Testing the Relative Importance of Mass and Heat Resistances in Solid Catalysts

Roman Petrus and Mirosław Szukiewicz
Rzeszów University of Technology, Dept. of Chemical Engineering and Process Control, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

Criteria for isothermal conditions and/or absence of diffusion resistances in catalytic reaction were derived using approximate profiles of reagents concentration and temperature for the important reaction $\nu_A A + \nu_B B \rightarrow \nu_R R$ and for a power-law type of the kinetic equation, which are quite often applied in practice. The method can be easily adapted to another type of kinetic rate equation and/or more complicated reaction schemes. The developed criteria were applied to some data from the literature with good result.

Introduction

Is external diffusion limiting? Does temperature gradient in a catalyst pellet play a major role? Is internal diffusion important? In many instances it is of interest to obtain quick estimates to these questions. It could widen researcher experience on a process and could make designing easier, and also modeling and simulating, which are more and more commonly applied and useful methods of process analysis. It should be pointed out that answers to the questions can help to build correct mathematical models of catalytic processes that are highly nonlinear and coupled. The lack of mass- or heat-transport resistances or, especially, isothermal conditions result in a substantially simplified model equation set and a method of solution.

The literature on chemical reactor engineering includes a number of diagnostic criteria. Major reviews on this topic are given by Froment and Bischoff (1979) and Doraiswamy and Sharma (1984). In addition, an interesting criterion on the importance of temperature and concentration gradients in catalyst pellets was given by Dogu and Dogu (1984). These are the criteria that still are the most often applied in practice. Some of the criteria from among those just listed will be discussed in detail in the following. Unfortunately, these criteria concern only the single-component reactions, which considerably lessens their usefulness in practice.

Dogu (1985) had developed a criteria for multicomponent reactions. He relied on parabolic concentration profiles and a hyperbolic-type temperature profile inside a pellet. The intrinsic reaction rate was expanded into a Taylor series. In this article, a number of criteria are developed with the intention of presenting a simple and general method of detecting interphase transport intrusions and intraparticle temperature and concentration gradients for the pellet. The relationships were derived using the parabolic concentration profiles and temperature profiles by Petrus (1988a,b) [a parabolic temperature profile was first used by Anderson (1963)] and a modified power series expansion of effectiveness factor terms. The changes result in simplified algebra with no loss of accuracy. The method applied is explained using an important example, quite often used in practice reaction $\nu_A A + \nu_B B \rightarrow \nu_R R$, and for a power-law type of the kinetic equation. The method can be easily adapted to another type of kinetic rate equations and/or more complicated reaction schemes.

Theory

Consider a case where the active material is supported on nonactive core (it is often seen in practice, such as this type of catalyst is commonly used in selective hydrogenation of acetylene—a very important commercial process). The steady-state mass and heat balances for the two-component single nonisothermal reaction

$$\nu_A A + \nu_B B \rightarrow \nu_R R \tag{1}$$

Correspondence concerning this article should be addressed to R. Petrus.

can be expressed in dimensionless form as follows

$$D_i \frac{1}{x^a}\frac{d}{dx}\left(x^a \frac{dc_i}{dx}\right) - \frac{\nu_i}{\nu_A}\Phi^2 R_{(c_i,\varphi)} = 0, \quad i = A,B \tag{2}$$

$$\frac{1}{x^a}\frac{d}{dx}\left(x^a \frac{d\varphi}{dx}\right) + \beta_0 \Phi^2 R_{(c_i,\varphi)} = 0 \tag{3}$$

with boundary conditions

$$\frac{dc_i}{dx} = 0 \quad \frac{d\varphi}{dx} = 0 \quad \text{at } x = 0 \tag{4}$$

$$\frac{dc_i}{dx} = Sh^* \frac{K_i}{D_i}(E_i - c_{i,s}) \quad \frac{d\varphi}{dx} = Nu^*(1 - \varphi_s) \quad \text{at } x = 1 \tag{5}$$

where $R_{(c_i,\varphi)}$ is the kinetic expression, and is equal to 0 for the nonactive core. The subscript i denotes a component of a reaction ($i = A,B$). Parameters D_A, K_A, E_A are equal to 1 and will be omitted in the following.

The dimensionless radius of the pellet is defined as follows

$$x = \frac{r - R_{nc}}{R_0 - R_{nc}} \tag{6}$$

where R_{nc} denotes the radius of the nonactive core of the pellet.

Note that:

- The model includes the case of the fully active pellet; then $R_{nc} = 0$;
- The model includes the case of reaction $\nu_A A \rightarrow \nu_R R$; then $\nu_B = 0$ and the equation for component B should be omitted;
- For isothermal processes the rate equation does not depend on temperature and proper terms in kinetic equation $R_{(C_i,\varphi)}$ and are neglected in the model. Hence, Eq. 3 with boundary conditions can be omitted. This rule will be applied in the following, as well.

