

NONSTEADY FLOW AND HEAT TRANSFER OF POLYMERIZING LIQUIDS IN A  
LONG TUBULAR REACTOR

A. M. Grishin and V. B. Nemirovskii

UDC 532.517.4:541.12:536.24

Low-temperature polymerization regimes with laminar flow of the reactants in a pipe were studied numerically in a two-dimensional formulation in [1].

The requirements of high productivity and an initial material (monomer) of low viscosity lead to the occurrence of turbulent flow regimes in a number of reactors. Intensive mixing taking place during turbulent flow of the reactants provides justification for introducing an assumption of complete equalization of the parameters of the reacting medium across the reactor and the use of the unidimensional "ideal substitution" model to analyze reactor performance. This was done in [2] in a modeling of the polymerization of ethylene in a high-pressure tubular reactor. However, under conditions leading to the formation of a sufficiently large quantity of polymer, a significant increase in the viscosity of the reacting medium may change the character of flow and heat transfer. In this case, the assumptions underlying the "ideal substitution" model may not be valid, and the performance of the reactor must be analyzed within the framework of a two-dimensional formulation.

The study of [3] employed such a formulation to numerically investigate the steady turbulent flow of a polymerizing liquid. It was established that with a sufficient content of polymer in the mixture, the turbulent flow may become laminar.

The present study, being an outgrowth of [3], numerically investigates the nonsteady high-temperature flow of polymerizing liquids with a high degree of conversion of the monomer into the polymer. It is shown that with the formation of a large concentration of polymer in the reacting medium, the effect of a significant change in viscosity on hydrodynamics and heat transfer leads to the formation of several flow regions along the reactor and to a non-monotonic change in flow velocity and temperature during the reaction in sections distant from the reactor inlet. It is established that over a certain time interval a steady flow forms in the case of a low degree of conversion of the monomer to the polymer. The transient period, meanwhile, becomes shorter with an increase in the rate of flow of the reacting liquid.

1. Formulation of the Problem. We are examining the turbulent flow of an incompressible, initially low-viscosity liquid which undergoes a thermal or induced polymerization in a long tubular reactor with noncatalytic walls. The flow rate of the liquid is constant. The liquid (monomer), with a temperature  $T_n$ , moves under the influence of a pressure gradient with a velocity corresponding to the specified flow rate. At the initial moment of time a heat carrier with the temperature  $T_0 > T_n$  is instantaneously fed into the jacket of the reactor. This causes heating of the reacting liquid and the beginning of the polymerization reaction (in the case of induced polymerization, a mixture of the monomer and a reaction initiator is also delivered at the initial moment of time). Thermal polymerization is modeled as the total zero- or first-order reaction, while in the case of induced polymerization we examine a kinetic model of ethylene polymerization at high pressure proposed in [2]. The temperature of the liquid entering the pipe is equal to  $T_n$ , while at the pipe inlet the velocity profile is uniform. The liquid is assumed to be Newtonian. It is also assumed that the density of the reacting medium changes negligibly during the reaction and can be considered constant.

Given these assumptions, turbulent flow of the polymerizing liquid in a long pipe is described in dimensionless variables for the general case by the following system of simplified Navier-Stokes equations:

$$\frac{\partial(u\eta)}{\partial\xi} + \frac{\partial(v\eta)}{\partial\eta} = 0; \quad (1.1)$$

---

Tomsk. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 1, pp. 72-81, January-February, 1985. Original article submitted December 20, 1983.

$$\frac{\partial u}{\partial \tau} + u \frac{\partial u}{\partial \xi} + v \frac{\partial u}{\partial \eta} = \text{Pr} \left[ \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \mu_{\Sigma} \eta \frac{\partial u}{\partial \eta} \right) - \frac{\partial \pi}{\partial \xi} \right]; \quad (1.2)$$

$$c_p \left( \frac{\partial \theta}{\partial \tau} + u \frac{\partial \theta}{\partial \xi} + v \frac{\partial \theta}{\partial \eta} \right) = \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \lambda_{\Sigma} \eta \frac{\partial \theta}{\partial \eta} \right) - \text{Le} \sum_{i=1}^n c_{pi} D_{\Sigma} \frac{\partial c_i}{\partial \eta} \frac{\partial \theta}{\partial \eta} + \delta w_j + \kappa \mu_{\Sigma} \left( \frac{\partial u}{\partial \eta} \right)^2; \quad (1.3)$$

$$\frac{\partial c_i}{\partial \tau} + u \frac{\partial c_i}{\partial \xi} + v \frac{\partial c_i}{\partial \eta} = \text{Le} \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( D_{\Sigma} \eta \frac{\partial c_i}{\partial \eta} \right) - \delta \gamma_i w_i \quad (i = \overline{1, n-1}); \quad (1.4)$$

$$\sum_{i=1}^n c_i = 1. \quad (1.5)$$

The system is closed by using the condition of constancy of the flow rate

$$Q = \int_0^1 u \eta d\eta = \text{const.} \quad (1.6)$$

System (1.1)-(1.6) must be solved with allowance for the initial and boundary conditions:

$$\tau = 0: u = 2Q, \theta = \theta_n, c_j = 1, c_i = 0 \quad (i = \overline{1, n-1}; i \neq j); \quad (1.7)$$

