Dissociation of Gas Hydrates in a Combustion Environment

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***Abstract* — This paper proposes mathematical models of gas hydrate decomposition in high-temperature media. These models are based on heat and mass balances with a set of assumptions about transfer mechanisms and features of chemical reactions. The calculations provide an insight into dynamics of hydrate particles in a flame environment and shed light on possible results of interaction between the combustion front and emission of gas and vapor. Several examples are provided to illustrate the potential of hydrates as a fuel and as a flame extinguishing material. The developed models enable the generation of numerical estimates, which can be employed to design technologies for beneficial uses of gas hydrates.**

***Index Terms* — gas hydrates, thermal processing, diffusion flame, dissociation kinetics.**

I. Introduction

Gas hydrates are widespread in nature and constitute a significant part of hydrocarbon reserves [1, 2]. However, gas hydrates are not viewed as a significant energy resource and, according to technological forecasts, will not become significant for decades to come [3, 4]. This is due to their physicochemical and geochemical characteristics [5–7]. There are a small number of projects aimed at extracting gas hydrates (mostly research projects), or using them as materials or energy carriers (due to their specific properties) [8–10]. Interest in hydrates is associated, among other things, with their possible role in climate change processes [11].

Hydrates of combustible gases can be considered as a low-grade fuel (the water content in the crystals usually exceeds 70–80%). Nevertheless, there are still combustion conditions that enable efficient use of combustible matter. First of all, this is the diffusion combustion of powders: as experiments show [12–14], it is possible to select the conditions under which the emitted gas burns above the layer, providing the required level of combustion temperature at which the flame-to-surface heat flow maintains hydrate decomposition sufficient for self-sustained combustion.

Hydrates of non-flammable gases can be used as extinguishing agents [10]. In addition to high water content (also in crystalline form), hydrates are characterized by a higher latent heat of decomposition (since dissociation is an endothermic process), while the decomposition itself leads to the release of non-flammable gases that dilute the reacting medium.

Most studies on the interaction of gas hydrates with flames focus on experiments. Theoretical works usually rely on rather rough assumptions about the occurrence of physicochemical processes, especially in interphase regions. The authors of [15, 16] consider the one-dimensional non-stationary problem of the dissociation front propagation and phase transitions during the diffusion combustion of released methane. In [17, 18], the hydrate layer is considered as a bundle of pipes through which the

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components of the combustible mixture flow. The numerical description of experimentally observed non-stationary features of surface behavior remains impossible (although it is not clear whether such details are required for plausible modelling). In the study of combustion processes, we encounter a multitude of temporal and spatial scales associated with different components of the overall process, and significant changes in their ratios during the development of the process.

Mathematical models of flat hydrate layer dissociation are proposed in the papers [19] (for the diffusive gas transfer in the continuous approximation) and [20] (for the filtration intraparticle transfer). In [21], the latter model was verified using experimental data. In this case, however, the conditions on the outer surface of the powder layer are approximate. In [22], this model is used to estimate the stability of a methane-air-steam diffusion flame (such flames are considered experimentally and theoretically in [23, 24]).

Extinguishing flames with carbon dioxide hydrate is investigated in several experimental works [25, 26], where the hydrate is used in various forms (falling powder, stationary backfill). These experiments show the greater relative efficiency of hydrate compared to ice and water. In order to conduct a more detailed analysis of flame extinction mechanisms, suitable mathematical models are needed to study the impact of various factors, such as hydrodynamics and chemical reactions. Generally, such mathematical models tend to be quite complex. As in the case of the combustion of flammable gases emitted during hydrate dissociation, they must include a full-scale description of involved physicochemical processes, including interphase interactions. The huge number of elementary chemical reactions and multiple coexisting phases practically prevent any attempts to study numerically any realistic problem. In this regard, "computable", simplified models that contain the main features, and at the same time are not overloaded with a large number of details (that do not always have a decisive influence) are of greater interest.

The purpose of this work is to construct simple mathematical models of the stability of hydrocarbon flames in the presence of gas hydrates and to conduct numerical studies based on these models to clarify the basic mechanisms of observed critical phenomena. Exclusion of a detailed chemical description of flames inevitably reduces the problem to the thermal stability problem. On the one hand, this significantly simplifies the analysis of flame thermal stability, since it has a very wide range of tools [27], but on the other hand, this reduction narrows the applicability of the results, since the analysis does not allow the other features (for example, the chain reaction development) to be explained [28].

II. Models of Gas Hydrate Granule and Pellet Dissociation

Further, the difference between a single granule of gas hydrate and an agglomerate of such granules plays a significant role. The gas hydrate properties at the granule level are described in isothermal approximation, and the dissociation kinetics depends on the granule conversion degree. Since dissociation is a heterogeneous process, the interface between the fresh hydrate phase and the porous ice (that remains after the gas escapes into the gas phase) is of primary importance. This study, similarly to the classical works on the hydrate dissociation kinetics [29] assumes that the granules can be approximately considered spherical and the shrinkage of reacting surface is related to the granule conversion degree by simple geometric relationships. Other models of heterogeneous reactions are constructed in a similar manner (for example, thermochemical conversion of solid fuels [30]). In some cases, it is possible to approximate hydrate dissociation front movement as a Stefan problem [31] (when temperature gradients are high enough).

