Engineering Science & Technology
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Research Article

Improved LDF Model for Unsteady-State Diffusion and Reaction in Porous Catalysts

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Received: 7 February 2025; **Revised:** 23 June 2025; **Accepted:** 27 June 2025

Abstract: Partial Differential Equations (PDEs) describe chemical or biochemical diffusion and reaction processes and result from the principles of conservation of mass and heat. They most often require numerical solutions due to non-linearity. Approximate Models (ApM) are transient models described by Ordinary Differential Equations (ODEs) that operate with an average concentration or temperature. Replacing PDEs with appropriate ODEs simplifies both the model solution and the analysis of results. Therefore, ApMs are applied as part of a more complex model, for example, to describe mass or heat balances for the gas phase in a heterogeneous reactor [1]. The ApMs are also a suitable tool for the analysis of a steady state; for example, the effectiveness factor for heterogeneous catalysis processes or biochemical processes that are realised in the real world can easily be found [2]. The work presents the idea of improving the Generalised Linear Driving Force approximation Model (GLDFM), previously presented in [3]. Its application is limited. For fast processes inside porous pellets or biofilms, sharp profiles of concentration, temperature, or both appear, in which cases the GLDFM fails. To improve the precision of GLDFM, we introduce an additional factor into the model and develop a robust way of determining its value. The appropriate relationship for that factor is presented based only on correction parameters, replacing the Thiele modulus by a modified value. An appropriate relationship is presented. To achieve this, we use computational experiments (simulations). The improvement extends the range of operating conditions for which the GLDFM model can be applied without loss of precision. This means that the error observed by the Modified Approximate Model referred to as ApMM the main text under the steady state of $a = 2$ and $\Phi \leq 20$ should be less than 5%. As presented in the main part, this restriction results from the nonlinearity of a generation term bounded by $0 \leq D_R \leq 5$. Various examples previously presented by various authors confirm the correctness of the idea applied. The results are discussed, and intentions for future research are presented.

***Keywords*:** heterogeneous catalysis, biocatalysis, porous media, diffusion with reaction, linear driving-force approximation

1. Introduction

Process analysis based on the mathematical model requires a sufficiently precise model, software, and hardware. Generally, in the real world, the term 'sufficiently precise model' in applied sciences always means a compromise between theory and practice; currently, some coefficients of the theoretical model or even its terms cannot be

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determined theoretically. The exemplary case for the diffusion-reaction process is the kinetic term in Equations (7)-(8). It is commonly accepted that real kinetic equations are determined on the basis of experiments, with their coefficients typically obtained through regression methods. Various cases demonstrating this can be found in references [4]-[6]. For scientific purposes, mathematical models should be based on theory (termed 'theoretical models'). However, in applied sciences like technology, this condition cannot be met. In the above-mentioned papers, a power-law kinetic equation with fractional exponents was successfully employed. The acceptable precision level is of paramount importance and remains at the investigator's discretion. For practical purposes, empirical models often prove sufficient. Alternatively, semi-empirical models offer a compromise—certain coefficients in theoretically derived models are adjusted through experimental data or simulations (for example, [7]). The ApMM model falls into this semi-empirical category.

The problems of diffusion and reaction are currently of primary importance in chemical practice. Increasingly advanced catalysts with improved activity, selectivity, or both are frequently presented at various congresses and scientific meetings. However, implementing these ideas in practice requires analysis based on process calculations. The issue combines flow, mass, and heat transfer both in the reactor and within the catalyst pellet. Mathematically, the problem is described by Partial Differential Equations (PDEs). Mass balances should be established for all reagents and inert components. If necessary, the equation set should be complemented with heat balance equations. Solving this equation set is a hard task; numerical solutions are typically required. Moreover, as diffusion-reaction problems are often stiff, even numerical solutions can prove difficult or at least computationally intensive. For this reason, many ideas for simplification have been reported. Steady-state problems are commonly analysed using the effectiveness factor or key factor concepts (which are not mutually exclusive). Approximate models, often called low-order ones, are applied for unsteady diffusion with reaction. Obviously, they are also helpful for analysis of steady state. The characteristic feature of approximate models is their use of average concentration within the pellet, which reduces the transient-diffusion problem to an ordinary differential equation.

