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RADIALLY SYMMETRIC FLOW OF REACTING LIQUID WITH CHANGING VISCOSITY*

S. E. SOLOVYOV†, V. A. VOLPERT‡, AND S. P. DAVTYAN§

Abstract. Frontal regimens for one-dimensional flow of reacting liquid with changing viscosity are studied. Stationary solutions are investigated for the case of narrow reaction zones that shrink to a front. The results of numerical solution of the nonstationary problem are presented. Complex oscillations resulting from period-doubling bifurcations are found.

Key words. reacting liquid, frontal regimes, changing viscosity, oscillations, period doubling

AMS(MOS) subject classifications. 34B15, 49G99, 80A25

1. Introduction. In this work, we investigate frontal regimes of an exothermic reaction with radially symmetric injection of reactants. We consider a reactor for which the reaction zone is located between two porous infinite coaxial cylinders. A reactive liquid is injected through the inner cylinder and removed through the outer one. The reactants are driven by an externally applied pressure gradient, with the pressure difference between the outer and inner cylinders assumed to be given. This model has various applications. We apply it to investigate polymerization processes. Therefore we take into account some specific features of these processes. We suppose that the species are in the liquid phase throughout the reactor and their viscosity changes due to the reaction. The density of the reactants is assumed to be constant, since its change is small for a number of polymerization processes. Moreover, we neglect the diffusion of the reactants since diffusion for many monomer-polymer systems is very slow. Such assumptions are conventional in polymer science [1]–[8].

Under these assumptions, the conservation laws for energy, mass fraction, momentum, and mass for one-step irreversible reaction in a one-dimensional flow can be written in polar coordinates as

$$(1.1) \quad \frac{\partial T}{\partial t} = \kappa \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - V \frac{\partial T}{\partial r} + qK(T)(1 - \alpha),$$

$$(1.2) \quad \frac{\partial \alpha}{\partial t} = -V \frac{\partial \alpha}{\partial r} + K(T)(1 - \alpha),$$

$$(1.3) \quad \rho \left(\frac{\partial V}{\partial t} + V \frac{\partial V}{\partial r} \right) = - \frac{\partial p}{\partial r} + \eta \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial V}{\partial r} \right) - \frac{V}{r^2} \right) + 2 \frac{\partial \eta}{\partial r} \frac{\partial V}{\partial r},$$

$$(1.4) \quad \frac{\partial V}{\partial r} + \frac{V}{r} = 0.$$

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Here T is the temperature, α is the degree of conversion, r is the radial coordinate ($r_0 \leq r \leq r_1$), κ is the thermal diffusivity, q is the adiabatic heat release, and ρ is the density of the reactants. We take $K(T)$ to have the Arrhenius form

$$K(T) = k_0 \exp(-E/R_0T),$$

where E is the activation energy, R_0 is the universal gas constant, and k_0 is preexponential factor. It is assumed that the velocity V of the medium and the pressure p , as well as T and α , depend on the radial coordinate only. The viscosity η is a function of T and α . Its form will be discussed below.

The boundary conditions are

$$r = r_0: T = T_i, \alpha = 0; \quad r = r_1: \partial T / \partial r = 0.$$

We consider the reactants to be premixed. They do not react before they enter the reactor because their temperature is low. We also assume that the reaction zone is not very close to the outer cylinder, so that $\alpha \approx 1$ for $r = r_1$.

There are a number of works devoted to the model presented above in the case when the velocity at the inlet of the reactor is given. Stationary solutions, their stability and two-dimensional solutions resulting from instabilities of stationary solutions are studied in [3]–[5]. More complex chemistry is considered in [7], while [8] deals with hydrodynamical stability of the reaction front.

In this work, we consider the value $\Delta p = p_1 - p_0$ to be prescribed. Here p_0 and p_1 are the values of the pressure for $r = r_0$ and $r = r_1$, respectively. In this case, the velocity at the entrance of the reactor is unknown and should be found as part of the solution of the problem.

From (1.4), we have

$$(1.5) \quad V(r, t) = V_0(t) \frac{r_0}{r},$$

where $V_0(t)$ is the velocity at the entrance of the reactor. Substituting (1.5) into (1.3) and integrating (1.3) from r_0 to r_1 , we obtain

$$(1.6) \quad \frac{\partial V_0}{\partial t} = - \frac{1}{\rho r_0 \ln(r_1/r_0)} \left(\Delta p + 2V_0 r_0 \int_{r_0}^{r_1} \frac{1}{r^2} \frac{\partial \eta}{\partial r} dr \right).$$

We have omitted the quadratic term here since the Reynolds number is sufficiently small [1].