Particle dissociation becomes possible under thermobaric conditions above the equilibrium curve. The equilibrium curve, which defines the boundaries of the hydrate phase stability, is usually given in the form of a parametric equation:

$$\ln\left(\frac{P_{eq}}{P_0}\right) = C_0 - \frac{C_1}{T}. \qquad (1)$$

Here P_{eq} is equilibrium pressure, P_0 is atmospheric pressure, T is temperature, C_0 and C_1 are empirical constant. Note that for gas mixtures, there can be corrections, which we do not consider here. The equations of the equilibrium curves for methane hydrate and carbon dioxide hydrate are given in [32].

Following the work [29], we consider the dissociation process driving force to be the difference between the equilibrium and current gas pressure above the hydrate.

Then the equation for dissociation kinetics can be approximately written as follows [33]:

$$-\frac{dX}{dt}=\frac{K_d\left(P_{eq}-P_{out}\right)}{6B\rho_H d_0}X^{2/3}\frac{Da'}{1+Da'}, \qquad (2)$$

where X is a conversion degree, K_d is the apparent kinetic constant, and Da' is a coefficient taking into account the pore resistance of the hydrate particle, P_{out} is output pore pressure, B is hydrate-forming gas mass fraction, ρ_H is hydrate mass density, d_0 is an average granule diameter. In a more precise formulation, when considering quasi-stationary filtration through a particle with spherical symmetries, one can obtain the equation:

$$-\frac{dX}{dt}=\frac{K_d}{6B\rho_H d_0}X^{2/3}\times \\ \times\left\{P_{eq}-P_{out}\left[\sqrt{\frac{1}{4Da^2}+\frac{P_{eq}}{P_{out}}\frac{1}{Da}+1}-\frac{1}{2Da}\right]\right\}, \qquad (3)$$

where Da is a ratio of dissociation and filtration rates: when Da is large, the gas hydrate granule decomposition is controlled by kinetics (these conditions favor K_d measurements); when Da is small, the decomposition is controlled by filtration. In the latter case, data on the decomposition kinetics are disturbed by the porous structure influence - from here, for example, it is possible to estimate the characteristic pore sizes and gas permeability [34]. The difference between equations (2) and (3) is determined by the assumed approximation (see Appendix).

Agglomerates of granules (we will call them pellets) are formed when granules stick together (for example, under the action of a press, or due to partial melting). Such objects consist of a large number of granules. Each of them reacts along its trajectory, yet depending on neighbor granules, since they exchange heat and/or mass. The pellet density is less than the granule density due to the porous space between the particles, through which the gas flows during dissociation. Usually, with a good degree of approximation, the hydraulic resistance of the pellet can be assumed to be lower than the hydraulic resistance of the pores in the granules, therefore, the gas pressure drop in the pore space of the pellet is considered negligible. Conditions for heat transfer, however, are opposite: whereas for an individual granule, temperature can be considered uniform, for a pellet, it is necessary to factor in temperature inhomogeneity.

Then, given the granules are motionless, we obtain heat transfer equation for the pellet:

$$c_p\rho\frac{\partial T}{\partial t}=\frac{1}{r^n}\frac{\partial}{\partial r}\left(r^n\lambda\frac{\partial T}{\partial r}\right)+Q\left(t,r\right), \qquad (4)$$

where Q is a heat sink, concerned with dissociation and phase transition latent heat; T is the temperature; c_p is the heat capacity; ρ is the pellet density; r is a characteristic spatial coordinate (radius or depth); λ is the thermal conductivity; n is a geometric (symmetry) exponent. The location of the reaction and phase transition fronts are calculated using an option of the enthalpy scheme. The boundary conditions are as follows:

$$\frac{\partial T}{\partial r}(0)=0, \\ -\lambda\frac{\partial T}{\partial r}(R)=\alpha\left(T_{env}-T\right)+\varepsilon\sigma\left(T_{rad}^4-T^4\right)-Q_{ev}J_{ev}, \qquad (5)$$

where α is a heat transfer coefficient, σ is the Stefan-Boltzmann constant, ε is the emissivity, Q_{ev} is the evaporation heat, J_{ev} is the evaporation rate. Depending on environment conditions, values of T_{env} and T_{rad} may coincide or differ (for example, for muffle conditions T_{rad} is a wall temperature, and T_{env} is a flame temperature).

Surface water evaporation rate is calculated using the formula:

$$J_{ev}=\beta\left(C_{eq}-C_{env}\right), \qquad (6)$$

where C_{eq} is the equilibrium water vapor concentration, C_{env} is the environmental water vapor concentration (usually close to zero). Mass transfer coefficient β is calculated taking into account Stefan flow [35]. Solving equations (1)–(6) yileds the dynamics of changes in temperature and pellet mass under high-temperature conditions. In this case, as mentioned above, quite serious simplifications are made. Namely, the water flow on the pellet surface is neglected (as is shown below, water flow losses can be partially factored in by introducing the effective evaporation heat); the structure of the boundary layer is not considered (all features are contained in the integral coefficients of heat and mass transfer), the multiphase flow in the porous space is not taken into consideration. The validity of these assumptions can be proved only by comparing calculation with experimental data. Model (1)–(6) is simplified because it includes only some basic balance equations. However, it contains a large number of coefficients. As is known, by varying these coefficients, we can achieve the agreement between

calculations and experiments as close as desired. Therefore, restrictions are imposed on the values of the coefficients, depending on the degree of their certainty.

