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MODELING OF THE NONSTATIONARY PROCESS OF CONVERSION OF METHANE TO HYDROGEN IN A FILTRATION-COMBUSTION WAVE

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Experimental data on incomplete oxidation of methane in air are analyzed for the stoichiometric relation $\gamma = 4$ using a numerical model; the data are obtained with different charges and for different flow rates of feed of a mixture. In order to explain the experimental data, it is proposed that a heterogeneous reaction that ensures the beginning of the processes of oxidation of methane at lower temperatures be introduced into the chemical model.

Introduction. Results of an experimental investigation of incomplete oxidation of methane with the aim of applying such a process to the production of hydrogen were given in [1]. Experimental data were compared to the results of a numerical modeling of filtration combustion. Only the homogeneous scheme of chemical processes involving 946 chemical reactions and a thermodynamic base of the properties of components from CHEMKIN was used in a two-temperature one-dimensional numerical model. A particular feature of such a model was the assumption that the traveling wave of filtration combustion had fully reached the steady state, i.e., steady-state equations were solved and the wave velocity was determined by iteration. Such an approximation was chosen because of the fact that the employment of such a large kinetic scheme required too much computer time for modeling a nonstationary process.

Comparison of the maximum temperatures in the combustion-wave front showed a considerable excess of the calculated values over the measured ones [1]. It was particularly difficult to compare the component composition since the reactor length turned out to be insufficient from the viewpoint of the development of a steady-state traveling wave. The dimensions of the heating zone (i.e., the leading edge of the wave) were such that the legitimacy of the comparison of the data obtained using the model and the experimental data could be expected just in the experiments with the lowest flow rates of a gas mixture ($G \leq 0.3$ kg/(m^2·sec)). Most of the experiments, conversely, were conducted for considerable flow rates, which was dictated by the desire to attain higher temperatures and accordingly a higher than usual content of hydrogen in the mixture going out of the reactor. However, for the experiments conducted with low flow rates where the model seemed to be applicable we observed no agreement between calculation and measurement. This suggested that the problem was more serious, and it, apparently, would not be solved by simple passage to a nonstationary modeling. Analysis of measuring the composition of the products of chemical reactions in [1] enabled us to make the assumption of heterogeneous processes even in such noncatalytic charges as Al_2O_3 and ZrO_2.

The nonstationary formulation of the model proposed below makes it possible to study transient (unsteady) regimes. Modeling of the process of filtration combustion in such an approximation requires much computer time but solves the question of the correctness of comparing calculation to measurement in [1]. Within the framework of such a model we can analyze the features of the ignition (initiation) and development (or decay) of a filtration-combustion wave by the measured profiles of the initial heating of a porous

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medium. The nonstationary modeling makes also it possible to use all evolution data measured in the experiment.

Formulation of the Problem and Method of Solution. A mathematical model of filtration combustion involves the equations of conservation of energy (energy equations) for a gas mixture and a solid phase and the equations describing a change in the concentration of chemical components with time.

The energy equation for a gas phase is written in the quasistationary approximation in an enthalpy formulation:

$$G\frac{dE}{dx} = \alpha_{\text{vol}}\,(\Theta - T_{\text{g}})\,. \tag{1}$$

The convective heat exchange of a porous charge and gases is modeled by the volumetric coefficient of heat exchange α_{vol} which depends on the filtration rate and the parameters of the porous charge. In the model, α_{vol} is determined in terms of Nu_{ef} from semiempirical dependences proposed in [2]: $\alpha_{\text{vol}} = 9(1-\varepsilon_{\text{p}})^2\lambda_{\text{g}}\text{Nu}_{\text{ef}}/(\varepsilon_{\text{p}}d^2)$. The model includes the dependences of the dynamic viscosity of the gas μ_{g} and of the thermal conductivity λ_{g} on T_{g} and the dependence of the heat capacity of the solid phase c_{s} on Θ. The specific enthalpy of the gas mixture E is a sum of specific enthalpies of all the components of the mixture:

$$E = \sum_{k=1}^{K} h_k\,(T_{\text{g}})\,Y_k\,, \tag{2}$$

where h_k is the specific enthalpy of the kth component (including the formation energy).

