Simulation of combustion of a flat layer of methane hydrate

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Abstract. A mathematical model of the combustion of a flat layer of methane hydrate is presented, which includes the continuity equations for the gas mixture, the conservation of the mass of each of its components, as well as the heat balance in the gas and gas hydrate layers. In addition, the system is supplemented by the conditions following the laws of conservation of mass and heat at the boundary of the "gas hydrate - gas" phase transition. The distributions of the concentration fields of the gas mixture, as well as the temperature fields in the gas hydrate and gas, are plotted.

1. Introduction
Gas hydrates are currently considered a promising source of hydrocarbons. According to estimates, the world's gas reserves in gas hydrates amount to about 500 trillion m$^3$ [1]. Another aspect of the study of hydrates is the fact that they can accumulate sufficient volumes of greenhouse gases [2–4]. For example, a number of scientists propose various models for the injection of carbon dioxide (both in liquid and gaseous forms) into natural accumulations of hydrates, which, along with their conservation, allows the release of natural gas (mainly methane) from the hydrate composition. Mathematical models of the processes of formation and decomposition of gas hydrate, as well as injection of CO$_2$ (both in liquid and gaseous forms) were considered, in particular, in [5–7].

The combustion of hydrates was considered in works [8, 9]. A mathematical model of the combustion of a solid gas hydrate core is presented in [10]. Note that the combustion of gas is a unique process, because the mass content of water in the hydrate is 87.1%. The experimental data [8, 11] shows that if we ensure the flow of water from the surface of the gas hydrate, then the heat of combustion of methane released during the dissociation is sufficient to maintain combustion.

This paper presents a mathematical model of the combustion process of a flat layer of methane gas hydrate placed in a gaseous medium with an oxidizer. The mathematical model includes the continuity equations for the gas mixture, as well as for each of its individual components. In addition, the model is supplemented by the equations of thermal conductivity for gas and gas hydrate, as well as the conditions following from the laws of conservation of mass and heat at the boundary of the “gas hydrate - gas” phase transition.

2. Problem statement and basic equations
Let us consider a flat hydrate layer with the initial thickness $a_0$ and temperature $T_0$, placed in an atmosphere with an oxidizing agent. The temperature and pressure of the atmosphere are set equal to $T_a$ and $p_a$ will be assumed to be $T_a > T_i(p_a)$ where $T_i(p_a)$ is the equilibrium temperature of hydrate formation corresponding to the pressure $p_a$. Then, because the temperature of the atmosphere exceeds the equilibrium temperature of hydrate formation at a given pressure, the methane gas hydrate begins...
to decompose into methane and water. Thus, in a certain layer near the gas hydrate there will be a fuel - methane (sufficient for ignition), the combustion of which is carried out according to the equation [12]:

\[ CH_4 + 2O_2 + 2 \cdot 3,762N_2 \rightarrow CO_2 + 2H_2O + 2 \cdot 3,762N_2 + Q. \]

Here \( Q \) is the amount of heat released during the combustion of methane. We will assume that the system consists of two regions, one of which \((0 \leq z \leq z_{(s)})\) contains gas hydrate, and the other \((z > z_{(s)})\) corresponds to the gas phase. Coordinate \( z_{(s)} \) - corresponds to the boundary of the «gas hydrate – gas»

The system of basic equations for the region \((z > z_{(s)})\), which is the continuity equations for the gas mixture as a whole and each of its components, heat flow, and Dalton's law has the form:

\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho v}{\partial z} = 0, \\
\frac{\partial}{\partial t} \left( \rho k_i \right) + \frac{\partial}{\partial z} \left( \rho v k_i \right) = \frac{\partial}{\partial z} \left( \rho D \frac{\partial k_i}{\partial z} \right) + J_i, \\
\frac{\partial}{\partial t} \left( \rho c_p T \right) + \frac{\partial}{\partial z} \left( \rho v c_p T \right) = \frac{\partial}{\partial z} \left( \lambda \frac{\partial c_p T}{\partial z} \right) - \sum_{i=1}^{s} J_i h_i^0, \\
p = \rho R_g T \sum_{i=1}^{5} \frac{k_i}{m_i}.
\]