The thermal conductivity coefficient of backfills and pellets is calculated using the formulas for granular structures recommended in [36]. The porosity required for calculations is usually uncertain, with its value varying from 0.3 to 0.6 (a lower porosity corresponds to a sparse backfill and a larger porosity corresponds to a dense compaction). The particle sizes of the powder are determined by the synthesis conditions, but they can also change during preparation and measurement (for example, due to sticking or fragmentation). In calculations, it is necessary to use a certain average effective granule size. Due to experimental procedures, the powder bed is rarely uniform in height, therefore, the local height is also an uncertain value (although the average height can be determined quite accurately). The thermodynamic properties of the hydrate depend on the ice saturation degree. This value depends on the synthesis method and the sample preparation. In some cases, an undersaturated sample manages to lose a significant part of the gas during preparation for the experiment. Therefore, the gas content in the hydrate can range from the theoretical limit to half of this value. Some properties (for example, thermal conductivity and kinetic coefficients) can be determined only in a narrow temperature range. Therefore, they have to be replaced by averaged values (the uncertainty is quite high).

The previous paragraph is intended to show how uncertain is the choice of the quantities that are necessary for calculations. Trying to describe the effects of interfacial interactions and detailed kinetics of chemical reactions, we encounter a multiply growing uncertainty of the input information. In this context, as mentioned above, it is more reliable to use simplified models.

The main result of solving equations (1)–(6) is the numerical estimate of the characteristic decomposition times for a gas hydrate pellet (dissociation time, melting time, evaporation time), as well as the characteristic values of the gas-vapor surface mass flows. These data are

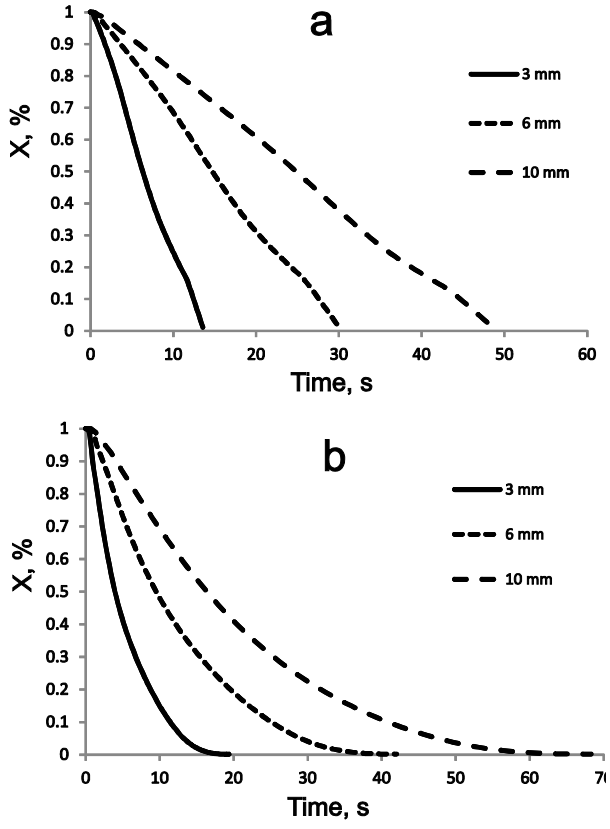

Fig. 1. Dynamics of CO_2 hydrate dissociation at 800°C: (a) – flat layer, (b) – cube.

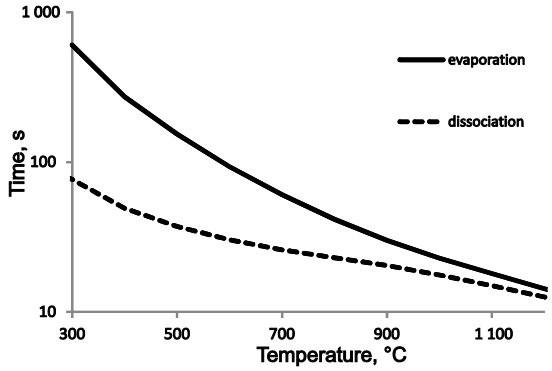

Fig. 2. Dynamics of CO_2 hydrate dissociation at 800°C: (a) – flat layer, (b) – cube.

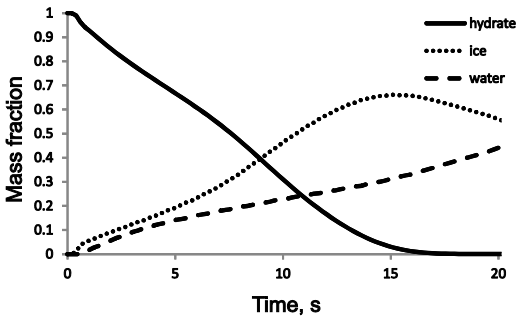

Fig. 3. Time dependence of CO_2 hydrate pellet composition (initial size – 5 cm, environment temperature – 900°C).

necessary for the next modelling stage, where the gas mixture compositions and heat flows associated with the hydrate particles conversion are needed to calculate the flame characteristics.

