

Characteristic features of polymerizing fluid flow in tubular reactor are the strong dependence of viscosity depth of transformation and temperature, and low viscosity of the initial substance, viz, the monomer, which leads to turbulent flow at sufficiently large mass flows. Two-dimensional laminar flow of viscous chemically reacting fluids was numerically and analytically studied in [1, 2] taking temperature dependence of viscosity into consideration, and in [3] the simultaneous dependence of viscosity on temperature as well as on the depth of transformation of the reagent was taken into account. In the present paper a numerical study is carried out on turbulent flow of reacting fluid in long pipes with strong dependence on the depth of transformation, temperature, and variable boundary conditions along the pipe length

1. Consider stationary turbulent flow of chemically reacting Newtonian fluid in a long pipe with noncatalytic walls, at constant mass flow. Assume that the velocity profile at inlet is uniform, fluid inlet temperature is T_0 , the pipe walls are maintained at constant temperature, equal to the inlet temperature or the wall temperature is a function of stream-wise coordinate. A binary mixture is assumed.

The system of equations describing the stationary turbulent flow of reacting fluid in a long pipe, expressed in nondimensional variables, has the form

$$\begin{aligned} \frac{\partial(u\eta)}{\partial\xi} + \frac{\partial(v\eta)}{\partial\eta} &= 0, \\ u \frac{\partial u}{\partial\xi} + v \frac{\partial u}{\partial\eta} &= \text{Pr} \left[\frac{1}{\eta} \frac{\partial}{\partial\eta} \left(\mu_{\Sigma} \eta \frac{\partial u}{\partial\eta} \right) - \frac{\partial\pi}{\partial\xi} \right], \\ \bar{c}_p \left(u \frac{\partial\Theta}{\partial\xi} + v \frac{\partial\Theta}{\partial\eta} \right) &= \frac{1}{\eta} \frac{\partial}{\partial\eta} \left(\lambda_{\Sigma} \eta \frac{\partial\Theta}{\partial\eta} \right) - \text{Le} (1 - \bar{c}_{p2}) D_{\Sigma} \frac{\partial c_1}{\partial\eta} \frac{\partial\Theta}{\partial\eta} \\ &\quad + \delta c_1 \exp \frac{\Theta}{1 + \beta\Theta} + \kappa \mu_{\Sigma} \left(\frac{\partial u}{\partial\eta} \right)^2, \\ u \frac{\partial c_1}{\partial\xi} + v \frac{\partial c_1}{\partial\eta} &= \text{Le} \frac{1}{\eta} \frac{\partial}{\partial\eta} \left(D_{\Sigma} \eta \frac{\partial c_1}{\partial\eta} \right) - \delta \gamma c_1 \exp \frac{\Theta}{1 + \beta\Theta}, \\ Q &= \int_0^1 u \eta d\eta = \text{const}. \end{aligned} \quad (1.1)$$

Equations (1.1) have to be solved with the following boundary and initial conditions:

$$\begin{aligned} \partial u / \partial \eta |_{\eta=0} &= 0, \quad v(\xi, 0) = 0, \quad \partial \Theta / \partial \eta |_{\eta=0} = 0, \quad \partial c_1 / \partial \eta |_{\eta=0} = 0, \\ u(\xi, 1) &= 0, \quad \Theta(\xi, 1) = \varphi(\xi), \quad \partial c_1 / \partial \eta |_{\eta=1} = 0, \\ u(0, \eta) &= 2Q, \quad \Theta(0, \eta) = 0, \quad c_1(0, \eta) = 1, \end{aligned} \quad (1.2)$$

where

$$\begin{aligned} \Theta &= (E/RT_0^2)(T - T_0); \quad \bar{c}_p = c_1 + \bar{c}_{p2}(1 - c_1); \quad \bar{c}_{p2} = c_{p2}/c_{p1}; \quad \text{Pr} = \\ &= \mu(T_0, 1) c_{p1} / \lambda; \\ \text{Le} &= \frac{D(T_0, 1) \rho c_{p1}}{\lambda}; \quad \delta = \frac{r_0^2 E q k_0 \exp(-E/RT_0)}{\lambda RT_0^2}; \quad \kappa = \frac{\mu(T_0, 1) \lambda E}{r_0^2 \rho_1^2 RT_0^2}; \end{aligned}$$

