Kinetics and Catalysis, Vol. 44, No. 6, 2003, pp. 827–833. Translated from Kinetika i Kataliz, Vol. 44, No. 6, 2003, pp. 902–908.
Original Russian Text Copyright © 2003 by Kuchaev, Shapatina, Zyskin, Christiansen, Avetisov.

Method for Estimating Efficiency Factors for Complex Reactions: I. Reactions Occurring via Several Stoichiometric Equations

V. L. Kuchaev*, E. N. Shapatina*, A. G. Zyskin*, L. Christiansen, and A. K. Avetisov***
** Karpov Research Institute of Physical Chemistry (Russian State Scientific Center), Moscow, 103064 Russia*
*** Haldor Topsøe A/S, Lingby DK-2800, Denmark*

Received April 26, 2001; in final form, Iune 10, 2002

Abstract—The method for estimating the efficiency factors proposed by Temkin for a multicomponent reaction described by a single stoichiometric equation is extended to reactions described by several stoichiometric equations. The proposed approach makes it possible to find the efficiency factors of key substances by solving a set of nonlinear equations. The capabilities of the method are illustrated using the reaction of steam reforming of methane as an example.

Temkin [1] proposed a simple method for estimating the efficiency factor for a porous heterogeneous catalyst for the case when the reaction occurs via a single stoichiometric equation. The goal of this work is to extend the method to reactions described by several independent stoichiometric equations.

According to [1], the stoichiometric equation can be described in the form

$$0 = \sum_{i=1}^{m} b_i \mathrm{B}_i, \tag{1}$$

where B_i are the substances participating in the reaction; b_i are the stoichiometric coefficients, which are positive for the products and negative for the initial substances; and m is the number of substances participating in the reaction.

The rate of such a reaction w is positive in the absence of diffusion control, and the rate of formation of each substance participating in the reaction is described by the formula

$$w_i = b_i w. \tag{2}$$

The values of w_i are negative for the initial substances and positive for the products. The reaction rate refers to the unit volume of the catalyst grain. The following assumptions were made when carrying out calculations: (1) the effective coefficient of diffusion of each reaction participant does not change over the catalyst grain and (2) the catalyst grains are spherical with the same radius a.

To determine the efficiency factor, one should know the dependence of the reaction rate on the concentrations of reaction participants. In [1], the problem was solved using an approximation that the reaction rate inside the grain linearly depends on the concentration of all components of the reaction mixture:

$$w = w_a + \sum_{i=1}^{m} \left(\frac{\partial w}{\partial C_i}\right)_a [C_i - (C_i)_a], \tag{3}$$

where w and C_i are the reaction rate and the concentration of B_i at a certain distance from the center of the grain ($r \le a$); w_a, $(C_i)_a$, and $\left(\frac{\partial w}{\partial C_i}\right)_a$ are the values of the reaction rate, the concentration of B_i, and the derivative $\frac{\partial w}{\partial C_i}$ at $r = a$, that is on the grain surface. (Henceforth, subscript a means that the value refers to the case of r equal to a.)

Formula (3) is approximate because it does not include further terms of expansion in a series of w over powers of $[C_i - (C_i)_a]$. The closer the efficiency factor to unity, the more accurate the estimate.

The diffusion flow of any substance through the sphere with radius r in the catalyst grain is equal to the amount of substance formed inside the sphere. Taking into account Eq. (2), we obtain

$$-4\pi r^2 D_i^* \frac{\mathrm{d}C_i}{\mathrm{d}r} = b_i \int_0^r 4\pi r^2 w \mathrm{d}r, \tag{4}$$

where D_i^* is the effective diffusion coefficient of B_i in the catalyst grain and r is the distance from the grain center. The flow is negative for initial substances and positive for the products.