Several months ago, we presented a Generalised Linear Driving Force approximate Model (GLDFM) [3]. The aim of that article was to develop the GLDFM equations, or more precisely, their coefficients, on the basis of the process operation conditions. The GLDFM equations are computationally simple to solve, which represents the fundamental purpose of all approximate models, not just those of the LDF type. 'Approximate model' usually does not preserve exactness of the former one, but its application in practice is much simpler.

Solving the model equations helps to anticipate the results of the real process running. A simpler solution method, from a practical point of view, is better, provided that the results of simulations are sufficiently precise. Reference [3] presents a broad description of the derived Linear Driving Force (LDF) models, one of the types of approximate models, along with the examples of application of various LDF models. To avoid redundancy, here we present only the crucial one. The conversion of partial differential equation set describing mass and energy balances (the Exact Model (ExM)) into ordinary differential equation set in complex domain was achieved using integral transforms rules. As integral transforms require model linearity, the only nonlinear term (that is, the generation term resulting from reaction kinetics) was linearised using Taylor series expansion limited to linear terms. The GLDFM was derived using strict mathematical rules, preserving the physical properties of the ExM. The solution of the ODE set, along with the subsequent mathematical manipulations, leads to a complex-domain model that can be easily transformed into a real domain (using inverse integral transform). As shown in [3, Figure 1], the resulted model has limited precision. That is, for any process, the GLDFM is valid for a sufficiently long time and a sufficiently small Thiele modulus value. The first mentioned limitation appears as a consequence of linear driving force for external mass and heat transfer, an inherent characteristic of LDF models. It should be noted that transient precision rapidly increases as time passes. In most practical applications of the approximate models, such imprecisions for short times can simply be neglected. The second limitation arises from the different steady-state values calculated from the exact and approximate models. To simplify the description in the considerations presented below, this difference will be termed as 'stationary error' for brevity. The stationary error for the linear kinetic rate equation is negligible, as was shown in [8]. For any nonlinear kinetic that appears, we accept its maximal value as 5%. It poses some problems for practical applications of the GLDFM.

As mentioned, reference [3] presents a broad description of approximate models, including their derivation methods and applications in various areas, mainly in heterogeneous catalysis and biocatalysis. For convenience of the reader, we recall the essential ones. The approximate models and mathematical methods are presented in [2], [8]-[13]. The crucial attempt of application integral transforms to obtain the LDF-type model is presented in [8]. Other

researchers presented solutions for more sophisticated cases [9], [10] and introduced some new important ideas such as the transient effectiveness factor [11]. Additional mathematical methods have also been suggested to improve LDF models [12], [13]. Applications of the type of model mentioned in various chemical processes present [14]-[17]. For example, a description of the dynamics of simultaneous adsorption, diffusion, and reaction in catalysts can be found in [15], [16] and reactor dynamics [15]-[17]. It should be noted that applications of approximate models are presented not only for chemical processes but also for bioprocesses that take place in biofilms [18]-[20].

The need to reduce stationary errors confirms numerous applications of the approximate models widely presented in [3]. The GLDFM operates a parameter M that can be directly calculated from the relationship between kinetic and operating conditions, which influences the Thiele modulus and Prater parameter β. Next, parameter Ψ should be calculated using M. As was proved [8], the parameter Ψ reflects the intensification of diffusional mass transfer caused by the progress of the chemical reaction. The GLDFM can be readily solved using typical software and algorithms, and allows for fast analysis of complex processes, for example, to obtain the largest yield. These properties, first of all, the lower requirements of hardware and software, enable calculations using GLDFM to support investigations made in laboratories and help determine directions for future investigations. As new catalysts are developed mainly to obtain 'faster' processes, the narrow region of GLDFM limits its application. Therefore, the stationary error must be reduced.