$$\beta = \frac{RT_0}{E}; \quad \gamma = \frac{c_{p1} \rho RT_0^2}{qE}; \quad \mu_\Sigma = \mu_M + \mu_T; \quad \lambda_\Sigma = 1 + \mu_T \frac{Pr}{Pr_T};$$

$$D_\Sigma = \frac{1}{\mu_M} + \mu_T \frac{Pr}{Pr_T} \frac{Le_r}{Le}; \quad \mu_M = \exp \left[W(1 - c_1) - \frac{b_1 + b_2(1 - c_1)}{1 + \beta\theta} \theta \right];$$

$$W = A_0 + A_1/RT_0; \quad b_1 = E_0/E; \quad b_2 = A_1/E; \quad \pi = \frac{p \rho c_{p1} r_0^2}{\mu(T_0, 1)\lambda};$$

$$Pr_T = 1; \quad Le_r = 1.$$

Here x , r , U , and V are dimensional streamwise and transverse coordinates, and streamwise and transverse velocity components respectively; r_0 is the pipe radius; p is the pressure; ρ , c_{p1} are the density and specific heat of the monomer; T is the temperature, E , q are the activation energy and thermal effect of the chemical reaction; R is the universal gas constant; k_0 is the pre-exponential constant; μ , λ , and D are dimensional coefficients of molecular viscosity, heat conductivity, and binary diffusion. The index M denotes non-dimensional molecular viscosity coefficient, T denotes nondimensional eddy viscosity and turbulent similarity parameters for Prandtl and Lewis numbers, Σ is the effective viscosity coefficient, which, according to the hypothesis on total viscosity [4], is equal to the sum of molecular and eddy viscosities.

The dependence of molecular viscosity coefficient was given by the equation obtained in [5] from experimental results on the flow of polymer solutions in monomer:

$$\mu = \mu_0 \exp \{A_0(1 - c_1) + [E_0 + A_1(1 - c_1)]/(RT)\},$$

where μ_0 , A_0 , E_0 , and A_1 are empirical coefficients determined from experiment or reference data. Molecular viscosity coefficient was computed from equations given by Wilkes and Cheng [6] for binary mixtures (solutions), and the coefficient of molecular heat conductivity was assumed constant.

As a concrete example, the polymerization of ethylene at high pressure in a tubular reactor was studied under turbulent flow conditions of the reagent. Effective thermokinetic reaction constants of polymerization of ethylene at high pressure, as given in [7] was used to compute nondimensional parameters that determine the heat release. Thermophysical and mechanical parameters of the medium were computed at polymerization temperature and a pressure of 200 MPa at which the reacting medium is homogeneous and the compressed ethylene has the properties of incompressible liquid droplet [8]. Experimental data from [7, 9, and 10] were used to compute these parameters. The coefficient of eddy viscosity was computed from equations based on "mixing length" theory [4] which has the following form in the chosen nondimensional variables

$$\mu_T = (1/Pr)(l\varepsilon)^2 |\partial u / \partial \eta|. \quad (1.3)$$

Some semiempirical turbulent models suggested in [11-14] for pipe flows were considered:

$$l = 0.14 - 0.08\eta^2 - 0.06\eta^4, \quad \varepsilon = 1; \quad (1.4)$$

$$l = 0.4(1 - \eta), \quad \varepsilon = 1 - \exp \left[\left(-\sqrt{\frac{\tau_w}{Pr}} \frac{1 - \eta}{\mu_M} \right) / 26 \right]; \quad (1.5)$$

$$l = 0.13 - 0.06\eta^2 - 0.07\eta^4, \quad \varepsilon = 1 - \exp \left[\left(-\sqrt{\frac{\tau_w}{Pr}} \frac{1 - \eta}{\mu_M} \right) / 26 \right]. \quad (1.6)$$

Here Eq. (1.4) corresponds to Prandtl-Nikuradze turbulent model [11], (1.5) corresponds to Van Driest model [12-14], and (1.6) represents Van Driest model in the form suggested in [14], and τ_w is the nondimensional shear stress at the wall.

