TECHNICAL TRANSACTIONS 3/2017
CZASOPISMO TECHNICZNE 3/2017

CHEMISTRY

DOI: 10.4467/2353737XCT.17.020.6213

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DIFFUSION WITH CHEMICAL REACTION – ASSESSMENT OF THE ACCURACY OF AN APPROXIMATE KINETIC MODEL FOR SPHERICAL PELLETS

DYFUZJA Z REAKCJĄ CHEMICZNĄ – OCENA DOKŁADNOŚCI PRZYBLIŻONEGO MODELU KINETYCZNEGO DLA ZIAREN KULISTYCH

Abstract

Diffusion with a first-order chemical reaction in a spherical pellet of a catalyst with third-type boundary conditions was considered; such a process can be described by a kinetic model based on the continued fraction approximation. Results of calculations obtained from an approximate kinetic model were compared with the exact solution. It was found that the application of this approximate model provides a good level of accuracy and requires short calculation times.

Keywords: diffusion, chemical reaction, approximate kinetic model

Streszczenie

Rozważono dyfuzję z reakcją chemiczną I rzędu w kulistym ziarnie katalizatora z warunkami brzegowymi III rodzaju. Taki proces można opisać modelem kinetycznym opartym na aproksymacji ułamkami łańcuchowymi. Wyniki obliczeń uzyskane z przybliżonego modelu kinetycznego porównano z rozwiązaniem ścisłym. Stwierdzono, że stosowanie przybliżonego modelu zapewnia dobrą dokładność wyników oraz krótkie czasy obliczeń.

Słowa kluczowe: dyfuzja, reakcja chemiczna, przybliżony model kinetyczny

Nomenclature

Bi – Biot number
c – component concentration, mol/m^3
D_e – effective diffusion coefficient, m^2/s
k_1 – reaction rate constant, 1/s
k_c – mass transfer coefficient, m/s
n – approximation order
r – spatial coordinate, m
R_p – radius of pellet, m
t – time, s
Y – dimensionless component concentration

Greek symbols
β_n – eigenvalues
ξ – dimensionless spatial coordinate
η – effectiveness factor
η_G – global effectiveness factor
τ – dimensionless time
Φ – Thiele modulus

Subscripts and superscripts
app – approximate
b – bulk
ex – exact
– – average value

1. Introduction

Mathematical models of catalytic reactors and adsorbers are systems of partial differential equations; the equation that refers to mass balance in a fluid flowing through the reactor/adsorber is an example of one of these. The other example refers to the kinetics of mass transport inside the catalyst/adsorbent. Solving such systems of equations is difficult. The problem of time-consuming calculations is especially significant in cases where a complex procedure is required in order to perform them. This is why it is favourable to use a simplification in the mathematical description of diffusion in porous pellets which results in the elimination of the spatial coordinate in a pellet. After the elimination of the spatial coordinate, the considered system is described by a system of ordinary differential equations.

The description of diffusive transport kinetics with approximate equations has been known for a long time. Historically, the LDF equation proposed by Glueckauf [1] was the first such equation. Due to substantial inaccuracies with this equation, a number of other approximate kinetic equations were proposed. They referred both to the process of diffusion with adsorption [2–5] and diffusion with chemical reaction [6–16].

In the work by Lee & Kim [17], a new approach to the problem of approximate equations of diffusive mass transport kinetics is presented. This model is based on: the application of the Laplace transform for the diffusion equation; the transformation of the solution to the form of a continued fraction; the truncation of the resulting expression for the number of terms which are needed to ensure the required level of accuracy. The first-order approximation corresponds to the LDF equation. The authors proposed their model for different pellet shapes (slab, cylinder, sphere) wherein they assumed that the mass transfer resistance in a fluid surrounding the catalyst/adsorbent pellet (external resistance) can be neglected. Moreover, it was assumed in the model that the concentration of the component in the fluid is time-invariant.

In work [18], the discussed model was extended for the case when transfer resistances are in both solid and fluid phases; therefore, a parameter characterising the relationship between the external and the internal resistance to mass transfer was introduced into the model – this is the Biot number (for a spherical pellet):

$$Bi = \frac{k_c R}{D_e} \tag{1}$$

In work [19], the changes of the component concentration in the bulk of a fluid surrounding a pellet was taken into account in the approximate model. It was shown [18, 19] that models using the continued fraction approximation give results consistent with exact solutions (analytical or numerical). This numerical verification, however, referred to systems without chemical reactions. Hence, processes of alternate adsorption-desorption in a pellet and moreover, adsorption in a perfect-mixing tank were considered.