It follows from (4) that, with a change in the radius from r to $r + dr$,

$$\frac{D_i^*}{b_i}\mathrm{d}C_i = \frac{D_j^*}{b_j}\mathrm{d}C_j. \qquad (5)$$

Equation (5) was called diffusional stoichiometry [1] and it is correct for any $r \le a$. This equation can be integrated:

$$C_i - (C_i)_a = \frac{D_j^* b_j}{D_j^* b_j}[C_j - (C_j)_a]. \qquad (6)$$

Upon substitution of Eq. (6) into Eq. (3), we obtain

$$w = w_a - \frac{D_j^* h^2}{b_j}[C_j - (C_j)_a, \qquad (7)$$

where

$$h^2 = -\sum_{i=1}^{m}\frac{b_i}{D_i^*}\left(\frac{\partial w}{\partial C_i}\right)_a. \qquad (8)$$

The minus sign in Eq. (8) is necessary for the condition $h^2 > 0$ (this condition is fulfilled if the reaction rate inside the grain is lower than on the grain surface).

The differentiation of (4) over r gives us equations for the concentration of each reaction participant:

$$\frac{\mathrm{d}^2 C_i}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}C_i}{\mathrm{d}r} + \frac{b_i w}{D_i^*} = 0. \qquad (9)$$

The boundary conditions are

$$C_i = (C_i)_a \text{ at } r = a \text{ and } \quad \frac{\mathrm{d}C_i}{\mathrm{d}r} = 0 \text{ at } r = 0. \qquad (10)$$

This equation is solved in elementary functions if w is a linear function of C_i (Eq. (7)). A solution that fulfills boundary conditions (10) at $h^2 > 0$ is

$$C_i = (C_i)_a + \frac{b_i w_a}{D_i^* h^2} - \frac{b_i w_a}{D_i^* h^2}\frac{a(\mathrm{e}^{hr} - \mathrm{e}^{-hr})}{r(\mathrm{e}^{ha} - \mathrm{e}^{-ha})} \qquad (11)$$

and at $h^2 < 0$,

$$C_i = (C_i)_a + \frac{b_i w_a}{D_i^* h^2} - \frac{b_i w_a}{D_i^* h^2}\frac{a\sin(r\sqrt{-h^2})}{r\sin(a\sqrt{-h^2})}. \qquad (12)$$

An efficiency factor for substance B_i is the ratio of the average rate of formation of this substance in a grain to the rate of formation in the absence of diffusion control. The following formula corresponds to this definition:

$$\eta_i = \frac{\int_0^a 4\pi r^2 w_i \mathrm{d}r}{\frac{4}{3}\pi a^3 (w_i)_a}. \qquad (13)$$

If the reaction occurs via a single stoichiometric equation, the efficiency factor for a substance coincides with the standard efficiency factor.

For the case when $h^2 > 0$ we obtain using formulas (4), (11), and (13) and notation $ha = \varphi$

$$\eta = \frac{3}{\varphi}\left(\coth\varphi - \frac{1}{\varphi}\right). \qquad (14)$$

For the case when $h^2 < 0$, we obtain using notation $\chi = a\sqrt{-h^2}$

$$\eta = \frac{3}{\chi}\left(\frac{1}{\chi} - \cot\chi\right). \qquad (15)$$

Formula (15) can be fulfilled at $0 < \chi < \pi$, in which case $\eta > 1$. When χ approaches zero, η approaches unity. When χ approaches π, the efficiency factor becomes infinite, which cannot be realized in practice.

Let us apply the above approach [1] to a reaction occurring via several independent stoichiometric equations. If their number is n ($n < m$), then the rates of formation of n key substances should be known. The rates of formation of other substances can be expressed in terms of the rates of formation of the key substances. The efficiency factors for different key substances are not the same. It is necessary to find the efficiency factors for all key substances and then to determine the efficiency factors for other substances.

By analogy to [1], for each key substance we take into account only linear terms with respect to the concentrations of m substances when expanding the rates of formation into the series. Formula (3) will be replaced in that case by the formulas for each of the n key substances:

$$w_j = (w_j)_a + \sum_{i=1}^{m}\left(\frac{\partial w_j}{\partial C_i}\right)_a [C_i - (C_i)_a]. \qquad (16)$$

Assuming that the amount of substance formed is equal to the respective diffusion flow, we obtain the formulas analogous to (4) for each of the reaction participants:

$$-4\pi r^2 D_i^* \frac{\mathrm{d}C_i}{\mathrm{d}r} = \int_0^r 4\pi r^2 w_i \mathrm{d}r. \qquad (17)$$

Let us assume that the efficient diffusion coefficients of substances are independent of r. Then, the differentiation of Eq. (17) over r gives the differential equations for all m reaction participants, including n key substances:

$$\frac{\mathrm{d}^2 C_i}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}C_i}{\mathrm{d}r} + \frac{w_i}{D_i^*} = 0. \qquad (18)$$

These can be solved in elementary functions if w_i is a linear function of C_i.