2. The boundary-value problem (1.1), (1.2) was solved on a computer using iterative-interpolation method (IIM) [15]. As a result of using IIM, an implicit six-point difference scheme is obtained with quasilinearization of sources by Newton's method. The method of factorization of momentum equations suggested in [16] was used to find the unknown pressure gradient.

Laminar flow of inert and reacting fluids at zero eddy viscosity coefficients was computed in order to verify the program. Computations on inert fluid in the stable region of the flow gave skin friction coefficient and Nusselt number Nu differing by 2 and 1.5%

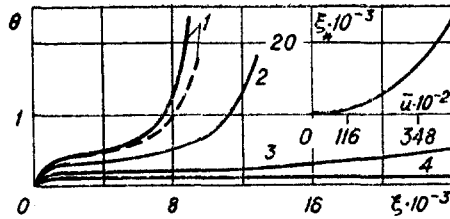


Fig. 1

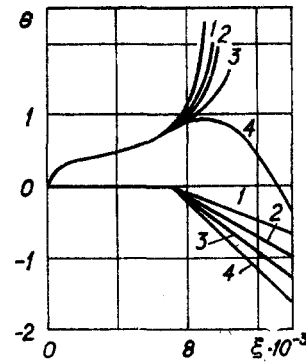


Fig. 2

respectively from the known values for stable laminar flow, viz., $\zeta = 64/\text{Re}$ [4] and $\text{Nu} = 3.65$ [17]. Velocity and temperature fields completely agreeing with results of [1] were obtained in the computation of reacting fluid flow, taking into consideration the dependence of viscosity on temperature

Besides, in order to select the turbulence model, computation was carried out for isothermal, inert fluid flow within a wide range of Reynolds numbers. Computed velocity profiles in the stable region were compared with Nikuradze's [4] experimental velocity profiles.

The best agreement was obtained by using Van Driest model in the form (1.6) when the deviation between experimental and computed profiles decreased with increase in Reynolds number. Thus, when $\text{Re} = 105 \cdot 10^3$, the maximum difference between these profiles did not exceed 1% at the core of the flow for the model defined by Eqs. (1.6), whereas for other models the deviation was appreciably more (up to 10%). Consequently, the modified Van Driest model (1.3), (1.6) was used in subsequent computations.

In the numerical investigation of polymerizing fluid, the flow region with constant wall temperature equal to the inlet temperature, i.e., $\varphi(\xi) = 0$ in boundary conditions (1.2) was initially studied. The variation in temperature along the pipe axis with increasing distance from the pipe entrance is shown in Fig. 1 for various mass flows. Curves were obtained for a pipe radius $r_0 = 0.015$ m with inlet temperature $T_0 = 500^\circ\text{K}$ ($\delta = 26$, $\kappa = 0.284 \times 10^{-14}$, $b_1 = 0.044$, $b_2 = 0.35$, $\text{Pr} = 1.56$, $\text{Le} = 0.3 \times 10^{-2}$, $\beta = 0.031$, $\gamma = 0.013$). Curves 1-4 represent mean section velocity of 0.25, 0.3, 0.5, 1.0 m/sec at $\text{Re}_0 = 37180, 44616, 74360, 148720$. Continuous curves were obtained for $W = 20.04$ which corresponds to viscosity of the final product, viz, the fusion of polyethylene (computed with $c_1 = 0$), given $\mu(T_0, 0) = 5 \times 10^4$ N·sec/m². Dashed curve was obtained for $W = 18.43$ ($\mu(T_0, 0) = 10^4$ N·sec/m²).

It is seen from computed results shown in Fig. 1 that for a given value of δ , different thermal conditions can be obtained depending on mass flow. At very small mass flow (curves 1 and 2) large heat release from intensive chemical reaction leads to progressive increase in reaction rate and a sharp increase in temperature at a distance from the entrance ξ_* (critical pipe length). When the pipe length exceeds ξ_* , the process becomes explosive in nature. According to the terminology suggested in [2], such a flow condition is called self-ignition.