Here \( t \) – time, \( v \) – speed, \( k_i = \rho_i/\rho \) – mass concentration of the \( i \)-th component of the gas mixture; \( \rho_i \) and \( \rho \) – respectively, the density and molar mass of the \( i \)-th component; \( \mu_i \) – mixture density; \( D \) – diffusion coefficient; \( L_5 \) is the specific heat of combustion of methane; \( R_g \) is the universal gas constant. We estimate the specific heat capacity of the mixture using the specific heat capacities of its components:

\[
c_p = \sum_{i=1}^{5} c_{pi} \cdot k_i.
\]

Further, \( i = 1, 2, ..., 5 \) corresponds to oxygen (O\(_2\)), carbon dioxide (CO\(_2\)), nitrogen (N\(_2\)), water vapour (H\(_2\)O) and methane (CH\(_4\)).

Since the problem estimates the motion of a gas mixture with velocities much lower than the speed of sound, then instead of the equation of momenta, we will consider the condition of homobaricity of the gas mixture [8]:

\[
p = p_a = \text{const}.
\]

In a layer of gas hydrate \((0 < z \leq z_{(s)})\) the heat conduction equation has the form:

\[
P_h c_h \frac{\partial T}{\partial t} = \lambda_h \frac{\partial^2 T}{\partial z^2}.
\]

Here \( \rho_h, \ c_h \) and \( \lambda_h \) are the density, specific heat, and thermal conductivity of the gas hydrate, respectively.

In addition, the system of equations (1)–(5) must be supplemented with the conditions for the balance of mass and heat at the boundary of the phase transition \( z = z_{(s)} \) between the surface of the gas hydrate and the gas mixture. The law of conservation of mass written for the entire system «gas hydrate - gas mixture» shows:
\[ u_{i} = \dot{z}_{i} \left( 1 - \frac{\rho_{h}}{\rho_{i}} \right). \] (4)

Here \( \dot{z}_{i} = \frac{dz_{i}}{dt} \) is the speed of the boundary movement \( z = z_{i} \); the subscript \( s \) in parentheses corresponds to the values of the parameters at the phase transition boundary. Considering that the mass content of gas in the composition of the hydrate equals to \( G \) (water, respectively, equals \( 1 - G \)) from the law of conservation of mass for water and methane, you can get:

\[ \rho_{i}(s) \frac{\partial k_{i}}{\partial z} \bigg|_{z = z_{i}(s)} = \rho_{h} \left( (1 - G) - k_{u}(s) \right) \dot{z}_{i}(s), \quad \rho_{i}(s) \frac{\partial k_{i}}{\partial z} \bigg|_{z = z_{i}(s)} = \rho_{h} \left( G - k_{s}(s) \right) \dot{z}_{i}(s). \] (5)

In a similar way, you can write the ratios for oxygen and carbon dioxide:

\[ \rho_{i}(s) \frac{\partial k_{i}}{\partial z} \bigg|_{z = z_{i}(s)} = -\rho_{h} k_{u}(s) \dot{z}_{i}(s), \quad \rho_{i}(s) \frac{\partial k_{i}}{\partial z} \bigg|_{z = z_{i}(s)} = -\rho_{h} k_{s}(s) \dot{z}_{i}(s). \] (6)

In addition, we write down the conditions for the absence of a temperature jump and heat balance at the boundary \( z = z_{i} \) as:

\[ T^{(-)} = T^{(+)} = T_{i}, \quad \frac{\lambda_{h}}{\partial z} \bigg|_{z = z_{i}(s)} + \lambda_{s} \frac{\partial T}{\partial z} \bigg|_{z = z_{i}(s)} = \left( \rho_{i} l_{h} + \left( 1 - G \right) \rho_{w} l_{w} \right) \dot{z}_{i}(s). \] (7)

Here \( \rho_{w} \) – density of water; \( l_{h} \) and \( l_{w} \) are specific heats of decomposition of hydrate and vaporization; symbols \((-)\) and \((+)\) mean that the parameter values correspond to gas hydrate and gas mixture. Note that, since the water released during the decomposition of the gas hydrate immediately transforms into a vapor state, the heat balance equation is written taking into account the costs for the decomposition of the gas hydrate and for the evaporation of water.

