NUMERICAL STUDY OF THE INFLUENCE OF DISPERSION EFFECTS ON PROPERTIES OF FILTRATION COMBUSTION WAVES WITH COMPLEX CHEMICAL KINETICS

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A one-dimensional, two-temperature stationary model of filtration combustion with complex chemical kinetics has been developed. The influence of the phenomena of gas diffusion and heat conduction on the properties of the filtration combustion wave has been investigated.

Over recent decades, combustion of gases under the conditions of filtration through a porous medium has been studied intensively, which is due to the high efficiency of the process of filtration combustion (FC) compared with free-volume combustion. Most published works are based on one- and two-temperature approximation and one- or two-stage chemical kinetics [1–6]. In modeling FC of gases with the simplified chemical kinetics the authors often neglect the phenomena of gas diffusion and heat conduction and eliminate corresponding terms from the equations, relying on the fact that the coefficient of heat conduction of the solid phase, as a rule, greatly exceeds the coefficient of gas heat conduction and a diffusion flow is negligibly small compared with a convection flow and does not exert a strong effect on modeling of brutto kinetics (see, e.g., [6]). At the same time, it is known that dispersion effects, which affect heat and mass transfer in the system gas–porous medium and which cannot be allowed for in the absence of diffusion and heat conduction in the mathematical model, can arise under certain conditions of gas filtration through a porous medium. In the present paper, we study the influence of dispersion effects on the properties of FC waves by the developed mathematical model containing a detailed description of the chemical kinetics of methane oxidation.

We consider a one-dimensional, stationary, two-temperature model that is determined by the following system of differential equations:

$$(c_p\rho)_g\,(U - u_w)\frac{dT_g}{dx} = \frac{d}{dx}\left(\lambda_g^*\frac{dT_g}{dx}\right) - \frac{\alpha}{\varepsilon}(T_g - T_s) - \sum_i \omega_i h_i \mu_i\,, \tag{1}$$

$$-(c_p\rho)_s\,u_w\frac{dT_s}{dx} = \frac{d}{dx}\left(\lambda_s\frac{dT_s}{dx}\right) - \frac{\alpha}{1-\varepsilon}(T_s - T_g) - \frac{\beta}{1-\varepsilon}(T_s - T_{env})\,, \tag{2}$$

$$\rho_g\,(U - u_w)\frac{dY_i}{dx} = \frac{d}{dx}(\rho_g Y_i V_i^*) + \omega_i\mu_i\,, \tag{3}$$

$$\rho_g = \frac{p\mu}{RT_g}\,. \tag{4}$$

Here (1) and (2) are, respectively, the equations of conservation of energy of the gas and solid phases; Eq. (3) describes the law of continuity of the mass component, and the equation of state of an ideal gas (4) closes the system. Equations (1)–(4) are written in the system of coordinates related to the wave. The boundary and initial conditions are determined as follows:
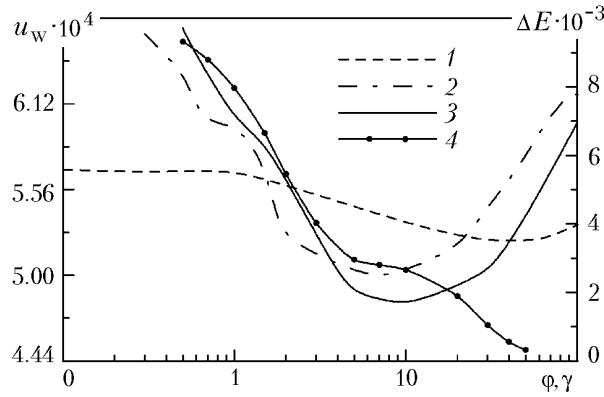
Fig. 1. Dependence of the velocity of the filtration combustion wave (1–3) and variation of the enthalpy of the reaction mixture (4) on the scaling coefficients: 1) $\varphi = 1.0$; 2) $\gamma = 1.0$; 3) $\gamma = \varphi$; 4) $\gamma = 1.0 = $ const. u_w, m/sec; ΔE, J/mole.

on the left-hand boundary (inlet)

$$T_g = T_0, \quad \frac{dT_s}{dx} = 0, \quad Y_i = Y_i^0;$$

(5)

on the right-hand boundary (outlet)

$$\frac{dT_g}{dx} = \frac{dT_s}{dx} = \frac{dY_i}{dx} = 0;$$

(6)

at the initial instant of time

$$T_g^0(x) = T_s^0(x) = T_0(x), \quad Y_i(x) = Y_i^0(x).$$

(7)

Within the entire computational domain, pressure is taken to be constant and equal to initial pressure.