When a chemical reaction occurs in a system, the diffusion equation describing the rate of transfer of a component in a porous pellet must be complemented with the source term which results from the elimination or formation of the component. For diffusion with a chemical reaction, the kinetic relationships contain (except from the Biot number) the Thiele modulus (internal diffusion modulus), which for a spherical pellet and a first-order reaction is defined as follows [20]:

$$\Phi = R\sqrt{\frac{k_1}{D_e}} \tag{2}$$

In this work, the results of kinetic calculations for diffusion with a first-order chemical reaction occurring in a spherical pellet of a catalyst are presented. Calculations were conducted on the basis of the approximate kinetic model based on the approximation of the continued fraction and the obtained results were compared with the analytical solution. Calculations were conducted for different values of the Biot number, different values of the Thiele modulus and different orders of approximation. The aim of this work is to determine the effect of the approximation order on accuracy and calculation time.

2. The diffusion and chemical reaction equation

The equation of diffusion and chemical reaction in a spherical pellet of a catalyst has the form:

$$\frac{\partial c}{\partial t}=D_e\left(\frac{\partial^2 c}{\partial r^2}+\frac{2}{r}\frac{\partial c}{\partial r}\right)+R \tag{3}$$

while the first-order reaction rate is:

$$R=-k_1 c \tag{4}$$

The following initial condition was assumed:

$$t=0 \qquad c=0 \tag{5}$$

The boundary condition for the centre of a spherical pellet has the form:

$$r=0 \qquad \frac{\partial c}{\partial r}=0 \tag{6}$$

The external mass transfer resistance was taken into account in the condition for the pellet surface:

$$r=R \qquad -D_e\frac{\partial c}{\partial r}=k_c\left(c-c_b\right) \tag{7}$$

The equations were transformed to the dimensionless form. The following dimensionless variables were introduced:

$$Y=\frac{c}{c_b} \qquad \xi=\frac{r}{R} \qquad \tau=\frac{D_e t}{R^2} \tag{8}$$

these relate to component concentration, position variable and time, respectively.

The dimensionless equation of diffusion with a chemical reaction has the form:

$$\frac{\partial Y}{\partial \tau}=\frac{\partial^2 Y}{\partial \xi^2}+\frac{2}{\xi}\frac{\partial Y}{\partial \xi}-\Phi^2 Y \tag{9}$$

with the initial condition:

$$\tau=0 \qquad Y=0 \tag{10}$$

and boundary conditions:

$$\eta=0 \qquad \frac{\partial Y}{\partial \eta}=0 \tag{11}$$

$$\xi=1 \qquad \frac{\partial Y}{\partial \xi}=Bi\left(1-Y\right) \tag{12}$$

The average concentration of a component in a pellet results from the following relationship:

$$\bar{Y} = 3\int_{0}^{1} \xi^{2} Y \cdot d\xi \tag{13}$$

3. The approximate kinetic model

As a result of the applied approximation, a partial differential equation is replaced by a system of n ordinary differential equations where n is the approximation order. If the external mass transfer resistances are significant and have to be taken into account, this system of differential equations in the matrix form is as follows [18]:

$$\dot{\mathbf{x}} = \mathbf{d}^{-1}\mathbf{a}\mathbf{x} + \mathbf{d}^{-1}\mathbf{b} \tag{14}$$

where vectors $\dot{\mathbf{x}}$, $\mathbf{x}$ and $\mathbf{b}$ are defined in the following way:

$$\dot{\mathbf{x}} = \begin{bmatrix} \dot{x}_1 & \dot{x}_2 & \ldots & \dot{x}_n \end{bmatrix}^T \tag{15}$$

$$\mathbf{x} = \begin{bmatrix} x_1 & x_2 & \ldots & x_n \end{bmatrix}^T \tag{16}$$

$$\mathbf{b} = \begin{bmatrix} 3 & 3 & \ldots & 3 \end{bmatrix}^T \tag{17}$$

Matrix $\mathbf{d}$ has the form:

