On the Possibility of Increasing the Effectiveness of a Porous Catalyst Granule for a Simple Reaction in a Non-stationary Regime

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The possibility of increasing the effectiveness factor of a porous catalyst grain for a simple reaction in non-stationary conditions is shown.

In some papers (*e.g.*, refs. 1 and 2) the problem of increasing the effectiveness of a non-porous catalyst granule has been studied when a chemical reaction proceeds on it in a non-stationary regime. Some papers have also considered this problem taking into account the granule porosity. A simple reaction with *n*th-order kinetics proceeding on isothermal porous catalyst granules of different geometric forms was considered; however, chemical reactions are accompanied by heat radiation or absorption.

The intensity of the process in a porous catalyst granule is to some extent determined by the hydrodynamic factors in the surrounding space. So, an analysis of the problem of increasing the effectiveness of a porous catalyst granule is of both theoretical and practical interest. This can be done when a chemical reaction proceeds on it in a non-stationary regime taking into account the non-isothermity of a granule and resistance in a boundary layer to mass- and heat exchange in a reaction mixture stream.

Let us analyse a reaction of the following form:

$$\mathrm{A}_1 \xrightarrow{r_1} \text{products} \tag{1}$$

The reaction exhibits arbitrary kinetics r_1 and proceeds on porous catalyst granules of different geometric forms. To simplify the analysis let the concentration C_1 of substance A_1 and the temperature T in the nucleus of the reaction mixture stream change rather slowly, taking into account the duration of the process proceeding in the granule pores (quasi-stationary conditions). In this case, for a description of joint reaction (1) proceeding on a porous catalyst granule and reagent diffusion in pores the stationary quasi-homogeneous model[4] can be used. In ref. 3 an analysis was performed based on the same assumption. The proposed model for reaction (1) has the following form:

$$\begin{aligned} &x^{-\alpha}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^{\alpha}D_1^*\frac{\mathrm{d}C_1}{\mathrm{d}x}\right) - R_s^2 r_1 = 0 \\ &x^{-\alpha}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^{\alpha}\lambda^*\frac{\mathrm{d}T}{\mathrm{d}x}\right) + R_s^2 Q r_1 = 0 \end{aligned} \tag{2}$$

with boundary conditions:

$$x = 0: \ \frac{\mathrm{d}C_1}{\mathrm{d}x} = \frac{\mathrm{d}T}{\mathrm{d}x} = 0; \ x = 1: \ D_1^*\frac{\mathrm{d}C_1}{\mathrm{d}x} = R_s\beta_1(C_{01} - C_{s1}),$$

$$\lambda^*\frac{\mathrm{d}T}{\mathrm{d}x} = R_s\beta_T(T_0 - T_s) \tag{3}$$

where x is a given dimensionless distance from the granule centre of radius R_s; C_{01} and C_{s1} are concentrations of substance A_1, respectively, in the reaction stream nucleus and near the external surface of a granule; T_0 and T_s are the temperatures in a stream nucleus and at the external surface of a granule, respectively; D_1^* is a constant describing the effective coefficient of diffusion of substance A_1 in the pores; λ^* is a constant describing the effective coefficient of a granule's heat conductivity; Q is the heat effect of the reaction; β_1 and β_T are, respectively, coefficients of mass-exchange on substance A_1 and heat exchange between a granule and reaction mixture stream; and α is a parameter which is determined by a granule geometric form ($\alpha = 0$-plate; $\alpha = 1$-cylindrical; $\alpha = 2$-spherical).

Let values C_{01} and T_0 change with time as follows:

$$C_{01}(t) = \tilde{C}_{01} + \hat{C}_{01}(t), \ \int_0^{\tau}\hat{C}_{01}(t)\mathrm{d}t = 0, \ \hat{C}_{01}(t) \ll \tilde{C}_{01} \tag{4}$$

$$T_0(t) = \tilde{T}_0 + \hat{T}_0(t), \ \int_0^{\tau}\hat{T}_0(t)\mathrm{d}t = 0, \ \hat{T}_0(t) \ll \tilde{T}_0$$

where $\tilde{C}_{01}$ and $\tilde{T}_0$ do not depend on time and τ is the period of changing functions $\hat{C}_{01}(t)$ and $\hat{T}_0(t)$.