Thus we consider the system of equations (1.1), (1.2), (1.6). Section 2 is devoted to the analytical investigation of the stationary problem. We discuss the results of numerical computations for the nonstationary problem in § 3.

2. Stationary regimes. In this section, we apply the narrow reaction zone approximation developed by Zeldovich and Frank-Kamenetskii (see [9], [10]) to find a solution of the stationary problem. We denote by R the radius of the reaction zone and solve the linear equations

$$(2.1) \quad \kappa \frac{1}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) - V_0 \frac{r_0}{r} \frac{dT}{dr} = 0, \quad V_0 \frac{r_0}{r} \frac{d\alpha}{dr} = 0$$

for $r_0 < r < R$ and $R < r < r_1$. These solutions should be matched at $r = R$ as follows:

$$(2.2) \quad T|_{R-0} = T|_{R+0}, \quad \left. \frac{dT}{dr} \right|_{R-0} - \left. \frac{dT}{dr} \right|_{R+0} = \frac{qV_0 r_0}{\kappa R},$$

$$(2.3) \quad \left(\frac{dT}{dr} \right)_{R-0} - \left(\frac{dT}{dr} \right)_{R+0} = \frac{q}{\kappa} \int_{T_i}^{T(r)} K(T) dT.$$

From (2.1) and (2.2), we have

$$T(r) = \begin{cases} T_b - q + q(r/R)^{V_0 r_0/\kappa}, & r_0 \leq r \leq R, \\ T_b, & R \leq r \leq r_1, \end{cases}$$

$$T_b = T_0 + q - q(r_0/R)^{V_0 r_0/\kappa},$$

$$a(r) = \begin{cases} 0, & r_0 \leq r \leq R, \\ 1, & R < r \leq r_1, \end{cases}$$

where T_b is the temperature in the reaction zone. From (2.3), we obtain the equation for R ,

$$(2.4) \quad \left(\frac{V_0 r_0}{R}\right)^2 = \frac{\kappa}{q} \int_{T_i}^{T_b} K(T) dT.$$

Using the Frank-Kamenetskii transform [10]

$$\int_{T_i}^{T_b} K(T) dT \approx k_0 \frac{R_0 T_b^2}{E} \exp\left(-\frac{E}{R_0 T_b}\right)$$

and denoting

$$w = \frac{V_0}{V_n}, \quad \delta = \frac{\kappa}{V_n r_0}, \quad V_n = \left(\frac{\kappa}{q} k_0 \frac{R_0 T_a^2}{E} \exp\left(-\frac{E}{R_0 T_a}\right)\right)^{1/2},$$

$$T_a = T_i + q, \quad \sigma = \frac{q}{T_a}, \quad Z = \frac{E(T_a - T_i)}{2 R_0 T_a^2}, \quad s = \frac{R}{r_0},$$

we rewrite (2.4) in the form

$$(2.5) \quad s = w \left(1 + \frac{\sigma}{s^{w/\delta} - \sigma}\right) \exp \frac{Z}{s^{w/\delta} - \sigma}.$$

We note that V_n is an approximate value of the normal velocity of the front in an unmoving medium for first-order reactions [11]; w and s are the dimensionless velocity at the entrance of the reactor and the radius of the reaction zone, respectively.

To simplify (2.5), we consider the case when $s^{w/\delta} \gg \sigma$. This inequality is specific for the process under consideration if the reaction zone is not very close to the entrance of the reactor. Thus we can replace (2.5) by

$$(2.6) \quad s = w \exp(Z s^{-w/\delta}).$$

This allows us to find s as a function of w for various values of Z and δ . This function has been studied in detail in [3], and we do not study it here.

Thus we have the system of two equations (1.6), (2.6) from which w and s can be found. In the approximate analysis, we consider η as a piecewise constant function,

$$\eta = \begin{cases} \eta_0, & \alpha = 0, \\ \eta_1, & \alpha = 1. \end{cases}$$

This means that $\eta = \eta_0$ for $r_0 \leq r \leq R$ and $\eta = \eta_1$ for $R < r \leq r_1$. We can take η in this form, since the dependence of polymer viscosity on the degree of conversion is much stronger than its dependence on temperature [12], [13]. Moreover, computations for