$$\tau > 0, \xi = 0: u = 2Q, \theta = \theta_n, c_i = c_{i0} \quad (i = \overline{1, n-1}); \quad (1.8)$$

$$\tau > 0, \xi > 0, \eta = 0: \partial u / \partial \eta = 0, v = 0, \partial \theta / \partial \eta = 0, \quad (1.9)$$

$$\partial c_i / \partial \eta = 0 \quad (i = \overline{1, n-1});$$

$$\tau > 0, \xi > 0, \eta = 1: u = 0, \partial \theta / \partial \eta = -\text{Bi} \theta, \quad (1.10)$$

$$\partial c_i / \partial \eta = 0 \quad (i = \overline{1, n-1}).$$

Here  $\tau = t/t_0$ ,  $\xi = x/r_0$ ,  $\eta = r/r_0$ ,  $u = U/u_0$ ,  $v = V/u_0$  are dimensionless values of time, the longitudinal and transverse coordinates, and the longitudinal and transverse components of velocity;  $r_0$ , internal radius of the pipe;  $t_0 = r_0^2 \rho \bar{c}_{pj} / \bar{\lambda}$ , characteristic time of thermal relaxation of the reacting medium;  $u_0 = r_0/t_0$ ;  $c_i$ , mass concentrations of the components;  $n$ , number of components;  $c_p = \sum_{i=1}^n c_i \bar{c}_{pi}$ , dimensionless specific heat of the mixture;  $c_{pi} = \bar{c}_{pi} / \bar{c}_{pj}$ ;  $\bar{c}_{pj}$ , dimensional specific heat of the monomer;  $\pi = p/p_0$ , dimensionless pressure;  $p_0 = \mu(T_0, 0) \bar{\lambda} / r_0^2 \rho \bar{c}_{pj}$ ;  $\theta = E_j (T - T_0) / RT_0^2$ , dimensionless temperature;  $R$ , universal gas constant;  $E_j$ , effective activation energy for polymerization or for growth of the chain;  $w_j$ , dimensionless reaction rates;  $w_j$ , rate of the chain growth reaction, with which most of the heat liberation is connected;  $\rho$ ,  $\bar{\lambda}$ , dimensional density and dimensional thermal conductivity of the reacting medium;  $\mu_{\Sigma} = \mu_t + \mu$ ,  $\lambda_{\Sigma} = \lambda_t + \lambda$ ,  $D_{\Sigma} = D_t + D$ , dimensional heat-transfer coefficients, calculated on the basis of the total-viscosity hypothesis;  $\mu_t$ ,  $\lambda_t = \mu_t \text{Pr} / \text{Pr}_t$ ,  $D_t = \mu_t \text{Pr} \text{Le}_t / \text{Pr}_t \text{Le}$ , dimensionless coefficients of turbulent transport;  $\mu$ ,  $\lambda$ , and  $D$ , dimensionless value of the coefficient of molecular viscosity, thermal conductivity, and effective coefficient of binary diffusion.

The dimensionless parameters:  $\delta = \frac{r_0 \rho q k_{0j} E_j \exp(-b_3 E_j / RT_0)}{\bar{\lambda} RT_0^2}$  is the Frank-Kamanetskii criterion;  $\text{Pr} = \mu(T_0, 0) \bar{c}_{pj} / \bar{\lambda}$  is the Prandtl number;  $\text{Le} = \bar{D}(T_0, 0) \rho \bar{c}_{pj} / \bar{\lambda}$  is the Lewis-Semenov number;  $\beta = RT_0 / E_j$ ;  $\gamma_i = \gamma_j \frac{k_{0i}}{k_{0j}} \exp\left(\frac{b_3 E_j - E_i}{RT_0}\right)$ ;  $\gamma_j = \frac{\rho \bar{c}_{pj} RT_0^2}{q E_j}$ ;  $\kappa = \frac{\mu(T_0, 0) \bar{\lambda} E_j}{r_0^2 \rho^2 c_p^2 RT_0^2}$ ;  $q$  is the thermal effect of the reaction;  $b_e$  is a dimensionless parameter which accounts for the effect of pressure on the reaction rate;  $\text{Pr}_t$  and  $\text{Le}_t$  are the turbulent Prandtl and Lewis-Semenov numbers (in the present work, we took  $\text{Pr}_t = \text{Le}_t = 1$ ). The subscript  $j$  pertains to the monomer.

The second boundary condition of (1.10) was obtained on the assumption that the characteristic time of thermal relaxation of the reacting medium is such longer than the time of thermal relaxation of the steel wall of the reactor. In this case, heat conduction in the reactor wall is quasisteady in character, and the heat-conduction equation is easily integrated with allowance for compatibility conditions for heat flux and temperature on the inside wall of the pipe and conditions of heat transfer in accordance with Newton's law with the heat carrier on the outside wall. This leads to the second condition of (1.10), where  $\text{Bi} = k_t r_0 / \bar{\lambda}$ . The heat-transfer coefficient  $k_t$  accounts for the combined thermal resistance of the wall and the heat carrier and is determined by the expression

$$k_t = \frac{1}{\left( \frac{1}{\alpha_n r_n} + \frac{\ln r_n / r_0}{\lambda_c} \right) r_0},$$

where  $r_n$  and  $\alpha_n$  are the outside radius of the pipe and the heat-transfer coefficient on the outside surface;  $\lambda_c$  is the thermal conductivity of the wall.