Solving the model equations gives the reaction components and/or temperature profiles. Unfortunately it is a rather hard problem to solve, although the key-component concept and the Prater relationship, which relates the temperature and concentration profiles, can make the task easier. However, the aim of this work can be achieved without finding an exact solution, by assuming parabolic profiles of reagents and/or temperature. But this simple assumption is complicated due to internal diffusion. It is common knowledge that for small and medium internal diffusion resistance, reagent concentrations, and in consequence reaction rate in an active part of a catalyst pellet, are positive (cf. curve 1 in Figure 1). Thus, the reaction zone (that is, the area for which a reaction rate is significant) is equal to the active part of the catalyst pellet. As diffusional resistances grow, the reagent concentration in the active part drops (cf. curve 2, for which the concentration drops to null at $r = R_{nc}$), and finally the reaction zone narrows (cf. in curve 3, the resistance is significant, and R_c represents the position of the hypothetical reaction interface).

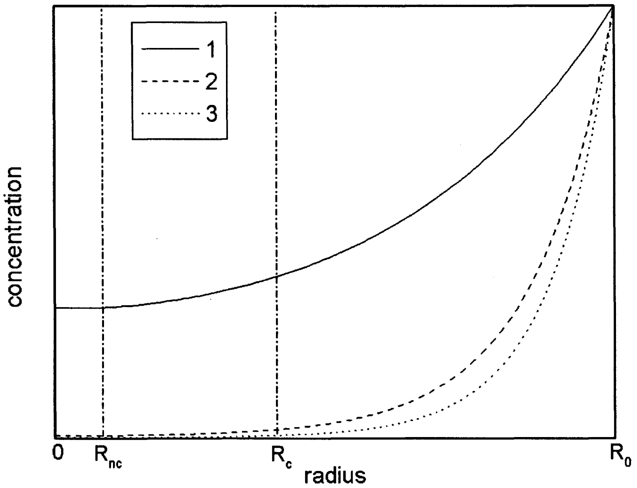

Figure 1. Reagent concentration vs. radius of the pellet.

It is easy to see in Figure 1 that the parabolic approximation of the concentration profile in the whole active part of the pellet is correct only for curves 1 and 2; that is, for small and medium internal diffusion resistance. Otherwise the parabolic approximation should concern only the reaction zone. Note, that curves 2 and 3 differ from each other in principle by the location of the border of the reaction zone. It follows that the narrower reaction zone can be taken into consideration relatively easily by substituting the radius of the nonactive core, R_{nc}, by the hypothetical reaction interface, R_c, in the model. Thus, coordinate x should be substituted by

$$\xi = \frac{r - R_c}{R_0 - R_c} \tag{7}$$

At first the region of the small internal diffusion resistance will be considered. Parabolic concentrations and temperature profiles are given by

$$c_A(x) = c_{As} + a_{cA}(1 - x^2) \tag{8}$$

$$c_B(x) = c_{Bs} + a_{cB}(1 - x^2) \tag{9}$$

$$\varphi(x) = \varphi_s + a_\varphi(1 - x^2) \tag{10}$$

The unknown parameters a_{cA}, a_{cB}, and a_φ can be found by using boundary conditions (Eq. 5)

$$a_{cA} = -\frac{Sh^*(1 - c_{As})}{2}U \tag{11}$$

$$a_{cB} = -\frac{Sh^* \frac{K_i}{D_i}(E_B - c_{Bs})}{2}U \tag{12}$$

$$a_\varphi = -\frac{Nu^*(1 - \varphi_s)}{2}U \tag{13}$$

where

$$U = 1 - \frac{R_{nc}}{R_0} \tag{14}$$

On the other hand, the mass and heat fluxes at steady state can be expressed as

$$\Psi_{0A} = (a+1)Sh^*(1-c_{As}) \tag{15}$$

$$\frac{\nu_B}{\nu_A}\Psi_{0A} = (a+1)Sh^*\frac{K_i}{D_i}(E_B - c_{Bs}) \tag{16}$$

$$\Psi_{0A}\,\beta_0 = (a+1)Nu^*(\varphi_s - 1) \tag{17}$$

Combining Eqs. 8, 11, 15; 9, 12, 16; and 10, 13, 17, respectively, the concentration and temperature profiles are expressed by

$$c_A(x) = 1 - \frac{\Psi_{0A}}{a+1}\left[\frac{1}{Sh^*} + \frac{1}{2}U(1-x^2)\right] \tag{18}$$

$$c_B(x) = E_B - \frac{\nu_B\Psi_{0A}}{(a+1)\nu_A}\left[\frac{1}{Sh^*K_B} + \frac{1}{2D_B}U(1-x^2)\right] \tag{19}$$

$$\varphi(x) = 1 + \beta_0\frac{\Psi_{0A}}{a+1}\left[\frac{1}{Nu^*} + \frac{1}{2}U(1-x^2)\right] \tag{20}$$

The profiles are valid if the reaction zone is the same as the active zone of the pellet. Curve 2 in Figure 1 represents an extreme case for the concentration profiles, which means that either the concentration of component A or the concentration of component B is equal to 0 for $x = 0$. This observation can help to evaluate the region of validity of Eqs. 18–20, namely, they are valid if

$$\Psi_{0A} < \Psi_{0A,\text{crit}} = \min\left(\frac{2(a+1)}{2+Sh^*U}, \frac{2\nu_A(a+1)Sh^*K_BD_BE_B}{\nu_B(2D_B + Sh^*K_BU)}\right) \tag{21}$$