$$\mathbf{d} = \mathbf{I} + \frac{1}{3Bi} \cdot \mathbf{bq} \tag{18}$$

while matrix $\mathbf{a}$:

$$\mathbf{a} = \begin{bmatrix} -p_1q_1 & -p_1q_2 & -p_1q_3 & \ldots & -p_1q_{n-1} & -p_1q_n \\ -p_1q_1 & -p_2q_2 & -p_2q_3 & \ldots & -p_2q_{n-1} & -p_1q_n \\ -p_1q_1 & -p_2q_2 & -p_3q_3 & \ldots & \ldots & -p_1q_n \\ \ldots & \ldots & -p_3q_3 & \ldots & \ldots & \ldots \\ \ldots & -p_2q_2 & \ldots & \ldots & -p_{n-1}q_{n-1} & -p_{n-1}q_n \\ -p_1q_1 & -p_2q_2 & -p_3q_3 & \ldots & -p_{n-1}q_{n-1} & -p_nq_n \end{bmatrix} - \Phi^2\mathbf{I} \tag{19}$$

where the values of p_i and q_i are:

$$p_i = 2i^2 + i \tag{20}$$

$$q_i = 4i + 1 \tag{21}$$

In the above formulas, $i = 1, 2, \ldots, n$, while $\mathbf{I}$ is the identity matrix. The system of equations (14) should be solved with the initial condition:

$$\tau = 0; \qquad \mathbf{x} = [0\,0 \ldots 0]^T \tag{22}$$

As a result of solving the system of differential equations (14), one gets the vector function $\mathbf{x}(\tau)$, on the basis of which the scalar function $\bar{Y}(\tau)$ can be determined:

$$\bar{Y} = \mathbf{qx} \tag{23}$$

The calculation problem is as follows: for the given values of the Thiele modulus Φ and the Biot number Bi, the average dimensionless concentration of a component in a catalyst pellet $\bar{Y}$ after time τ should be determined. For calculation purposes, the approximation order n should be assumed – the accuracy of calculations depends on it.

The calculation algorithm is presented below. Elements of vectors **p** and **q** are determined according to (20) & (21), elements of matrices **d** and **a** are then found according to formulas (18) & (19), respectively. In the next step, one should find the inverse of matrix **d** and determine products $\mathbf{d}^{-1}\mathbf{a}$ and $\mathbf{d}^{-1}\mathbf{b}$. As the result of solving the system of differential equations (14), values of function **x** are found, which after substitution into relationship (23), provide the solution.

4. Analytical solution

The analytical solution of equation (9) with conditions (10–12) for spherical pellets has the form [9]:

$$\bar{Y} = \eta_G + \frac{6Bi}{\Phi^3}\sum_{i=1}^{\infty}\frac{-\Phi\sqrt{\beta_i}\cdot\cos\left(\Phi\sqrt{\beta_i}\right)+\sin\left(\Phi\sqrt{\beta_i}\right)}{\left(\beta_i+1\right)\sqrt{\beta_i}\left[Bi\cdot\cos\left(\Phi\sqrt{\beta_i}\right)-\Phi\sqrt{\beta_i}\cdot\sin\left(\Phi\sqrt{\beta_i}\right)\right]}\cdot\exp\left[-\left(\beta_i+1\right)\Phi^2\tau\right] \tag{24}$$

where the global effectiveness factor η_G is given by the relationship:

$$\eta_G = \frac{\eta}{1+\dfrac{\Phi^2\eta}{3Bi}} \tag{25}$$

The effectiveness factor η depends only on the Thiele modulus according to the following formula for spherical pellets:

$$\eta = \frac{3}{\Phi}\left[\frac{1}{\tanh(\Phi)} - \frac{1}{\Phi}\right] \tag{26}$$

If there are no external mass transfer resistances ($Bi \to \infty$), then $\eta_G = \eta$.