For the general case, we obtain an approximate solution. Using formulas (13) and (17) we obtain upon the substitution of the upper limit of integration $r = a$ that

$$-4\pi a^2 D_i^*\left(\frac{\mathrm{d}C_i}{\mathrm{d}r}\right)_a = \frac{4}{3}\pi a^3 (w_i)_a \eta_i. \qquad (19)$$

It follows from (19) that near the grain surface ($r \cong a$)

$$C_j - (C_j)_a = \frac{D_i^*}{D_j^*}\frac{(w_j)_a\eta_j}{(w_i)_a\eta_i}[C_i - (C_i)_a]. \qquad (20)$$

To allow w_i to be linear functions of C_i, we assume that Eq. (20) is correct for arbitrary distance from the center of the catalyst grain. The closer the efficiency factors of B_i and B_j to unity, the more exact Eq. (20) is.

Upon the substitution of (20) into (16), we obtain the formula analogous to (7)

$$w_i = (w_i)_a - D_i^* h_i^2 [C_i - (C_i)_a], \qquad (21)$$

where

$$h_i^2 = -\frac{1}{(w_i)_a\eta_i}\sum_{j=1}^{m}\frac{1}{D_j^*}\left(\frac{\partial w_i}{\partial C_j}\right)_a (w_i)_a \eta_j, \qquad (22)$$

Now w_i in Eq. (18) becomes a linear function of one variable C_i. For boundary conditions (10), the solution to Eq. (18) is determined by formula (11) or (12) where $(w_i)_a$ substitutes for $b_i w_a$. For the efficiency factors of substances η_i, formulas (14) and (15) remain valid. However, according to Eq. (22), each h_i is a function of m unknowns η_i. The number of such unknowns can be reduced to n if the efficiency factors for non-key substances are expressed in terms of the efficiency factors for the key substances.

The rates of formation of non-key substances can be described in the form of a linear combination of the rates of formation of key substances:

$$w_{n+j} = b_{ij}w_1 + b_{2j}w_2 + \ldots + b_{nj}w_n, \qquad (23)$$

where j changes from 1 to $m - n$. Upon multiplying the right-hand and left-hand sides of this equation by $4\pi r^2 \mathrm{d}r$ and integrating from 0 to a, we obtain

$$\begin{aligned} &\eta_{n+j}(w_{n+j})_a \\ &= b_{1j}\eta_1(w_1)_a + b_{2j}\eta_2(w_2)_a + \ldots + b_{nj}\eta_n(w_n)_a. \end{aligned} \qquad (24)$$

By substituting (24) into (22) and multiplying the right-hand and left-hand sides by a^2 we obtain the system

$$\begin{aligned} h_1^2 a^2 &= -a^2\left(a_{11} + a_{21}\frac{\eta_2}{\eta_1} + \ldots + a_{n1}\frac{\eta_n}{\eta_1}\right) \\ h_2^2 a^2 &= -a^2\left(a_{12}\frac{\eta_1}{\eta_2} + a_{22} + \ldots + a_{n2}\frac{\eta_n}{\eta_2}\right) \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ h_n^2 a^2 &= -a^2\left(a_{1n}\frac{\eta_1}{\eta_n} + a_{2n}\frac{\eta_2}{\eta_n} + \ldots + a_{nn}\right). \end{aligned} \qquad (25)$$

The coefficients a_{kl} are determined from the preset kinetic equations using the formula

$$a_{kl} = \frac{(w_k)_a}{(w_l)_a}\left[\frac{1}{D_k^*}\left(\frac{\partial w_l}{\partial C_k}\right)_a + \sum_{i=1}^{m-n}\frac{b_{ki}}{D_{n+i}^*}\left(\frac{\partial w_l}{\partial C_{n+i}}\right)_a\right]. \qquad (26)$$

The system includes unknowns $(h_1a)^2$, $(h_2a)^2$, …, $(h_na)^2$ and $\eta_1, \eta_2, \ldots, \eta_n$, and each η_i is a function of h_ia (formulas (14), (15)). Thus, system (25) consists of n equations with n unknowns and it can be solved by inspection as in the example below where $n = 2$.