By analogy, if $\Psi_{0A} \geq \Psi_{0A,\text{crit}}$, then

$$c_A(\xi) = 1 - \frac{\Psi_{0A}}{a+1}\left[\frac{1}{Sh^*} + \frac{1}{2}V(1-\xi^2)\right] \tag{22}$$

$$c_B(\xi) = E_B - \frac{\nu_B\Psi_{0A}}{(a+1)\nu_A}\left[\frac{1}{Sh^*K_B} + \frac{1}{2D_B}V(1-\xi^2)\right] \tag{23}$$

$$\varphi(\xi) = 1 + \beta_0\frac{\Psi_{0A}}{a+1}\left[\frac{1}{Nu^*} + \frac{1}{2}V(1-\xi^2)\right] \tag{24}$$

where

$$V = 1 - \frac{R_c}{R_0} = \min\left(\frac{2(a+1)}{\Psi_{0A}} - \frac{2}{Sh^*}, \frac{2\nu_A(a+1)E_BD_B}{\nu_B\Psi_{0A}} - \frac{2D_B}{Sh^*K_B}\right) \tag{25}$$

Equation 25 results from the observation that either the concentration of component A or the concentration of component B is equal to 0 for $\xi = 0$ (cf. curve 3 in Figure 1).

And finally two additional notes. The value of the Weisz modulus is restricted by physical considerations so that in this extreme case, V approaches 0, which leads to the following equation

$$\Psi_{0A} < \Psi_{0A,\text{bound}} = \min\left((a+1)Sh^*, \frac{\nu_A}{\nu_B}(a+1)Sh^*K_BE_B\right) \tag{26}$$

Note that the use of Eqs. 18–20 is sufficient to achieve the aim of the work. The only exception concerns heat-transfer resistances and will be presented later.

The way to obtain the profiles as well as to calculate the reaction zone depth, V, and limiting values $\Psi_{0A,\text{crit}}$ and $\Psi_{0A,\text{bound}}$ is described in more detail by Petrus (1988a,b).

Next we present an evaluation of the importance of temperature or concentration gradients based on the *effectiveness factor*, a very important particle parameter. It is common knowledge that an overall effectiveness factor

$$\eta_0 = (a+1)\int_0^1 x^a R_{(c_i,\varphi)}\,dx \tag{27}$$

is a reflection of mass and heat resistances, both outside and inside of the catalyst pellet. It can be presented as a product of two factors

$$\eta_0 = \eta_{\text{ex}}\eta \tag{28}$$

The first (called η_{ex}) is a reflection of interphase transport intrusions and can be expressed as

$$\eta_{\text{ex}} = R_{(c_{is},\varphi_s)} \tag{29}$$

while the second η (the well-known local effectiveness factor) is a reflection of intraparticle temperature and concentrations gradients, and is expressed as

$$\eta = \frac{(a+1)\int_0^1 x^a R_{(c_i,\varphi)}dx}{R_{(c_{is},\varphi_s)}} \tag{30}$$

And so, in order to derive the criteria we assume that the influence of the overall transport limitation can be neglected if maximal deviation of η_0 does not exceed 5%. Similarly, the influence of external transport resistances or internal temperature and concentration gradients can also be ignored if the maximal deviation of η_{ex} or η, respectively, does not exceed 5%. This approach is in many instances sufficiently exact and permits the criteria obtained to be shown as closed mathematical formulas.

To derive the criteria for reactions frequently found in industrial practice (Eq. 1) with power-law kinetics, we can write

$$R_{(c_i,\varphi)} = \frac{c_A^{n1}c_B^{n2}}{E_B^{n2}}\exp\left[\gamma_0\left(1 - \frac{1}{\varphi}\right)\right] \tag{31}$$

Since both concentrations and temperature profiles are determined, all that is left to be shown is a way to derive the criteria and mathematical manipulations.

External mass- and heat-transfer resistances

In the first instance, considering the most general case, the simultaneous intrusion of both external resistances, it is enough to take the parameter η_{ex} into account, that is, its value should be found in the range

$$0.95 < \eta_{ex} < 1.05 \tag{32}$$

Substituting Eq. 29 into Eq. 32 and combining with Eq. 31 leads to

$$0.95 < \frac{c_{As}^{n1} c_{Bs}^{n2}}{E_B^{n2}} \exp\left[\gamma_0 \left(1 - \frac{1}{\varphi_s}\right)\right] < 1.05 \tag{33}$$

where c_{As}, c_{Bs}, and φ_s can be obtained by substituting $x = 1$ into Eqs. 18–20. By combining the resulting equation with Eq. 33, the following inequality can be obtained

$$0.95 < \left(1 - \frac{\Psi_{0A}}{(a+1)Sh^*}\right)^{n1} \left(1 - \frac{\nu_B \Psi_{0A}}{(a+1)\nu_A K_B E_B Sh^*}\right)^{n2} \times \exp\left[\gamma_0 \left(1 - \frac{1}{1 + \beta_0 \dfrac{\Psi_{0A}}{(a+1)Nu^*}}\right)\right] < 1.05 \tag{34}$$