The numerical model was used to calculate dependencies. These dependencies make it possible to estimate the duration of decomposition stages under various temperature conditions. Figure 1 shows that geometric factor plays an important part in dissociation process. During conversion of flat layer, dissociation front surface does not change, and conversion rate is close to constant. When cubic sample is heated, dissociation front surface shrinks, leading to a decrease in conversion rate.

Figure 2 shows that evaporation time is much more sensitive to environment temperature (equilibrium vapor pressure in equation (6) exponentially depends on temperature). Dissociation forms an ice layer, which melts forming a liquid cover layer (its temperature does not exceed 100°C, but is quite close to this value most of the evaporation time). The processes of dissociation, melting, and evaporation occur simultaneously (Fig. 3). At the same time, the water can leave pellet not only by evaporation but also by flowing down. To allow for this effect, a slight modification of the model is proposed: non-evaporative water losses are simulated by lowering the evaporation heat. Figure 4 presents the results of calculations for coefficients 0.75, 0.5, and 0.25. As expected, reducing the evaporative water losses enhances dissociation kinetics and increases surface temperature. Liquid layer width for all cases is of the order of tenth mm.

Since the dissociation stage is the fastest stage of all, gas is released in a high, short-lived peak. Further, depending on the sample size, the surface temperature increases until intense evaporation begins. The evaporation is very energy-consuming, therefore, the water vapor flux is usually lower than the gas flux. Due to the high water content in the hydrate, evaporation lasts much longer. Thus, when hydrate enters the flame zone, a large injection of hydrate-forming gas occurs, and then evaporation begins. There is a short time period when the gas-vapor mixture composition is determined by the position of the dissociation front and phase transition fronts. If the hydrate releases flammable gas, the release of flammable gas should enhance the flame stability, but it is necessary to remove the condensed ice residue in order to reduce the heat sink. If the hydrate releases non-flammable gas, the initial injection of gas leads to dilution of the reacting medium, therefore, quenching by inert diluent has higher possibility in the first period of decomposition. After this, extinction may occur due to the heat losses, and stability depends on the conditions of heat and mass transfer between ice particles and the flame zone.

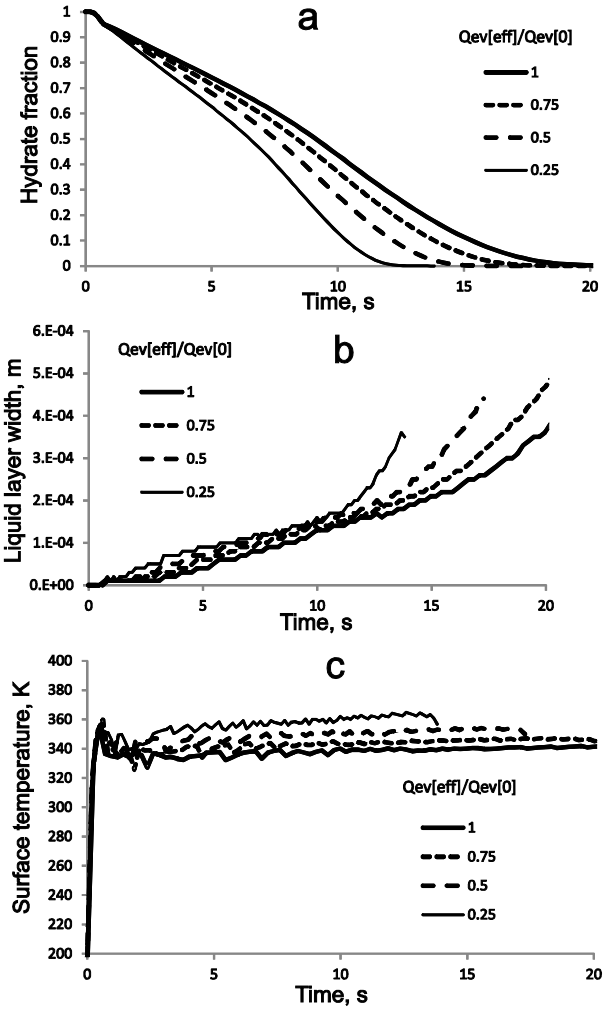

Fig. 4. CO_2 pellet decomposition for varying evaporation heat: (a) – hydrate fraction; (b) – width of surface water layer; (c) – surface temperature.

III. Diffusion Flame Model

Typically, the combustion of gas during hydrate decomposition is diffusion combustion. The authors of [37, 38] propose mathematical models of flame near a single suspended hydrate particle and flame propagation in a cloud of such particles. These models are based on the

Shvab-Zeldovich approximation widely used in combustion theory [39, 40]. Gas combustion above a decomposing hydrate powder can be considered as a reaction process in the boundary layer above a permeable surface [41] (in this case, the injection velocity is, as a rule, low enough to consider its effect insignificant and to use the approximation for an impermeable surface [12, 22]). In some experimental setups, air is supplied through the hydrate layer [42, 17]. In such cases, we can assume that the mixture has already been mixed before entering the space above the layer. In this work, however, we address a diffusion flame and the limits of its stability during interaction with hydrates of flammable and non-flammable gases. The diffusion flame models are even more adequate to consider extinguishing liquid fuel flames by hydrate particles.