The method for estimating the efficiency factors described above was applied to the reaction of steam reforming of methane using data presented in [2, 3]. In those papers, the reaction kinetics were studied on supported nickel catalyst in a flow-type system at a pressure of 3–15 bar and 500, 525, and 550°C. The equations for the rates of formation of all substances in the kinetics-controlled regime were proposed. These included the numeric values of the rate constants.

For the catalyst used with grain sizes of 0.18–0.25 mm [2, 3] or 0.3–0.4 mm [3], the distribution of pores [4] over radii and the tortuosity coefficient are known. This makes it possible to calculate the effective diffusion coefficients in the catalyst under reaction conditions. Thus, available data are sufficient for estimating the efficiency factors for all substances for the proposed kinetic model. According to this model, methane and water form CO and CO_2 via independent routes, and H_2 and CO_2 are formed from CO and H_2O. The following equations were derived:

$$r_1 = \frac{k_1 P_{CH_4} P_{H_2O}(1 - X_1)}{P_{H_2}^{5/2}(DEN)^2}, \qquad (27)$$

$$r_2 = \frac{k_2 P_{CO} P_{H_2O}(1 - X_2)}{P_{H_2}(DEN)^2}, \qquad (28)$$

$$r_3 = \frac{k_3 P_{CH_4} P_{H_2O}^2(1 - X_3)}{P_{H_2}^{7/2}(DEN)^2}, \qquad (29)$$

$$\begin{aligned} (DEN) &= 1 + K_{H_2O}\frac{P_{H_2O}}{P_{H_2}} + K_{CH_4}P_{CH_4} \\ &\quad + K_{CO}P_{CO} + K_{H_2}P_{H_2}, \end{aligned} \qquad (30)$$

where r_1 and r_3 are the rates of formation of CO and CO_2 from methane and water and r_2 is the rate of formation of CO_2 and H_2 from CO and H_2O,

$$X_1 = \frac{1}{K_{(1)}}\frac{P_{CO}P_{H_2}^3}{P_{CH_4}P_{H_2O}}, \tag{31}$$

$$X_2 = \frac{1}{K_{(2)}}\frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}}, \tag{32}$$

$$X_3 = \frac{1}{K_{(3)}}\frac{P_{CO_2}P_{H_2}^4}{P_{CH_4}P_{H_2O}^2}, \tag{33}$$

$K_{(1)}$, $K_{(2)}$, $K_{(3)}$ are the equilibrium constants of the reactions

$$CH_4 + H_2O = CO + 3H_2, \tag{34}$$

$$CO + H_2O = CO_2 + H_2, \tag{35}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2. \tag{36}$$

The goal of this work was to obtain the estimates of efficiency factors using the method described above and the kinetic model proposed in [2] and compare them with those obtained by numerically solving the set of differential equations (18).

For the numeric calculation, we made a computer program using a set of differential equations of Fick's law for each component (isothermal grain and neglected external mass transfer). The coefficients of molecular diffusion are calculated from the composition of the mixture near the catalyst grain surface and are assumed constant in the depth of a grain. The effective diffusion coefficients of reactants in a grain are calculated from the known relations that take into account the molecular and Knudsen components of diffusion as well as by their averaging over the distribution of pore volumes over radii. The assumption that the diffusion coefficients are constant over grain radii makes it possible to use the well-known relationship of "diffusional stoichiometry" and to simplify calculations (the number of differential equations to be solved is equal to the number of key substances). This assumption is usually allowable.

Such an approach to calculating the internal diffusion is used in the literature rather widely. The algorithm for an arbitrary complex heterogeneous catalytic reaction was presented in [5].