In addition, at the boundary \( z = z_{i} \) the partial vapor pressure \( p_{u}(s) \) and the temperature \( T_{i} \) fulfill the Clapeyron – Clausius equation, which can be written as [15]:

\[ p_{u}(s) = p_{*} \exp \left( -\frac{T_{*}}{T_{i}} \right), \] (8)

where \( p_{*} \) and \( T_{*} \) are empirical parameters.

On the other hand, for steam and the entire gas mixture on it, the following relations are valid:

\[ p_{u}(s) = \rho_{u}(s) R_{u} T_{i}, \quad p_{i} = \rho_{i} R_{i} T_{i}, \quad R_{i} = \frac{R_{g}}{\mu_{i}}, \quad R_{i} = \frac{R_{g} \sum_{i=1}^{s} k_{u}(s)}{\mu_{i}}. \] (9)

Here \( \rho_{u}(s) \) and \( \rho_{i} \) are the partial vapour density and the mixture density at the phase transition boundary. From (9) you can get:

\[ p_{u}(s) = p k_{u}(s) R_{u} / R_{i}. \] (10)

Equations (8) and (10) make it possible to determine the temperature \( T_{i} \) from the known value of \( k_{u}(s) \).

We represent the initial conditions \( (t = 0) \) as:

\[ z > z_{i}: T = T_{a}, k_{1} = k_{a}, k_{2} = k_{b}, k_{3} = 1 - k_{a}, k_{i} = 0 \quad (i = 2, 4, 5), \]

\[ 0 \leq z \leq z_{i}: T = T_{b}. \] (11)
Conditions far from the gas hydrate layer \((z \to \infty)\) in the form:

\[ z \to \infty : T = T_0, k_i = k_{10}, k_i = 1 - k_{10}, k_i = 0 \quad (i = 2, 4, 5). \] (12)

At the boundary \(z = 0\), the conditions are as follows:

\[ z = 0 : T = T_0. \] (13)

The resulting system of equations (1)-(13) is closed. To solve it, the method of catching the front into the node of the spatial grid is used [13]. According to this method, for the unknown time step \(\tau\) to be determined, the front of the phase transition moves along the coordinate by the value \(h\). At the same time, to find the concentration and temperature fields in the gas region, we use the Schwab-Zeldovich analytical method by analogy with the works [14] under the assumption of a diffusion combustion mode, according to which there is no oxidizer below the flame surface, and fuel (methane) above.

3. Calculations results

In figure 1 for the moment of time \(t = 1.5\) s, the temperature distribution of the system is shown during combustion of a flat layer of methane hydrate with a thickness of \(a_0 = 0.5\) m in a gaseous medium with an oxidizer. For other parameters characterizing the system, the following values are taken: \(T_0 = 280\) K, \(T_a = 300\) K, \(p_a = 10^5\) Pa, \(D = 10^{-5}\) m²/sec, \(c_h = 913\) J/(kg · K), \(c_d = 837\) J/(kg · K), \(c_a = 1146\) J/(kg · K), \(c_r = 2020\) J/(kg · K), \(c_m = 2483\) J/(kg · K), \(\lambda = 0.0469\) W/(m · K), \(\lambda_h = 0.45\) W/(m · K), \(m_t = 0.032\) kg/mol, \(m_d = 0.044\) kg/mol, \(m_a = 0.028\) kg/mol, \(m_r = 0.018\) kg/mol, \(m_m = 0.016\) kg/mol, \(T_f = 4616\) K, \(p_f = 27542\) MPa, \(\rho_h = 900\) kg/m³, \(\rho_w = 1000\) kg/m³, \(G = 0.12\), \(l_h = 5 \times 105\) J/kg, \(l_w = 2.26 \times 10^6\) J/kg. The specific heat of combustion of methane was assumed to be \(L = 50\) MJ/kg. It follows from the figure that the temperature in the area of the gas hydrate changes insignificantly (it is necessary to put \(a_0\) on the figure). In this case, the temperature in the gas moving from the phase transition boundary first increases and then decreases to the initial value. This is due to the fact that the highest temperature is observed at the point \(z = z^*\), the coordinate of which corresponds to the combustion front. The temperature at the peak reaches a value of about 2000 K, which corresponds to the flame front.