The derivation of an approximate model free from unacceptably large stationary errors can help to analyse research in many areas that handle heterogeneous processes with porous pellets, biofilms, etc. The model presented here may be classified as a semi-theoretical model. In the GLDFM equations, derived directly from the heat and mass conservation rules [3], we corrected only one parameter. The relationship for modification of Φ was developed. More details are presented in the main part of the article. Such an approach to the problem helps preserve main advantages of GLDFM, that is, the simplicity of model solution that helps analyses processes; however, due to high nonlinearity diversity kinetic terms, we strongly recommend testing the goodness of the GLDFM, and if it is insufficient, using ApMM.

Taking into account the above remarks, the ApMM model is mainly aimed at readers interested in simple and fast practical analysis of diffusion-reaction processes that can help determine directions for further investigation than the strictly scientific study. Examples that show the effectiveness of the developed approximate model include various processes: isothermal and nonisothermal, exothermic and endothermic, where mass or heat transfer resistances may or may not be omitted, and finally, where one or more reagents influence kinetics. The results will be discussed, and intentions for future investigations will be presented.

2. Materials & methods

All models will be presented in dimensionless form. If a process under consideration is isothermal, the equation of heat balance and the conditions that corresponded to them can be omitted.

Consider a transient nonisothermal process with n components for a single reaction, so $i = 1, ..., n$ and $a = 0$ for planar, $a = 1$ for cylindrical, and $a = 2$ for the spherical geometry of the pellet. As the key component, we accept the reagent 'A'. The model is described by Equations (1)-(5). External mass and heat resistances affect the process

$$\frac{1}{D_i}\frac{\partial C_i}{\partial \tau} = \frac{1}{x^a}\frac{\partial}{\partial x}\left(x^a \frac{\partial C_i}{\partial x}\right) - \frac{e_i}{D_i}\Phi^2 \cdot R\left(C_1, \ldots, C_n, T\right) \tag{1}$$

$$\frac{1}{Le}\cdot\frac{\partial T}{\partial \tau} = \frac{1}{x^a}\frac{\partial}{\partial x}\left(x^a \frac{\partial T}{\partial x}\right) + \beta \cdot \Phi^2 \cdot R\left(C_1, \ldots, C_n, T\right) \tag{2}$$

$$IC: \tau = 0: \; C_i = C_{i,in} \; T = T_{in} \tag{3}$$

$$BC: \tau > 0: \; \left.\frac{\partial C_i}{\partial x}\right|_{x=0} = 0 \left.\frac{\partial T}{\partial x}\right|_{x=0} = 0 \tag{4}$$

$$\tau > 0 \left.\frac{\partial C_i}{\partial x}\right|_{x=1} = Bi_{m,i}\left(C_{i,b} - C_{i,s}\right) \quad \left.\frac{\partial T}{\partial x}\right|_{x=1} = Bi_h\left(T_b - T_s\right) \tag{5}$$

Where C_i is dimensionless concentration of component '*i*', T is dimensionless temperature, Φ is Thiele modulus, *Le* is Lewis number, Bi_m, Bi_h are mass and heat Biot numbers, respectively, β is Prater number, e_i is a ratio of the stoichiometry coefficients of species '*i*' and '*A*', and D_i is a ratio of the effective diffusion coefficients of species '*i*' and '*A*'.

If external mass and heat resistances are negligible, the boundary condition (5) are described by

$$\tau > 0: \; C_i(x=1) = C_{i,s} T(x=1) = T_s \tag{6}$$

This model will henceforth be called the Exact Model (ExM).