The preceding relationship is rather complicated. A power-series expansion of concentrations and temperature terms (with truncating nonlinear terms) allows us to simplify it to the inequality

$$0.05(a+1) > \left| \frac{\Psi_{0A}}{Sh^*}\left[n1 + n2 \frac{\nu_B}{\nu_A K_B E_B}\left(1 - n1 \frac{\Psi_{0A}}{(a+1)Sh^*}\right)\right] - \frac{\Psi_{0A}}{(a+1)Sh^*} \cdot \frac{\gamma\beta_0}{Nu^*}\left\{Sh^* - \frac{\Psi_{0A}}{3} \times \left[n1 + n2 \frac{\nu_B}{\nu_A K_B E_B}\left(1 - n1 \frac{\Psi_{0A}}{(a+1)Sh^*}\right)\right]\right\} \right| \tag{35}$$

In this inequality, the first term gives information on the diffusion limitations, and the second term gives information on the heat effects. If heat-transfer resistance is negligible (such as for isothermal processes), Eq. 35 can be simplified by substitution of $Nu^* \to \infty$. This leads to

$$0.05(a+1) > \left| \frac{\Psi_{0A}}{Sh^*}\left[n1 + n2 \frac{\nu_B}{\nu_A K_B E_B}\left(1 - n1 \frac{\Psi_{0A}}{(a+1)Sh^*}\right)\right] \right| \tag{36}$$

Similarly if the external mass-transfer resistance is negligible (Sh^* approaches infinity), then to examine heat resistance it is enough to check the simple inequality

$$0.05(a+1) > \left| \frac{\gamma\beta_0 \Psi_{0A}}{Nu^*} \right| \tag{37}$$

Equations 36 and 37 also can be derived on the basis of Eq. 33 by neglecting the terms concerning concentration or heat dependence, respectively.

Internal mass- and heat-transfer resistances

Equations concerning internal mass- and heat-transfer resistances can be derived in the same way as was described in the preceding subsections. The only difference is the use of the following equation

$$0.95 < \eta < 1.05 \tag{38}$$

instead of Eq. 32.

So substituting Eq. 30 into Eq. 38 and combining with the equations that describe the concentration and temperature profiles, linearization (by expanding a result into a power series and truncating nonlinear terms) and then integrating leads to the following inequality

$$0.05(a+1)(a+3) > \left| \Psi_{0A}\left\{ n1 + n2 \frac{\nu_B}{\nu_A E_B D_B} - \gamma_0 \beta_0 - \frac{\Psi_{0A}}{a+1}\left[n1 \cdot n2 \frac{2\nu_B}{(a+5)\nu_A E_B D_B} - \gamma_0 \beta_0 \times \left(\frac{2n1}{(a+5)} + \frac{2\nu_B n2}{(a+5)\nu_A E_B D_B} \times \left(1 - \frac{3\Psi_{0A} n1}{(a+1)(a+7)}\right)\right)\right]\right\} \right| \tag{39}$$

If the preceding inequality is true, then both concentration and temperature gradients inside the pellet are neglected. Similarly, as in the preceding point, a criterion concerning only internal mass-transfer resistances if heat-transfer resistance is negligible can be derived. The following equation presents it

$$0.05(a+1)(a+3) > \Psi_{0A}\left[n1 + n2 \frac{\nu_B}{\nu_A E_B D_B} \times \left(1 - n1 \frac{2\Psi_{0A}}{(a+1)(a+5)}\right)\right] \tag{40}$$

Finally a criterion on the lack of an internal temperature gradient (if concentration gradients can be omitted) derived in the proposed way is given by

$$0.05(a+1)(a+3) > |\gamma_0 \beta_0 \Psi_{0A}| \tag{41}$$

Overall mass- and heat-transfer resistances

Using the following equation

$$0.95 < \eta_0 < 1.05 \tag{42}$$

and following the reasoning in the same way as described earlier, one can obtain three expressions. First, all resistances can be neglected if the following inequality is true

$$\begin{aligned}0.05(a+1)(a+3) > \Bigg| \Psi_{0A} \Bigg[& n1\left(\frac{(a+3)}{Sh^*}+1\right) \\ & + \frac{\nu_B n2}{\nu_A E_B}\left(\frac{(a+3)}{K_B Sh^*}+\frac{1}{D_B}\right) \\ & - \gamma_0 \mathrm{B}_0\left(\frac{(a+3)}{Nu^*}+1\right) - \frac{\Psi_{0A}}{(a+1)} \\ & \times \Bigg\{ \frac{\nu_B n1 \cdot n2}{\nu_A E_B} \Bigg(\frac{1}{K_B Sh^*} + \frac{1}{Nu^*} \\ & + \frac{2}{(a+5)D_B} \Bigg) - \gamma_0 \beta_0 \Bigg[n1 \Bigg(\frac{1}{Sh^*} + \frac{1}{Nu^*} \\ & + \frac{2}{(a+5)} \Bigg) + \frac{\nu_B n2}{\nu_A E_B D_B}\left(\frac{1}{Nu^*}+\frac{2}{(a+5)}\right) \\ & - n1 \cdot n2 \frac{2\Psi_{0A}}{(a+1)(a+5)D_B E_B} \\ & \times \left(\frac{1}{Nu^*}+\frac{1}{Sh^*}+\frac{3}{(a+7)}\right) \Bigg] \Bigg\} \Bigg] \Bigg| \end{aligned} \qquad (43)$$