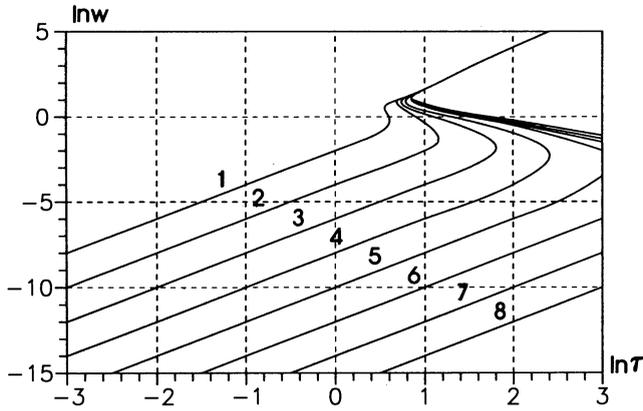


FIG. 1. Dependence $w(\tau)$ for a fixed δ (in $\ln - \ln$ coordinates): $\delta = 1.2$, 1.— $Z = 1$, 2.—2, 3.—3, 4.—4, 5.—5, 6.—6, 7.—7, 8.—8.

the nonstationary problem show that the specific form of the function $\eta(\alpha, T)$ is not very important (see § 3). Thus we have

$$\int_{r_0}^{r_1} \frac{1}{r^2} \frac{d\eta}{dr} dr \approx \frac{\Delta\eta}{R^2},$$

where $\Delta\eta = \eta_1 - \eta_0$. From (1.6), we obtain

$$(2.7) \quad s = \tau w^{1/2},$$

where

$$\tau = \left(-\frac{2V_n\Delta\eta}{\Delta p r_0} \right)^{1/2}.$$

From (2.6), (2.7), we numerically find w as a function of τ for various δ and Z (Figs. 1 and 2). We see that there is only one solution for $\tau < \tau_1(\delta, Z)$ and $\tau > \tau_2(\delta, Z)$, while there are three solutions for $\tau_1(\delta, Z) \leq \tau \leq \tau_2(\delta, Z)$. For w sufficiently large, (2.6) can be rewritten approximately as $s = w$. Thus we obtain the asymptotic result $w \simeq \tau^2$ for large τ .

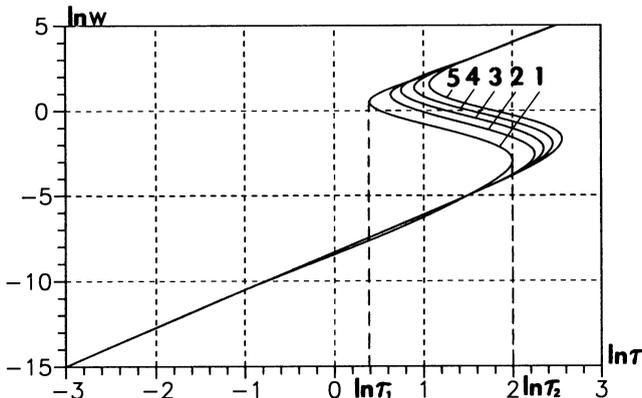


FIG. 2. Dependence $w(\tau)$ for a fixed Z (in $\ln - \ln$ coordinates: $Z = 3.88$, 1.— $\delta = 0.25$, 2.—1, 3.—1.5, 4.—2, 5.—2.5).

3. Numerical results.

3.1. Numerical method. For the numerical computations, a conservative finite-difference scheme with upwind differences was used. We applied the Thomas algorithm for inversion of tridiagonal matrices and used an adaptive space mesh with at least 15–20 grid points in the reaction zone. The accuracy of the simulations was verified by increasing the number of the grid points and by decreasing the timestep, which was taken to be constant.

3.2. Viscosity formula. We have considered three different forms of the function $\eta(\alpha, T)$ in the numerical simulations

$$(3.1) \quad \eta = \begin{cases} \eta_0, & r_0 \leq r \leq R, \\ \eta_1, & R < r \leq r_1, \end{cases}$$

$$(3.2) \quad \eta = \eta_0 + (\eta_1 - \eta_0)\alpha^n,$$

$$(3.3) \quad \eta = \eta_0 + \Delta\eta\alpha^n k_1 \exp(-E_1/R_0T).$$

Here R is the radius of the reaction zone. In the numerical simulations, we find R as the distance from the point $r = 0$ to the point where the degree of conversion equals 0.5. We take the values of the parameters specific for methylmetacrylate polymerization [3], [13]: $\kappa = 0.3 \text{ cm}^2/\text{min}$, $T_i = 300 \text{ K}$, $q = 170 \text{ K}$, $E = 20 \text{ kcal/mol}$, $\eta_0 = 0.1 \text{ Pa}\cdot\text{sec}$, $\eta_1 = 1000 \text{ Pa}\cdot\text{sec}$. The value of n is varied from 1 to 10, and k_1 is taken in such a way that $k_1 \exp(-R_1/R_0T_b) = 1$.