The approximate model is described by Equations (7)-(9).

$$\frac{1}{D_i}\frac{dC_{i,av}}{d\tau} = \frac{(a+1)}{\frac{1}{\Psi_a} + \frac{1}{Bi_{m,i}}}\left(C_{i,b} - C_{i,av}\right) - \frac{e_i}{D_i}\Phi^2 \cdot R\left(C_{1,av}\ldots, C_{n,av}, T_{av}\right) \tag{7}$$

$$\frac{1}{Le}\frac{dT_{av}}{d\tau} = \frac{(a+1)}{\frac{1}{\Psi_a} + \frac{1}{Bi_h}}\left(T_b - T_{av}\right) + \beta \cdot \Phi^2 \cdot R\left(C_{1,av}\ldots, C_{n,av}, T_{av}\right) \tag{8}$$

$$\tau = 0: \; C_{A,av} = C_{A,in} T_{av} = T_{in} \tag{9}$$

For convenience, let us use the following notation,

$$D_R = \sum_{i=1}^{n} \left.\frac{\partial R}{\partial C_i}\right|_{\substack{C_i = C_{is} \\ T = T_s}} - \beta \left.\frac{\partial R}{\partial T}\right|_{\substack{C_i = C_{is} \\ T = T_s}} \tag{10}$$

and

$$M = \Phi^2 D_R \tag{11}$$

Parameter Ψ_a is defined in Table 1.

If external mass and heat resistances are negligible, the model reduces to the following

$$\frac{1}{D_i}\frac{dC_{i,av}}{d\tau} = (a+1)\Psi_a\left(C_{i,b} - C_{i,av}\right) - \frac{e_i}{D_i}\Phi^2 \cdot R\left(C_{1,av}\ldots, C_{n,av}, T_{av}\right) \tag{12}$$

$$\frac{1}{Le}\frac{dT_{av}}{d\tau} = (a+1)\Psi_a\left(T_b - T_{av}\right) + \beta \cdot \Phi^2 \cdot R\left(C_{1,av}\cdots, C_{n,av}, T_{av}\right) \tag{13}$$

The initial conditions are presented by Eq. (9). This model will henceforth be called the General Linear Driving Force Model (GLDFM).

Eq. (11) indicates that for various kinetic equations, whether for isothermal or non-isothermal processes, the

precision of ApM depends on the D_R value; that is, the Thiele modules and kinetic rate equation influence it. It further suggests that the ApM precision can be improved using the same model equations as (7)-(8) but with a modified Thiele modulus value Φ_m (in all equations containing Φ, it should be replaced by Φ_m). The aim of this work will be to determine the useful correlation between Φ and Φ_m.

Table 1. Relationships that define Ψ_a [3]

	$M < 0$	$M = 0$	$M > 0$
Ψ_0 ($a = 0$)	$\frac{M \sin\sqrt{-M}}{\sqrt{-M}\cos\sqrt{-M} - \sin\sqrt{-M}}$	3	$\frac{M \sinh\sqrt{M}}{\sqrt{M}\cosh\sqrt{M} - \sinh\sqrt{M}}$
Ψ_1 ($a = 1$)	$\frac{MJ_1(\sqrt{-M})}{\sqrt{-M}J_0(\sqrt{-M}) - 2J_1(\sqrt{-M})}$	4	$\frac{MI_1(\sqrt{M})}{\sqrt{M}I_0(\sqrt{M}) - 2I_1(\sqrt{M})}$
Ψ_2 ($a = 2$)	$\frac{M(\sqrt{-M}\cos\sqrt{-M} - \sin\sqrt{-M})}{M\sin\sqrt{-M} - 3\sqrt{-M}\cos\sqrt{-M} + 3\sin\sqrt{-M}}$	5	$\frac{M(\sqrt{M}\cosh\sqrt{M} - \sinh\sqrt{M})}{M\sinh\sqrt{M} - 3\sqrt{M}\cdot\cosh\sqrt{M} + 3\sinh\sqrt{M}}$

We will present a new approach for stationary error reduction, based on regularities observed in results obtained for different reaction schemes and kinetics. The aim of this work is to obtain an approximate model free from unacceptable stationary errors. We propose a procedure based on statistical analysis of numerical solutions, which will be used to find correlation between Φ and Φ_m. In the present paper, we use computational experiments (simulations) to improve precision of the GLDFM. It is common knowledge that reaction interacts diffusion; the factor Ψ reflects this fact (as discussed in details in [8]). Since the Taylor series expansion reduced to linear terms is a source of imprecision of the GLDFM, we decided to introduce a correction term to this model to reduce errors resulting from this simplification. We choose the simplest way from the user's point of view, that is, calculating the correction term based on constant values b_0, b_1, c_0, c_1 determined by us and moduli Φ, β, Bi_m, Bi_h that can be calculated from operation conditions and kinetic relationships.

