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Heat and mass transfer during polymerization process in a chemical reactor

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ABSTRACT

The study consists of two parts. In the first part a computer model of the frontal polymerization process in cylindrical force out reactor is presented. Free convectional phenomena is taken into account.
In the second part analytical investigation is carried out for the case of one-dimensional model. The uniqeness conditions for the boundary value problem solution have been analysed and the solution is calculated within given accuracy with a help of specially constracted analytical iterative procedure.

INTRODUCTION

In our study we present complicated model for detailed analysis of heat transfer and chemical kinetics taking forced and free convection of reacting mixture into account. For the case even of one-dimensional model we have not seen analytical results in scientific literature, only mean values are analysed. So we have symplified the initial model neglecting dissipation and some other effects but we reserved radius dependense of temperature, monomer and initiator concentrations and constracted a special analytical procedure for investigating conditions of uniqueness for the relating boundary value problem solution and a special iterative algorithm for constructing numerical solution. Temperature, monomer and initiator concentrations as functions of reactor radius have been calculated with the arbitrary given accuracy without using finite-differense or other discreat methods.

Two-dimensional Flow Model

Mathematical model of polymerization process in cylindrical force out reactor with an inner feeder is concidered. The reacting mass places between two coaxial vertical cylinders. Axial symmetry is assumed. Initial mixture of monomer and initiator runs through the inner cylyndrical surface of a feeder, products of the polymerization process leave the working zone through external penetratible cylindrical surface of the reactor. Flow rates of the feeding and taking out of the products are assumed to be constant along the altitude. Polymerizing mass is considered to be viscous incompressible fluid with heat and physical characteristics depending on temperature and on the depth of chemical conversion.
Free radical mechanism according the following kinetic scheme of origining polymer chains is assumed:

Initiation: $I \xrightarrow{k_1} 2R_0\ ,\quad k_1 = A_1 \exp(-E_1/RT);$

Chain grow: $R_i + M \xrightarrow{k_p} R_{i+1}\ ,\quad k_p = A_p \exp(-E_p/RT);$

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Precipice by disproportion and recombining:

$$R_i + R_j \xrightarrow{k_{td}} P_i + P_j \quad , \quad R_i + R_j \xrightarrow{k_{tr}} P_{i+j} \;;$$

$$k_t = k_{tr} + k_{td} = A_t exp\,(-E_t/RT) \;;$$

Transmission of the chain to monomer:

$$R_i + M \xrightarrow{k_m} P_i + R_1 \quad , \qquad k_m = A_m exp\,(-E_m/RT) \;;$$

Mathematical model includes the following differential equations written in cylindrical coordinates:

$$\frac{\partial T}{\partial \tau} + \frac{1}{r}\frac{\partial}{\partial r}(ruT) + \frac{\partial}{\partial z}(vT) = \qquad (1)$$

$$\frac{1}{\rho c}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(\lambda r\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(\lambda\,\frac{\partial T}{\partial z}\right) + Q_0 kM + 2\mu\dot{S}^2\right];$$

$$\frac{\partial \omega}{\partial \tau} + \frac{\partial}{\partial r}(u\omega) + \frac{\partial}{\partial z}(v\omega) = \qquad (2)$$

$$\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(r\nu\omega)\right) + \frac{\partial^2}{\partial z^2}(\nu\omega) - g\beta\,\frac{\partial T}{\partial r} \;;$$

$$\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial \Psi}{\partial r}\right) + \frac{1}{r}\frac{\partial^2 \Psi}{\partial z^2} = -\,\omega \;; \qquad (3)$$

$$u = -\frac{1}{r}\frac{\partial \Psi}{\partial z} \;; \qquad v = \frac{1}{r}\frac{\partial \Psi}{\partial r} \;;$$

$$\frac{\partial M}{\partial \tau} + \frac{1}{r}\frac{\partial}{\partial r}(ruM) + \frac{\partial}{\partial z}(vM) = \qquad (4)$$

$$D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial M}{\partial r}\right) + \frac{\partial^2 M}{\partial z^2}\right] - V_1 - kM \;;$$