The basis for our calculations is the model proposed in [43]. This model relies on correspondence between the original stationary diffusion combustion problem and the simpler problem of a stoichiometric well-mixed combustion (stoichiometry condition follows from the Shvab-Zeldovich approximation). Such a replacement is possible due to the similar nature of critical phenomena in the thermal theory of flames. The mentioned work [43] examines the thermal balance of a diffusion flame, taking into account the combustion heat and heat losses (conductive, convective, and radiative). The residence time of the reagents in the flame zone is determined by the flow velocity and the characteristic spatial scale. The model allows calculating the critical conditions for flame extinction (including local extinction in turbulent flows [44]). In [22], we calculated the stability limits of combustion for methane/water vapor mixtures (using data from the experimental work [24]). In addition, it is shown that with the accurately chosen spatial scale, it is possible to reproduce the extinction conditions for methane above the methane hydrate layer.

The model is constructed by analogy with the description of a perfectly stirred flow reactor. The material balance equation can be written as follows:

$$n_j^0 - n_j = \tau \sum_i \gamma_{ij} w_i \,, \qquad (7)$$

where n_j is the amount of the j-th substance, τ is a residence time, γ_{ij} is a stoichiometric coefficient, and w_i is a rate of the i-th reaction.

The simplest choice of kinetic description of a chemical reaction is to use a lumped mechanism with effective kinetic coefficients. This approach is also used in [43] (kinetics constants can be found in the paper). For hydrocarbon fuels, the lumped equation is written as follows:

$$C_n H_m + \left(n + \frac{m}{4}\right) O_2 = nCO_2 + \frac{m}{2} H_2 O \,. \qquad (8)$$

Heat balance is written in the following form:

$$\sum_j h_j(T_0) n_j^0 = \sum_j h_j(T) n_j + q_{cond} + q_{conv} + q_{rad} \,, \qquad (9)$$

where h_j is the specific enthalpy of the j-th component (calculated using the database from [45]), and q is heat losses:

$$q_{cond} = \tau \frac{\lambda_g}{L^2} (T - T_{env}) \,, \qquad (10)$$

$$q_{conv} = \tau \frac{\alpha}{L} (T - T_{env}) \,, \qquad (11)$$

$$q_{rad} = \tau \frac{\kappa}{L} \left(T^4 - T_{rad}^4\right) . \qquad (12)$$

Here λ_g is heat conductivity, and L is characteristic length (reaction zone width).

To obtain adequate numerical results, it is important to select appropriate scales. In the simplest configurations of diffusion flames, the linear and time scales are uniquely determined by the distance between the nozzles and the flow rate of the reagents. In the combustion of a boundary layer, the linear scale is related to its thickness; therefore, in general, it depends on the position of the flame front. Even for moving flame front, it is possible to choose an averaged length that allows calculating its stability under conditions of convective heat transfer [22]. The calculations show that the radiative term (12) cannot be neglected due to high concentration of CO_2 and H_2O [20]. The value of κ is estimated using recommendations given in [46].

For the combustion conditions of methane-vapor mixtures, it is possible to calculate the theoretical dependences of the combustion temperature on the composition and characteristic scales. For one-stage reactions, such dependences usually show the existence of regions with one solution and three solutions (in the latter case, two of them are stable). At large degrees of dilution, the stationary solutions form closed curves (isolas) [27, 47]. The separation of isola from the region of low-temperature solutions indicates the impossibility of self-ignition in such mixtures, which is consistent with the

