A MATHEMATICAL MODEL AND ALGORITHM FOR CALCULATING REACTIONS TAKING PLACE WITH INTENSE LIBERATION OF HEAT AND CHANGE OF VOLUME

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We present a model and an algorithm for the calculation of a strongly exothermic reaction with a change in volume. We give examples of numerical calculations of the basic characteristics of a layer.

Investigators are drawn, more and more, in the solution of energy problems to questions relating to the catalytic oxidation of the simplest hydrocarbons (see [1, 2]). These reactions are characterized by a significant liberation of heat and a pronounced change in volume during the conversion of the initial materials into the reaction products; this leads to a change in the flow rate and, as a consequence, to variation in the hydrodynamic parameters over the length of the catalyzer layer. The methods of calculation, customarily adoped, involving an averaged rate of motion may, therefore, yield invalid results.

In the present paper we consider the reaction of catalytic oxidation of hydrocarbons, which can be represented roughly in the form

$$n_1A_1+n_2A_2\rightarrow n_3A_3+n_4A_4,$$

where A_1 is the hydrocarbon being oxidized; A_2 is the oxidizer (for example, atmospheric oxygen); A_3 and A_4 are the reaction products; n_j is the number of moles of the j-th reaction component.

1. Mathematical Description. A mathematical model of the process in a one-dimensional setting includes the material balance equations for each component and the momentum and energy equations for the gaseous mixture and catalyzer:

$$\frac{d}{dl}(\rho_j v)=\nu_j W_1,\quad j=1,\ 2,\ 3,\ 4, \tag{1}$$

$$G\frac{dv}{dl}=-\frac{dP}{dl}-F_{\text{fr}}, \tag{2}$$

$$GC_V\frac{dT}{dl}=\gamma(\Theta-T)-P\frac{dv}{dl}+F_{\text{fr}}\,v, \tag{3}$$

$$\varepsilon_{\text{к}}\rho_{\text{к}}C_{\text{к}}\frac{\partial\Theta}{\partial t}=\lambda_{\text{ск}}\frac{\partial^2\Theta}{\partial l^2}-\gamma(\Theta-T)+W_1Q. \tag{4}$$

For closure of the system (1)-(4) we use the equation of state

$$P=\rho R_{\text{m}}T, \tag{5}$$

where $\rho=\sum_{j=1}^{4}\rho_j;\quad R_{\text{m}}=\sum_{j=1}^{4}y_jR_j,\ R_j=R/M_j.$

The boundary and initial conditions are the following:

$$\text{for } l=0:\ GC_V(T-T_{\text{en}})=\alpha(\Theta-T),\ \rho_j=\rho_j^0,\ v=G/\rho^0,\ \lambda_{\text{CK}}\frac{\partial\Theta}{\partial l}=\alpha(\Theta-T); \tag{6}$$

$$\text{for }\ l=L:\ \frac{\partial\Theta}{\partial l}=0;\quad \text{for }\ t=0:\ \Theta(0,\ l)=\Theta_0(l). \tag{7}$$

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Ordinarily, in chemical reactor calculations no account is taken of the effect of a change in pressure and speed of the flow along the length of the apparatus on the speed of the chemical conversion, the temperature in the apparatus, and the transport process. The present system of equations allows one to make estimates when such simplification is admissible. For this purpose we obtain explicit expressions for the determination of $dP/d\ell$, $dv/d\ell$, $dT/d\ell$ in terms of the parameters of the model and we present them in a dimensionless form:

$$\frac{d\ln\bar{P}}{d\eta}=-\frac{M^2kSL}{1-M^2}\left\{\frac{RW_1}{(k-1)C_PG}\sum_{j=1}^{4}\frac{\nu_j}{M_j}+\frac{\mathrm{St}(\Theta-T)}{T}+\frac{\xi'}{2}[1+(k-1)M^2]\right\}, \tag{8}$$

$$\frac{d\ln\bar{v}}{d\eta}=\frac{LS}{1-M^2}\left\{\frac{RW_1}{(k-1)C_PG}\sum_{j=1}^{4}\frac{\nu_j}{M_j}+\frac{\mathrm{St}(\Theta-T)}{T}+\frac{\xi'}{2}kM^2\right\}, \tag{9}$$

$$\frac{d\ln T}{d\eta}=\frac{LS}{1-M^2}\left\{-\frac{RW_1}{GC_P}\sum_{j=1}^{4}\frac{\nu_j}{M_j}+(1-kM^2)\frac{\mathrm{St}(\Theta-T)}{T}-\frac{kM^2\xi'v^2}{2C_PT}\right\}. \tag{10}$$