The value which characterizes the intensity of a catalytic reaction proceeding on a porous granule is a factor of catalyst effectiveness.[4] In this paper, for an arbitrary chemical reaction of any given kinetics we have obtained a relation for the effectiveness factor in the form of a row according to a size of the radius of a porous catalyst granule. In this case we suppose that there is now resistance to mass- and heat exchange between a granule and a reaction stream ($\beta_1 \to \infty$ and $\beta_T \to \infty$). According to the solution which is given in ref. 4 for models (2) and (3), taking into account relation (4), we obtain the following relation for an average effectiveness factor of a porous catalyst granule during the period τ:

$$\tilde{\eta} \simeq 1 - \frac{R_S^2}{(\alpha+1)(\alpha+3)}\left\{\left(\left.\frac{\partial r_1}{\partial C_1}\right|_{\substack{C_1 = \tilde{C}_{01} \\ T = \tilde{T}_0}} + \Im_1\right)\left(1 + \frac{\alpha+3}{B_1}\right)/D_1^* - \right.$$

$$\left. Q\left(\left.\frac{\partial r_1}{\partial T}\right|_{\substack{C_1 = \tilde{C}_{01} \\ T = \tilde{T}_0}} + \Im_2\right)\left(1 + \frac{\alpha+3}{B_T}\right)/\lambda^*\right\}$$

$$\Im_i = \left\{\varepsilon_1\left[\left.\frac{\partial r_{01}}{\partial \hat{C}_{01}}\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}} * \frac{\partial}{\partial \hat{C}_{01}}\left(\left.\frac{\partial r_1}{\partial C_i}\right|_{\substack{C_1 = C_{01} \\ T = T_0}}\right)\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}} + \right.\right.$$

$$\left.\left.\frac{\tilde{r}_{01}}{2}\frac{\partial^2}{\partial \hat{C}_{01}^2}\left(\left.\frac{\partial r_1}{\partial C_i}\right|_{\substack{C_1 = C_{01} \\ T = T_0}}\right)\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}}\right] +$$

$$\varepsilon_2\left[\left.\frac{\partial r_{01}}{\partial \hat{C}_{01}}\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}} * \frac{\partial}{\partial \hat{T}_0}\left(\left.\frac{\partial r_1}{\partial C_i}\right|_{\substack{C_1 = C_{01} \\ T = T_0}}\right)\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}} + \right.$$

$$\left.\frac{\partial r_{01}}{\partial \hat{T}_0}\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}} * \frac{\partial}{\partial \hat{C}_{01}}\left(\left.\frac{\partial r_1}{\partial C_i}\right|_{\substack{C_1 = C_{01} \\ T = T_0}}\right)\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}} +$$

$$\left.\tilde{r}_{01}\frac{\partial^2}{\partial \hat{C}_{01}\partial \hat{T}_0}\left(\left.\frac{\partial r_1}{\partial C_i}\right|_{\substack{C_1 = C_{01} \\ T = T_0}}\right)\right|_{\substack{\hat{C}_{01} = 0 \\ \hat{T}_0 = 0}}\Bigg] +$$

$$\varepsilon_3\left[\frac{\partial r_{01}}{\partial \hat{T}_0}\Bigg|_{\substack{\hat{C}_{01}=0\\ \hat{T}_0=0}} * \frac{\partial}{\partial \hat{T}_0}\left(\frac{\partial r_1}{\partial C_i}\Bigg|_{\substack{C_1=C_{01}\\ T=T_0}}\right)\Bigg|_{\substack{\hat{C}_{01}=0\\ \hat{T}_0=0}} + \right.$$

$$\left.\frac{\tilde{r}_{01}}{2}\frac{\partial^2}{\partial \hat{T}_0^2}\left(\frac{\partial r_1}{\partial C_i}\Bigg|_{\substack{C_1=C_{01}\\ T=T_0}}\right)\Bigg|_{\substack{\hat{C}_{01}=0\\ \hat{T}_0=0}}\right]\Bigg\}/\tilde{r}_{01} \qquad (5)$$

$$\varepsilon_1 = \int_0^\tau \frac{\hat{C}_{01}^2(t)\mathrm{d}t}{\tau},\ \varepsilon_2 = \int_0^\tau \frac{\hat{C}_{01}(t)\hat{T}_0(t)\mathrm{d}t}{\tau},\ \varepsilon_3 = \int_0^\tau \frac{\hat{T}_0^2(t)\mathrm{d}t}{\tau}$$