As a porous medium we take a dense packing of aluminum dioxide spheres with a mean diameter $d = 5 \cdot 10^{-3}$ m. The length of the computational domain $L = 0.4$ m, and the initial velocity of gas is 1 m/sec. The specific heat capacity and thermal conductivity of aluminum dioxide were determined as $c_{ps} \approx 0.92 + 3.0 \cdot 10^{-7} T_s$ and $\lambda_s \approx 1.4 \cdot 10^4 T_s^{-1.07}$. The coefficient of porosity for a dense packing of spheres $\varepsilon = 0.4$, and the density of the material of the spheres in the packing $\rho_s = 3.9 \cdot 10^3$ kg/m^3. The coefficient of bulk interphase heat exchange was calculated by the formula given in [7]:

$$\alpha \approx \frac{3.0}{d^2} \pi \lambda_g (2 + 1.1 Re^{0.6} Pr^{1/3}).$$

The coefficient of volumetric heat losses is estimated on the basis of the experimental data: $\beta = 3 \cdot 10^4$ W/(m^3·K). The composition and parameters of the original mixture: $CH_4:O_2:N_2 = 2:1:4$ at $T_0 = 300$ K and $p = 1$ atm. To calculate the thermophysical and transport properties of the gas mixture we developed a set of subprograms similar to the utility programs of the CHEMKIN II package [8].

CRI-Mech version 3.0 [9] was used as the kinetic mechanism for calculation. This kinetic mechanism contains 53 chemical components and 325 elementary chemical reactions.

It is obvious that the solution of the system of equations (1)–(4) is a combination of the boundary-value problem and the problem of determination of the eigenvalue of the system u_w. To solve the described system of differential equations, we developed a program that uses an algorithm realized in the PREMIX program of the CHEMKIN II package [10] and is based on the modified Newton method. In contrast to [10], the program developed allows one to solve an additional equation of energy conservation for a porous medium.
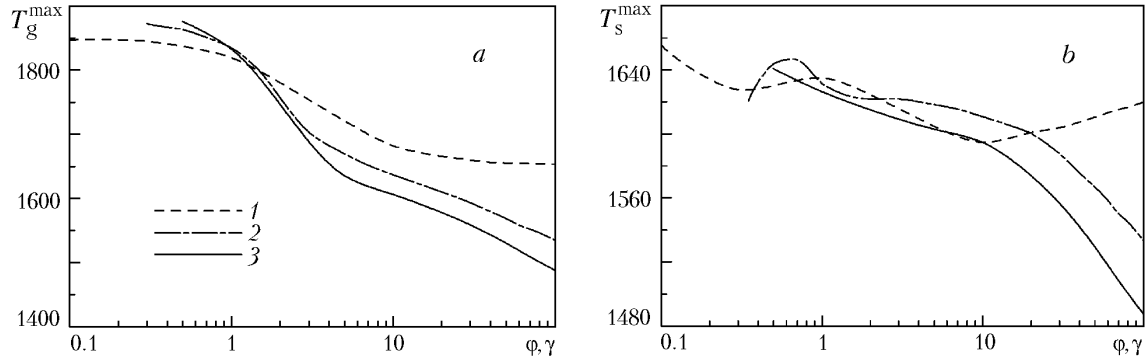
Fig. 2. Dependence of the maximum temperature of gas (a) and maximum temperature of the porous packing (b) on the scaling coefficients. For notation 1–3, see Fig. 1. T_g^{max}, T_s^{max}, K.