Most studies investigating the turbulent flow of liquids with variable physical properties use semiempirical models of turbulence developed for liquids with constant properties to calculate turbulent transport coefficients. Allowing for the variable properties of calculating the physical properties entering into the turbulent transport coefficients with local temperatures or at the wall temperature. The literature contains no information on the use of well-known semiempirical models to study the turbulent flow of polymerizing liquids. In the present work, as in [3], the turbulent transport coefficient was calculated from a modification of the van Driest formula. Here, the variability of the properties was accounted for by calculating the coefficient of molecular viscosity entering into the van Driest damping factor with local values of temperature and polymer concentration. The mutual effect of turbulent pulsations and the chemical reaction was not considered in our calculations due to the extreme complexity and the lack of generally accepted data on this subject. It was assumed that the usual gradient representations [4] are valid for the turbulent flows of heat and mass. The coefficient of molecular thermal conductivity was assumed constant. As in [3], the dependence of the coefficient of molecular viscosity on polymer concentration and temperature was calculated from the formula obtained in [5] on the basis of analysis of empirical data on the flow of solutions of a polymer in a monomer. This formula appears as follows in dimensionless variables

$$\mu(\theta, c_g) = \exp\left(Wc_g - \frac{b_1 + b_2 c_g}{1 + \beta\theta}\theta\right),$$

where  $W = A_0 + A_1/RT_0$ ;  $b_1 = E_0/E_j$ ;  $b_2 = A_1/E_j$ ;  $A_0, A_1, E_0$  are empirical coefficients determined from experiment or from literature data.

In the case of thermal polymerization it was assumed that the mixture consists of two components ( $n = 2$ ): monomer and polymer. In induced polymerization we assumed four components ( $n = 4$ ): initiator, monomer, active radicals, and polymer. In the last case, in the calculation we introduced the assumption that the reacting medium was binary, since the molecules can tentatively be divided into two groups ("heavy" molecules of radicals and the polymer and "light" molecules of the initiator and monomer). The effective coefficients of binary diffusion were calculated from the Wilke and Chang formula from [6] for the case of low solute concentration.

2. Solution Algorithm and Numerical Analysis of a Model Problem. Boundary-value problem (1.1)-(1.10) was solved numerically by an iteration-interpolation method [7].

The solution algorithm was similar to that described in [3], the only difference being that we used a difference scheme obtained by the iteration-interpolation method to solve non-steady two-dimensional parabolic equations.

First we used the program written to compute the problem to calculate several test variants. In particular, we studied the case of transition to steady flow regimes, with a change from turbulent to laminar flow, as described in [3].

We then computed the model problem. Here, the effective kinetics of the thermal polymerization corresponds to a first-order reaction. A distinctive feature of the model problem was the specification of a large value to the parameter  $\gamma_j = \gamma$ , which made it possible to study basic features of a polymerization involving a high degree of conversion of monomer to polymer.

Also, we assumed that the wall temperature was equal to the temperature of the heat carrier  $T_0(\theta)|_{\eta=1} = 0$ , i.e., the thermal resistance of the wall and heat carrier was not considered. This corresponds to the case  $Bi \rightarrow \infty$ . Thus, we examined conditions of the first type for the temperature at the wall.

Figure 1 shows the main results of the solution of the model problem. The figure shows transverse profiles of flow velocity and monomer temperature and concentration in several sections of the pipe at different moments of time. The results were obtained with  $\gamma = 0.5$ ,  $\theta_n = -8.8$ ,  $\delta = 171$ ,  $\kappa = 0.132 \cdot 10^{-14}$ ,  $\beta = 0.033$ ,  $W = 20.04$ ,  $b_1 = 0.044$ ,  $b_2 = 0.35$ ,  $b_3 = 1$ ,  $Bi = \infty$ ,