$$\frac{\partial I}{\partial \tau} + \frac{1}{r}\frac{\partial}{\partial r}(ruI) + \frac{\partial}{\partial z}(vI) = \qquad (5)$$

$$D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial I}{\partial r}\right) + \frac{\partial^2 I}{\partial z^2}\right] - k_1 I \;;$$

$$\frac{\partial \bar{R}}{\partial \tau} + \frac{1}{r}\frac{\partial}{\partial r}(ru\bar{R}) + \frac{\partial}{\partial z}(v\bar{R}) = \qquad (6)$$

$$D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \bar{R}}{\partial r}\right) + \frac{\partial^2 \bar{R}}{\partial z^2}\right] + V_1 - k_t\bar{R}^2$$

We denoted: $k = (k_p + k_m)\bar{R}$; $V_1 = 2 \cdot I \cdot f \cdot k_i$; $\bar{R} = \sum_{i=1}^{\infty} R_i$

Heat energy equation (1) is written taking exothermal polymerization effect and viscous dissipation into account. The vorticity equation (2) accounts free thermogravital convection. The equations (4)-(5) determin concentration fields for monomer, initiator and growing macro-radicals. The depth of chemical conversion is determined by monomer concentration relatively its initial value

$$\eta = 1 - M / M_0 ;$$

Equations (1)-(6) are completed by natural boundary conditions. The solution of the non-stationary boundary value problem is found numerically with a help of finite-difference method upto the steady-state conditions are satisfied.

Figure 1 presents calculated state of reacting mixture for radial forced flow of reagents. The reaction has a clear frontal character. The zone of intensive chemical reactions, where gradients of all quantities are localized, arrives in a form of a relatively thin cylindrical layer. Conditions of polymerization process change essentially if we take thermo-gravital convection into account. Closed circulation contour appears. Maximum of the flow intensity localizes at the feeders surface.

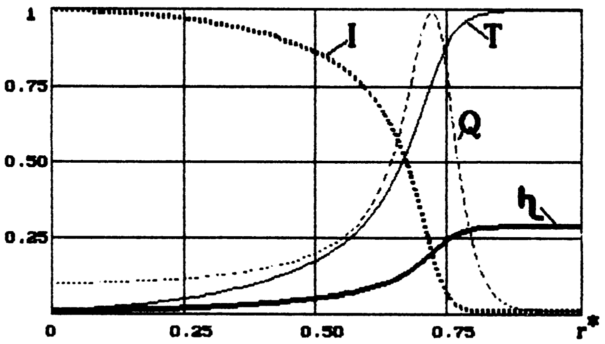

Figure 1: Radius dependence of the main process quantities for forced flow.

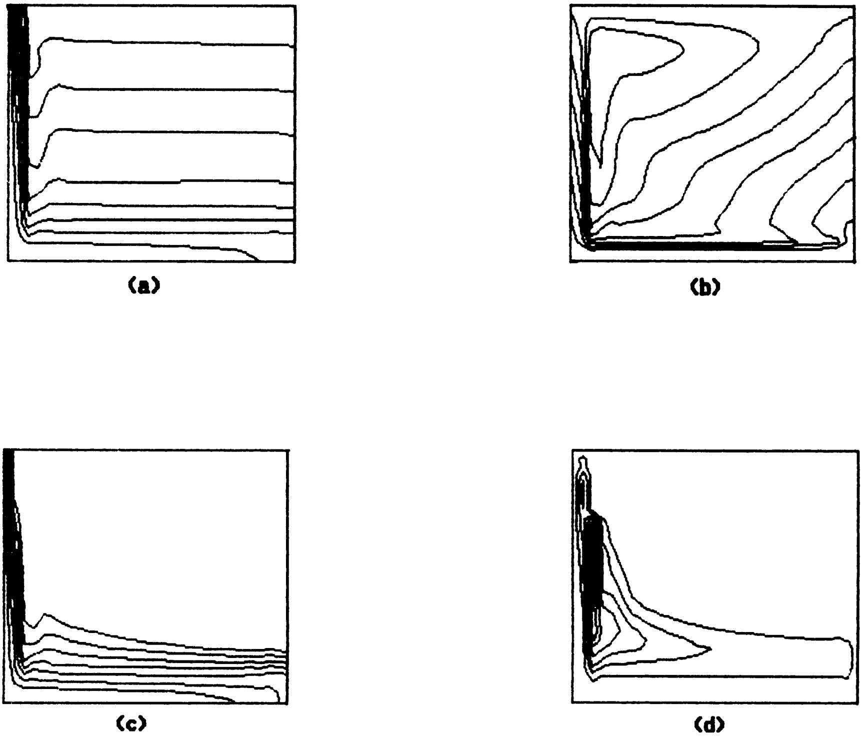
(a)
(b)
(c)
(d)