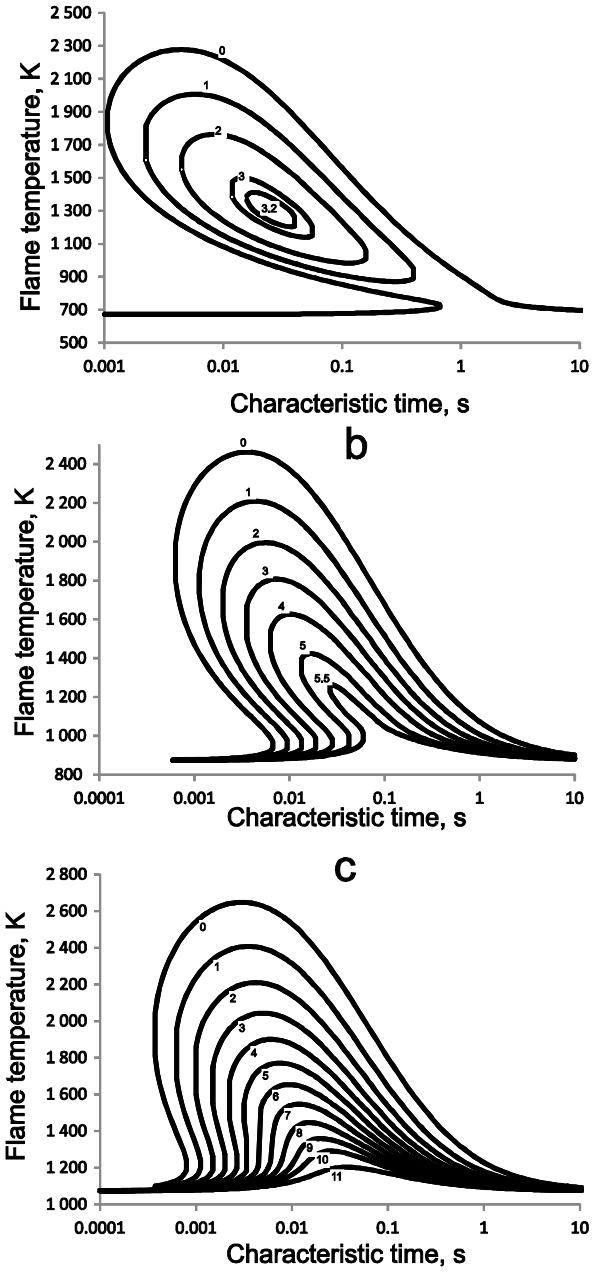

Fig. 5. Dependence of calculated flame temperature for methane-water vapor mixtures (numbers near curves are dilution ratios) on environment temperature: (a) – 400°C; (b) – 600°C; (c) – 800°C.

reality (methane hydrate flames are usually initiated by pilot heat source). The critical concentration of water vapor in a mixture with methane for the room temperature environment is of the order of 70% [22]. The higher the environment temperature, the wider the flame stability limits. Figure 5 shows calculated temperature curves for various environment conditions (400°C, 600°C, and 800°C). At the temperature of 600°C, isolas merge with the low-temperature solution branch; at the temperature of 800°C, critical points degenerate at dilution ratios larger than 5.

In the case of flame extinguishing by gas hydrate, the composition of the diluent has a significant influence on the flame stability limits [43]. Since the lumped chemical mechanism is not sensitive to the composition of the diluent (although some diluents can act as chain reaction inhibitors), specific heat capacity is the major factor. For example, carbon dioxide is more effective than water vapor, which, in turn, is more effective than nitrogen. The calculations performed using the model align with these concepts. During the hydrate decomposition, it is possible to distinguish three main stages: release of the hydrate-forming gas; release of the gas-water vapor mixture; release of the water vapor. For carbon dioxide hydrate, these stages correspond to the compositions of the diluents CO_2, CO_2/H_2O (for simplicity, we take an equimolar mixture for calculation), and H_2O. Then it is possible to find the conditions for the extinction of hydrocarbon flames when gas hydrate particles enter them.

Depending on the size of the particles and the average flame temperature (such an approximation inevitably has to be made, because of both the uncertainty of the particle trajectory and the perturbations of the flame front), the decomposition takes various amounts of time to complete. Calculated decomposition time gives the average gas and water vapor flows entering the flame region. Then, knowing the average burning rate of an undisturbed flame, we can approximately calculate the quantity of hydrate particles, which allows creating diluent mass flow sufficient for flame extinction (assuming that the particles are distributed evenly). When considering diffusion combustion, the fuel combustion rate is related to the area. Then the calculations give the critical mass of hydrate particles per unit area of flame (which is enough to extinguish the flame). For liquid fuel combustion, we consider a dispersed particle flow with an average particle diameter of 2 mm and an average decomposition rate of 0.4 mg/s. The environment temperature is 300 K.

Figure 6 shows dependences of flame temperature on mass flow for CO_2 hydrate: right termination points correspond to extinction. The stable combustion limits depend on fuel heat value (as expected, the higher the heat value, the higher the hydrate mass flow required for the

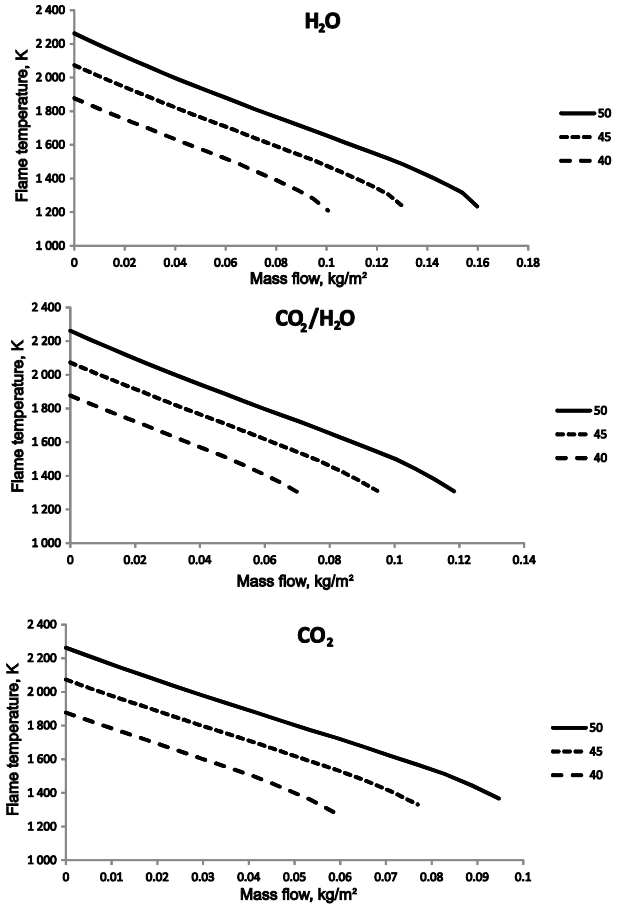

Fig. 6. Influence of diluting gas flow composition on stability limits of diffusion flame (for fuel heat value, MJ/kg).