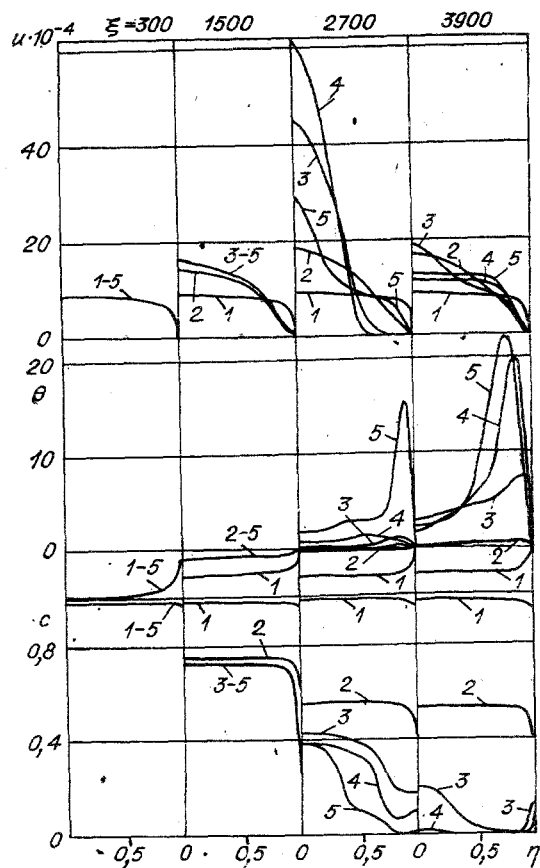


Fig. 1

and a flow rate corresponding to a mean velocity of 0.5 m/sec (the Reynolds number at the pipe inlet  $Re_0 = 105,400$ ). Curves 1 correspond to  $\tau = 0.0059$ ; 2) 0.0193; 3) 0.0294; 4) 0.0359; 5) 0.0696.

It is apparent from the graphs that at a short distance from the inlet ( $\xi = 300$ ) the process quickly changes over to a nearly steady regime. Developed turbulent flow of the "cold" liquid, containing almost no polymer, is established here. Somewhat farther from the inlet ( $\xi = 1500$ ) the liquid is heated almost to the temperature of the wall, remaining a bit colder than it. The concentration of polymer increases as a result of chemical conversion. Here, laminar flow takes place due to the significant increase in the viscosity of the reacting medium [3]. For this flow region the running Reynolds number  $Re|_{\xi=1500} = \bar{u}2r_0\rho/\mu_0(T, c_g)|_{\xi=1500} \approx 700$  ( $\bar{u}$  is the flow velocity averaged over the cross section, while  $\mu_0(T, c_g)$  is the viscosity of the medium in the center of the pipe, calculated from the temperature and concentration of the polymer on the axis), i.e., it becomes significantly less than the critical value.

The velocity profile is deformed from that for developed turbulence to an almost parabolic form, with an inflection point near the wall. The inflection point is due to the presence of a thin layer of substantially more viscous liquid near the wall (containing a large quantity of polymer), which is in turn due to the fact that the temperature of the wall is significantly higher than the temperature of the interior portion of the pipe. Still farther from the inlet ( $\xi = 2700$ ), the pattern of flow over time develops in a more complicated manner. During laminarization of the flow the additional heat liberation from the reaction caused the temperature in the pipe to become higher than the wall temperature. This is accompanied by a substantial increase in the concentration of polymer in the mixture and a substantial increase in the viscosity of the medium. These developments enhance the role of mechanical heat sources, the intensity of which is greatest in the region of the greatest velocity gradients. A maximum appears on the temperature profile. Polymerization is rapidly completed in the vicinity of the maximum, and a layer of very viscous, low-mobility liquid is formed near the wall. Due to the constant flow rate, velocity increases in the center of the pipe, and a stream of considerably less viscous liquid is formed. Later, mechanical heat liberation in the layer of low-mobility viscous polymer leads to a sharp increase in temperature near the wall (hydrodynamic ignition [8]), so that a temperature peak occurs. In the vicinity of this