To change the scale of gas diffusion and heat conduction in the system of equations (1)–(4), we determine the coefficient of λ_g^* and the rate of diffusion V_i^* in the form

$$\lambda_g^* = \varphi \lambda_g \,, \tag{8}$$

$$V_i^* = \gamma V_i \,, \quad i = 1 \dots N \,, \tag{9}$$

where λ_g and V_i are the real coefficient of heat conduction and the rate of gas diffusion; φ and γ are the scaling coefficients, which for specific calculation are taken to be constant. The choice of the range of variation of the parameters φ and γ is governed by the following consideration. To emulate the absence of the phenomena of diffusion and heat conduction in gas it is necessary that the scaling coefficients be equal to zero. However, in this case, Eqs. (1) and (3) become equations of the first order and lead to a singular Jacobian in the Newton method, thus making determination of the system impossible. As is shown by the experience of calculations by the developed model, even at values of the scaling coefficients smaller than 0.1 the convective terms in Eqs. (1) and (3) become predominant and strongly impede solution of the problem by the mathematical method realized. Because of this, the lower boundary of the range of variation of the coefficients is taken to be equal to 0.1. As is shown in [11], at rates of gas filtration that exceed a certain value (~0.5 for the conditions under consideration), which is determined predominantly by the geometric parameters of the elements in the packing and the mutual position of them, additional effects related to mixing of macrovolumes (called dispersion) begin to influence heat and mass transfer in gas. As the rate of filtration increases further, the dispersion phenomena can lead to such enhancement of heat and mass transfer processes at which the effective coefficients of heat conduction and diffusion increase by one to two orders [11]. Proceeding from this fact, we take the upper boundary of the range of variation of the scaling coefficients equal to 100.

Figures 1–4 give the results of modeling the filtration combustion wave at different values of the scaling coefficients. At $\varphi = 1.0 = $ const, scaling is performed only over γ and only for the coefficients of diffusion, at $\gamma = 1.0 = $ const, scaling is performed over φ and only for the heat-conduction equation, and at $\varphi = \gamma$ — with simultaneous variation of the scaling coefficients.

Figure 1 gives the dependence of the velocity of the combustion wave on the scaling coefficients. It is found that the velocity of the FC wave is more sensitive to variation of the rates of diffusion of the chemical components than to variation of the heat-conduction coefficient of the gas. In order to explain the presence of the extremum of the function $u_w(\varphi)$, in the figure we give the dependence of variation of the enthalpy ΔE of the reaction mixture, which was calculated as the difference between the enthalpy of the mixture cooled to 1100 K after the reaction zone and the enthalpy of the original mixture, on the scaling coefficient φ. As φ changes from 1 to 40, an increase in heat dissipation leads to a decrease in the gas temperature (see Fig. 2), a decrease in the rates of chemical reactions, and, consequently, to decrease of heat release ΔE in the system. However, this is partially compensated by an increase in the thermal effect of reactions due to preliminary heating of the gas mixture in front of the reaction zone, which also
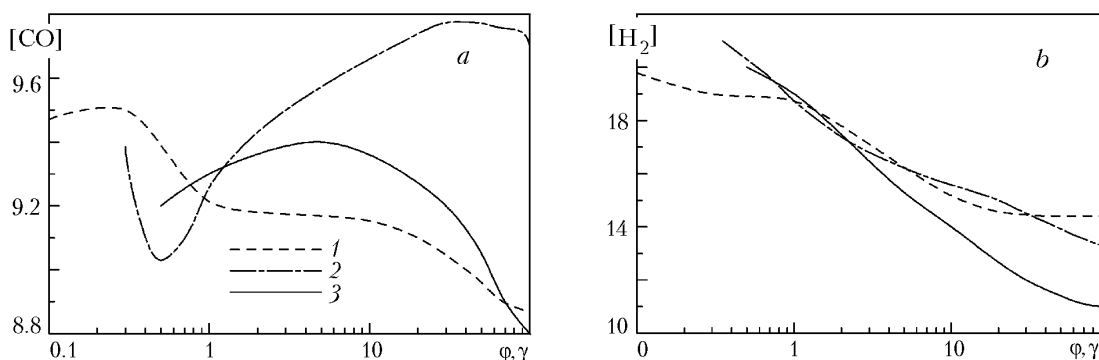
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Fig. 3. Dependence of the concentration of CO (a) and H_2 (b) at the outlet on the scaling coefficients. For notation 1–3, see Fig. 1. [CO], [H_2], %.
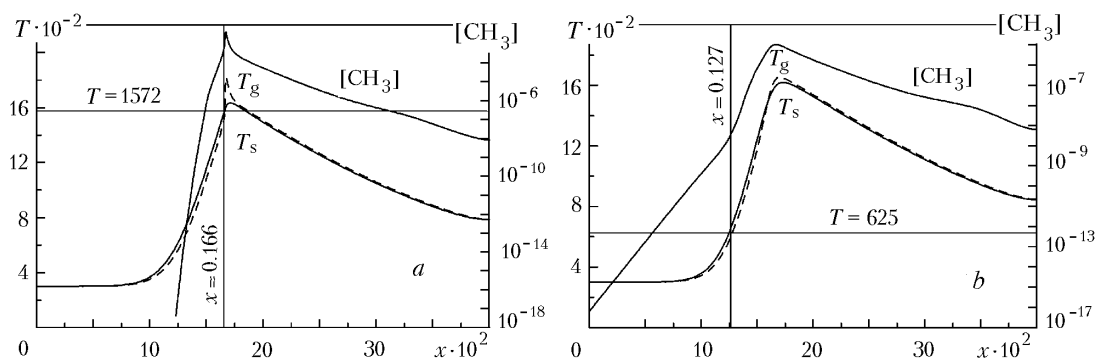

