Increasing the productivity of a porous catalyst granule with respect to the target compound for an arbitrary chemical reaction in a non-stationary regime

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The productivity of a porous catalyst granule with respect to the target compound for an arbitrary chemical reaction in a non-steady-state regime is increased.

In a previous study[1] we have considered the problem of increasing the effectiveness of a porous catalyst granule during a simple chemical reaction occurring on the granule in a non-stationary regime.

The present work studies the possibility of increasing the yield of the target compound in an arbitrary chemical reaction on a porous catalyst granule.

Consider an arbitrary reaction, equation (1), where

$$0 = \sum_{i=1}^{n} a_{ip} A_i \tag{1}$$

a_{ip} are stoichiometric coefficients (for initial substances, $a_{ip} < 0$, while for the reactions products, $a_{ip} > 0$); A_i represent the substances that participate in this reaction; $p = 1, ..., k$), where p is the reaction route.

Let us suppose that in the nucleus of the reaction mixture flowing around a porous granule, the concentrations $C_{0i}(t)$ of compounds A_i ($i = 1, ..., n$) and the temperature $T_0(t)$ vary as functions of time t according to equations (2) and (3).

$$C_{0i}(t) = \tilde{C}_{0i} + \bar{C}_{0i}(t), \int_0^{\tau_i} \bar{C}_{0i}(t)\mathrm{d}t = 0 \tag{2}$$

$$i = 1, ..., n$$

$$T_0(t) = \tilde{T}_0 + \bar{T}_0(t), \int_0^{\tau_{n+1}} \bar{T}_0(t)\mathrm{d}t = 0 \tag{3}$$

$$\tau_0 = \min(\tau_1, ..., \tau_{n+1}), \tau_i = \frac{\tau_0 p_i}{d_i}, \; i = 1, ..., n+1$$

Here, $\tilde{C}_{0i}$, $i = 1, ..., n$ and $\tilde{T}_0$ are constant values; τ_i are the periods of the variation of the concentrations and temperature; p_i and d_i are any positive integers. To simplify the analysis, we assume, as in the previous study,[1] that the concentrations of the substances and the temperature in the nucleus of the reaction mixture stream vary fairly slowly with respect to the duration of the process occurring in the granule pores (the condition for the quasi-stationary state). In this case, the reaction [equation (1)] proceeding on a porous catalyst granule and the diffusion of substances in the pores may be described simultaneously[3] in terms of the stationary quasi-homogeneous model.[2] It is noteworthy that numerous experimental data[4] indicate that stationary processes occurring on porous catalyst granules can be adequately described in terms of this model. With allowance for the resistance to heat and mass transfer between a porous granule and the external reaction mixture, the quasi-homogeneous model for a type (1) reaction is written as equation (4):[5]

$$x^{-\alpha}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^{\alpha}\frac{\mathrm{d}C_i}{\mathrm{d}x}\right) + R_\mathrm{s}^2 \sum_{p=1}^{k} a_{ip}\frac{r_p}{D_i^*} = 0 \tag{4}$$

$$i = 1, ..., n+1$$

with boundary conditions, equation (5).

$$x = 0: \frac{\mathrm{d}C_i}{\mathrm{d}x} = 0; \; x = 1: D_i^*\frac{\mathrm{d}C_i}{\mathrm{d}x} = R_\mathrm{s}\beta_i(C_{0i} - C_{si}) \tag{5}$$

$$i = 1, ..., n+1$$

Here x is the dimensionless distance from the centre of a porous granule of radius R_s; C_i and C_{si} are concentrations of substance A_i in the pores and near to the external surface of the granule, respectively; ($i = 1, ..., n$); $C_{n+1} = T$, the temperature inside the granule; $C_{0n+1} = T_0$; $C_{sn+1} = T_\mathrm{s}$, the temperature on the external surface of the granule; D_i^* is the effective diffusion coefficient of substance A_i in the pores; $D_{n+1}^* = \lambda^*$ is the effective heat conductivity coefficient for the porous catalyst granule; $a_{n+1p} = Q_p$ is the thermal effect of the reaction occurring according to the route p; r_p is the rate of the reaction occurring according to the route p; β_i is the coefficient of mass exchange with the reaction flow for substance A_i ($i = 1, ..., n$), β_{n+1} is the coefficient of heat exchange with the reaction flow; α is the parameter determined by the shape of the granule ($\alpha = 0$ for a plate, $\alpha = 1$ for a cylinder, and $\alpha = 2$ for a sphere). Thus, in the model (4) with (5) at $i = n+1$, the equation describes the temperature distribution in a porous catalyst granule. It is also assumed in this model that the D_i^* values ($i = 1, ..., n$) and λ^* values are constants.