With an increase in mass flow, the process just described extends along the pipe length as a result of convective heat transfer along the flow (ξ_* increases) and with sufficiently large mass flow the fluid is only negligibly heated near the pipe entrance due to chemical heat release and further down-stream the temperature remains practically constant (curve 4). Thus, for a reasonable length of the pipe, a quasiisothermal flow condition is maintained. Chemical transformation in this case is small, the depth of transformation does not exceed a few percent over a large distance from the inlet.

At the top right hand corner of Fig. 1 is shown the dependence of critical pipe length ξ_* on the mean flow velocity for the same nondimensional parameters ($W = 20.04$). It is seen that the dependence of ξ_* on mass flow is nonlinear. With an increase in mass flow, ξ_* increases very rapidly and at very large mass flows self-ignition does not occur even in a very long pipe.

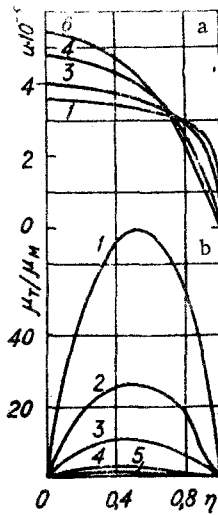


Fig. 3

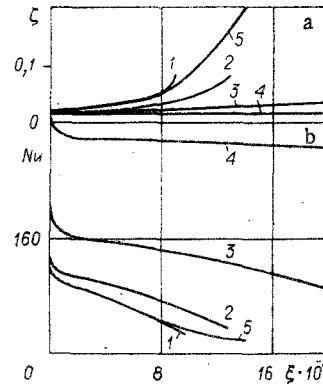


Fig. 4

It is seen from a comparison of the continuous and dashed curves in Fig. 1 that for a large viscosity of the end product ξ_* decreases. This can be explained by an increase in the role of mechanical heat sources with large viscosity of the reacting medium. It is worth mentioning that the role of mechanical source $\kappa \mu_{\Sigma} (\partial u / \partial \eta)^2$ in the general energy balance even in laminar flow of a very viscous fluid is considerably weaker than the role of chemical source or the term $\frac{1}{\eta} \frac{\partial}{\partial \eta} \left(\lambda_{\Sigma} \eta \frac{\partial \Theta}{\partial \eta} \right)$ [1] and results in only an additional heat release.

Since the governing system is nonlinear, small effects can lead to large changes in the nature of the flow and heat transfer and even, as shown in [1, 2], become the cause of hydrodynamic ignition.

It follows from computations that self-ignition condition in turbulent flow of polymerizing fluid occurs with a transformation depth of about 20%. Here, as a result of an increase in the viscosity of the reacting medium, the velocity profile begins to deform and becomes less fully developed.

The variation in temperature boundary conditions along the pipe was studied for flow control. The case of linear drop in wall temperature at a certain distance from the inlet was considered, i.e.,

$$\varphi(\xi) = \begin{cases} 0, & \xi < \xi_1, \\ \Theta_1 \frac{\xi - \xi_1}{\xi_2 - \xi_1}, & \xi \geq \xi_1, \end{cases}$$

where $\xi_2 - \xi_1$ is the length of the cooled segment; Θ_1 is the temperature at the end of the cooled segment. The beginning of the cooled segment ξ_1 was chosen in the region of inflection in the temperature curve in the self-ignition zone.

Figure 2 shows the variation of temperature along the axis of the pipe and the corresponding change in wall temperature for the same values of the nondimensional parameters as in Fig. 1, and a mass flow corresponding to the mean velocity of 0.25 m/sec ($\xi_1 = 7 \times 10^3$, $\xi_2 = 14 \times 10^3$, curves 1-4 correspond to $\Theta_1 = -0.64, -0.96, -1.28, -1.6$). The curve without a number was obtained at constant wall temperature

It follows from an analysis of Fig. 2 that with an increase in the rate of cooling of the wall the critical pipe length increases (curves 1-3). Finally, for a certain cooling rate the heat transfer to the pipe wall exceeds the heat input from chemical reaction and the temperature of the reacting medium begins to fall rapidly (curve 4). In this case the self-ignition condition is not realized and the flow laminarization takes place. When the transformation depth is more than 20%, the initial turbulent flow becomes completely laminar as a result of a rapid increase in the viscosity of the reacting medium.