flame extinction). CO_2 has a higher specific heat capacity, which is why, CO_2-added flame demonstrates narrower stability boundaries.

According to Fig. 7, heat values of real liquid fuels fill a narrow band between boundary values (40 and 50 MJ/kg). Given the hydrate powder particle size of 2 mm, we obtain a critical amount of powder of about 100 g/m^2, which corresponds to a heat flow ranging from 100 to 200 kW. The figure shows the dependence of calculated flame temperature and heat losses on mass flow during diffusion combustion of evaporating liquid fuels in the presence of CO_2 hydrate powder.

IV. Conclusions

Interaction of gas hydrates with high-temperature media is considered using a set of simplified mathematical models, which allow estimating individual particle (pellet) behavior and stability of hydrocarbon-air diffusion flames. The behavior of flame and hydrate particles is interdependent, and the simplest approximation splits overall process into two subsystems: one providing boundary conditions (temperature, mass flows) for the other.

The calculations show the influence of geometric, thermal, and reactivity factors on hydrate decomposition macrokinetics and flame stability. In the first scenario, dissociation and phase transitions under external heat supply determine the expected decomposition time and product gas composition. In the second scenario, saturation of the zone of flame with inert gases determines its stationary temperature.

Problems related to combustion stability are interesting from the perspective of safe storage and transport of hydrates: in the case of flammable gas emissions (for example, during unplanned heating or depression), a large amount of water does not guarantee that ignition will not occur (although it may contribute to faster extinction).

On the other hand, determining the conditions for stable combustion, especially in confined spaces, may be of crucial importance for the technologies of gas production

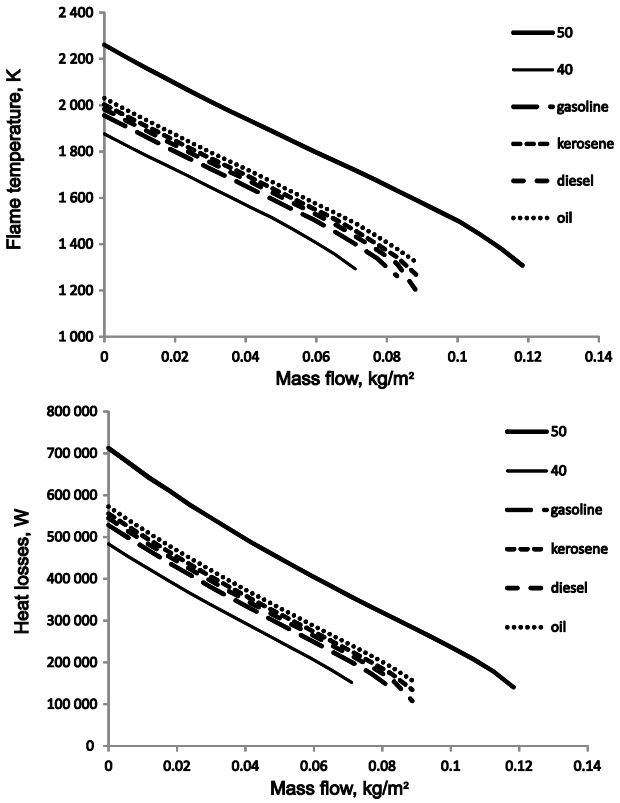

Fig. 7. Flame temperature and heat losses at different CO_2 hydrate power mass flows for various liquid fuels.

from hydrates associated with thermal stimulation of gas-saturated formations due to the heat of combustion of additional fuel or part of the gas produced [48]. The effectiveness of such methods depends significantly on the intensity of heat exchange in the area of contact between the hot medium and the rock. These problems may be a subject for the future works.

APPENDIX

The problem of gas hydrate granule dissociation is very similar to those of droplet evaporation or carbon particle combustion [35].

Let us consider a one-dimensional problem of filtration between two concentric spherical surfaces. The fluid is an ideal gas with the molecular mass M_r. The stationary Darci flow conditions give the equation:

$$\frac{d}{dr}\left(r^2 \frac{k_F}{\mu} \frac{PM_r}{R_g T} \frac{dP}{dr} \right) = 0, \qquad (A1)$$

where P is the gas pressure, μ is the viscosity, k_F is the permeability, R_g is a gas constant. Further, we use a set of approximations: the permeability is uniform; the area is isothermal; the gas composition is uniform. The internal boundary is maintained at pressure P_{in} and the outer boundary – at P_{out}. This set allows us to obtain the formula for the stationary Darci flow rate:

$$J = \frac{P_{in}^2 - P_{out}^2}{1 - r/R} \frac{k_F M_r}{2r\mu R_g T}, \qquad (A2)$$

where r and R are the radii of the two spheres (if $r << R$, equation (A2) becomes the Darci flow for a thin flat layer).