Here $\eta = \ell/L$; $k = C_p/C_V$; $St = \alpha/\rho C_p v$; $M^2 = v^2/c^2$; $c^2 = kR_mT$; $\bar{P} = P/P_0$ $\bar{v} = v/v_0$; $W_1 \doteqdot k_1\rho y_1 P$; $k_1 = k_{01}\exp(-E/R\Theta)$: $y_1P = y_1\beta/(k_1 + \beta)$; $\xi' = (1/\varepsilon^3)[54.45(1 - \varepsilon)/Re + 0.4]$.

From equations (8)-(10) it follows that changes in the pressure, speed of the flow, and temperature of the flow occur at the expense of a change in the number of the moles in the chemical reaction, heating of the flow at the expense of convective heat exchange and phase friction.

We now estimate the order of the terms appearing on the right sides of the equations, whereby we restrict ourselves to the case most typical for chemical reactors, namely, $M^2 \ll 1$, $Re \geqq 100$, $\varepsilon \approx 0.4$, $k = 1.4$, Θ and $T \leqq 1000$°K.

We transform some of the terms on the right sides of the equations:

$$\frac{RW_1}{(k-1)C_PG}\sum_{j=1}^{4}\frac{\nu_j}{M_j}=\frac{RW_1}{(k-1)C_PG}\sum_{j=1}^{4}\frac{n_j}{M_1}=\frac{R_1\Delta nW_1}{(k-1)C_PG}=$$

$$=\frac{R_1\Delta nW_1}{R_mkG},\quad\text{since}\quad C_P=\frac{R_mk}{(k-1)},\quad R_1=R/M_1;$$

$$\frac{d(\rho_1v)}{dl}=-W_1S\rightarrow G\frac{dy_1}{dl}=-W_1S\rightarrow\frac{W_1}{G}\sim\frac{\Delta y_1}{LS},$$

where Δy_1 is the change in concentration of the reacting component along the length of the layer; Δn is the change in the number of moles as a result of the reaction.

We now rewrite the system of equations (8)-(10), taking into account estimates of the order of the quantities appearing on the right sides of the equations:

$$\frac{d\ln\bar{P}}{d\eta}=-M^2kSL\left\{\Delta n\frac{\Delta y_1}{LS}+(10^{-2}-10^{-4})+1\right\},$$

$$\frac{d\ln\bar{v}}{d\eta}=LS\left\{\Delta n\frac{\Delta y_1}{LS}+(10^{-2}-10^{-4})+(10^{-3}-10^{-5})\right\}$$

$$\frac{d\ln T}{d\eta}=LS\left\{\underset{\mathrm{I}}{-\Delta n\frac{\Delta y_1}{LS}}+\underset{\mathrm{II}}{(10^{-2}\div10^{-4})}+\underset{\mathrm{III}}{(10^{-6}\div10^{-10})}\right\}$$

(I: chemical reaction; II, interphase heat exchange; III, phase friction).

Analyzing this system, we make the following conclusions.

1. Pressure change along the catalyzer layer is mainly due to phase friction, i.e., only the last term is important in Eq. (8).

2. For small speeds of the reacting mixture the variation of $\bar{v}$ is determined through convective heat exchange among the phases and by the variation in the number of moles as a result of the chemical reaction; for flow speeds greater than about 10 m/sec it is necessary to take into account phase friction. For catalyzer layers of sufficient extent or large specific surface the effect of a change in the number of moles on $\bar{v}$ can prove to be negligible.