This conclusion follows from an analysis of Fig. 3* where flow velocity profiles are shown at different distances from the inlet (a) and profiles of the ratio of eddy viscosity to molecular viscosity are shown in (b) for laminarization conditions corresponding to curve 4 of Fig. 2 ($\xi = 100, 4000, 7000, 10,000, 13,000, 14,000$, curves 1-6 respectively).

It is seen clearly that as the reacting mixture moves into the depth of the pipe, the velocity profile changes from fully developed turbulent flow near the inlet to a laminar profile at a distance $\xi = 14,000$ from the inlet, similar to profiles obtained in [1]. Reynolds number for the laminar flow region, computed on the basis of mean velocity, is considerably less than the critical value and for the example shown in the figures it is 390.

It is interesting to observe that in the turbulent region the concentration profile is practically homogeneous whereas in the fully laminar flow within a very narrow region close to the wall there is a sharp decrease in reagent concentration to a value differing from the core by 10% and more. A thin film of a substance more viscous than the fluid at the center of the pipe is formed near the wall. This is probably because the velocity decreases near the wall during the transition from turbulent to laminar flow but the transition time increases. As a result of this the depth of transformation also increases.

As seen from Fig. 3b, the ratio of eddy viscosity to molecular viscosity which is much greater than unity in turbulent flow, rapidly decreases as the flow moves deeper into the pipe and becomes less than unity in the fully laminar region.

Thus, a decrease in wall temperature in the case of high temperature polymerization in flow-through reactors can be used for process control by increasing the critical reactor length or through flow transition from turbulent to laminar flow without a rapid rise in the temperature of the reacting medium.

It is mentioned in [18] that laminarization of inert fluids by variations in temperature or mass flow was discovered a number of decades ago. The possibility of laminarization by chemical reaction has been obtained, apparently, for the first time.

The variation in nondimensional skin friction coefficient (a) $\zeta = 8Pr_w \tau_w / (4Q^2)$ and local Nusselt number (b) $Nu = (2\partial\theta/\partial\eta|_{\eta=1}) / (\theta_w - \theta^0)$ (θ^0 is the temperature at the core of the flow, θ_w is the pipe wall temperature) with distance from pipe inlet is shown in Fig. 4. Curves 1-4 were obtained for constant wall temperature and correspond to conditions of laminarization of turbulent flow with drop in wall temperature and the values of the parameters correspond to the curve 4 of Fig. 3.

In the quasiisothermal case (curve 4) the transformation depth is small and the flow resembles the inert fluid flow. A comparison of the skin friction coefficient for quasiisothermal condition at a large distance from pipe inlet, with the skin friction coefficient for a stable flow of an inert fluid using Nikuradze's equation [4] $\zeta = 0.0032 + 0.221/Re^{0.237}$, shows that the difference does not exceed 2-3% (depending on the distance from the inlet) because of reactivity of the medium and certain change in viscosity during the reaction. For the same case, a comparison has been made for the local Nusselt number at a distance $\xi = 100$ (where the singularity is still practically absent) with the value of Nu computed from the formula recommended for fully developed turbulent flow in pipes and channels [17]:

$$Nu = 0.021Re^{0.8}Pr^{0.43}(Pr/Pr_w)^{0.25}\epsilon,$$

where Pr_w is Prandtl at wall temperature, $\epsilon = 1$ when $\xi > 30$. The error in this numerical experiment was 1%.