Values β_j ($j = 1, 2, \ldots$) are subsequent roots of the algebraic equation:

$$\Phi\sqrt{\beta}\cdot\cos\left(\Phi\sqrt{\beta}\right)+\left(Bi-1\right)\cdot\sin\left(\Phi\sqrt{\beta}\right)=0 \tag{27}$$

The interpretation of roots of this equation is presented in Fig. 1. Substituting into (27):

$$x=\Phi\sqrt{\beta} \tag{28}$$

one obtains:

$$\cot\left(x\right)=\frac{1-Bi}{x} \tag{29}$$

In Fig. 1, the graphs of functions $y_1(x)$ and $y_2(x)$ are presented; these functions are given as follows:

$$y_1=\cot\left(x\right) \qquad y_2=\frac{1-Bi}{x} \tag{30 a, b}$$

The abscissas of the intersection points of these functions are the solutions to equation (29). The graph of function y_1 does not depend on *Bi*, while the graph of function y_2 depends on this parameter. In Table 1, the first three roots of equation (29) for different values of *Bi* are presented.

Table 1. The zeros of equation (29) for different values of *Bi*

Bi	0.1	0.2	0.5	1	2	5	10	20	50	100
x_1	0.5423	0.7593	1.1656	1.5708	2.0288	2.5704	2.8363	2.9857	3.0788	3.1102
x_2	4.5157	4.5379	4.6042	4.7124	4.9132	5.3540	5.7173	5.9783	6.1582	6.2204
x_3	7.7382	7.7511	7.7899	7.8540	7.9787	8.3029	8.6587	8.9831	9.2384	9.3308

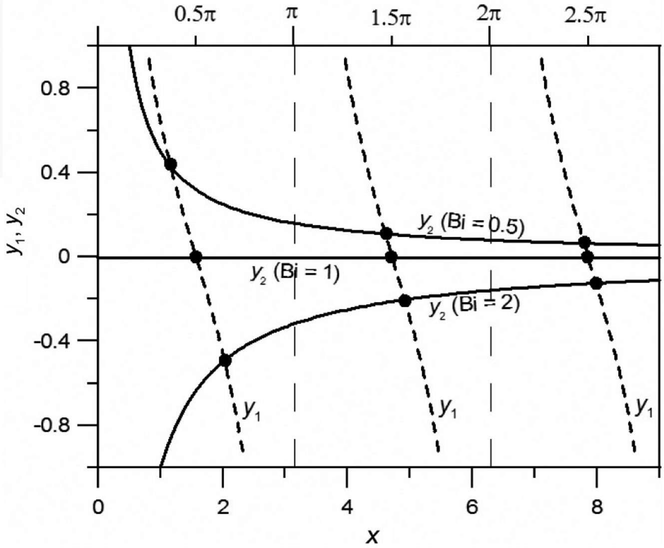

Fig. 1. The zeros of equation (29) for *Bi* = 0.5, *Bi* = 1 and *Bi* = 2

5. Results of calculations

The exact values of $\overline{Y}_{ex}$ were determined according to the analytical solution (24–27). The approximate values of $\overline{Y}_{app}$ were determined on the basis of the algorithm presented in Section 3 for the approximation order $n = 5$. The obtained results are presented in charts.

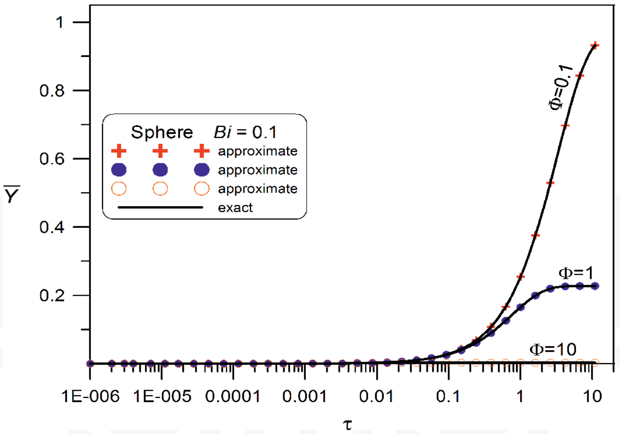

Fig. 2a. Comparison between the results of approximate and exact calculations for spherical pellets and different values of the Thiele modulus. The results refer to $Bi = 0.1$ and $n = 5$

In Figs. 2a, b, c & d, the relationships between the average dimensionless concentration of a component in a pellet and the dimensionless time of the process of diffusion with chemical reaction in a spherical pellet of a catalyst are presented. The charts determined on the basis of the approximate model and the charts resulting from the exact solution for different combinations of the values of the Biot number and Thiele modulus are presented. The consistency between the approximate and exact charts is very high.