Next, the mass-transfer resistances can be omitted (if the heat-transfer resistances are negligible) if

$$\begin{aligned}0.05(a+1)(a+3) > \Psi_{0A} \Bigg\{ & n1\left(1+\frac{(a+3)}{Sh^*}\right) \\ & + n2 \frac{\nu_B}{\nu_A E_B} \Bigg[\frac{(a+3)}{K_B Sh^*} + \frac{1}{D_B} \\ & - n1 \frac{\Psi_{0A}}{3} \Bigg(\frac{(a+3)}{K_B Sh^{*2}} + \frac{1}{K_B Sh^*} \\ & + \frac{1}{D_B Sh^*} + \frac{2}{(a+5)D_B} \Bigg) \Bigg] \Bigg\} \end{aligned} \qquad (44)$$

Finally, the heat-transfer resistances can be omitted (if the mass-transfer resistances are negligible) if

$$0.05(a+1)(a+3) > \left| \gamma_0 \beta_0 \Psi_{0A} \left(1+\frac{(a+3)}{Nu^*}\right) \right| \qquad (45)$$

But a more detailed analysis leads to the conclusion that the pellet can be isothermal apart from the mentioned case if the internal heat-transfer resistance is neglected instead of the external one and the reaction zone is narrow; that is, the value of parameter V is close to 0 [this problem was considered in earlier works by Petrus (1988a,b)]. In this case, the following inequality should be considered

$$0.05 > |\gamma_0 \varphi_s (1-\varphi(0))| \qquad (46)$$

where φ_s and $\varphi(0)$ can be obtained by substituting $\xi = 1$ or $\xi = 0$ respectively, into Eq. 24. By the substitution of φ_s and $\varphi(0)$ into Eq. 46 and using Eq. 25, the following inequalities can be obtained

$$0.05 > \left| \frac{\gamma_0 \beta_0 \left(1 - \frac{\Psi_{0A}}{(a+1)Sh^*}\right)}{\left(1+\beta_0 \frac{Sh^*}{Nu^*}\right)^2} \right| \qquad (47)$$

or

$$0.05 > \left| \frac{\gamma_0 \beta_0 \left(\frac{\nu_A E_B D_B}{\nu_B} - \frac{\Psi_{0A} D_B}{(a+1)Sh^* K_B} \right)}{\left(1+\beta_0 \frac{\nu_A E_B K_B Sh^*}{\nu_B Nu^*}\right)^2} \right| \qquad (48)$$

Inequality 47 is valid if component B is in excess in the reaction mixture and, vice versa, inequality 48 is valid if component A is in excess in the reaction mixture.

Discussion

The criteria were derived using the approximate temperature and concentration profiles. The choice of the profile type has an immediate impact on the accuracy and simplicity of the criteria. The chosen profiles should satisfy the basic relationships for a catalyst pellet, for example, the Prater relationship. If necessary, the accuracy can be improved at the expense of the simplicity of the outcome by considering high-order terms of the series expansion (see Eqs. 53 and 54).

In the previous section many criteria were derived for the diffusion-reaction process in a catalyst particle. Experimental data published in the literature do not allow all of the criteria to be tested. For this reason only some of them are verified and discussed here. Moreover, the criteria derived in this article involve only two-component reactions, and this limitation makes a comparison with criteria available in the literature difficult. However, the criteria can be easily adapted to one-component reactions by the simple substitution of $n2 = 0$ and $\nu_B = 0$ (with the single exception of Eq. 48, which concerns only two-component reactions). It allows us to both compare developed criteria with published ones and to prove their correctness. All cited criteria will be expressed using the notation of this work.

At first, inequalities 36, 37, and 40, are considered. For a one-component reaction and for a spherical particle, they can be expressed as

$$0.15 > n1 \frac{\Psi_{0A}}{Sh^*} \qquad (49)$$

$$0.15 > \left| \frac{\Psi_{0A}}{Nu^*} \beta_0 \gamma_0 \right| \qquad (50)$$

$$0.75 > n1 \Psi_{0A} \qquad (51)$$

respectively. Inequalities 49–51 were published earlier, and they were verified by Hudgins (1981) and Hudgins and Silveston (1984). This confirms indirectly that inequalities 36, 37, and 40, are correct for two-component reactions.