Figure 2: Trajectories (a), temperatute isolines (b), isolines of monomer conversion (c) and intensity of heat exchange (d) for the case of free motion.

The suggested method allows to analyse differential evaluation of inhomogeneous characteristics of polymer products at the exit of the reactor.

Analitical Iterative Procedure for the Steady-State Solution

For the steady-state one-dimensional case the simplified system of equations (1)-(6) can be written as

$$\frac{1}{r}\frac{d}{dr}(ruT) = \frac{1}{\rho c}[\ \frac{1}{r}\frac{d}{dr}(\lambda r\frac{dT}{dr})+ \tag{7}$$

$$+\frac{Q_0}{\rho c}MI^{1/2}k_p'(\frac{2fk_u'}{k_{ob}'})^{1/2}\exp(\frac{-2E_p-E_u+E_{ob}}{2RT}),$$

$$\frac{1}{r}\frac{d}{dr}(ruM) = -MI^{1/2}k_p'(\frac{2fk_u'}{k_{ob}'})^{1/2}\exp(\frac{-2E_p-E_u+E_{ob}}{2RT}), \tag{8}$$

$$\frac{1}{r}\frac{d}{dr}(ruI) = -k_u'I\exp(\frac{-E_u}{RT}) \tag{9}$$

with the boundary conditions

$$I(R_1)=I\ ,\qquad M(R_1)=M_0\ ,\qquad T(R_1)=T_0 \tag{10}$$

$$\lambda\frac{dT}{dr} = \overset{\rightharpoonup}{W} - \alpha(T-T_{cp}),\ r = R_3 \tag{11}$$

R_1 is a radius of an inner cylinder (the feeder) and R_3 is a radius of external cylinder of the reactor.

After integration the system (7)-(9) can be written in the form of the following equations

$$T = -\frac{\hat{c}}{\hat{J}}\,[(r/R_1)^{\hat{J}/a} - 1] + \qquad (12)$$

$$+\, T_0(r/R_1)^{\hat{J}/a} + \frac{\beta}{a}\, r^{\hat{J}/a} \int_{R_1}^{r} M r^{-\hat{J}/a-1}\, dr,$$

$$I(r) = I_0 \exp[-\frac{k_u'}{\hat{J}} \int_{R_1}^{r} r \exp(-\frac{E_u}{RT})dr] \qquad (13)$$

$$M(r) = M_0 \exp[-\frac{\hat{k}}{\hat{J}} \int_{R_1}^{r} r I^{1/2} \exp(-\frac{E}{RT})dr] \qquad (14)$$

We denote

$$-E = \frac{-2E_p - E_1 + E_t}{2}, \qquad F = \frac{\lambda}{\rho c}, \qquad \hat{W} = \frac{W}{2\pi R_3 L},$$

$$\hat{k} = (\frac{2 f k_u'}{R_{ob}'})^{1/2} k_p', \qquad \hat{J} = \frac{J}{2\pi L \rho}, \qquad \beta = \frac{Q_0}{\rho c}\hat{J}$$