The simulations show that the qualitative behavior of the solutions depends on the form of the function $\eta(\alpha, T)$ only weakly, though the duration of the transition period and other quantitative characteristics of the observed modes can depend on it. In the case when $\eta_1 \gg \eta_0$, which is specific for polymerization processes, we can approximate $\Delta\eta$ by η_1 , which is a basic parameter that characterizes the viscosity as a function of the temperature and the degree of conversion.

3.3. Results and discussion. We note that different stationary regimes can exist in plug-flow reactors: high-temperature, low-temperature, and intermediate (see, for example, [3]). In the model under consideration, there are from one to three high-temperature regimes (Figs. 1 and 2). The numerical simulations show that these stationary modes are unstable but the type of the instability is different for the different branches of the curve $w(\tau)$. If the initial conditions are chosen in such a way that they are close to the stationary solution on the second branch, then an oscillatory instability occurs. We describe the observed modes below. If the initial conditions are close to the stationary solutions on the third branch, then the reaction zone leaves the reactor and the low-temperature mode appears instead of the high-temperature one, or a transition to the oscillations mentioned above occurs. Finally, if the initial conditions are taken corresponding to the first branch, then we also observe a transition to the oscillations around the second branch or the reaction zone tends toward the entrance of the reactor. In the last case, the width of the reaction zone increases considerably and the maximal temperature in the reactor decreases. This is another form of the transition to the low-temperature regime.

Thus we conclude that the stationary solutions on the first and third branches are unstable, corresponding to a real eigenvalue crossing into the right half plane. Solutions on the second branch are unstable, corresponding to a pair of complex conjugate eigenvalues crossing into the right half plane.

We discuss now the oscillations observed in the numerical simulations. We varied k_0 and Δp while the other parameters were fixed. Namely, for each chosen value of k_0 ,

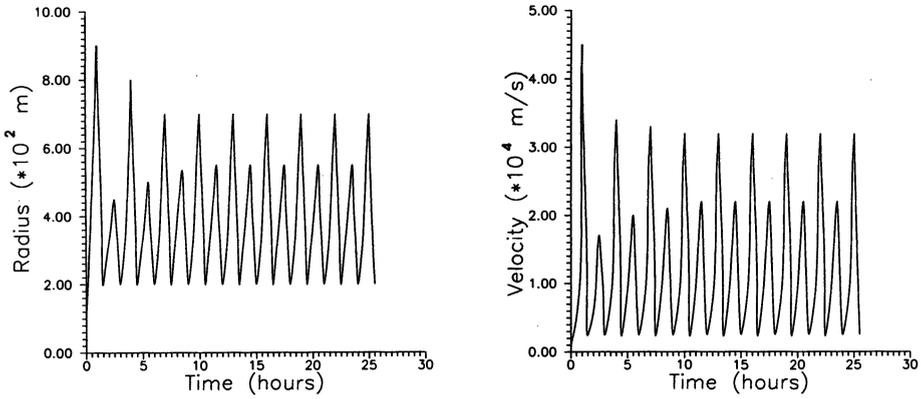


FIG. 3. Double-period oscillations: (a) the radius of the reaction zone versus time, (b) the velocity at the entrance of the reactor versus time, $\delta = 0.79$, $\tau = 3.98$.

we performed a series of simulations for various values of Δp . The variation of k_0 and Δp is equivalent to the variation of δ and τ . For δ and τ sufficiently small ($\delta < 0.5$), the velocity exhibits harmonic oscillations that develop into relaxation oscillations as τ increases.

For higher values of δ ($\delta = 0.79$), period-doubled oscillations are observed for $3.74 < \tau < 9.12$ and for $\tau > 25.2$. Figure 3 shows the radius of the reaction zone and the velocity at the entrance of the reactor as a function of time. Figure 4 shows the amplitude of the velocity oscillations for a single period mode and two amplitudes (for each half-period) for the double-period oscillations, in the $\tau - w$ plane. We note that the oscillations are observed for values of τ for which stationary solutions are not found by the analytical approach.

When δ increases, period four ($\delta = 1.73$, $\tau = 5.84$, see Fig. 5), period eight ($\delta = 1.9$, $\tau = 5.62$), and aperiodic oscillations ($\delta \geq 2.5$) are observed. Thus we conclude that this is a sequence of period-doubling bifurcations that leads to chaos. The critical values of the parameters here depend on the form of the function $\eta(\alpha, T)$.