Inequality 39 concerning internal mass- and heat-transfer resistances for a one-component reaction and for a spherical particle can be expressed as

$$0.75 > \left| n1\Psi_{0A}\left[1-\frac{\gamma_0\beta_0}{nl}\left(1-n1\frac{2\Psi_{0A}}{21}\right)\right]\right| \tag{52}$$

A criterion concerning internal mass- and heat-transfer resistances also has been presented earlier by Dogu and Dogu (1984)

$$0.75 > \left| n1\Psi_{0A}\left(1-\frac{\gamma_0\beta_0}{n1}\right)\right| \tag{53}$$

and by Dogu (1985)

$$\begin{aligned}0.75 > \Bigg| & n1\Psi_{0A}\left(1-\frac{\gamma_0\beta_0}{n1}\right)+\frac{1}{21}(n1\Psi_{0A})^2\\ &\times\left[-\frac{n1-1}{n1}+2\frac{\gamma_0\beta_0}{n1}-\left(\frac{\gamma_0\beta_0}{n1}\right)^2\right]+\frac{1}{567}(n1\Psi_{0A})^3\\ &\times\left[\frac{(n1-1)(n1-2)}{n1^2}-3\frac{n1-1}{n1}\frac{\gamma_0\beta_0}{n1}+3\left(\frac{\gamma_0\beta_0}{n1}\right)^2\right.\\ &\left.-\left(\frac{\gamma_0\beta_0}{n1}\right)^3\right]+\frac{1}{18{,}711}(n1\Psi_{0A})^4\\ &\times\left[-\frac{(n1-1)(n1-2)(n1-3)}{n1^3}+4\frac{(n1-1)(n1-2)}{n1^2}\frac{\gamma_0\beta_0}{n1}\right.\\ &\left.-6\frac{n1-1}{n1}\left(\frac{\gamma_0\beta_0}{n1}\right)^2+4\left(\frac{\gamma_0\beta_0}{n1}\right)^3-\left(\frac{\gamma_0\beta_0}{n1}\right)^4\right]\Bigg|\end{aligned} \tag{54}$$

Based on the results given by Maymo and Smith (1966), inequalities 52–54 can be compared. Table 1 presents the comparison.

In agreement with the earlier assumption, the lack of resistances is indicated by the value of the effectiveness factor—if its value is included in the range (0.95, 1.05), then resistances can be neglected. Inequality 52 is true only for run 8-7, and a measured value of the effectiveness factor $\eta = 0.96$ confirms it. In the remaining circumstances, inequality 52 indicates that the resistances cannot be neglected. In contrast to inequality 52, inequality 53, given by Dogu and Dogu (1984), indicates the lack of resistances for as far as four runs (8-4, 8-7, 11-2, 10-2). If the error for runs 8-4 and 11-2 is not big (effectiveness factor values are close to an extreme value of 0.95), then for run 10-2 inequality 53 completely fails. Inequality 54 does not have this drawback. What is the reason? Inequality 52 can be easily rearranged to get

$$0.75 > \left| n1\Psi_{0A}\left(1-\frac{\gamma_0\beta_0}{n1}\right)+\frac{2\gamma_0\beta_0}{21}\Psi_{0A}^2 n1\right| \tag{55}$$

Inequalities 53–55 differ from one another by the last terms on the righthand side, which describe the interaction between the mass and heat fluxes in the pellet. In some circumstances, the interaction plays a major role and it primarily impacts on process behavior. The core of the importance of the interaction between the mass and heat fluxes is presented in Figure 2. This figure presents the relation $\Psi_{0A} = f(\beta_0)$ for run 10-2 (Table 1). The single point (square) represents data for run 10-2. The area below the solid line includes processes for which internal mass- and heat-transfer resistances can be omitted, in agreement with Eq. 53. It is easy to see that if $\gamma_0\beta_0/n1$ is sufficiently close to 1, then the Ψ_{0A} value can be unlimited, which cannot be found in practice. Taking the interaction between the mass and heat fluxes in the pellet into account eliminates this drawback by limiting the Ψ_{0A} value for which the internal mass- and heat-transfer resistances can be omitted. The area under the dashed line in Figure 2 represents the processes for which the resistances can be omitted (in agreement with Eq. 52). Equation 54 correctly indicates the lack of resistance, because its accuracy was improved by considering the high-order terms of the series expansion. The area for which internal mass- and heat-transfer resistances can be omitted in agreement with Eq. 53 is similar to the area under the dashed line (but smaller). Similar outcomes were obtained for other values of parameters β_0, γ_0, Ψ_{0A}, and n.

Inequality 43, which concerns all mass- and heat-transfer resistances, can be verified on the basis of results presented

Table 1. Verification of Criteria (Eqs. 52 and 53)*

Run	β_0	γ_0	$\gamma_0\beta_0/n1$	Ψ_{0A}	η	Eq. 52	Eq. 53	Eq. 54
7-1	0.030	7.00	0.261	4.47	0.67	2.97	2.65	3.13
8-4	0.131	6.81	1.109	5.53	0.93	1.60	0.49	1.28
8-7	0.136	7.27	1.230	3.84	0.96	0.41	0.71	0.06
11-2	0.116	7.03	1.014	4.33	0.92	1.12	0.048	0.92
*E*1	0.339	6.75	2.846	5.18	1.10	2.98	7.68	8.47
10-2	0.116	6.58	0.949	12.31	0.60	9.35	0.504	12.06

*Based on data given by Maymo and Smith (1966).