Fig. 4. Influence of the scaling coefficient on the time of induction of the gas mixture at the coefficient of diffusion: a) $\gamma = 1.0$; b) 100.0. T, K; [CH_3], %; x, m.

stipulates earlier ignition of the mixture and decrease of the velocity of the FC wave. Further increase of φ leads to such decrease of the gas temperature and heat release that the heat flux toward the gas flow becomes insufficient for compensation of the decrease of heat release, thus causing an increase in the velocity of the wave. When $\varphi < 1$ the velocity of the FC wave does not change.

The dependence of the maximum temperature of the porous packing and the maximum temperature of the gas on the scaling coefficients is shown in Fig. 2. As is seen, the change in the maximum temperature of the gas reaches $\pm 12\%$ and the maximum temperature of the packing $\pm 5\%$. Figure 3 presents the dependence of the concentration of carbon oxide (a) and hydrogen (b) at the outlet on the scaling coefficients. The filtration combustion wave can be used in chemical reactors for conversion of hydrocarbon fuels to hydrogen. It is seen from Fig. 3b that the hydrogen concentration at the outlet changes almost twofold. The conducted analysis showed that the decrease in temperature in the pick leads to the slip of methane and thus to a decrease in the degree of conversion of methane to hydrogen. It becomes evident that when the effects of diffusion and heat conduction in gas are neglected or are described incorrectly, the results of the modeling can greatly differ from the actual ones.

In analysis of the time of induction (ignition) of the mixture, which is estimated as the instant of 10% decay of the original fuel, we found much earlier ignition of the original mixture in the presence of dispersion (Fig. 4). This is caused by intense diffusion of the radicals, most important of which are CH_3, H, and OH, from the reaction zone toward the gas flow.

Thus, in modeling filtration combustion waves with complex chemical kinetics it is desirable to take into account the phenomena of diffusion and heat conduction in gas. This is of importance at large rates of diffusion when there appear dispersion effects that must be allowed for and included in the form of the corresponding corrections to the coefficients of diffusion and heat conduction of the gas.

NOTATION

c_p, specific heat capacity, J/(kg·K); d, mean diameter of spheres, m; ΔE, change of the enthalpy of the gas mixture, J/mole; h_i, enthalpy of the ith component, J/mole; L, length of the computational domain, m; N, number of chemical components in the system; p, pressure, atm; Pr, Prandtl number; Re, Reynolds number; R, universal gas constant; T_{env}, temperature of the environment, K; T, temperature, K; T_s, temperature of the porous medium, K; U, gas velocity, m/sec; u_w, velocity of the combustion wave, m/sec; V_i and V_i^*, rates of diffusion of the ith component, m/sec; x, spatial coordinate, m; Y_i, mass fraction of the ith component; α, coefficient of interphase heat transfer, W/(m³·K); β, coefficient of heat exchange with the environment, W/(m³·K); ε, porosity; γ, scaling coefficient for the rate of diffusion; φ, scaling coefficient for the heat-conduction coefficient; λ_g and λ_g^*, coefficients of gas heat conduction, W/(m·K); λ_s, heat-conduction coefficient of the skeleton, W/(m·K); μ_i, molar mass of the ith component, kg/mole; ρ, density, kg/m³; ω_i, rate of production of the ith component, mole/(m³·sec). Indices: s, solid phase; g, gas; i, index of the considered chemical element; 0, initial value; w, wave of filtration combustion; env, environment; max, maximum.

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