The energy equation for a solid phase is nonstationary and involves the heat source that describes interphase heat exchange:

$$c_{\text{s}}\,\rho_{\text{s.bulk}}\frac{\partial\Theta}{\partial t} = \frac{\partial}{\partial x}\left(\lambda_{\text{ef}}\frac{\partial\Theta}{\partial x}\right) - \alpha_{\text{vol}}\,(\Theta - T_{\text{g}})\,, \tag{3}$$

where $\lambda_{\text{ef}} = \lambda_{\text{s}}(1-\varepsilon_{\text{p}}) + \dfrac{32\sigma d\varepsilon_{\text{p}}\Theta^3}{9(1-\varepsilon_{\text{p}})}$ is the effective coefficient of thermal conductivity, which is the sum of the conductive $\lambda_{\text{s}}(1-\varepsilon_{\text{p}})$ and radiative $32\sigma^2 d\varepsilon_{\text{p}}\Theta^3/[9(1-\varepsilon_{\text{p}})]$ components, while c_{s} and λ_{s} are the heat capacity and the thermal conductivity of the solid material (the grain material proper), respectively. The radiative thermal conductivity is written in the approximation of an optically thick layer.

By adding Eqs. (1) and (3) we can obtain a divergent form of the energy equation in which the enthalpy of the gas appears instead of its temperature:

$$c_{\text{s}}\,\rho_{\text{s.bulk}}\frac{\partial\Theta}{\partial t} = \frac{\partial}{\partial x}\left(\lambda_{\text{ef}}\frac{\partial\Theta}{\partial x} - GE\right). \tag{4}$$

Such a form of the energy equation makes it possible to use a rather coarse grid for finding the temperature of the solid material. Even in the combustion front where a very detailed (fine) grid is used for modeling chemical kinetics, no special techniques of calculation of the solid-phase temperature are required.

The equations of chemical kinetics, which describe the change in the mass concentration of the components $\rho_{\text{g}}\dfrac{dY_k}{dt} = \dot{\omega}_k^{\text{hom}}W_k$ ($k = 1, ..., K$), can be rewritten in the quasistationary approximation, using the relation $dx = udt = \dfrac{G}{\rho_{\text{g}}\varepsilon_{\text{p}}}dt$:

$$\frac{G}{\varepsilon_p}\frac{dY_k}{dx} = \dot{\omega}_k^{\mathrm{hom}} W_k \quad (k = 1, ..., K)\,, \tag{5}$$

where $\dot{\omega}_k^{\mathrm{hom}}$ is the rate of formation of the kth component in homogeneous reactions. In the first stage, we used the complete base of Konnov [5]; the base involved 121 gas components and took account of 1027 reactions. The thermodynamic properties of the components were taken from the CHEMKIN base.

Thus, the mathematical model of the process is fully determined by Eqs. (1), (2), (4), and (5). The procedure for finding a numerical solution consists of several parts. At first we prescribe the distribution of the skeleton temperature Θ_0; as a rule, it corresponds to the reading of thermocouples at the instant of ignition of a combustion wave, i.e., at the instant of feeding of a mixture with $\gamma = 4$. From this prescribed profile we find the spatial distributions of Y_k, E, and T_g. In this stage, we employ the standard procedure DVODE for solution of the system of equations (1) and (5); this procedure provides the prescribed accuracy due to automatic choice of an integration step. The distribution of E is stored on the same grid that is used for discretization of Θ. The solution for Θ at a new time step is found using an explicit difference scheme for Eq. (4). As the test calculations showed, for a reasonable size of the spatial step (of about $1 \cdot 10^{-3}$ m) restrictions on the size of the time step which are associated with the stability of an explicit difference scheme are less severe than restrictions due to the quasistationary description of a gaseous medium. In the calculations, the size of the time step was chosen from the condition of convergence of the velocity of the steady-state filtration-combustion wave.

Such a numerical algorithm ensured the conservatism of solution for energy and required approximately 50 sec on a Pentium II 400 computer for 1 sec of physical time. This considerable lagging of the counting rate behind the actual process made it impossible to analyze the model effectively; therefore, we made attempts to substantially reduce the kinetic scheme.