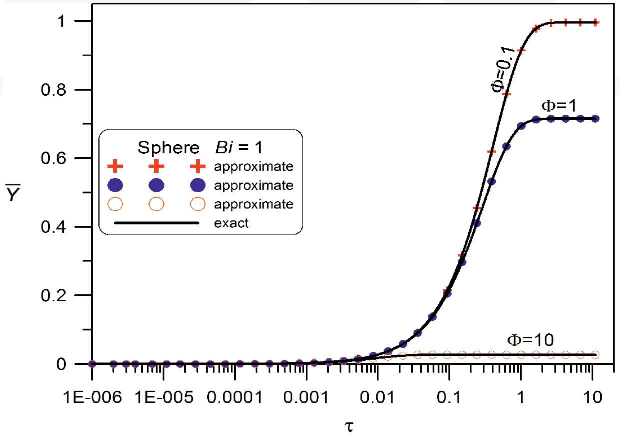

Fig. 2b. Comparison between the results of approximate and exact calculations for spherical pellets and different values of the Thiele modulus. The results refer to $Bi = 1$ and $n = 5$

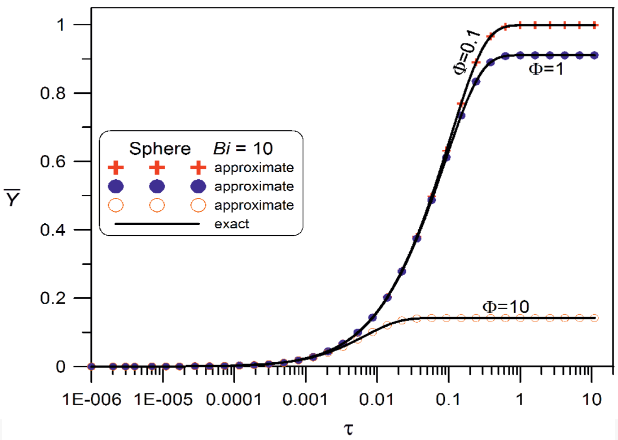

Fig. 2c. Comparison between the results of the approximate and exact calculations for spherical pellets and different values of the Thiele modulus. The results refer to *Bi* = 10 and *n* = 5

Concentration of the component increases over time; moderately at first, then the concentration increase is greater. For long durations, the average dimensionless concentration in pellets stabilises at the value of the global effectiveness factor. For small values of the Thiele modulus (which correspond to a small rate reaction), the limit concentrations in pellets have high values. For large values of Φ, which correspond to the high-rate reactions, concentrations in pellets have smaller values because of the reaction of the component.

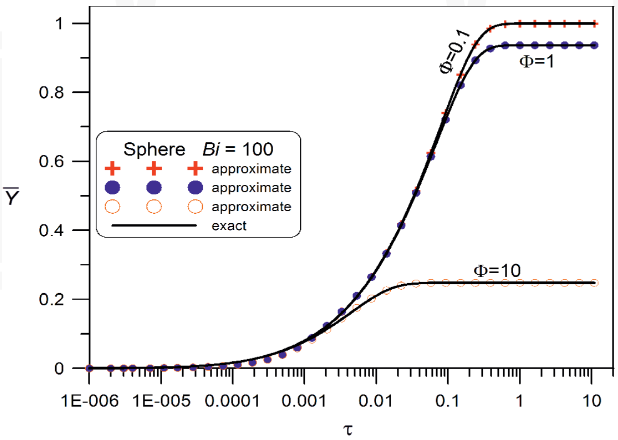

Fig. 2d. Comparison between the results of approximate and exact calculations for spherical pellets and different values of the Thiele modulus. The results refer to *Bi* = 100 and *n* = 5

In Fig. 3, temporal variations of the dimensionless concentrations of a component for a constant value of Φ = 1 and different values of the Biot number are presented. The greater the Biot number, the greater the concentration values – this results from the fact that the mass transfer resistance gets smaller.