The values of the rate constants for 550°C borrowed from [2] are presented below:

$k_1 = 2.41$ mol bar$^{1/2}$ h^{-1} g^{-1},
$k_2 = 107$ mol bar^{-1} h^{-1} g^{-1},
$k_3 = 0.334$ mol bar$^{1/2}$ h^{-1} g^{-1},
$K_{CO} = 2.52$ bar^{-1},
$K_{H_2} = 1.12 \times 10^{-3}$ bar^{-1},
$K_{CH_4} = 0.179$ bar^{-1},
$K_{H_2O} = 0.415$,
$K_{(1)} = 0.08317$ bar^2,
$K_{(2)} = 3.534$,
$K_{(3)} = 0.2939$ bar^2.

Let us first choose CH_4 and CO as key substances. As will be seen from the subsequent discussion below this pair provides the least deviation of approximate efficiency factors from the exact ones.

The rates of formation of key substances is determined by the formulas

$$w_{CH_4} = -r_1 - r_3, \tag{37}$$

$$w_{CO} = r_1 - r_2. \tag{38}$$

The rates of formation of other substances can be expressed via the rates of formation of key substances:

$$w_{H_2O} = 2w_{CH_4} + w_{CO}, \tag{39}$$

$$w_{H_2} = -4w_{CH_4} - w_{CO}, \tag{40}$$

$$w_{CO_2} = -w_{CH_4} - w_{CO}. \tag{41}$$

Using formulas (24), (25), and (39)–(41), we obtain

$$\begin{aligned} h_{CH_4}^2a^2 = -a^2\Bigg\{&\frac{1}{D^*_{CH_4}}\left(\frac{\partial w_{CH_4}}{\partial C_{CH_4}}\right)_a + \frac{2}{D^*_{H_2O}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2O}}\right)_a \\ &- \frac{4}{D^*_{H_2}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2}}\right)_a - \frac{1}{D^*_{CO_2}}\left(\frac{\partial w_{CH_4}}{\partial C_{CO_2}}\right)_a \\ &+ \left[\frac{1}{D^*_{CO}}\left(\frac{\partial w_{CH_4}}{\partial C_{CO}}\right)_a + \frac{1}{D^*_{H_2O}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2O}}\right)_a \right. \\ &\left. - \frac{1}{D^*_{H_2}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2}}\right)_a - \frac{1}{D^*_{CO_2}}\left(\frac{\partial w_{CH_4}}{\partial C_{CO_2}}\right)_a\right]\frac{(w_{CO})_a}{(w_{CH_4})_a}\frac{\eta_{CO}}{\eta_{CH_4}}\Bigg\}, \end{aligned} \tag{42}$$

$$\begin{aligned} h_{CO}^2a^2 = -a^2\Bigg\{&\frac{1}{D^*_{CO}}\left(\frac{\partial w_{CO}}{\partial C_{CO}}\right)_a + \frac{1}{D^*_{H_2O}}\left(\frac{\partial w_{CO}}{\partial C_{H_2O}}\right)_a \\ &- \frac{1}{D^*_{H_2}}\left(\frac{\partial w_{CO}}{\partial C_{H_2}}\right)_a - \frac{1}{D^*_{CO_2}}\left(\frac{\partial w_{CO}}{\partial C_{CO_2}}\right)_a \\ &+ \left[\frac{1}{D^*_{CH_4}}\left(\frac{\partial w_{CO}}{\partial C_{CH_4}}\right)_a + \frac{2}{D^*_{H_2O}}\left(\frac{\partial w_{CO}}{\partial C_{H_2O}}\right)_a \right. \\ &\left. - \frac{4}{D^*_{H_2}}\left(\frac{\partial w_{CO}}{\partial C_{H_2}}\right)_a - \frac{1}{D^*_{CO_2}}\left(\frac{\partial w_{CO}}{\partial C_{CO_2}}\right)_a\right]\frac{(w_{CH_4})_a}{(w_{CO})_a}\frac{\eta_{CH_4}}{\eta_{CO}}\Bigg\}. \end{aligned} \tag{43}$$

The effective diffusion coefficients were calculated using the Fuller-Schettler-Gidding formula [6] for binary diffusion coefficients. To calculate the coefficients of molecular diffusion of gaseous mixture, Knudsen diffusion coefficients, and the effective diffusion coefficients, we used formulas taken from [7]. The distribution of pores over radii and the tortuosity coefficients for a given catalyst were taken from [4].