It should be emphasised that the statistical method helps minimise the risk of determining inadequate relationships but cannot ensure precision in all cases, especially for nonlinear equations. Such phenomena are observed, for example, when kinetic equations are determined using regression methods, and this limitation is generally accepted.

At first, we show that a relationship between Φ_m and Φ really exists. To achieve this milestone, we used the following scheme:

1. The exact model was solved using the shooting method based on the original procedure of boundary value problems solution. The scheme is described in detail in [21]. The solution obtained helps to calculate the exact value of the effectiveness factor η_{ExM}.

2. The stationary version of the GLDFM was solved to obtain η_{ApMM} for the same process parameters as used in the point 1. In stationary model, left-hand sides of (7) and (8) or (12) and (13) are equal to zero; from a mathematical point of view, there are sets of nonlinear algebraic equations.

3. Step 2 was repeated until condition $\eta_{\mathrm{ApMM}} = \eta_{\mathrm{ExM}}$ was met. Such a value of Φ_m corresponds to Φ.

4. Steps 1-3 were repeated for selected values of Φ from the range $0 < \Phi < 20$ and for various kinetic equations for which the D_R value is between 0 and 5.

Results of the above procedure are presented in Figure 1. It confirms the correctness of the concept.

Figure 1 indicates that relationship between Φ_m and Φ is linear for small Thiele modulus values (D_R is the slope coefficient [3]). Next, as Φ rises, the deviations from linearity grow. We try to find a relationship using a statistical method called Multiple Linear Regression (MLR). MLR is a statistical technique that uses several explanatory variables (here Φ and D_R) to predict the outcome of a response variable (here Φ_m). The data necessary to employ this statistical technique were obtained the same way as the data used for the construction of Figure 1, but in more wide ranges of D_R values, that is $0 \leq D_R \leq 5$. This range resulted from an arbitrary accepted set of kinetic equations that covers different

types of kinetics, including power law and Langmuir-Hinshelwood-like kinetics for both isothermal and non-isothermal cases.

$$\Phi_m = \Phi + \left(b_0 + b_1 D_R\right)\Phi^3 + \left(c_0 + c_1 D_R\right)\Phi^5 \tag{14}$$

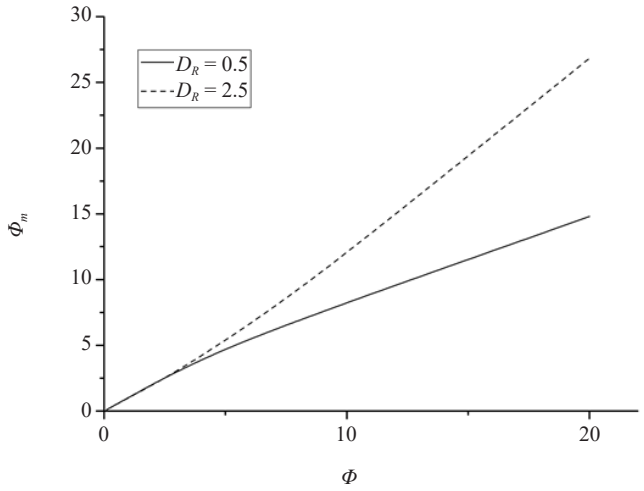

Figure 1. Modified Thiele modulus versus Thiele modulus for various D_R parameters

The coefficients determined with some statistical indicators for the spherical geometry corresponding to them are presented in Table 2.