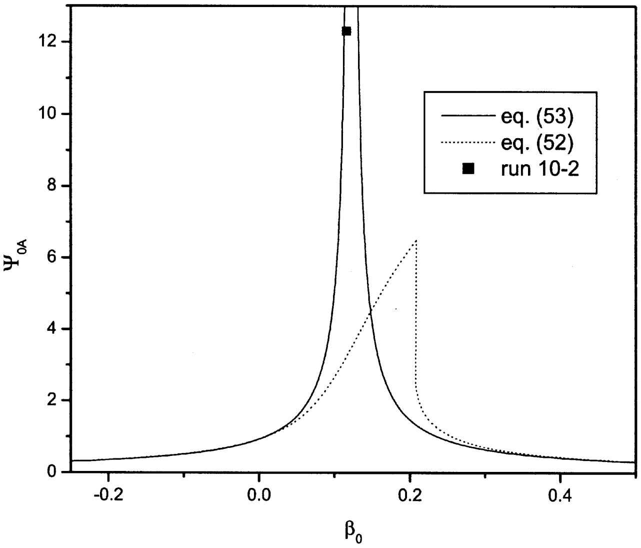

Figure 2. Ψ_{0A} vs. β_0 for the run 10-2 (Table 1).

Table 2. Verification of Criteria (Eqs. 56 and 57)*

Sh^*	Nu^*	γ_0	β_0	$\gamma_0\beta_0/n1$	Ψ_{0A}	η_0	Eq. 56	Eq. 57
1.0	1.0	10.0	−0.4	−4.0	0.0098	0.98	0.29	0.29
1.0	1.0	10.0	−0.4	−4.0	0.176	0.669	5.18	5.40
50.0	1.0	10.0	−1.0	−10.0	0.0096	0.961	0.59	0.59
50.0	1.0	10.0	−1.0	−10.0	0.138	0.554	8.35	8.90
69.16	10.06	9.65	0.0428	1.160	38.13	0.937	19.46	7.04
67.25	9.77	9.63	0.065	1.758	33.31	1.092	14.43	15.27
61.53	8.74	9.89	0.082	2.278	22.05	1.032	0.14	16.73

*Based on data given by Tan and Smith (1984) (upper part), Respondek and Petrus (1978), Petrus and Respondek (1979) (lower part).

by Tan and Smith (1984), and by Respondek and Petrus (1978) and Petrus and Respondek (1979). For a one-component reaction and for a spherical particle it can be expressed as

$$0.75 > \left| n1\Psi_{0A}\left\{ \frac{5}{Sh^*} + 1 - \frac{\gamma_0\beta_0}{n1} \times \left[\frac{5}{Nu^*} + 1 - n1\frac{\Psi_{0A}}{3}\left(\frac{1}{Sh^*} + \frac{1}{Nu^*} + \frac{2}{7} \right) \right] \right\} \right| \quad (56)$$

The criterion by Dogu (1985) has the form

$$0.75 > \left| n1\Psi_{0A}\left[\frac{5}{Sh^*} + 1 - \frac{\gamma_0\beta_0}{n1} \frac{1 + \frac{5}{Nu^*}\left(1 + \frac{\Psi_{0A}}{3}\frac{\beta_0}{Nu^*}\right)}{\left(1 + \frac{\Psi_{0A}}{3}\frac{\beta_0}{Nu^*}\right)^2} \right] \right| \quad (57)$$

The verified results are presented in Table 2.

Inequality 56 is valid for data included in the first, third, and last rows of the Table 2, and without error indicates cases for which $0.95 < \eta_0 < 1.05$; that is, cases for which all mass- and heat-transfer resistances can be omitted. Inequality 57 fails for the last case, unfortunately.

Finally, we discuss inequality 40 for two-component reactions. For a spherical particle, it can be expressed as

$$0.75 > \Psi_{0A}\left[n1 + n2\frac{\nu_B}{\nu_A E_B D_B}\left(1 - n1\frac{2\Psi_{0A}}{21} \right) \right] \quad (58)$$

The criterion by Dogu (1985) has the form

$$0.75 > \Psi_{0A}\left(n1 + n2\frac{\nu_B}{\nu_A E_B D_B} \right) \quad (59)$$

The verification is based on results given by Baldi et al. (1974). The results are presented in Table 3.

In all cases, both inequalities 58 and 59 are not true, so internal mass-transfer resistances cannot be neglected. Experimental values of the effectiveness factor confirm these outcomes.

Table 3. Verification of Criteria (Eqs. 58 and 59)*

E_B	D_B	ν_B/ν_A	$n1$	$n2$	Ψ_{0A}	η	Eq. 58	Eq. 59
2.6	0.4	2	1	1	0.462	0.92	1.31	1.35
2.6	0.4	2	1	1	1.060	0.87	2.89	3.09

*Based on data given by Baldi et al. (1974).

All of the outcomes presented previously suggest that the criteria developed here are correct. The method of verification also proves that the criteria can be successfully applied after being simplified for one-component reactions and in some circumstances are better than the criteria published earlier, because they take the interaction between mass and heat fluxes in the pellet into account. The method can be particularly easily adapted to another type of kinetic rate equation (such as the Langmuir-Hinshelwood type or any type of experimental relationship). In that case, the kinetic equation of the power-law type is replaced with a "new" one (determination of parabolic profiles of reagent concentrations and temperature can be omitted). For more complicated reaction schemes, the full methodology of the criteria derivation should be utilized. And finally one last note. If the criteria are not sufficiently precise, they can be easily improved by considering the high-order the terms of the series expansion.