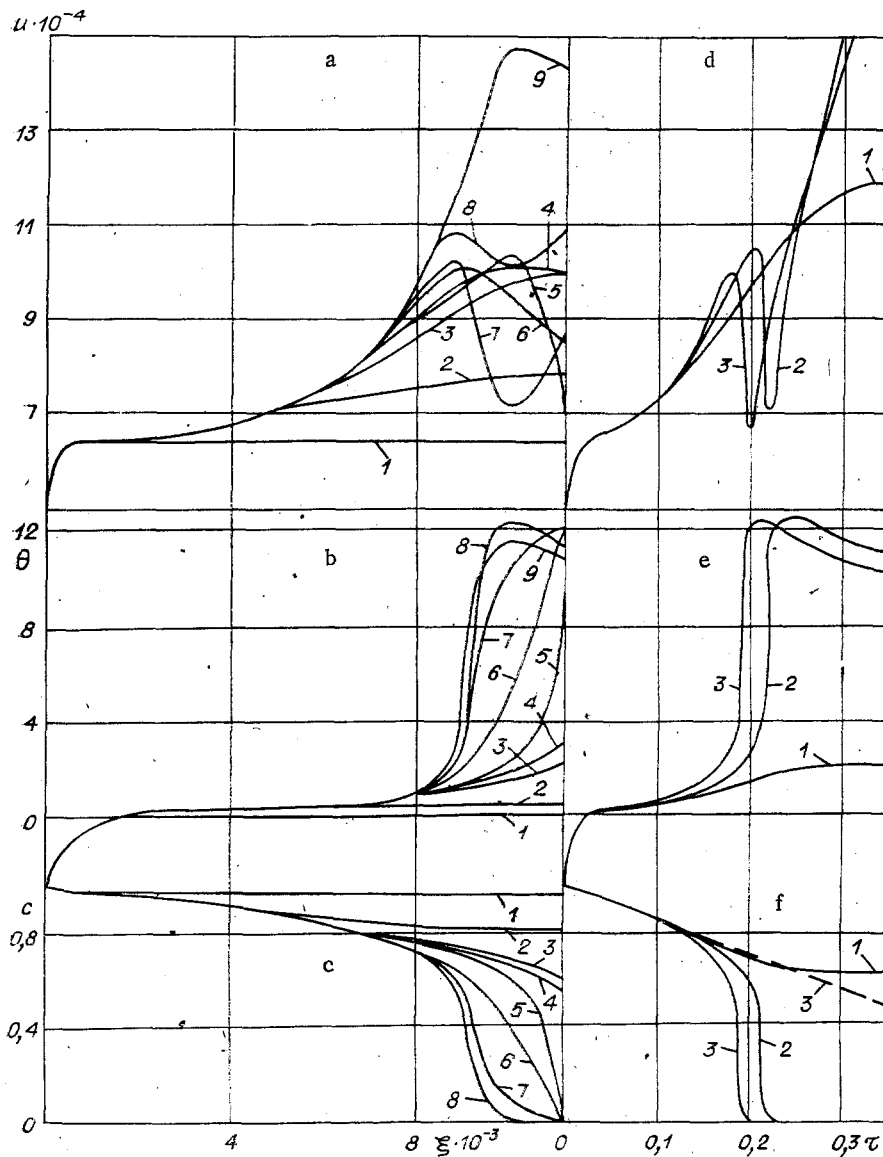


Fig. 2

peak, polymer viscosity decreases, while flow velocity increases. The velocity profile is deformed again (see curve 5, Fig. 1) to a complex shape with two inflection points.

Still farther from the inlet ( $\xi = 3900$ ), where a mixture containing a high concentration of polymer is present, the combined heat liberation from the chemical reaction and the mechanical heat sources leads to rapid polymerization across the entire pipe. In the vicinity of the temperature peak the viscosity of the polymer melt decreases, and the complicated velocity profile with two inflection points changes into a planar profile outwardly similar to the velocity profile for turbulent flow.

Thus, the strong effect of the chemical reaction on hydrodynamics and heat transfer leads to the formation of four regions of flow along the pipe: a region of developed turbulent flow of a low-viscosity liquid; a region of laminarized flow; a region of laminar flow with a low-mobility boundary layer and a stream of less viscous liquid in the center of the pipe; a region of flow of polymer melt with a quasiturbulent velocity profile.

3. Results of Numerical Solution of a Problem on Thermal Polymerization and Their Analysis. Together with the model problem, we calculated flow variants with the effective kinetics of the thermal polymerization of styrene presented in the literature and well approximating the actual kinetics [9].

Here, for a pipe of a certain length, we calculated both laminarization of the flow — with a monotonic transition to a steady regime and a moderate degree of monomer-to-polymer conversion — and nonsteady flow with a high degree of conversion and a nonmonotonic change in

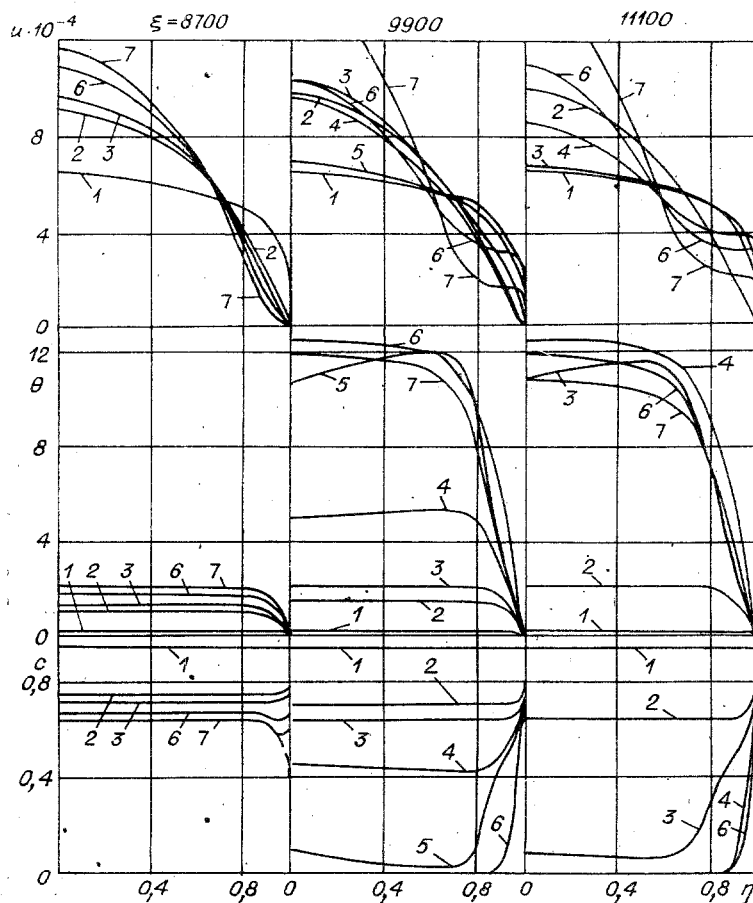


Fig. 3

flow velocity and temperature. Both variants were calculated as functions of flow rate.