![Figure 1. Temperature distribution of the «gas hydrate - atmosphere» system.](image)

Figure 2 shows the distributions of the dependence of the concentrations of the gas phase components on the coordinate for the time instant \(t = 1.5\) s. From the figure, according to the presented model, it follows that before the combustion front \((z < z^*)\) the methane concentration decreases, and oxygen is absent. After the combustion front \((z > z^*)\), there is no fuel (methane), and the oxidizer concentration, on the contrary, increases to its initial value. The nitrogen concentration increases from zero to its original value. For carbon dioxide, the concentration increases from zero at the phase transition boundary to a maximum value at the combustion front, then it decreases to zero. The concentration of water vapor reaches a maximum value at the front of the phase transition and then decreases to zero far from the hydraion layer.
Figure 2. Dependences of the concentrations of the components of the gas mixture on the coordinate: a: 1 – O₂, 2 – CO₂, 5 – CH₄; b: 3 – N₂, 4 – H₂O.

4. Conclusion
A mathematical model of the combustion of a flat gas hydrate layer in an atmosphere with an oxidizer is presented, which includes the continuity equations for the gas mixture, the conservation of the mass of each of its components, as well as the heat balance in the gas and gas hydrate layers. The solution of the resulting system of equations in the gas phase is carried out using the Schwab-Zel’ dovich method. The distributions of the concentration field of the gas mixture, as well as the temperature field in the gas hydrate and gas are plotted.

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References
[1] Sloan E D and Koh C A 2008 Clathrate hydrates of natural gases (Boca Raton: CRC Press Taylor and Francis Group)
[2] Lee Y, Kim Y, Lee J et al. 2015 Appl. Energy 150 120-7
[3] Lee H, Seo Y, Seo Y-T et al. 2003 Angew. Chem. Int. Ed. 42 5048-51
[4] Yuan Q, Sun C-Y, Yang X et al. 2012 Energy 40 47-58
[5] Shagapov V Sh and Musakaev N G 2016 Dynamics of hydrate formation and decomposition in gas production, transportation and storage systems (Moscow: Nauka)
[6] Khasanov M K, Stolpovsky M V and Gimaltdinov I K 2018 International Journal of Heat and Mass Transfer 127 21-8
[7] Khasanov M K, Stolpovsky M V and Gimaltdinov I K 2019 International Journal of Heat and Mass Transfer 132 529-38
[8] Nakoryakov V E, Misyura S Ya, Elistratov S L et al. 2013 Journal of Engineering Thermophysics 22(3) 169-73
[9] Misyura S Y 2016 Energy 103 430-9
[10] Dagan Y and Kohany T B 2018 Combustion and Flame 193 25-35
[11] Roshandell M, Santacana-Vall J, Karnani S et al. 2016 Combustion Science and Technology 188 2137-48
[12] Warnatz J, Maas W and Dibble R 2003 Combustion. Physical and chemical aspects, modeling.
experiments, the formation of pollutants (Moscow: FIZMATLIT)

[13] Vasiliev V I, Popov V V and Timofeeva T S 2000 Computational Methods in the Development of oil and gas fields (Novosibirsk)

[14] Zverev I N and Smirnov N N 1987 Gas Dynamics of Combustion (Moscow: Publishing house of Moscow. University)

[15] Nigmatulin R I 1987 Dynamics of Multiphase Media (Moscow: Nauka)