Conclusions

The derived criteria of mass and transfer that are relatively important concern quite a large class of reactions, and they are characterized by good accuracy. Moreover, the method of derivation presented for the chosen reaction and kinetic equation can be easily extended to practically any type of reaction in accordance with the following scheme:

- Determination of approximate (parabolic) profiles of reagent concentrations and temperatures inside the pellet using mass and heat balances and stoichiometry;
- Substitution of the profiles or values of the concentrations and/or temperatures at the characteristic points of the pellet (surface, center, and so on) into the proper inequality;
- Mathematical manipulations (expansion into a power series, integration, and so on) to obtain the final version of the criterion

The criteria are straightforward, and their use should not cause difficulties, even though they have the disadvantage of rather complex formulas if the number of species taking part in a process is large and/or the reaction kinetics are not in a power-law form.

Notation

a = coefficient (equal to 0, 1, 2 for planar, cylindrical, and spherical geometry of the pellet, respectively)
A, B, R = components
a_{cA}, a_{cB}, a_{φ} = coefficients in Eqs. 11–14
c_i = dimensionless concentration of component i (related to the bulk concentration)
c_{is}, φ_s = surface concentration/temperature
D_i = ratio of effective diffusion coefficients of components i and A
E_i = ratio of bulk concentrations of components i and A
K_i = ratio of mass-transfer coefficients of components i and A
ni, $i = 1, 2$ = order of reaction in respect to component i
Nu^* = modified Nusselt number
r = distance in the pellet
$R_{(c,\varphi)}$ = kinetic expression

R_0 = radius of the pellet
R_c = hypothetical reaction interface
R_{nc} = dimensionless radius of nonactive core
Sh^* = modified Sherwood number
U = active zone
V = reaction zone
x = dimensionless distance in the pellet

Greek letters

β_0 = Prater parameter
γ_0 = dimensionless activation energy
η, η_0, η_{ex} = local effectiveness factor, overall effectiveness factor, and effectiveness factor with regard to external transport resistances, repectively
ν_i = stoichiometric coefficient for component i
ξ = dimensionless coordinate defined by Eq. 7
φ = dimensionless temperature
Φ = Thiele modulus
Ψ_{0A}, $\Psi_{0A,\mathrm{crit}}$, $\Psi_{0A,\mathrm{bound}}$ = Weisz modulus, critical value of Weisz modulus, and extreme value of Weisz modulus, respectively

Subscripts

s = surface

Literature Cited

Anderson, J. B., “A Criterion for Isothermal Behavior of a Catalyst Pellet,” *Chem. Eng. Sci.*, **18**, 147 (1963).

Baldi, G., S. Goto, C.-K. Chow, and J. M. Smith, “Catalytic Oxidation of Formic Acid in Water. Intraparticle Diffusion in Liquid-Filled Pores,” *Ind. Eng. Chem. Process Des. Dev.*, **13**, 447 (1974).

Dogu, T., “A General Criterion to Test the Relative Importance of Intraparticle and External Heat and Mass Transfer Resistances in Porous Catalysts,” *Can. J. Chem. Eng.*, **63**, 37 (1985).

Dogu, T., and G. Dogu, “Testing the Relative Importance of Temperature and Concentration Gradients in Catalyst Pellets,” *AIChE J.*, **30**, 1002 (1984).

Doraiswamy, L. K., and M. M. Sharma, *Heterogeneous Reactions: Analysis, Examples and Reactor Design*, Wiley, New York (1984).

Froment, G. F., and K. B. Bischoff, *Chemical Reactor Analysis and Design*, Wiley, New York (1979).

Hudgins, R. R., “Inadequacy of the Criteria for Detecting Interphase Transport Intrusions,” *Chem. Eng. Sci.*, **36**, 1579 (1981).

Hudgins, R. R., and P. L. Silveston, “Testing of the Intraparticle Mass Transfer Criterion,” *Chem. Eng. Sci.*, **40**, 667 (1984).

Maymo, J. A., and J. M. Smith, “Catalytic Oxidation of Hydrogen—Intrapellet Heat and Mass Transfer,” *AIChE J.*, **12**, 845 (1966).

Petrus, R., “Róznica Temperatury i Głębokość Strefy Reakcji w Porowatym Ziarnie Katalizatora,” *Inz. Chem. Proc.*, **9**, 203 (1988a).

Petrus, R., “Róznica Temperatury i Głębokość Strefy Reakcji w Porowatym Ziarnie Katalizatora II,” *Inz. Chem. Proc.*, **9**, 427 (1988b).

Petrus, R., and J. Respondek, “Współczynnik Efektywności Oraz Minimalne Róznice Temperatur w Porowatych Ziarnach Katalizatora,” *Inz. Chem.*, **IX**, 195 (1979).

Respondek, J., and R. Petrus, “Model Kinetyczny Uwodornienia Propylenu na Katalizatorze Platynowym,” *Inz. Chem.*, **VIII**, 155 (1978).

Tan, Ch., S., and J. M. Smith, “Catalyst Particle Effectiveness with Unsymmetrical Boundary Conditions,” *Chem. Eng. Sci.*, **39**, 1329 (1984).

Manuscript received Oct. 2, 2002, and revision received Feb. 19, 2003.