In the first stage, all the components and corresponding reactions involving chemical transformations of nitrogen were removed from the Konnov base. Upon such a transformation of nitrogen to an "inert" gas the base was reduced to 49 components while the time of computation of one time step decreased to 13 sec. With such a modification of the base we observed no significant change in the solution. It is obvious that the base "Konnov-49" is quite applicable to our case. Further "simplification" of the scheme of chemical reactions occurred with a certain change in the solution. The more simplified base "Konnov-38," which uses 38 components, yielded results quite similar to the initial solution. Taking account of the fact that the inaccuracy of the base "Konnov-38" is lower than the measurement error in the experiments [1], we used precisely this kinetic scheme for modeling. In this case, one time step took about 8 sec of processor time. Apart from the Konnov base, we also considered the base GRI [4], from which the chemical compounds of nitrogen were similarly removed. The truncated base GRI-35 has no marked advantage for the counting rate but yielded a somewhat different composition of the end products and differed somewhat in the initial stage of ignition. The Konnov base was preferable to us since it is better tested for oxidation of methane and propane.

Analysis of Results of Calculations According to a Homogeneous Chemical Model and Modification of the Model. The first series of calculations was carried out to check the numerical algorithm and test the code. In this stage, we checked the conservatism of the scheme and made a comparison with the existing solutions. In particular, the maximum skeleton temperatures calculated in a steady-state wave coincided with the results of calculations [1] for different mass flow rates.

Nonstationary modeling showed that for many regimes the initial temperature profiles of the solid phase do not ensure the ignition of the mixture but in the reactor, in the case of such a start, we observed the formation of a filtration-combustion wave. The "decay" was obtained for both the GRI base and the Konnov base. Variation of α_{vol} and of the remaining parameters of the model (exclusive of the chemical part) even beyond the real values yielded no positive result.

Forced ignition of the mixture could be provided – either by higher temperatures in the initial distribution or by substantially extending the heated region. In all the cases with both forced ignition and the natural one, solutions with significantly overstated maximum temperatures of the solid phase $\Theta_{\max}$ as compared to those measured experimentally were formed. Naturally, in this high-temperature solution, the component composition of the gases at the exit from the reactor differed very strongly from the composition measured in the experiments.

We can assume that under experimental conditions, ignition occurs owing to certain heterogeneous reactions which produce radicals on hot surfaces of a porous structure, whereas the gas is not sufficiently heated yet for these radicals to be produced in the volume. On the basis of such a scheme we made attempts to introduce irreversible homogeneous reactions that initiate the formation of radicals at low temperatures in the gas. Different reactions and different rates of them were tested, but the results were the same: if the mixture was ignited the maximum temperature was higher than in the experiment. The replacement of the heterogeneous processes by homogeneous ones leads to the release of the heat of chemical reactions in the gas medium rather than on the solid-phase surface. Passage to a more consistent heterogeneous concept required that Eqs. (1), (3), and (5) be written in the following form:

$$G \frac{dE}{dx} = \alpha_{\mathrm{vol}} (\Theta - T_{\mathrm{g}}) - Q^{\mathrm{het}} , \tag{6}$$

$$c_{\mathrm{s}} \rho_{\mathrm{s.bulk}} \frac{\partial \Theta}{\partial t} = \frac{\partial}{\partial x} \left(\lambda_{\mathrm{ef}} \frac{\partial \Theta}{\partial x} \right) - \alpha_{\mathrm{vol}} (\Theta - T_{\mathrm{g}}) + Q^{\mathrm{het}} , \tag{7}$$

$$\frac{G}{\varepsilon_{\mathrm{p}}} \frac{dY_k}{dx} = \dot{\omega}_k^{\mathrm{hom}} W_k + \dot{\omega}_k^{\mathrm{het}} W_k \quad (k = 1, ..., K) , \tag{8}$$