The efficiency factors were calculated for the spherical grains of the catalyst with radii a = 0.108 and 0.175 mm. The first of these radii corresponds to the average size of particles (0.18–0.25) mm used in [2], and the second corresponds to grains with a size of 0.3–0.4 mm, on which some of the experiments were carried out in [3].

Table 1 shows the partial pressures of substances P_i (for a total pressure of 3 bar), the rates of their formation $(w_i)_a$ at 550°C, the derivatives $(\partial w_i/\partial C_j)_a$ calculated using formulas (27)–(30) with the above constants, and the values of the effective diffusion coefficients of substances inside the catalyst grain calculated for these conditions.

The substitution of the rates of substance formation, their derivatives, and the effective diffusion coefficients into (42) and (43) at a = 0.108 mm leads to the equations

$$h_{CH_4}^2 a^2 = 1.5738 + 1.1377\frac{\eta_{CO}}{\eta_{CH_4}}, \tag{44}$$

$$h_{CO}^2 a^2 = 19.8860 - 2.1418\frac{\eta_{CH_4}}{\eta_{CO}}. \tag{45}$$

It was found by inspection that $\eta_{CO}/\eta_{CH_4} = 0.6371$, $\varphi_{CH_4} = \sqrt{h_{CH_4}^2 a^2} = 1.5163$, $\varphi_{CO} = 4.0656$, $\eta_{CH_4} = 0.8741$, $\eta_{CO} = 0.55707$. Table 2 shows the approximate values of efficiency factors calculated assuming different key substances and the values of the efficiency factors for all substances obtained by numeric simulations of the set of differential equations. If CH_4 and CO are chosen to be the key factors approximate values are close to the exact ones.

The difference between the values of the efficiency factors for CO and CO_2 is notable. This is due to the high value of the term containing D_{CO}^* in formula (43). A high concentration of CO inside the catalyst grain leads to a drastic increase in the rate of CO_2 formation from CO.

For another pair of key substances (CO_2 and CH_4), the rate of their formation is determined by the formulas

$$w_{CH_4} = -r_1 - r_3, \tag{46}$$

$$w_{CO_2} = r_3 + r_2. \tag{47}$$

For other substances

$$w_{CO} = -w_{CH_4} - w_{CO_2}, \tag{48}$$

$$w_{H_2O} = w_{CH_4} - w_{CO_2}, \tag{49}$$

$$w_{H_2} = -3w_{CH_4} + w_{CO_2}. \tag{50}$$

Table 1. The partial pressure, the rates of formation, their derivatives with respect to the concentrations, and the effective diffusion coefficients

Parameter	CH_4	H_2O	H_2	CO_2	CO
P, bar	0.3355	1.869	0.7344	0.0541	0.007237
$D_i^* \times 10^5$, m^2/s	0.192	0.237	0.523	0.134	0.164
$(W_i)_a$, mol m^{-3} s^{-1}	–510.83	–685.23	1706.9	174.40	336.43
$\left(\frac{\partial W_{CH_4}}{\partial C_i}\right)_a$	–102.72	–6.2934	91.704	8.0116	285.80
$\left(\frac{\partial W_{H_2O}}{\partial C_i}\right)_a$	–129.02	–18.889	143.44	265.24	–1927.7
$\left(\frac{\partial W_{H_2}}{\partial C_i}\right)_a$	334.45	31.476	–326.85	–281.26	1356.1
$\left(\frac{\partial W_{CO_2}}{\partial C_i}\right)_a$	26.30	12.596	–51.738	–257.23	2213.5
$\left(\frac{\partial W_{CO}}{\partial C_i}\right)_a$	76.42	–6.3023	–39.966	249.22	–2499.2