3. In the thermal balance equation we can neglect the contribution of energy due to phase friction. Variation in temperature along the length of the layer is determined by heat exchange with the catalyzer and, in the case of a change in the number of moles, by the chemical reaction. The influence of the latter is important either only for large Δn or for intensive processes taking place over short layers of catalyzer.

The situation in which variation of $\bar{v}$ and T is determined through heat exchange with the catalyzer is of special interest. In this case $d\ln \bar{v}/d\eta = d\ln T/d\eta$, i.e., the speed of the flow in the catalyzer layer can be calculated in terms of the known temperature distribution. A situation of this kind is usually accepted without proof when chemical reactor calculations are made. As follows from these estimates, this holds only for a definite relationship among the parameters of the mathematical model.

To illustrate these results we carry out a numerical analysis of the complete system of equations (1)-(7). Since for problems of this kind the computational scheme and algorithm are, to our knowledge, not available in the literature, we shall dwell on them here in some detail.

2. An Algorithm for the Solution. We obtain difference schemes approximating the momentum, continuity, and thermal balance equations upon integrating the equations (1)-(3) from $\ell_{i-1/2}$ to $\ell_{i+1/2}$ and also applying the Newton–Leibnitz formula and the mean value theorem:

$$\int\limits_{l_{i-1/2}}^{l_{i+1/2}} g(l)\,dl = g(l_i)\int\limits_{l_{i-1/2}}^{l_{i+1/2}} dl.$$

Since the values of the variables at the resulting nodes are not known, for a positive flow rate the values at the points $\ell_{\ell-1/2}$ and $\ell_{i+1/2}$ "carry over" into the points ℓ_{i-1} and ℓ_i, respectively [3]. Carrying out these procedures, we obtain the following difference equations:

$$(\rho_j v)_i - (\rho_j v)_{i-1} = W_{ji-1}\hbar_i, \quad j = 1, 2, 3, 4, \tag{11}$$

$$G(v_i - v_{i-1}) = P_{i-1} - P_i - \xi G\hbar_i v_i/2, \tag{12}$$

$$GC_V(T_i - T_{i-1}) = \gamma\hbar_i(\Theta_i^{m+1} - T_i) - P_i(v_i - v_{i-1}) + (F_{\text{fr}})_{i-1}v_i\hbar_i, \tag{13}$$

where v_i, T_i, Θ_i^{m+1}, P_i are the values of the flow rate, the gas temperature, the catalyzer temperature, and also the pressure in the apparatus on the (m + 1)-st time layer, respectively; $\hbar_i = (h_i + h_{i-1})/2$; $W_{ji} = \nu_j W_{1i}$.

The data in this scheme are conservative since they reflect the basic properties of a continuous medium. The difference equations (11)-(13) approximate the initial system of differential equations with first order of accuracy in the spatial variable ℓ and they guarantee conservation of the mass outflow G.

The difference scheme for equation (4) is formulated by a well known method (see [4]):

$$\varepsilon_{\text{к}}\rho_{\text{к}}C_{\text{к}}\frac{\Theta_i^{m+1} - \Theta_i^m}{\tau} = \frac{\lambda_{\text{ск}}}{\hbar_i}\left(\frac{\Theta_{i+1}^{m+1} - \Theta_i^{m+1}}{h_{i+1}} - \frac{\Theta_i^{m+1} - \Theta_{i-1}^{m+1}}{h_i}\right) + (W_1Q)_i - \gamma(\Theta_i^{m+1} - T_i^m). \tag{14}$$

In the system of difference equations (11)-(14) the values of the variables at the i-th point in the (m + 1)-st time layer are not known. We effect the solution in the following order: first, with the aid of the driver method we calculate the catalyzer temperature, and then determine the values of all the flow variables with the help of an algorithm for the reduction of the system (11)-(13) to a quadratic equation in v_i and the selection of one of the roots of this equation. With the value of the speed known, determination of the remaining variables offers no difficulty.

Since the values of the catalyzer temperature and of the flow in the term $\gamma(\Theta_i^{m+1} - T_i^m)$ in the equation for the catalyzer temperature are taken from different time layers, it is necessary to organize the iterations. In solving the equation (14) a time step is chosen in an automatic way by comparing the results over a whole step and two time half-steps. After this we make a correction in accordance with Richardson's scheme, which enables us to increase the accuracy of the approximation with respect to the time to $O(\tau^2)$.