Figures 2 and 3 show results corresponding to nonsteady flow with almost complete conversion of monomer to polymer. The results were obtained for a pipe with the radius  $r_0 = 0.01$  m with  $T_n = 373^\circ\text{K}$  ( $\theta_n = -2.76$ ),  $T_0 = 423^\circ\text{K}$ ,  $\delta = 34.15$ ,  $\kappa = 0.447 \cdot 10^{-14}$ ,  $W = 17.5$ ,  $b_1 = 0.123$ ,  $b_2 = 0.99$ ,  $b_3 = 1$ ,  $\beta = 0.043$ ,  $\gamma = 0.061$ ,  $Bi = \infty$  and a flow rate corresponding to a mean velocity of 0.4 m/sec ( $Re_0 = 33,600$ ).

Figure 2a-c shows, respectively, the change along the pipe in the flow velocity  $u$ , temperature  $\theta$ , and concentration  $c$  of the monomer on the pipe axis at different moments of time [1)  $\tau = 0.0234$ ; 2) 0.1184; 3) 0.1734; 4) 0.1825; 5) 0.1925; 6) 0.2144; 7) 0.2176; 8) 0.2475; 9) 0.238]; Fig. 2d-f shows the time change in the same parameters of the reacting medium in three sections far from the inlet [1)  $\xi = 8700$ ; 2) 9900; 3) 11,100]. The dashed line in Fig. 2f shows the change in the concentration of the monomer at the pipe wall in the last-noted section.

It follows from analysis of Fig. 2 that in the last section the liquid is first heated to the temperature of the wall. Then additional heat liberation from the reaction results in a further increase in polymer temperature and concentration. This in turn increases the viscosity of the reacting medium, and at a certain polymer concentration the flow becomes laminar. This development is accompanied by an increase in flow velocity in the center of the pipe and a decrease in flow velocity in the wall region. The temperature in the central region of the pipe subsequently increases sharply due to the combined effect of chemical and mechanical heat sources, and very rapid polymerization to the point of almost complete conversion of monomer to polymer occurs in this region. Here, in contrast to the model problem calculation above, the monomer concentration in a thin layer near the wall remains significantly greater than in the center due to the temperature difference. The thin layer of appreciably less viscous liquid plays the role of a lubricant over which flows the melt of viscous polymer. This results in the occurrence of rod-type flow. Flow velocity increases at the wall and sharply decreases in the center. However, the concentration of polymer at the wall continues to increase (although slowly), the viscosity of the lubricating layer

increases, and flow velocity in and near the layer falls. Due to the constancy of the flow rate, velocity in the center of the pipe again begins to increase and temperature slowly decreases due to the cessation of functioning of the chemical heat sources and redistribution of the mechanical heat sources. With a certain time shift, a similar pattern develops in sections closer to the inlet. However, in the sections closest to the inlet, where little polymer is formed and the change in the viscosity of the medium is small, the velocity, temperature, and concentration change monotonically over time and rapidly assume values nearly constant over time. The time over which these quantities become quasisteady is shorter, the closer the section to the pipe inlet. Thus, as the calculations showed, in a long reactor allowing polymerization to proceed to complete conversion of monomer to polymer, it is possible to establish a quasisteady flow regime in sections fairly close to the inlet. However, on the whole the process is nonsteady in character — at least up to the times to which the calculations were performed.

Figure 3 shows profiles of flow velocity, temperature, and concentration of the monomer in three sections far from the inlet at different moments of time [1)  $\xi = 0.0484$ ; 2) 0.1734; 3) 0.1925; 4) 0.2144; 5) 0.2176; 6) 0.2475; 7) 0.2980]. The dashed line at  $\xi = 8700$  shows a stationary monomer concentration profile. It is apparent that on the whole the pattern of development of the process is similar to that described in the case of the model problem. The main feature is the presence of less viscous liquid near the wall in the lubricating layer. This liquid is due to the lower rate of polymerization near the wall compared to the rate of the reaction in the central region of the pipe, which is heated by chemical and mechanical heat liberation. The presence of the lubricating layer also explains the absence of the second inflection point on the velocity profiles, with a characteristic "shelf" near the wall. Thus, the change in the composition of the medium during polymerization significantly alters the viscosity of the medium, with the formation of a large quantity of polymer in the reactor. The effect of this change on flow hydrodynamics and heat and mass transfer ensures a process which is nonsteady on the whole, a nonmonotonic change in flow velocity and temperature far from the inlet, and pronounced nonuniformity of the parameters of the reacting medium across the reactor.

4. Results of Mathematical Modeling of Induced Polymerization and Their Analysis. The above examples of calculation of nonsteady flow in a polymerization reactor were obtained for relatively low flow rates with allowance for the effective kinetics of thermal polymerization, where there are no formal reasons limiting the degree of conversion of monomer to polymer.

In the case of induced radical polymerization, the amount of polymer formed in the reactor is determined in particular by the concentration of initiator at the inlet and is usually not great. Having the process occur at high flow rates helps increase the rate of turbulent mixing and increases the uniformity of the parameters of the reacting medium across the reactor.

Presented below is an example of a calculation of the radical polymerization of ethylene in a high-pressure tubular reactor. We used the kinetic model of induced radical polymerization proposed in [2]. Oxygen was examined as the initiator.