where the heterogeneous-reaction rate $\dot{\omega}_k^{\mathrm{het}}$ for the kth component is rewritten in the Arrhenius approximation $\dot{\omega}_k^{\mathrm{het}} = S_{\mathrm{vol}} A_{\mathrm{het}} Y_k \exp(-\Theta_{\mathrm{het}}/\Theta)$. In Eqs. (6) and (7), the magnitude of the heat source Q^{het} that is related to the heterogeneous reactions is determined in terms of the difference of the enthalpies of components disappearing on the surface and the enthalpies of components produced on the surface. Such a model implies that the thermal effect of a heterogeneous reaction is released in the solid phase. In Eq. (8), the appearance of heterogeneous reactions is reflected by an additional term proportional to $\dot{\omega}_k^{\mathrm{het}}$, i.e., to the rate of formation of the kth component in heterogeneous processes. The magnitude of $\dot{\omega}_k^{\mathrm{het}}$ is determined in terms of such a characteristic of a charge as the "surface in unit volume." We note that changes in the form of Eqs. (1) and (3) had no effect on the form of Eq. (4). Upon modification the mathematical model is represented by Eqs. (2), (4), (6), and (8).

We have no information on the representation of any actual heterogeneous model that is related to adsorption processes and reactions on the surface. What is proposed is a simple model scheme ensuring the heterogeneous ignition of the mixture earlier than it would otherwise occur as a result of homogeneous processes. The purpose of such an approach is an attempt to bring into agreement the calculated and measured maximum temperatures in waves for different flow rates. Although it is clear that in bringing the temperatures into agreement there cannot be particularly strong differences in composition — this will not be allowed by the laws of thermodynamics. A heterogeneous chemical model for the above purpose must be as simple as possible, in the best case consisting of a single model reaction. Let us choose such a reaction that ceases as oxygen disappears. By doing so we assume that a heterogeneous reaction provides just ignition and has no effect on homogeneous processes when oxygen is consumed. From these considerations, we chose the following heterogeneous reaction:

$$O_2 \Rightarrow O + O\,. \tag{9}$$

In an oxygen-rich atmosphere, the active centers of a catalyst are primarily filled with atomic oxygen that initiates heterogeneous reactions on the solid-phase surface [5, 6]. Thus, the form of reaction (9) has a definite meaning. As a temperature dependence of this reaction's rate, we used the Arrhenius approximation with two parameters: the activation energy and the pre-exponential factor. The heterogeneous-reaction rate $\dot{\omega}_k^{\text{het}}$ proper was calculated as a product of the Arrhenius exponent and the parameter that characterizes the specific surface of the solid phase. The maximum value of the reaction rate was bounded by a diffusion limit. In order to calculate the maximum flux per unit surface, we used the mass-exchange coefficient χ_k calculated in terms of the already introduced coefficient of heat exchange α_{vol} and the coefficients of diffusion D_k and thermal conductivity λ_δ of the gas: $\chi_k = \alpha_{\text{vol}} D_k/\lambda_g$.

Calculation Results. The parameters of the rate of reaction (9) were chosen on the basis of a rather large number of calculations; however, the choice made is most likely to be not optimum. The magnitudes of the coefficients $A_{\text{het}} = 2\cdot10^{13}$ mole/(m^2·sec) and $\Theta_{\text{het}} = 28{,}200$ K were found by selection of the parameters for just a single experiment, namely, for an Al_2O_3 charge of spheres of diameter $d = 3.5\cdot10^{-3}$ m. Even such an imperfect choice enabled us to solve the existing problems. The model with reaction (9) ensures the ignition of a mixture for all regimes with the initial distributions Θ_0 measured experimentally. On the other hand, the calculated maximum temperatures are much lower than in the model with homogeneous chemistry and agree better with the experimental ones.

Table 1 gives the calculated and experimental data of the maximum temperature of the solid phase for different filtration-combustion waves. The largest deviation does not exceed 125$^{\text{o}}$ (~10%) for all the investigated filtration regimes, which is quite satisfactory since such an agreement is observed for the strongly differing charges.

It is seen from the table that for low flow rates the correspondence of the calculations to the experimental measurements is poorer than for high G. This is mainly caused by the choice of the parameters of a heterogeneous chemical model A_{het} and Θ_{het}. Along with experimental data, Fig. 1 gives for comparison the results of modeling for two values of A_{het} ($2\cdot10^{13}$ and $9.2\cdot10^{11}$ mole/(m^2·sec)) that were selected with allowance made for the experimental data for flow rates of 1.06 and 0.3 kg/(m^2·sec) respectively. The qualitative behavior of the curves changed little with change in A_{het}. The heterogeneous chemical model can be adjusted to any flow rate by selection of the corresponding magnitude of A_{het}.