Table 2. Estimate coefficients of Eq. (14) and statistical indicators

Coefficients	Estimate	Standard error	Lower Control Limit (LCL)	Upper Control Limit (UCL)	*p*-value
b_0	-3.300×10^{-3}	5.19×10^{-4}	-4.328×10^{-3}	-2.265×10^{-3}	8.13×10^{-9}
b_1	1.980×10^{-3}	1.84×10^{-4}	1.613×10^{-3}	2.347×10^{-3}	0
c_0	5.820×10^{-6}	1.31×10^{-6}	3.220×10^{-6}	8.420×10^{-6}	2.44×10^{-5}
c_1	-3.383×10^{-6}	4.65×10^{-7}	-4.307×10^{-6}	-2.459×10^{-6}	1.15×10^{-10}

$R^2 = 0.941620$

A *p*-value of 0.05 or lower is generally considered statistically significant; a confidence interval determined by LCL and UCL values indicates that we are 95% confident that the real value of parameter is between LCL and UCL values (that is, the more narrow the confidence interval, the better), *R*-squared is a goodness-of-fit measure, generally the closer to one value the better.

The values of the statistical indicators presented in Table 2 show that formula (14) correctly estimates the relationship sought. Standard errors are small, confidence levels are narrow, and, finally, the *p* values show that all parameters are statistically significant. The GLDFM model with the Thiele modulus calculated from relationship (14) will henceforth be called the modified Approximate Model (ApMM).

In our opinion, the short calculation time and the simplicity of the solution are 'value added' of the LDF models. Therefore, the key factor in the profitability of using the GLDFM or ApMM is the assessment of potential gains and

losses resulting from the use of a more complex development model and, most of the time, time-consuming ExM model for a specific process with simpler and less time-consuming GLDFM and ApMM models. Too many factors impact the rating to present sharp relationship like, for example, 'valid for $\Phi < 1$'. Furthermore, diffusion-reaction processes are processes with nonlinear characteristics, so it is impossible to transfer the characteristics of one process to another. For this reason, the LDF models are based on modules of physical significance, which should facilitate application to a specific process and thus make it easier for the researcher to assess the usefulness of GLDFM or ApMM. The coefficients that do not make physical sense are the coefficients that correct the value of the Thiele modulus b_0, b_1, c_0, c_1, appearing in the ApMM model. Therefore, for any real process, we propose trying to solve the ExM first. If the rate is negative, the next option is the GLDFM. Finally, ApMM should be tested.

3. Results

To confirm the usefulness of the ApMM, we performed numerical experiments based on both theoretically investigated kinetic models and experimentally determined values. For the examples presented in the following, the ExM and ApMM results were compared in terms of precision or both precision and calculation time.

In Figure 2, we present a comparison of the results for a highly nonlinear kinetic equation for a nonisothermal process. Within the entire applicability region of ApMM, differences do not exceed 3.5%.

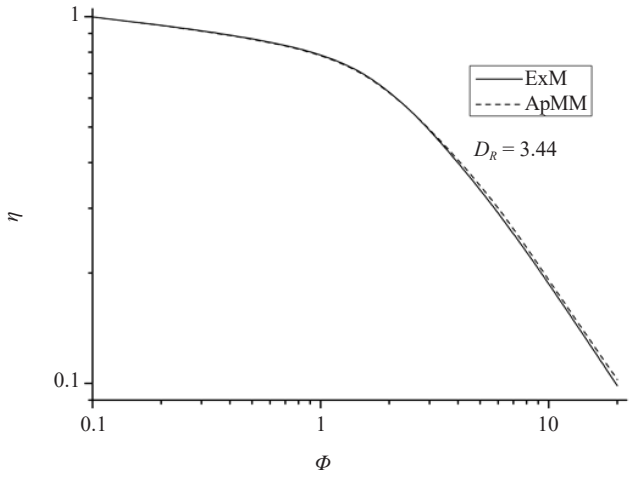

Figure 2. The comparison of effectiveness factor resulted from solution of ExM and ApMM in a broad range of Thiele modulus values. Results obtained for: $R = \frac{(1+3.5)^2 c^3}{(1+3.5c)^2} exp\left(20\left(1-\frac{1}{T}\right)\right)$, $\beta = -0.1$