Next, the internal boundary condition is changed: instead of constant pressure, we deal with the chemical reaction whose rate is proportional to kinetic coefficient K_d and pressure difference between equilibrium and boundary pressure values. Pressure P_{in} becomes a variable. Then, applying the stationary condition again, we obtain:

$$K_d \left(P_{eq} - P_{in} \right) = \frac{P_{in}^2 - P_{out}^2}{1 - r/R} \frac{k_F M_r}{2r\mu RT}. \qquad (A3)$$

Equation (A3) is a quadratic equation having the only physical (non-negative) root:

$$P_{in} = P_{out} \left[\sqrt{\frac{1}{4Da^2} + \frac{P_{eq}}{P_{out}} \frac{1}{Da} + 1} - \frac{1}{2Da} \right], \qquad (A4)$$

where Da is the Damkohler number, which is a ratio between characteristic times of heterogeneous reaction and filtration transport:

$$Da = \frac{k_F}{2r\mu} \frac{1}{K_d} \frac{P_{out} M_r}{R_g T} \frac{1}{1 - r/R}. \qquad (A5)$$

Now, we can write the formula for reaction rate in the following way:

$$J = K_d \left\{ P_{eq} - P_{out} \left[\sqrt{\frac{1}{4Da^2} + \frac{P_{eq}}{P_{out}} \frac{1}{Da} + 1} - \frac{1}{2Da} \right] \right\}. \qquad (A6)$$

Equation (A6) looks clumsy, but it can be reduced to a simpler form by using some approximations. Let us first show that it gives a reasonable kinetic behavior for small and large values of Da. For $Da >> 1$ we immediately obtain $P_{in} \to P_{out}$, which corresponds to kinetics-controlled heterogeneous reaction. For $Da << 1$, we need to operate more accurately. First, we consider P_{out} in (A4) as a function of $P_{eq}/P_{out} = w$. If $Da^{-1} > 1$, w becomes a small parameter, and we have the estimate (the first two terms of the Taylor series):

$$P_{in} \approx P_{out} \left\{ \left[\sqrt{\frac{1}{4Da^2} + \frac{1}{Da}} - \frac{1}{2Da} \right] + \frac{w}{\sqrt{1 + 4Da}} \right\}. \qquad (A7)$$

Now, we take the limit $Da \to 0$ and obtain $P_{in} \to P_{eq}$. This range of Da corresponds to filtration-controlled decomposition, and the flow rate J in (A6) becomes close to zero (compared to kinetic equation).

Now, let us solve an easier problem. Instead of compressed gas, we consider an equivalent fluid with the averaged density ρ, and obtain a simplified solution for the stationary Darci flow:

$$J = \frac{P_{in} - P_{out}}{1 - r/R} \frac{k_F \rho}{\mu r}. \qquad (A8)$$

Using stationary conditions and the same kinetic equation, we have the simplified formula for the boundary pressure:

$$P_{in} = \frac{P_{eq} + P_{out} Da'}{1 + Da'}, \qquad (A9)$$

where Da' is a modified Damkohler number:

$$Da' = \frac{k_F}{r\mu} \frac{\rho}{K_d} \frac{1}{1 - r/R}. \qquad (A10)$$

The difference between equations (A5) and (A10) is the choice of gas density (in [48], a suitable approximation for averaged density is proposed). Then the reaction rate can be written as follows:

$$J = K_d \left(P_{eq} - P_{out} \right) \frac{Da'}{1 + Da'}. \qquad \text{(A11)}$$

It can be seen that $Da' << 1$ leads to low flow rates (filtration-controlled decomposition) and $Da' >> 1$ gives kinetic-controlled decomposition.

During the dissociation, reaction front moves from the outer surface towards the particle's core. It is important to note that the location of dissociation front is geometrically related to the conversion degree. Considering progress variable X (a relative amount of gas stored in a hydrate phase), we can write:

$$Da = \frac{k_F}{2R\mu} \frac{1}{K_d} \frac{P_{out} M_r}{R_g T} \frac{1}{X^{1/3} - X^{2/3}}, \qquad \text{(A5a)}$$

$$Da' = \frac{k_F}{R\mu} \frac{\rho}{K_d} \frac{1}{X^{1/3} - X^{2/3}}. \qquad \text{(A10a)}$$

The factors depending on X have a greater influence on dissociation kinetics in the vicinity of $X = 1$ and $X = 0$ (as shown in [33]). For the gas flow given by (A11), the decomposition time (which is finite) can be obtained in the following form:

$$\tau = \frac{B \rho_H d_0}{2K_d \left(P_{eq} - P_{out} \right)} \left(1 + \frac{6}{Da''} \right), \qquad \text{(A12)}$$

where $Da'' = Da'(X^{1/3} - X^{2/3})$, B is the gas mass fraction in fresh hydrate, ρ_H is the fresh hydrate density, d_0 is an effective particle diameter [49].

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