The results of the calculation are shown in Figs. 4 and 5 and were obtained for a reactor with an inside radius  $r_0 = 0.02$  m and an outside radius (of the pipe)  $r_n = 0.0475$  m, with  $T_n = 423^\circ\text{K}$  ( $\theta_n = -0.68$ ) and  $T_0 = 473^\circ\text{K}$ . The concentration of initiator at the inlet  $c_{10} = 1.95 \cdot 10^{-5}$ , while the flow rate corresponded to a mean velocity of 12.41 m/sec. The substantial thickness of the walls of the high-pressure reactor makes it necessary to allow for the thermal resistance of the walls and the heat carrier. The results were obtained with  $Bi = 150.4$ .

Figure 4 shows the change along the reactor of the temperature  $\theta$  (solid curves) and the concentration of the initiator  $c_1$  (dashed lines), monomer  $c_2$  (solid curves), and radicals  $c_3$  (dashed lines) on the reactor axis at different moments of time [1)  $\tau = 0.1$ ; 2) 0.2; 3) 0.3; 4) stationary longitudinal profiles for  $\tau > 0.5$ ].

It is apparent that the reacting mixture is first heated to a temperature at which an intensive reaction begins. There is then a further increase in temperature due to heat liberation from the chemical reaction. Meanwhile, prior to the moment the mixture is heated to the reaction temperature, there is only a small quantity of the conveyed flow in the sections of the reactor farthest from the inlet, and the initiator has not yet successfully reacted.

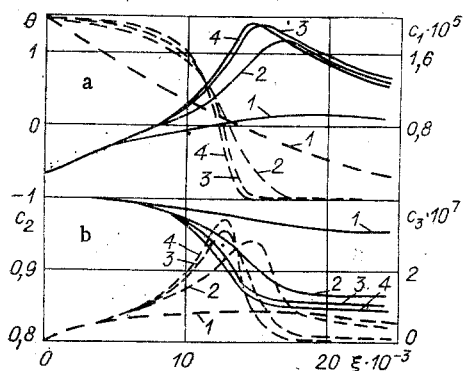


Fig. 4

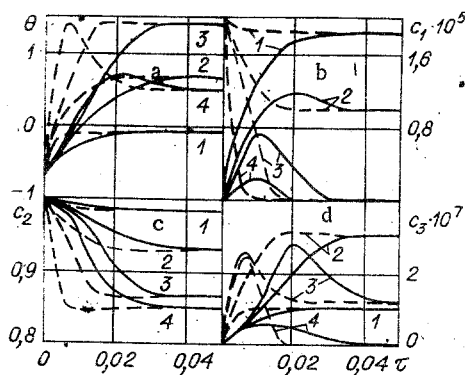


Fig. 5

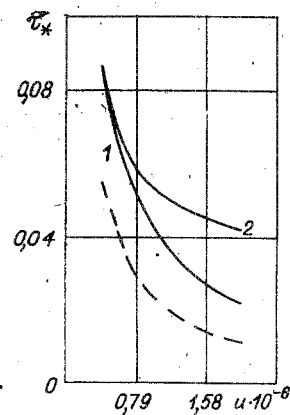


Fig. 6

Here, the rate of consumption of the initiator is significantly greater than the rate of its delivery by the flow, the reaction is completed quickly, and the mixture undergoes cooling.

The temperature maximum is formed closer to the inlet along with a region of intensive decomposition of the initiator, radical formation, and monomer polymerization (the reaction zone). As the region preceding the reaction zone becomes richer in initiator, the zone shifts in the direction of the inlet and the temperature maximum increases. The reaction rate here also increases, and all of the initiator decomposes. When equilibrium is established between the rate of delivery of initiator to the reaction zone and the rate of its consumption in the reaction, the shift in the reaction zone ceases, and a steady state is established (curves 4 in Fig. 4).

Figure 5a-d shows graphs depicting the change in temperature and the concentrations of the initiator, monomer, and radicals on the reactor axis with the elapse of time for several reactor sections [solid curves, 1)  $\xi = 7000$ ; 2) 12,000; 3) 14,500; 4) 24,500]. It is apparent from the figure that, given the above conditions, the polymerization process in the reactor reaches the steady regime fairly quickly. Meanwhile, the steady state is established later in the most distant sections of the reactor, where the initiator undergoes complete decomposition and the reaction is almost completed. The time required to reach the steady regime in this region of the reactor  $\tau_*$  can be termed the reactor start-up time. For comparison, Fig. 5 shows dashed curves obtained in the same reactor sections but with initial conditions such that at the initial moment of time the reactor is filled not with pure monomer but with a mixture of monomer and initiator having a temperature equal to the temperature at the inlet. The time required to reach the steady regime is considerably shorter in this case than with initial conditions of the first type (1.7). In the last sections of the reactor, where the reaction is completed, the concentration of the polymer is low (about 15%) and is determined by the flow rate and concentration of the initiator at the inlet and the temperature of the heat carrier. The transverse profiles of the temperature and concentration of the reactants, which are not presented here, are nearly uniform in all sections of the reactor.