We proceed now to a detailed consideration of the algorithm for solving the system of equations (11)-(13). We rewrite the continuity equations and also the value of the pressure P at the i-th point in the following form:

$$\rho_{ji} = a1_{ji}/v_i, \tag{15}$$

$$P_i = \sum_{j=1}^{4} \rho_{ji} R_j T_i = \Big(\sum_{j=1}^{4} a1_{ji} R_j\Big) \frac{T_i}{v_i} = \frac{B_i}{v_i} T_i, \tag{16}$$

where $a1_{ji} = \rho_{ji-1} v_{i-1} + W_{ji-1} \hbar_i$; $B_i = \sum_{j=1}^{4} a1_{ji} R_j$.

Using the equation (16), we can readily obtain an expression for T_i in terms of v_i from the difference equation (13):

$$T_i = \frac{v_i\,[GC_V T_{i-1} + \gamma \hbar_i \Theta_i^{m+1} + (F_{\text{fr}})_{i-1} \hbar_i v_i]}{v_i\,(G\tilde{C}_V + \gamma \hbar_i) + B_i\,(v_i - v_{i-1})}. \tag{17}$$

From equations (16) and (17) we obtain an expression for P_i in terms of v_i:

$$P_i = (S_1 v_i + S_2)/(Z_1 v_i + Z_2), \tag{18}$$

where $S_1 = B_i (F_{fr})_{i-1} \hbar_i$; $S_2 = B_i (G\tilde{C}_V T_{i-1} + \gamma \hbar_i \Theta_i{}^{m+1})$; $Z_1 = G\tilde{C}_V + \gamma \hbar_i + B_i$; $Z_2 = -B_i v_{i-1}$.

Substituting the values of the pressure from equation (18) into the momenum equation (12) and simplifying, we obtain a quadratic equation in the v_i:

$$a_i v_i^2 + b_i v_i + c_i = 0,$$

where $a_i = GZ_1(L + \xi \hbar_i/2)$; $c_i = S_2 - Z_2(P_{i-1} + Gv_{i-1})$; $b_i = S_1 + a_i Z_2/Z_1 - Z_1(Gv_{i-1} + P_{i-1})$. We write the roots of this equation in a form yielding minimum roundoff error in the calculations:

$$(v_i)_{1,2} = \frac{-2c_i}{b_i \pm \sqrt{b_i^2 - 4a_i c_i}}.$$

The choice of sign for the root here is based on the continuity of the solution $v_i(\hbar_i)$ as a function of $\hbar_i$. Actually, letting $\hbar_i \to 0$ in equation (12), we shall have

$$G(v_i - v_{i-1}) = P_{i-1} - P_i. \tag{19}$$

If we rewrite the equation of state (5) in the form $P = GR_m T/v$ and substitute the resulting expression for P into equation (19), we obtain, after simplifications, a quadratic equation for the v_i:

$$v_i^2 - [v_{i-1} + R_m T_{i-1}/v_{i-1}]\, v_i + R_m T_i = 0. \tag{20}$$

Providing we have continuity of the temperature $T_i = T_{i-1}$, the roots of the equation (20) have the form

$$(v_i)_{1,2} = \frac{1}{2}\left(v_{i-1} + R_m T_{i-1}/v_{i-1} \pm \sqrt{(v_{i-1} - R_m T_{i-1}/v_{i-1})^2}\right). \tag{21}$$

From equation (21) it is easy to see that if $v^2{}_{i-1} > R_m T_{i-1}$, then $(v_i)_1 = v_{i-1}$, $(v_i)_2 = 2R_m T_{i-1}/v_{i-1}$, and if $v^2{}_{i-1} < R_m T_{i-1}$, then $(v_i)_1 = 2R_m T_{i-1}/v_{i-1}$, $(v_i)_2 = v_{i-1}$. Noting that $R_m T = P/\rho$, we formulate a simple rule for the choice of sign: if $v^2{}_{i-1} > (P/\rho)_{i-1}$, choose the + sign; if $v^2{}_{i-1} \leq (P/\rho)_{i-1}$, choose the − sign.