Then, we obtain

$$\begin{aligned} h^2_{CH_4}a^2 = -a^2\Bigg\{ & \frac{1}{D^*_{CH_4}}\left(\frac{\partial w_{CH_4}}{\partial C_{CH_4}}\right)_a + \frac{1}{D^*_{H_2O}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2O}}\right)_a \\ & - \frac{3}{D^*_{H_2}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2}}\right)_a - \frac{1}{D^*_{CO}}\left(\frac{\partial w_{CH_4}}{\partial C_{CO}}\right)_a \\ & - \left[\frac{1}{D^*_{H_2O}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2O}}\right)_a - \frac{1}{D^*_{H_2}}\left(\frac{\partial w_{CH_4}}{\partial C_{H_2}}\right)_a \right. \\ & \left. - \frac{1}{D^*_{CO_2}}\left(\frac{\partial w_{CH_4}}{\partial C_{CO_2}}\right)_a + \frac{1}{D^*_{CO}}\left(\frac{\partial w_{CH_4}}{\partial C_{CO}}\right)_a\right]\frac{(w_{CO_2})_a\eta_{CO_2}}{(w_{CH_4})_a\eta_{CH_4}}\Bigg\}, \end{aligned} \quad (51)$$

$$\begin{aligned} h^2_{CO_2}a^2 = -a^2\Bigg\{ & \frac{1}{D^*_{CO_2}}\left(\frac{\partial w_{CO_2}}{\partial C_{CO_2}}\right)_a - \frac{1}{D^*_{H_2O}}\left(\frac{\partial w_{CO_2}}{\partial C_{H_2O}}\right)_a \\ & + \frac{1}{D^*_{H_2}}\left(\frac{\partial w_{CO_2}}{\partial C_{H_2}}\right)_a - \frac{1}{D^*_{CO}}\left(\frac{\partial w_{CO_2}}{\partial C_{CO}}\right)_a \\ & + \left[\frac{1}{D^*_{CH_4}}\left(\frac{\partial w_{CO_2}}{\partial C_{CH_4}}\right)_a + \frac{1}{D^*_{H_2O}}\left(\frac{\partial w_{CO_2}}{\partial C_{H_2O}}\right)_a \right. \\ & \left. - \frac{3}{D^*_{H_2}}\left(\frac{\partial w_{CO_2}}{\partial C_{H_2}}\right)_a - \frac{1}{D^*_{CO}}\left(\frac{\partial w_{CO_2}}{\partial C_{CO}}\right)_a\right]\frac{(w_{CH_4})_a\eta_{CH_4}}{(w_{CO_2})_a\eta_{CO_2}}\Bigg\}. \end{aligned} \quad (52)$$

Upon substitution of the values of the rates of formation of substances and their derivatives with respect to the concentrations at $r = a$, and $a = 0.108$ mm into (51) and (52), we obtain

$$h^2_{CH_4}a^2 = 3.3012 - 0.5898\frac{\eta_{CO_2}}{\eta_{CH_4}}, \quad (53)$$

$$h^2_{CO_2}a^2 = 18.1593 - 44.448\frac{\eta_{CH_4}}{\gamma_{CO_2}}. \quad (54)$$

We obtain by inspection that $\varphi_{CH_4} = 1.4747$ and $\chi_{CO_2} = \sqrt{-h^2_{CO_2}a^2} = 2.2609$.

For the pair of key substances CO and CO_2, analogous reasoning leads to the formulas

$$h^2_{CO}a^2 = 18.4754 - 0.7312\frac{\eta_{CO_2}}{\eta_{CO}}, \quad (55)$$

$$h^2_{CO_2}a^2 = 2.9844 - 29.2739\frac{\eta_{CO}}{\eta_{CO_2}}. \quad (56)$$

As mentioned above, the best agreement with exact values is achieved when methane and CO are chosen as key substances. It follows from comparison of Eqs. (43) and (45) obtained for this pair of key substances with Eqs. (53)–(56) that the approximate value is closer to the exact one if the value of the term that includes the ratio of the efficiency factor is low. The estimate of the approximation error will be considered in the next publication.

Table 2 also shows the approximate values of the efficiency factors of substances for $a = 0.175$ mm when choosing CH_4 and CO as key substances. It is seen that approximate values are close to exact if grains are larger.