It is interesting to note the dependence of the reactor start-up time on the flow rate (or mean flow velocity) and temperature of the reactants at the reactor inlet. Such a dependence was obtained with initial conditions of the second type, corresponding to the dashed curves in Fig. 5, and is shown in Fig. 6 [1)  $\theta_n = -0.68$ ; 2)  $\theta_n = -0.82$ ]. The curves were obtained with the same initial initiator concentration, and the initial temperature coincided with the temperature at the inlet. Values of the dimensionless mean flow velocity are plotted off the x axis. The start-up time  $\tau_*$  was determined at the distance  $\xi = 22,000$  ( $x = 440$  m) from the reactor inlet. As  $\tau_*$  we took the moment of time when the subsequent change in the temperature and concentration of the monomer in this section did not exceed 1% in relative value. The dashed line in Fig. 6 shows the dependence of the characteristic time of convection  $\tau_0 = L/\bar{u}$  ( $L$  is the length of the reactor,  $\bar{u}$  is the mean flow velocity) on the mean velocity. It is apparent that the value of  $\tau_*$  quickly decreases with an increase in flow velocity. Meanwhile, the character of this dependence is the same as for the characteristic time of convection  $\tau_0$ . A decrease in the initial temperature causes an increase in  $\tau_*$  in the case of high flow rates and causes almost no change for low flow rates. This occurs because the time required to reach the steady regime  $\tau_*$  is determined by the time of convective transport of a particle of the reacting liquid and the relaxation time. With low flow rates, the time of



convective transport is much longer than the time of the chemical reaction. Thus,  $\tau_*$  is slightly dependent on the reaction time, which in turn is determined by the initial temperature.

#### LITERATURE CITED

1. S. A. Bostandzhiyan, V. I. Boyarchenko, et al., "Low-temperature polymerization regimes in a flow-through reactor," *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 1 (1979).
2. B. L. Gutin, S. G. Lyubetskii, Z. N. Polyakov, et al., "Mathematical model and analysis of the operation of a tubular reactor for ethylene polymerization under high pressure," in: *Polymerization Processes. Equipment Design and Mathematical Modeling* [in Russian], ONPO "Plastpolimer," Leningrad (1976).
3. A. M. Grishin and V. B. Nemirovskii, "Laminarization of a turbulent flow of a polymerizing liquid in long pipes," *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 4 (1983).
4. B. S. Petukhov, "Turbulence in heat-transfer theory," in: *Heat and Mass Transfer - VI. Problem Documents of the VI All-Union Conference on Heat Transfer*, Pt. 1, Minsk (1981).
5. V. A. Khokhlov, V. V. Konsetov, G. I. Kozlova, and G. A. Balaev, "Study and modeling of optimum conditions for the polymerization of monomers in solution or bulk," in: *Modeling Chemical Processes and Reactors* [in Russian], Vol. 2, Novosibirsk (1971).
6. R. Reed and G. Sherwood, *Properties of Gases and Liquids* [Russian translation], Khimiya, Leningrad (1971).
7. A. M. Grishin and V. N. Bertsun, "Iteration-interpolation method and spline theory," *Dokl. Akad. Nauk SSSR*, 214, No. 4 (1977).
8. A. M. Grishin and V. B. Nemirovskii, "Regimes of flow of viscous reacting liquids in long long pipes," *Fiz. Goreniya Vzryva*, No. 3 (1979).
9. V. V. Korshak (ed.), *Plastics Engineering* [Russian translation], Khimiya, Moscow (1976).

#### TWO-PHASE FLOW IN A CHANNEL WITH ERODING WALLS

V. V. Kriklivyi, A. P. Trunev,  
and V. M. Fomin

UDC 532.529.5+629.7.036.54

The problem of two-phase flow in an axisymmetric channel, the walls of which can be destroyed through erosion, is considered in the paper. Two-phase flows in channels accompanied by wall erosion were studied in [1-4]. Since the mechanism of energy transfer to the eroding surface can differ depending on the conditions at the flow boundaries, each of these investigations is of independent interest. Here we consider erosion under the impact action of solid or liquid particles [5], while the main mechanism of energy transfer is assumed to be convective transport of the condensed phase. An erosion model describing this case was proposed in [6], and it lay at the basis of the present work. Certain exact relations connecting the parameters of the condensed phase with the parameters of the profile of the axisymmetric channel are obtained. It is shown that the process of erosion with convective transport of particles to the wall develops unstably, and the time of development of the instability is estimated. A numerical quasi-one-dimensional model of two-phase flow in a channel with eroding walls is developed, permitting a wide range of parametric research.

#### 1. Determination of Particle Trajectories in Two-Phase Flow

We consider the flow of a mixture of a gas and solid particles in an axisymmetric channel with curved walls. We take the gas to be inviscid and not thermally conducting in its interaction with the solid boundary and we neglect the intrinsic volume of the particles. To describe the flow we introduce a cylindrical coordinate system with the origin in the entrance cross section of the channel and we designate the axial coordinate as  $x$  and the radial coordinate as  $y$ . The following equations [7] are satisfied for the steady motion of particles of radius  $a$  along the trajectory of motion  $y_\alpha(x)$ :

$$u_a du_a/dx = \varphi_a(u - u_a), u_a dv_a/dx = \varphi_a(v - v_a),$$

---

Novosibirsk. Translated from *Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki*, No. 1, pp. 82-87, January-February, 1985. Original article submitted December 27, 1983.