For all the investigated charges the calculated maximum temperatures $\Theta_{\max}$ increase more rapidly with G than in the experiment. There can be several reasons for this: the imperfect model of thermal processes in the solid phase, the inaccurate dependence of the coefficient α_{vol} on the characteristics of the charge and on the operating parameters, and the simplified model of heterogeneous chemical processes. In describing the solid phase, we adopted the assumption of a single temperature inside the grain. It is quite acceptable for stationary processes or for small grains and low velocities of propagation of filtration-combustion waves. In order to evaluate the suitability of this approximation, we calculate the Fo number, having used the time of traversal of the grain by a heat wave as the characteristic time:

$$\text{Fo} = \frac{4\lambda_s d}{c_s \rho_s d^2 V_{\text{thermal}}} = \frac{4\lambda_s c_s \rho_s (1-\varepsilon_p)}{c_s \rho_s d c_g G} = \frac{4\lambda_s (1-\varepsilon_p)}{d c_g G}\,.$$

For the approximation of the temperature uniformity of the grain to hold true, the Fourier number must be rather large, Fo >> 1. From the equality Fo = 1 we obtain $d = 4\lambda_s(1-\varepsilon_p)/(c_g G)$ or for parameters characteristic of the charges in question $d \approx 2\cdot10^{-3} G$. Thus, even for grains $2\cdot10^{-3}$ m in diameter for flow rates

TABLE 1. Measured and Calculated Maximum Temperatures Θ_{max} in the Porous Charge of a Reactor in Different Filtration Regimes

G	Al_2O_3 cylinders ($\sim 8\cdot 10^{-3}$ m)			Al_2O_3 spheres ($6\cdot 10^{-3}$ m)			Al_2O_3 spheres ($3.5\cdot 10^{-3}$ m)			ZrO_2 spheres ($(2–3)\cdot 10^{-3}$ m)		
	experiment	calculation		experiment	calculation		experiment	calculation		experiment	calculation	
		I	II		I	II		I	II		I	II
0.30	1611	1667	1488	–	1735	1503	–	1780	1450	1507	1762	1400
0.42	1643	1737	1544	1654	1798	1560	1643	1829	1508	1596	1825	1483
0.61	1678	1760	1596	1656	1860	1622	1657	1897	1582	1631	1905	1560
0.78	1688	1827	1623	–	1894	1659	1671	1948	1626	1644	1950	1605
1.06	1693	1862	1656	1685	1935	1698	1680	1995	1677	1658	1996	1654
1.33	–	1889	1690	1697	1977	1721	1690	2046	1706	–	2027	1682

Notes: I, using just the homogeneous reactions; II, using the heterogeneous reaction $O_2 \Rightarrow O + O$ and the homogeneous reactions.

TABLE 2. Calculated Fourier Numbers

G	Al_2O_3 cylinders ($\sim 8\cdot 10^{-3}$ m)	Al_2O_3 spheres ($6\cdot 10^{-3}$ m)	Al_2O_3 spheres ($3.5\cdot 10^{-3}$ m)	ZrO_2 spheres ($(2–3)\cdot 10^{-3}$ m)
0.30	0.83	1.11	1.90	2.67
0.42	0.60	0.79	1.36	1.90
0.61	0.41	0.55	0.94	1.31
0.78	0.32	0.43	0.73	1.03
1.06	0.24	0.31	0.54	0.75
1.33	0.19	0.25	0.43	0.60

higher than 1 kg/(m^2·sec) we must take into account the temperature nonuniformity in the grain for a correct description of thermal processes. Table 2 gives the Fourier numbers for the porous charges and flow rates in question. As follows from the table, the Fourier numbers exceed 1 just for a very small number of experiments. All the experiments with $G \geq 0.6$ kg/(m^2·sec) should be described using a model that takes into account the temperature nonuniformity in the grain. In fact, only three experiments with a ZrO_2 charge, conducted for G of 0.3, 0.42, and 0.61 kg/(m^2·sec) and for which Fo ≈ 2, can be recognized as more or less corresponding to the model used, which is confirmed by comparison of the calculated and experimental data of Fig. 1a.