The productivity of a porous catalyst granule with respect to substance A_i is determined from equation (6):[2]

$$J_i(t) = -\xi R_\mathrm{s}^{\alpha-1} D_i^* \left(\frac{\mathrm{d}C_i}{\mathrm{d}x}\right)\Big|_{x=1} \tag{6}$$

where $i = 1, ..., n$, $\xi = 4\pi$ at $\alpha = 2$; $\xi = 2\pi l$ at $\alpha = 1$ (l is the height of the cylinder); $\xi = 2S$ at $\alpha = 0$ (S is the surface area of the plate, which is perpendicular to the x axis). Let us introduce the average $J_i(t)$ value over time τ; equation (7).

$$\tilde{J}_i = \tau^{-1}\int_0^{\tau} J_i(t)\mathrm{d}t, \; \tau = \tau_0 \prod_{i=1}^{n+1} p_i \tag{7}$$

Previously,[5] as a solution for the model (4), (5) was obtained as a power series in the powers of the granule radius R_s. If we use this solution to determine the $J_i(t)$ value, we can write the expression as a series up to the terms containing the second power of R_s, equation (8):

$$J_i \approx \frac{\xi R_s^{\alpha+1}}{\alpha+1}\sum_{p=1}^{k} a_{ip}\Big\{r_{0p} - \\ -\frac{R_s^2}{(\alpha+1)(\alpha+3)}\sum_{f=1}^{k}\sum_{l=1}^{n+1}\frac{a_{lf}r_{of}}{D_l^*}\left(1+\frac{\alpha+3}{B_l}\right)\frac{\mathrm{d}r_{sp}}{\mathrm{d}u_l}\Big|_{u_1=0,...,u_{n+1}=0}\Big\} \tag{8}$$

where $r_{op} = r_p(C_{01}, ..., C_{0n}, T_0)$ and $r_{sp} = r_p(C_{s1}, ..., C_{sn}, T_s)$, $p = 1, ..., k$; $C_{si} = C_{0i} - u_i$, $i = 1, ..., n+1$; $B_l = R_\mathrm{s}\beta_l/D_l^*$, $l = 1, ..., n+1$. Let us expand the functions r_{0p} and dr_{sp}/du_l in power series in $\bar{C}_{0i}(t)$ and $\bar{T}_0(t)$ up to the squared terms. Then, with allowance for equations (2) and (3), the substitution of the expression (8) to the formula (7) gives

$$\tilde{J}_i \approx \frac{\xi R_s^{\alpha+1}}{\alpha+1}\sum_{p=1}^{k} a_{ip}\Big\{\tilde{r}_{0p} + \\ +\sum_{m=1}^{n+1}\sum_{j=1}^{n+1}\frac{\varepsilon_{mj}}{2}\frac{\mathrm{d}^2 r_{0p}}{\mathrm{d}\bar{C}_{0m}(t)\mathrm{d}\bar{C}_{0j}(t)}\Big|_{\bar{C}_{01}(t)=0,...,\bar{C}_{0n+1}(t)=0} - \frac{R_s^2}{(\alpha+1)(\alpha+3)}\times \\ \times\sum_{s=1}^{k}\Big[\tilde{r}_{0s}\Big(\tilde{\Delta}_{sp} + \sum_{m=1}^{n+1}\sum_{j=1}^{n+1}\frac{\varepsilon_{mj}}{2}\frac{\mathrm{d}^2\Delta_{sp}}{\mathrm{d}\bar{C}_{0m}(t)\mathrm{d}\bar{C}_{0j}(t)}\Big|_{\bar{C}_{01}(t)=0,...,\bar{C}_{0n+1}(t)=0}\Big) + \\ +\sum_{m=1}^{n+1}\sum_{j=1}^{n+1}\varepsilon_{mj}\Big(\frac{\mathrm{d}r_{0s}}{\mathrm{d}\bar{C}_{0m}(t)}\Big|_{\bar{C}_{01}(t)=0,...,\bar{C}_{0n+1}(t)=0}\Big)\times \\ \times\Big(\frac{\mathrm{d}\Delta_{sp}}{\mathrm{d}\bar{C}_{0j}(t)}\Big|_{\bar{C}_{01}(t)=0,...,\bar{C}_{0n+1}(t)=0}\Big) + \\ +\frac{\tilde{\Delta}_{sp}}{2}\sum_{m=1}^{n+1}\sum_{j=1}^{n+1}\varepsilon_{mj}\frac{\mathrm{d}^2 r_{0s}}{\mathrm{d}\bar{C}_{0m}(t)\mathrm{d}\bar{C}_{0j}(t)}\Big|_{\bar{C}_{01}(t)=0,...,\bar{C}_{0n+1}(t)=0}\Big]\Big\},$$

$$\Delta_{sp} = \sum_{l=1}^{n+1}\frac{a_{ls}}{D_l^*}\left(1+\frac{\alpha+3}{B_l}\right)\frac{\mathrm{d}r_{sp}}{\mathrm{d}u_l}\Big|_{u_1=0,...,u_{n+1}=0} \tag{9}$$

$$\tilde{r}_{0p} = r_p(\tilde{C}_{01}, ..., \tilde{C}_{0n+1}),\ \tilde{\Delta}_{sp} = \Delta_{sp}(\tilde{C}_{01}, ..., \tilde{C}_{0n+1}),$$

$$\varepsilon_{mj} = \tau^{-1}\int_0^\tau \bar{C}_m(t)\bar{C}_j(t)\mathrm{d}t,\ \varepsilon_{mj} = \varepsilon_{jm}$$

