W/(m} \cdot \text{K}), \quad L = 5 \cdot 10^5 \text{ J/kg}, \quad L_h = 5 \cdot 10^3 \text{ J/kg}, \quad L_m = 2.38 \cdot 10^8 \text{ J/kg}, \quad E_0 = 1.7 \cdot 10^4 \text{ J/mol}, \quad k_r = 2 \cdot 10^5 \text{ m}^3/\text{s}, \quad L_t
\[ E_h = 3 \times 10^4 \text{J/mol}, \quad k_0 = 1.2 \times 10^4 \text{kg/(m}^2\text{s-K}), \quad R = 8.31 \text{J/(mol-K)}, \quad G = 0.12, \quad T_{l0} = 300 \text{K}, \quad T \approx 10 \text{K}, \]
\[ p_0 = 5.5 \text{MPa}, \quad T_0 = 280 \text{K}, \quad p_0 = 5 \text{MPa}, \quad h = 1.2 \text{m}, \quad a = 0.05 \text{m}. \]

Note that when writing the initial conditions (10), instead of the mass concentrations \( C_i \), we will use the volume concentrations \( \alpha_i \) according to the relation. In this case, we assume in all calculations that the volumetric content of methane in the layer \((a \leq x \leq a + L)\) \( \alpha_1 = 5 \% \), which corresponds to the combustion interval for the air mixture \((4 \% < \alpha_1 < 15 \%)\). In the other part of the computational domain, the gas is air. Thus, for the initial volumetric concentrations of the components of the gas mixture, we have the following values:

\[
\begin{align*}
\alpha_1 &= \begin{cases} 
0.05, & a \leq x \leq a + L \\
0, & a + L \leq x \leq h,
\end{cases} \\
\alpha_2 &= \begin{cases} 
0.19, & a \leq x \leq a + L \\
0.2, & a + L \leq x \leq h,
\end{cases} \\
\alpha_3 &= \begin{cases} 
0.0095, & a \leq x \leq a + L \\
0.01, & a + L \leq x \leq h,
\end{cases} \\
\alpha_4 &= \begin{cases} 
0.0095, & a \leq x \leq a + L \\
0.01, & a + L \leq x \leq h,
\end{cases} \\
\alpha_5 &= \begin{cases} 
0.0741, & a \leq x \leq a + L \\
0.78, & a + L \leq x \leq h.
\end{cases}
\end{align*}
\]

3. Discussion
We will assume that in the initial state in the layer \((a \leq x \leq a + L)\) methane and oxygen are mixed evenly, therefore the combustion of the gas mixture occurs rather quickly (~10^{-3} s). In this case, the process of heat transfer from gas to hydrate occurs within a few seconds. To initiate the combustion of the hydrate at the initial moment of time, a layer of a gas mixture containing methane with a thickness of \(L = 2 \text{ cm}\) was used.

Figure 1 shows the distributions of the temperature of the system and the mass concentration of the components of the gas mixture for the time instant \(t = 30 \text{s}\). The values of the transfer coefficients were assumed to be 0.1 m²/s. From figure 1, the concentrations of the oxidant (oxygen) and nitrogen increase with increasing coordinate, while the concentration of methane and water vapor, on the contrary, decreases. It also follows from figure 1 that, near a thin layer from the surface of methane hydrate, the concentration of carbon dioxide increases, and then, as we move to the right boundary, it decreases.

![Figure 1](image-url)

**Figure 1.** Distribution of mass concentration of gas components at the moment of 30 s. Lines 1, 2, 3, 4, 5 correspond to the concentrations of methane, oxygen, carbon dioxide, water vapor, nitrogen.

The dynamics of the maximum temperature of the gas mixture as a function of time is shown in figure 2. Curve 1 is plotted taking into account the kinetics of the hydrate decomposition process, line 2 - without taking it into account according to the model presented in [15]. As follows from figure, Taking into account the kinetics of the hydrate decomposition process, the highest temperature of the gas
mixture is 1700 K, and without taking it into account - about 1100 K. In this case, these temperatures are realized at the initial moment of the combustion process; then the maximum temperature of the gas mixture decreases.