From the viewpoint of the Fo numbers, adjustment of the parameters of heterogeneous chemistry to $G = 0.3$ kg/(m^2·sec) seems to be more consistent than to $G = 1.06$ kg/(m^2·sec). As is seen, in this case the disagreement between calculation and experiment increases with decrease in Fo, which can be interpreted as errors due to an incorrect description of the processes in the solid phase. Figure 1b gives data analogous to the data of Fig. 1a but for an Al_2O_3 charge with $d = 3.5\cdot 10^{-3}$ m. In this case, the Fo numbers are smaller and the disagreement between calculation and experiment is stronger.

The dependence of the volumetric coefficient of heat exchange α_{vol} on the parameters of the charge and on G is very important since it has an effect on both heat exchange and the rate of heterogeneous reactions. In order to refine this dependence, one must conduct special experiments with subsequent processing of data based on the model that takes into account the temperature nonuniformity inside grains.

The main difference in the composition of the products is an amount of methane greater in the experiment than in the predictions of the model. This difference is caused not only by the wrong level of temperatures but also by the too simplified model of heterogeneous processes; a change in this model can lead

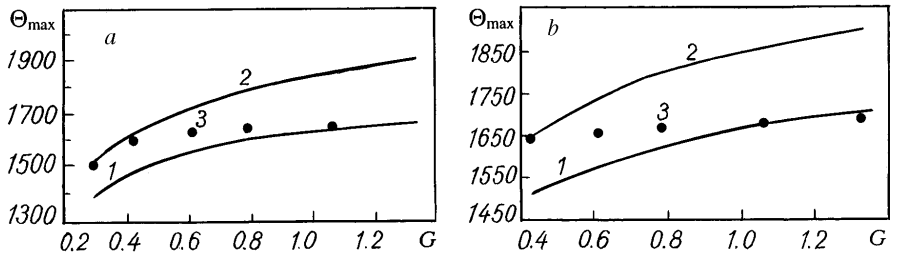

Fig. 1. Influence of A_{het} on the maximum temperature of the solid phase Θ_{max} calculated for a porous charge of ZrO_2 with $d = 2 \cdot 10^{-3}$ m (a) and of Al_2O_3 with $d = 3.5 \cdot 10^{-3}$ m (b): 1) $A_{het} = 2 \cdot 10^{13}$ mole/(m^2·sec); 2) $9.2 \cdot 10^{11}$; 3) experimental measurements.

to a change in both the composition of the gases and the attained maximum temperatures. Experiments measuring a wider spectrum of components than in [1] are required for the development of the heterogeneous model. In [1], chromatographic analysis was carried out after the condensation of a water stream and made it possible to measure the following components of the gas mixture: H_2, CO, CH_4, N_2, and O_2. The calculations, conversely, show the presence of such components as CO_2 and C_2H_2 in appreciable amounts (these components were not recorded in the experiments). In processing of chromatographic data, we employed a certain procedure for bringing the data into agreement that did not take into account the presence of CO_2 and C_2H_2 in the mixture. With allowance for the accuracy of the measurements proper and the errors of processing of the data, the error in determination of the concentration of nitrogen can be estimated at 5% and for the remaining components — at 10%.

Even with allowance for such errors we can say that the disagreement between the results of numerical modeling and experiment is of a systematic character for the concentrations of CO and CH_4 and is beyond the possible errors of measurement. At the exit from the reactor, the calculations always yield an understated amount of methane and an overstated amount of carbon oxide. This difference is most probably due to the incorrect heterogeneous chemistry adopted in the model.

Conclusions. Use of the enthalpy formulation of the energy equation and of the reduced base of chemical reactions enabled us to model the nonstationary processes in reactors with a porous charge. Primary analysis showed that the homogeneous model of chemical processes makes it impossible to explain experimental data. The introduction of a model heterogeneous chemical reaction demonstrated the possibility of restricting the maximum temperatures in a filtration wave and approximating experimental measurements.