The algorithm we have described for solving the nonlinear system of difference equations (11)-(13) is iterationless and exact. We used it on the BESM-6 computer employing FORTRAN-4 computer language.

3. Results of the Numerical Analysis. In Figs. 1 and 2 we display some of the results from our calculations based on the algorithm described above. In our example we chose a reactor with $\Delta n = 0.4$ and LS = 120. In accordance with the estimates presented above, the friction in this case is the main influence on the distribution of the pressure over the layer, while the heating up of the catalyzer and the change in the number of moles as a result of the reaction affect the distribution of temperatures and flow speed. This leads to the fact that the quantitative regularities in the variation of the rate of flow and its temperature are not alike (see Fig. 1).

Figure 2 shows a comparison of the drops in pressure calculated from the mathematical model and the ΔP determined from the formulas given in [5], the latter being obtained in the absence of a chemical reaction. As can be seen from the figure, the agreement of the results is fairly good, testifying to the validity of our estimates.

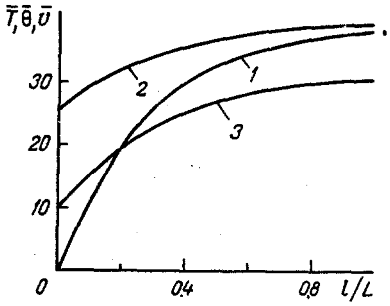

Fig. 1

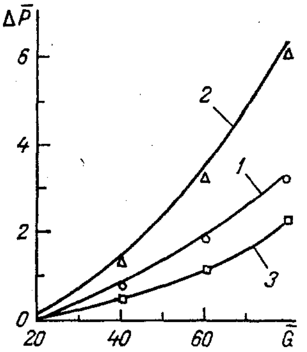

Fig. 2

Fig. 1. Stationary distribution of dimensionless flow temperature $\bar{T}$, catalyzer temperature $\bar{\Theta}$, and flow speed $\bar{v}$ along the length of the catalyzer layer: curve 1) $\bar{T} = (T - T_0)E/RT_0^2$; 2) $\bar{\Theta} = (\Theta - T_0)E/RT_0^2$; 3) $\bar{v} = (v/v_0)10$ (T_0, reference temperature; v_0, reactor inlet flow speed).

Fig. 2. Pressure drop $\Delta\bar{P}$, referred to the reference pressure, as a function of the reduced mass flow rate $\bar{G} = G/G_0$ for various grain sizes: curves labeled 1, 2, and 3 are for d_3/d_1 values of 1, 0.65, and 1.3, respectively; G_0, fixed mass flow rate; points shown are for $\Delta\bar{P}$ calculated from formulas in [5].

NOTATION

t, time; ℓ, length; ν_j, stoichiometric reaction coefficients; ρ_j, ρ, density of the j-th compnent and of the mixture, respectively: C_V, C_P, gaseous heat capacity at constant volume and pressure, respectively; v, flow velocity; G, mass flow rate; W_1, reaction rate; P, pressure; ξ, resistance coefficient; F_{fr}, interphase friction force = $\xi Gv/2$; T, Θ, flow and catalyzer temperatures, respectively; ε_K, ρ_K, C_K, fraction, density, and heat capacity of the catalyzer, respectively; λ_{CK}, coefficient of thermal conductivity on the layer; Q, thermal effect of reaction; $R_j = R/M_j$; R, universal gas constant; M_j, y_j, molecular weight and weight concentration of j-th component; R_m, gas constant of mixture; S, specific surface of layer; M, Re, St, Mach, Reynolds, and Stanton numbers, respectively; c, sound speed; L, apparatus length; α, β, coefficients of heat exchange and mass exchange, respectively; $\gamma = \alpha S$; T_{en}, flow temperature at entrance to layer; E, activation energy; k_{01}, preexponent; ε, voidage; τ, h_i, reactor time and space steps.

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