![Figure 2. Dependence of the maximum temperature of the gas mixture on time taking into account (1) and disregarding (2) the kinetics of the hydrate decomposition process.](image)

In figure 3 shows the time dependence of the motion of the phase transition boundary (a is the initial coordinate corresponding to the gas hydrate boundary) with allowance for (1) and without regard to (2) the kinetics of the decomposition process. As follows from figure 3, the rate of decomposition of the hydrate decreases with time, which corresponds to a decrease in the proportion of heat supplied to its boundary due to the burnout of methane. In addition, it follows from figure 3 that at the initial moment of time, the rate of hydrate decomposition according to the model that takes into account the kinetics of the decomposition process is higher than that according to the model that does not take it into account. This is explained by the fact that in the first case, as follows from figures 1 and 2, a more intense heat release occurs, which leads to an increase in the rate of hydrate decomposition and rapid combustion of methane. As a result, the rate of decomposition of the hydrate decreases with time even in comparison with the case when the calculation is carried out without taking into account the kinetics of the process.

![Figure 3. Time dependence of the movement of the gas hydrate boundary taking into account (1) and disregarding (2) the kinetics of the hydrate decomposition process.](image)
4. Conclusion
A mathematical model of the combustion process of methane gas hydrate in a closed volume is presented, taking into account the kinetics of its decomposition. It is shown that at the initial moment of time, the rate of decomposition of the hydrate according to the model that takes into account the kinetics of the decomposition process is higher than that according to the model that does not take it into account.

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References
[1] Soloviev V A 2003 Rossiyskiy Khimicheskiy Zhurnal 47(3) 59-69
[2] Anshits A, Kirik N and Shibistov B 2006 Advances in the Geological Storage of Carbon Dioxide 65 93-102
[3] Qi Li, Li X, Wei N and Fang Zh 2011 Energy Procedia 4 6015-20
[4] Gimaltdinov I K, Stolpovsky M V and Dodova M I 2017 Bulletin of the Tomsk Polytechnic University Geo Assets Engineering 328(6) 91-8
[5] Stolpovsky M V, Khasanov M K and Kulakov P A 2018 Izvestia of the Tula State University Earth sciences 2 101-12
[6] Davletshina M R, Stolpovsky M V and Chiglintseva A S 2020 Technologies for methane production from hydrogen using a heated liquid IOP Conf. Ser. Mater. Sci. Eng. 919 062070
[7] Ma S, Zheng J-N, Tian M, Tang D and Yang M 2020 Fuel 261 116364
[8] Misyura S Y 2021 AIP Conference Proceedings 2337 020013
[9] Nakoryakov V E, Misyura S Y, Elistratov S L, Manakov A Y and Sizikov A A 2013 Journal of Engineering Thermophysics 22 169-73
[10] Misyura S Y 2020 Applied Energy 270 115042
[11] Kitamura Y, Nakajo K and Ueda T 2002 Proceedings of the 4th International Conference on Gas Hydrate 4 1055-8
[12] Maruyama Y, Fuse M J, Yokomori T, Ohmura R, Watanabe S, Iwasaki T, Iwabuchi W and Ueda T 2013 Proc. Combust. Inst. 34 2131-8
[13] Nakamura Y, Katsuki R, Yokomori T, Ohmura R, Takahashi M, Iwasaki T, Uchida K and Ueda T 2009 Energy Fuels 23 1445-9
[14] Bar-Kohany T and Sirignano W A 2016 Combustion and Flame 163 284-300
[15] Davletshina M R, Gimaltdinov I K, Stolpovsky M V, Akchurina V A 2021 IOP Conf. Series: Materials Science and Engineering 1047 012159
[16] Wilcox D C 2006 Turbulence Modeling for CFD (Palm Drive, La Canada, California: DCW Industries) 515
[17] Smirnov N N, Nikitin V F and Legros J C 2000 Combustion and Flame 123 46-67
[18] Nigmatulin R I 1987 Dynamics of multiphase media 1 (Moscow: Nauka) 464
[19] Stromberg A G and Semechko D P 2001 Physical Chemistry (Moscow: Higher School of Economics)
[20] Belotserkovsky O M and Davydov Y M 1982 The method of large particles in gas dynamics (Moscow: Nauka)