On the other hand, it is seen that the model reaction proposed makes it impossible to obtain a composition of the products analogous to the experimental one in calculation. For a correct description of the chemical processes it is necessary to investigate more thoroughly heterogeneous processes, since it was shown that the existing homogeneous schemes cannot explain the experimental results. Investigation of this question necessitates the conduction of new experiments with thorough measurement of the thermal characteristics of the reactor and a purpose-oriented chemical analysis with allowance for all the components formed in considerable amounts.

In nonstationary processes, the temperature nonuniformities in the grain can have an effect on heat exchange between a gas and a porous charge and thus influence the characteristics of a filtration-combustion wave. In the case of small grains and low flow rates, the model with a constant temperature of the grain must correspond well to the actual situation. For large-grain charges and high flow rates the temperature nonuniformity in the grain is significant. The development of filtration-combustion waves and the maximum temperatures occurring under such conditions must be modeled with allowance for this feature.

NOTATION

A_{het}, frequency factor, mole/(m^2·sec); c_g, specific heat of the gas mixture, J/(kg·K); c_s, specific heat of the charge material, J/(kg·K); d, diameter of the charge grains, m; D_k, diffusion coefficient of the kth component in the gas, m^2/sec; E, specific enthalpy of the gas mixture, J/kg; Fo, Fourier number; G, specific mass flow rate of the gas mixture, kg/(m^2·sec); h_k, specific enthalpy of the kth component, J/kg; Nu_{ef}, effective Nusselt number; S_{vol}, specific surface, m^2/m^3; t, time, sec; T, gas temperature, K; u, velocity, m/sec; $V_{thermal}$, velocity of the heat wave, m/sec; W_k, molar mass of the kth component, kg/mole; x, space coordinate, m; Y_k, fractions of total mass of the components; Θ, skeleton temperature, K; Θ_{max}, maximum temperature in the porous charge, K; χ_k, mass-exchange coefficient, sec^{-1}; Θ_{het}, activation energy of the heterogeneous chemical reaction, K; $\dot{\omega}_k$, rate of formation of the kth component, mole/(m^3·sec); ε_p, intergranular porosity; α_{vol}, volumetric coefficient of interphase heat exchange, W/(m^3· K); γ, stoichiometric relation; λ_s, thermal conductivity of the charge material, W/(m·K); λ_{ef}, effective thermal conductivity of the charge, W/(m·K); λ_g, thermal conductivity of the gas mixture, W/(m·K); $\rho_{s.bulk}$, bulk density of the charge, kg/m^3; ρ_g, density of the gas mixture, kg/m^3; μ_g, dynamic viscosity of the gas mixture, Pa·sec; σ, Stefan–Boltzmann constant, W/(m^2·K^4). Subscripts and superscripts: ef, effective value; g, gas phase; hom, homogeneous; het, heterogeneous; k, index of the chemical element in question; p, porous; s, solid phase.

REFERENCES

1. V. V. Gavrilyuk, Yu. M. Dmitrenko, S. A. Zhdanok, V. G. Minkina, S. I. Shabunya, N. L. Yadrevskaya, and A. D. Yakimovich, in: *Proc. IV Minsk Int. Forum "Heat and Mass Transfer—MIF-2000* [in Russian], 22–26 May, 2000, Minsk, Vol. 4, Minsk (2000), pp. 21–31.
2. M. É. Aérov, O. M. Todes, and D. A. Narinskii, *Apparatuses with a Stationary Granular Bed* [in Russian], Leningrad (1979).
3. A. A. Konnov, *Detailed Reaction Mechanism for Small Hydrocarbons Combustion.* http://homepages.vub.ac.be/~akonnov/.
4. M. Frenklah, H. Wang, M. Goldenberg, G. P. Smith, D. M. Golden, C. T. Bowman, R. K. Hanson, W. C. Gardiner, Jr., and V. Lissianski, *Gas Research Institute Topical Report*, No. GRI-95/0058 (1995).
5. D. A. Hickman and L. D. Schmidt, *AIChE J.*, **39**, No. 7, 1164–1177 (1993).
6. O. Deutchmann and L. D. Schmidt, *AIChE J.*, **44**, No. 11, 2465–2477 (1998).