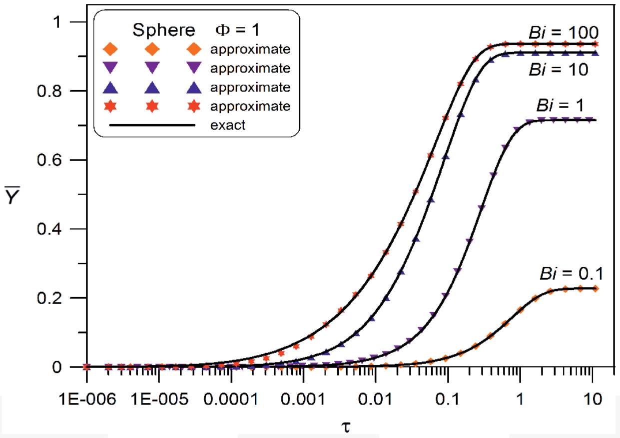

Fig. 3. Comparison between the results of approximate and exact calculations for spherical pellets and different values of the Biot number. The results refer to Φ = 1 and *n* = 5

6. The effect of the approximation order on the accuracy of results and calculation time

In Fig. 4, the effect of the approximation order on the accuracy of results obtained from the approximate model is presented. The ratio between the approximate $\overline{Y}_{app}$ and exact $\overline{Y}_{ex}$ values, which characterises the accuracy of approximation, is presented on the vertical axis. It can be seen from this figure that the accuracy considerably depends on the approximation order and process time; the shorter this time is, the less accurate is the approximation that is obtained. For short durations, it is useful to apply high approximation orders. For *n* = 10, the approximation model is accurate across the whole time range.

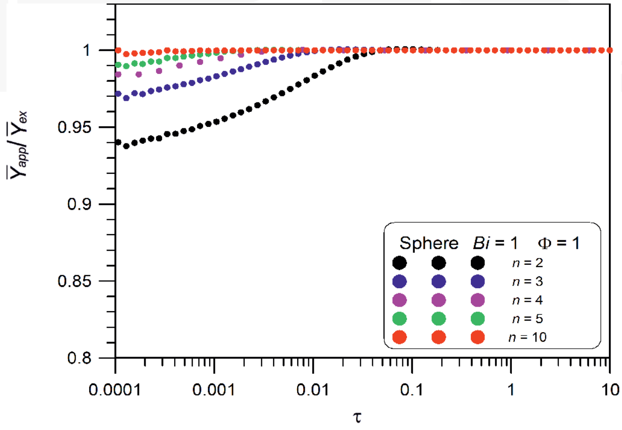

Fig. 4. Comparison of the results of approximate and exact calculations for spherical pellets and different orders of approximation. Calculations refer to *Bi* = 1 and Φ = 1

The times of calculations were also analysed. The results are presented in Fig. 5. The calculation time for the approximate model significantly depends upon the approximation order – this is obvious in view of the sizes of matrices which are used for algebraic calculations. For comparative reasons, the time of numerical calculations for the finite difference method is presented. For the considered process parameters ($Bi = 10$, $\Phi = 1$), the time of calculations according to the approximate model presented in this work is shorter than the time of numerical calculations when the approximation order $n < 7$.

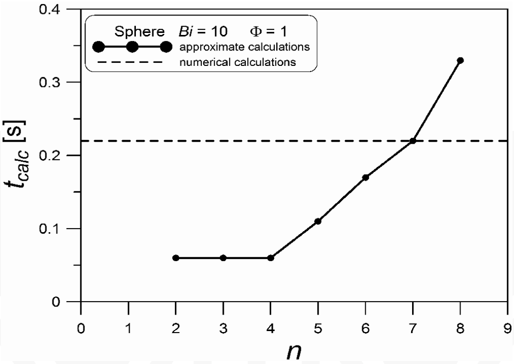

Fig. 5. Comparison of approximate and numerical calculation times

7. Conclusions

- The process of diffusion with a first-order chemical reaction with third-type boundary conditions can be described properly with the approximate kinetic model based on the approximation of continued fractions.
- The approximate model gives results consistent with the analytical solution.
- The accuracy of results obtained from the approximate model significantly depends upon the approximation order and process time. The longer the process lasts, the smaller is the order of approximation that is needed to ensure the required level of accuracy.
- Calculation times according to the approximate model are usually shorter than times required for conducting numerical calculations. It is only for high approximation orders that the times of approximate calculations do not fulfil this relationship.
- The model presented in this work is a calculation alternative for the classical numerical methods.

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