The constant $\hat{c}$ can be found from the boundary condition (11) in the form $\hat{c} = -\alpha R_1 T'(R_1) + \beta M_0 + \hat{J} T_0$ with the unknown $T'(R_1)$ defined by

$$T'(R_1)\{\lambda (R_3/R_1)^{\hat{J}/a-1} + \frac{\alpha R_1 a}{\hat{J}}[(R_3/R_1)^{\hat{J}/a} - 1]\} = \qquad (15)$$

$$= \frac{\alpha\beta M_0}{\hat{J}}[(R_3/R_1)^{\hat{J}/a} - 1] + \frac{\lambda\beta}{a R_3}[M_0 (R_3/R_1)^{\hat{J}/a} - M(R_3)] -$$

$$- (\frac{\lambda \hat{J}}{a R_3} + \alpha)\frac{\beta R_3^{\hat{J}/a}}{a} \int_{R_1}^{R_3} M(r) r^{-\hat{J}/a-1}\, dr + \hat{W} + \alpha(T_{cp} - T_0).$$

Uniqueness Conditions for the Solution of the System (7)-(11). It follows from equalities (13) and (14) that if the solution T(r) is unique then the functions I(r) and M(r) are unique as well. So the uniqueness of the boundary value problem (7)-(11)

solution follows the uniqueness of the solution T(r) for the equation (16) where $T'(R_1)$ is written in the form (15). It is proved that if the inequality (16) for the flow rate J

$$J > 2\pi\rho L_1 \frac{M_0 I_0^{1/2}}{T_0^2}\,\frac{\hat{k}E}{R}\,\frac{Q_0}{\rho c}\,\frac{(R_3^2 - R_1^2)}{2} = J_{kp} \qquad (16)$$

takes place then the continuous solution of the equation (12) with equality (15) is unique. The method of the provement is usual: two solutions $T_1(r)$ and $T_2(r)$ are proposed on the contrary and the differential mean value theorem is used for the differense $M(r,T_1(r)) - M(r,T_2(r))$ where $M(r,T(r))$ is defined by equality (14).

<u>Iterative Procedure for the Solution of the Boundary Value Problem</u> Let the conditions of uniqueness of the problem solution are fulfilled and zero approximation $T^{(0)}(r)$ for the temperature T(r) is chosen arbitrary. Then the first approximation $I^{(1)}(r)$ for the function I(r) can be presented in the form

$$I(r) \approx I^{(1)}(r) = I_0 \exp[-\int_{R_1}^{r} r \exp[\ln \frac{\hat{k}_u}{2J} - \frac{E_u}{RT^{(0)}(r)}] dr \qquad (17)$$

Substituting the function $I^{(1)}(r)$ into equation (14) we obtain the first approximation for the monomer concentration in the following form

$$M(r) \approx M^{(1)}(r) = M_0 \exp[-\int_{R_1}^{r} r (I^{(1)})^{1/2} \exp(\ln \frac{\hat{k}}{J} - \frac{E}{RT^{(0)}}) dr \qquad (18)$$

Then the algebraical equation for the first approximation of the unknown constant $T'(R_1)$ can be found from the equation (15) with

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$M^{(1)}(r)$ substituded instead of $M(r)$.

Substituting the function $M^{(1)}(r)$ into equation (12) we obtain the first approximation for the temperature in the following form

$$T^{(1)}(r) = T_0 + \left[\frac{c_1 \alpha R_1}{J} - \frac{Q_0 M_0}{\rho c}\right]\left[(r / R_1)^{\hat{J}/a} - 1\right] +$$

$$+ \frac{\beta}{\alpha}(r/R_3)^{\hat{J}/a} \int_{R_1}^{r} (r/R_3)^{-\hat{J}/a} M^{(1)}(r) r^{-1} dr$$

The zero approximation for the temperature can be chosen for example in the following form

$$T^{(0)}(r) = T_0 + (T_{cp} - T_0)(r - R_1)/(R_3 - R_1)$$

If the first approximation for the temperature is calculated then the above described algorithm can be repeated in a usual way untill the inequality

$$\max_{R_1 < r < R_3} \left| T^{(n+1)}(r) - T^{(n)}(r) \right| < \varepsilon$$

is satisfied for the given small ε.

Numerical calculations have been carried out for different arbitrary chosen $T^{(0)}(r)$. The constructed algorithm has shown to be extremely stable and quick. The results coinside (within the accuracy of finite-difference method) with those calculated in the first part of our study if the symplified model is used there.