Obviously, in a stationary regime, $\varepsilon_{mj} = 0$ (m, j = 1, ..., $n+1$). Analysis of equation (9) implies that if the inequality

$$\sum_{p=1}^{k} a_{ip} \sum_{m=1}^{n+1}\sum_{j=1}^{n+1} \varepsilon_{mj} \frac{\mathrm{d}^2 r_{0p}}{\mathrm{d}\bar{C}_{0m}(t)\mathrm{d}\bar{C}_{0j}(t)}\Big|_{\bar{C}_{01}(t)=0,...,\bar{C}_{0n+1}(t)=0} > 0 \qquad (10)$$

holds, the yield of product A_i in a reaction occurring on a porous catalyst granule in a non-stationary regime is higher than that in a similar stationary reaction. Here, we took into account that for the reaction products, $\tilde{J}_i > 0$. Since for the initial substances $\tilde{J}_i < 0$, then, if the condition

$$\sum_{p=1}^{k} a_{ip} \sum_{m=1}^{n+1}\sum_{j=1}^{n+1} \varepsilon_{mj} \frac{\mathrm{d}^2 r_{0p}}{\mathrm{d}\bar{C}_{0m}(t)\mathrm{d}\bar{C}_{0j}(t)}\Big|_{\bar{C}_{01}(t)=0,...,\bar{C}_{0n+1}(t)=0} < 0 \qquad (11)$$

is valid, a larger amount of the i-th initial substance is consumed in a non-stationary regime than in a stationary regime.

Let us use the results obtained to investigate the possibility of increasing the yield of the target product A_2 in a set of consecutive and competing reactions occurring in a non-stationary regime

$$\begin{tikzcd} A_1 \arrow[r, "r_1"] \arrow[rr, bend right, "r_3"'] & A_2 \arrow[r, "r_2"] & A_3 \end{tikzcd} \qquad (12)$$

where

$$r_1 = k_{01}C_1^n \exp\left(-\frac{E_1}{RT}\right),\ r_2 = k_{02}C_2^m \exp\left(-\frac{E_2}{RT}\right),$$

$$r_3 = k_{03}C_3^l \exp\left(-\frac{E_3}{RT}\right) \qquad (13)$$

Here, n, m and l are reaction orders; k_{0i} are pre-exponential factors (i = 1, 2, 3); E_i are the activation energies (i = 1, 2, 3).

Substitution of the reaction rates (13) to the inequality (10) gives the following inequality:

$$\tilde{r}_{01}\left[\frac{\varepsilon_{11}n(n-1)}{\tilde{C}_{01}^2} + \frac{2\varepsilon_{14}nE_1}{R\tilde{C}_{01}\tilde{T}_0^2} + \frac{\varepsilon_{44}E_1(E_1/R\tilde{T}_0 - 2)}{R\tilde{T}_0^3}\right] >$$

$$> \tilde{r}_{02}\left[\frac{\varepsilon_{22}m(m-1)}{\tilde{C}_{02}^2} + \frac{2\varepsilon_{24}mE_2}{R\tilde{C}_{02}\tilde{T}_0^2} + \frac{\varepsilon_{44}E_2(E_2/R\tilde{T}_0 - 2)}{R\tilde{T}_0^3}\right] \qquad (14)$$

In the case where this condition is fulfilled, the yield of substance A_2 in a reaction of type (12) occurring in a non-stationary regime is higher than that in a stationary regime.

It follows from the inequality (14) that the possibility of increasing the yield of the target product A_2 in a non-stationary regime with respect to that in a stationary regime does not depend on the variation with time of the concentration of substance A_3. The time variations of the concentration $C_{01}(t)$ (for n = 0 or 1) or $C_{02}(t)$ (for m = 0 or 1) also have no influence on the yield of the target product A_2. Analysis of the inequality (14) indicates that to obtain a higher yield of compound A_2, one should maintain the concentration $C_{01}(t)$ of compound A_1 (at $0 < n < 1$) and the concentration $C_{02}(t)$ of compound A_2 (at $m < 0$ or $m > 1$) invariable with time. For the majority of reactions, the dimensionless parameter E_i/RT_0 is close to 10. Therefore, as the inequality (14) implies, for $E_1 > E_2$, the temperature of the reaction (12) should vary with time.

Since the inequality (14) does not include the reaction rate r_3, all the above conclusions are also valid for consecutive reactions (*i.e.* r_3 = 0). For competing reactions (i.e. r_2 = 0) or for a simple reaction ($r_2 = r_3 = 0$), the right-hand term of the inequality (14) is equal to zero. In this case, the inequality (14) indicates that, in order to increase the yield of the target product, the competing and simple reactions need to be conducted at varying temperature $T_0(t)$.

It should be noted that the expressions (10) and (11) obtained are ordinary algebraic inequalities. It is much easier to analyse these inequalities than to perform numerical computer analysis of the initial model, equations (4) and (5).

The simple relations (10) and (11) are practical and apply to an arbitrary catalytic reaction (1). These relations are important when choosing an optimal catalysts for a particular reaction.

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