In high temperature polymerization, friction coefficient initially increases gradually due to the increase in viscosity. In the rapidly increasing temperature zone the friction coefficient increases rapidly due to an increase in reaction rate and the formation of viscous polymer near the pipe wall. Transition to laminar flow begins in this zone of the pipe. With a reduction in wall temperature in the segment where the reaction rate increases and further chemical transformation leads to complete laminarization, the skin friction coefficient (see Fig. 4a, curve 5) approaches a value determined by laminar skin friction coefficient $\zeta = 64/Re$ (the difference is nearly 20% and is explained by unstable flow situation). Local Nusselt number decreases rapidly as a result of a very large increase in viscosity, change in flow dynamics and the nature of heat transfer. The temperature profiles are

*Curves 2, 5 in Fig. 3a and 6 in Fig. 3b are not shown to preserve the clarity of other curves.

shifted in such a manner that the temperature gradient increases slower than the difference in the wall and core temperature. With a reduction in wall temperature the nature of heat transfer is again changed (see Fig. 4b, curve 5) due to wall temperature effects, Nusselt number becomes many times lower than the value that is characteristic for the fully developed turbulent flow near the pipe inlet. In the laminar flow region Nu is almost five times greater than the value $Nu = 3.65$ that is characteristic of stabilized laminar flow. Such a difference is also explained by thermally unstable nature of flow in this region.

Thus, there could be a transition from turbulent to laminar flow under conditions of continuous reaction in flow-through polymerization reactor of great length.

LITERATURE CITED

1. A. M. Grishin and V. B. Nemirovskii, "Flow conditions for viscous reacting fluids in long pipes," *Fiz. Goreniya Vzryva*, 15, No. 3 (1979).
2. A. M. Grishin and V. B. Nemirovskii, "Flow and heat transfer of viscous, reacting fluids in long tubes," *Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza*, No. 1 (1980).
3. S. A. Bostanzhiyan, V. I. Boyarchenko, et al., "Low temperature polymerization in flow-through pipes," *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 1 (1979).
4. L. G. Loitsyanskii, *Mechanics of Liquids and Gases* [in Russian], Nauka, Moscow (1978).
5. V. A. Khokhlov, V. V. Konsetov, et al., "A study and modeling of optimal conditions for the polymerization of monomers in mass or solution," in: *Modeling Chemical Processes and Reactors* [in Russian], Vol. 2, Novosibirsk (1971).
6. R. Reid and T. Sherwood, *Properties of Gases and Liquids: Their Estimation and Correlation*, McGraw-Hill (1966).
7. *Polyethylene and Other Polyolefins* [Russian translation], Mir, Moscow (1964).
8. A. P. Golosov and A. I. Dintses, *Polyethylene and Polyolefin Production Technology* [in Russian], Khimiya, Moscow (1978).
9. N. B. Vargaftik, *Handbook on Thermal and Physical Properties of Liquids and Gases* [in Russian], Fizmatgiz, Moscow (1963).
10. R. V. Torner, *Theoretical Principles of Processing Polymers* [in Russian], Khimiya, Moscow (1977).
11. H. Schlichting, *Boundary Layer Theory*, McGraw-Hill, New York (1978).
12. B. S. Petukhov, V. D. Vilenskii, and N. V. Medvetskaya, "Application of semi-empirical models to compute heat transfer in turbulent flow of single phase coolants in pipes with near-critical parameters," *Teplofiz. Vys. Temp.*, 15, No. 3 (1977).
13. O. A. Nekhamkina and M. A. Rotinyan, "Computation of turbulent flow of polyatomic gases in pipes," *Inzh.-fiz. Zh.*, 33, No. 4 (1977).
14. N. M. Galin and V. M. Esin, "Computation of heat transfer to turbulent flow in circular and annular pipes, taking into consideration thermophysical properties of the coolant as a function of temperature," *Teplofiz. Vys. Temp.*, 15, No. 6 (1977).
15. A. M. Grishin and V. N. Bertsun, "Iterative-interpolation method and the method of splines," *Dokl. Akad. Nauk SSSR*, 214, No. 4 (1974).
16. L. M. Simuni, "Numerical solution of nonisothermic flow of viscous fluid in a plane pipe," *Inzh.-fiz. Zh.*, 10, No. 1 (1966).
17. V. B. Kogan, *Theoretical Principles of Standard Processes in Chemical Engineering* [in Russian], Khimiya, Leningrad (1977).
18. M. M. Nazarchuk, M. M. Kovetskaya, and V. N. Panchenko, *Reverse Transition of Turbulent Flow into Laminar* [in Russian], Naukova Dumka, Kiev (1974).