Thus, the approximate method for calculating the efficiency factors for the substances in the reaction occurring via two stoichiometric equations gave the values that are about the same as those obtained using an exact solution to the set of differential equations (18). Note that this conclusion also refers to the case when the efficiency factors for some substances differ substantially from unity and from each other and when the notion of efficiency factor for a reaction makes no sense. When the reaction is controlled by internal diffusion, the reaction selectivity may change and this change will be described well by an approximate solution.

The above discussion assumed that the effective diffusion coefficients are constant over the grain. The numeric simulations showed that even at $a = 0.175$ mm, the effective diffusion coefficients in the center of the grain and on the surface differ by at most 2%, and the above assumption is correct.

Based on their experimental data, the authors of [2] believed that on the catalyst grains with sizes ranging from 0.18 to 0.25 mm (the average radius is 0.108 mm)

Table 2. Exact and approximate values of the efficiency factors of substances

a, mm	Calculation	η_i				
		CH_4	CO	CO_2	H_2O	H_2
0.108	Exact	0.88375	0.56981	1.4894	1.0379	0.94563
	From CH_4, CO	0.87414	0.55707	1.4858	1.0298	0.93664
	From CH_4, CO_2	0.87979	0.46470	1.6805	1.0836	0.96161
	From CO, CO_2	1.0139	0.56285	1.8839	1.2553	1.1028
0.175	Exact	0.77365	0.41378	1.4679	0.95035	0.84459
	From CH_4, CO	0.75191	0.39367	1.4430	0.92780	0.82252

the reaction occurred without internal diffusion control. As concerns the rate of methane consumption, this conclusion is consistent with our calculations (Table 2). The calculated value of the efficiency factor for methane at $a = 0.108$ mm ($\eta = 0.88$) is rather close to unity. The difference from unity can barely be found experimentally in [2]. With an increase in the size of catalyst grains to $a = 0.175$ mm, one should take into account a noticeable decrease in the efficiency factor of methane formation.

As concerns CO_2 and CO, our calculation shows that even at $a = 0.108$ mm the rates of formation of these substances may drastically change. It follows from Table 2 that 34% CO_2 and 66% CO are formed in the kinetic regime. Due to internal diffusion limitations, the composition of the reaction mixture should change to 58% CO_2 and 42% CO.

Note, however, that in papers [2, 3] the CO_2/CO concentration ratio in the reaction mixture formed is even higher. In our opinion, this shows that the corresponding change in the rate constants in Eqs. (27)–(29) is needed.

The error in determining the efficiency factors by the approximate solution depends on the kinetics of reactions and on the values of the efficiency factors found. The closer the efficiency factors of substances to unity, the more accurate the results of approximate calculation.

M.I. Temkin [1] showed that for some specific cases when the reaction occurs via a single stoichiometric equation, the approximate solution gives rather accurate values of efficiency factors. This was also done by comparing with the exact solutions. Further development of the Temkin method is needed to have a method for estimating the error of approximate solution when a reaction occurs via either a single or several stoichiometric equations.

The question of determining the errors in estimating the efficiency factors will be discussed in our next paper.

REFERENCES

1. Temkin, M.I., *Kinet. Katal.*, 1984, vol. 25, no. 2, p. 478.
2. Xu, J. and Froment, G.F., *AIChE J.*, 1989, vol. 35, no. 1, p. 88.
3. Xu, J. *Ph.D. Thesis, Gent: University of Gent*, 1989.
4. Xu, J. and Froment, G.F., *AIChE J.*, 1989, vol. 35, no. 1, p. 97.
5. Zyskin, A.G., Avetisov, A.K., and Khristiansen, L., *Teor. Osn. Khim. Tekhnol.*, 2002, no. 5, p. 506.
6. Reid, R.C, Prausnitz Y.M., and Sherwood, T.K. *The Properties of Gases and Liquids,* New York: McGraw-Hill, 1977.
7. Aris, R., *Introduction to the Analysis of Chemical Reactors*, Englewood Cliffs: Prentice Hall, 1963.