$$B_1 = R_\mathrm{S}\beta_1/D_1^*,\ B_\mathrm{T} = R_\mathrm{S}\beta_\mathrm{T}/\lambda^*,$$
$$r_{01} = r_1(C_{01}, T_0),\ \tilde{r}_{01} = r_1(\tilde{C}_{01}, \tilde{T}_0)$$

where $C_i = C_1$ at $i = 1$ and $C_2 = T$ at $i = 2$. If reaction (1) proceeds in a stationary regime, then values ε_1, ε_2 and ε_3 are 0. Hence, having analysed relation (5) we conclude that the effectiveness factor $\tilde{\eta}$ in a non-stationary regime is greater than in a stationary one if the following condition is fulfilled:

$$\Im_1\Big(1+\frac{\alpha+3}{B_1}\Big)/D_1^* - Q\Im_2\Big(1+\frac{\alpha+3}{B_\mathrm{T}}\Big)/\lambda^* < 0 \qquad (6)$$

Let us apply inequality (6) to the investigation of reaction (1) with kinetics of the following form:

$$r_1 = k_{01}C_1^n\exp[-E_1/(RT)] \qquad (7)$$

where k_{01} is the pre-exponential multiplier; n is the reaction order; E_1 is the activation energy; and R is the universal gas constant. In this case inequality (6), after being divided by value $\tilde{r}_{01}/(\tilde{C}_{01}D_1^*)$, will yield the following:

$$\Big\{n(n-1)\Big(\frac{3n}{2}-1\Big)\frac{\varepsilon_1}{\tilde{C}_{01}^2} + n(3n-2)\frac{\gamma\varepsilon_2}{(\tilde{T}_0\tilde{C}_{01})} +$$
$$n\gamma\Big(\frac{3\gamma}{2}-1\Big)\frac{\varepsilon_3}{\tilde{T}_0^2}\Big\}\Big(1+\frac{\alpha+3}{B_1}\Big) - \beta\gamma\Big\{n\Big(3n-1\Big)\frac{\varepsilon_1}{2\tilde{C}_{01}^2} +$$
$$\frac{n(3\gamma-4)\varepsilon_2}{\tilde{T}_0\tilde{C}_{01}} + \Big(\frac{3\gamma^2}{2} - 5\gamma + 3\Big)\frac{\varepsilon_3}{\tilde{T}_0^2}\Big\}\Big(1+\frac{\alpha+3}{B_\mathrm{T}}\Big) < 0, \qquad (8)$$

where $\gamma = E_1/(R\tilde{T}_0)$ and $\beta = QD_1^*\tilde{C}_{01}/(\lambda_0^*\tilde{T}_0)$. In the case of reactions of zero order ($n = 0$) inequality (8) takes the following form:

$$3\gamma^2/2 - 5\gamma + 3 > 0 \quad \text{for } \beta > 0 \qquad (9)$$

$$3\gamma^2/2 - 5\gamma + 3 < 0 \quad \text{for } \beta < 0 \qquad (10)$$

In the case of $\gamma < 0.785$ or $\gamma > 2.549$ the parameter γ satisfies inequality (9) and in the case of $0.785 < \gamma < 2.549$ it satisfies inequality (10). Usually the value of the parameter γ is *ca.* 10. Therefore, from inequalities (9) and (10) it follows that it is better to carry out exothermal reactions of zero order in a non-stationary regime. Endothermal reactions are better carried out in a stationary regime.

It is worth noting that in many cases a considerable amount of experimental data prove the possibility of describing stationary processes on porous catalyst granules with the help of a quasi-homogeneous model.[5] An analysis of these problems was performed, for example, in refs. 6 and 7. The application of a quasi-homogeneous model under the quasi-stationary conditions is given in ref. 7. The aim of our work is to obtain simple relations (5)–(6) suitable for practical application. Such relations would help to establish some regimes of processes proceeding on porous catalysts without computer processing of models (2)–(3). Under such regimes the mean value of the effectiveness factor in a non-stationary regime would be greater than in a stationary one.

Thus, the analysis shows that when inequality (6) is fulfilled, reaction (1) on a porous catalyst granule is better carried out in a non-stationary regime. This conclusion is important when choosing an optimal catalyst for a particular reaction.

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