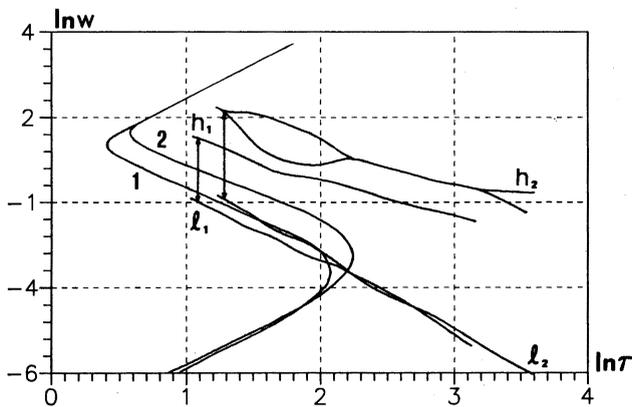


FIG. 4. Comparison of the analytical and numerical results: 1, 2—analytical solution, $Z = 3.88$, 1.— $\delta = 0.36$, 2.— 0.79 ; l_i and h_i , $i = 1, 2$ —minimal and maximal values of the velocity, respectively, during one period (simulations). Doubled-valued branch of the curve h_2 corresponds to period-two oscillations.

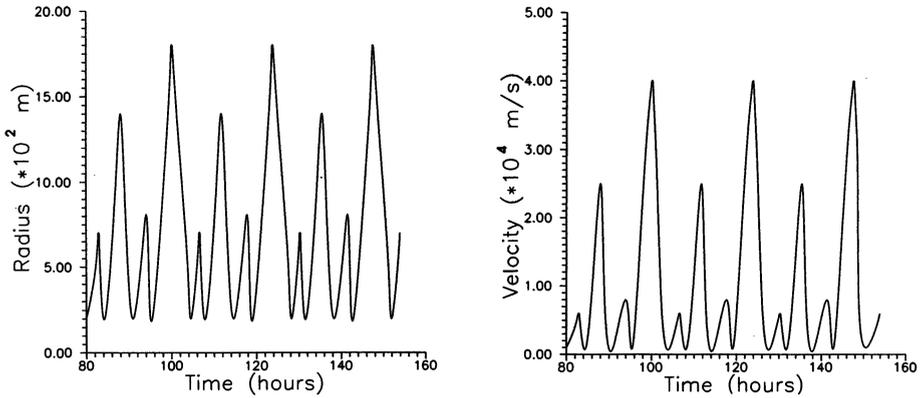


FIG. 5. Period-four oscillations: (a) the radius of the reaction zone versus time, (b) the velocity at the entrance of the reactor versus time, $\delta = 1.73$, $\tau = 5.84$.

Period doubling and irregular oscillations have been found for combustion waves traveling along a sample [14]–[17] and for gaseous combustion in a flow with a complex chemical reaction [18]. In the first case, these effects are caused by the interaction of the heat release and the heat transfer processes while in the second case by the salient features of consecutive reactions. Here we have found one more model for which a sequence of period-doubling bifurcations is observed. In this case, the complex oscillations are caused by the dependence of the flow velocity on the location of the reaction zone.

Qualitatively the mechanism of the instability can be explained as follows. If we perturb the radius of the reaction front so that it is, for example, greater than its value for the stationary solution, then the flow velocity increases (see (1.6)). There are then two possibilities. If thermal relaxation is slow, the velocity increase leads to further increase of the radius and the perturbation grows. In contrast, if thermal relaxation is fast, then each value of the velocity determines a fixed radius R of the reaction front, which is just a function of V_0 (see (2.4)), and system (1.1), (1.2), (1.6) can be reduced to the single equation

$$\frac{\partial V_0}{\partial t} = - \frac{1}{\rho r_0 \ln(r_1/r_0)} \left(\Delta p + \frac{2V_0 r_0 \Delta \eta}{R^2(V_0)} \right).$$

(For simplicity, we take $\eta(\alpha, T)$ in the form (3.1).) In this case, the perturbation decays.

Thus we can formulate a qualitative condition for instability. If the characteristic time of perturbation growth t_1 , which is proportional to $-\Delta \eta / \Delta p$, is less than the characteristic time of thermal relaxation, $t_2 \sim \kappa / V_n^2$, then the stationary solution is unstable. We note that $t_2 / t_1 \sim \delta / \tau^2$. Hence, increasing δ makes the stationary solution more unstable, and the oscillations become increasingly complex. This conclusion is in accordance with the results of the numerical computations presented in this paper.

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