For better presentation of ApMM advantages, we choose examples that refer to various, not commonly used, kinetic equations founded in the literature. The first two examples, based on [4], [5], concern heterogeneous catalytic processes in the real world. The data obtained by the experiments were processed. The next two examples are based on data derived from theoretical considerations published by Gottifredi et al. [22]. Also in this work, the values of the parameters do not differ from those encountered in practice. The typical values of the process parameter ranges presented in the [23], [24] are as follows: parameter β for exothermic reactions between 0.0 and 1.0, γ between 0.0 and 60.0, and Bi_m between 0.1 and 5,000.0.

The examples analysed in the following include various types of process:

• Nonisothermal, exothermic and endothermic processes for which mass and heat transfer resistances can be omitted [4],

• Nonisothermal where mass transfer resistance influences the process [5],

• Multicomponent reactions with two types of kinetic equations (Langmuir-Hinshelwood type and power law type) [22].

For comparison of calculation times, we used the numerical algorithm predefined in Maple for ODEs (ApMM) and our implementation of the method of lines algorithm for PDEs (ExM). The main idea of the Method of Lines (MOL) algorithm is discretizing spatial derivatives, which reduces PDEs to a system of ODEs and, following that, solutions can be computed via methods and software developed for the numerical integration of (ODEs) and Differential-Algebraic systems of Equations (DAEs).

In the beginning, the kinetics presented in the work [4] was analysed (data outside the application range of the ApMM were omitted). The results are presented in Table 3. The results of ExM and ApMM solutions are practically the same; the largest deviations do not exceed 2.5%. In Table 3, we present the time required to obtain a steady state solution. The last two columns show an acceleration more than twenty times for a single calculation point.

Table 3. The results for data presented in [4]. Results obtained for: $R = (cT)^{0.804} e^{\gamma\left(1-\frac{1}{T}\right)}$

Φ	β	γ	η_{ExM}	η_{ApMM}	t_{ExM}	t_{ApMM}
2.670	0.030	7.000	0.776	0.785	42.60	1.98
2.470	0.085	6.900	0.869	0.889	43.94	2.02
4.530	-0.116	6.580	0.465	0.477	44.25	2.03
3.040	-0.144	7.520	0.576	0.578	41.51	1.99

The next real-world example concerns our own experiments with hydrogenation of propylene. The results are presented in Table 4. We experimentally determined the coefficients of kinetics [5]. In the process, the resistance to mass transfer cannot be neglected. It does not make the precision of ApMM worse. Maximum errors were about 5%. The slightly larger errors result from larger values of the Thiele modulus. As in the previous example, the last two columns present the time required to obtain a steady-state solution. They again show a noticeable acceleration of computations. For this case, on average eight times. It should be noted that in this case process is very fast and a real time necessary to reach a steady state is less than 0.4 sec (calculated on data presented in [5]).

Table 4. The results for data presented in [5]. Results obtained for: $R = c^{0.5} e^{\gamma\left(1-\frac{1}{T}\right)}$

Φ	β	γ	Bi_m	η_{ExM}	η_{ApMM}	t_{ExM}	t_{ApMM}
8.59	0.035	7.91	140.8	0.363	0.344	14.42	1.94
9.49	0.036	7.72	132.9	0.330	0.316	16.79	1.89
10.32	0.037	7.50	123.1	0.303	0.295	17.47	2.00
8.25	0.035	7.91	150.6	0.377	0.357	16.51	1.93
9.13	0.036	7.72	142.1	0.343	0.326	16.89	1.87
9.93	0.037	7.50	131.7	0.316	0.305	17.29	1.93

The last two examples were found in [22]. The results are presented in Figures 3 and 4 for the Langmuir-Hinshelwood type kinetic equation and the power law type for two reagents, respectively. Since the examples are based

on theoretical values of parameters, the original Thiele modulus range was extended towards larger values of Φ. This helped to present the charts in the manner most often seen in textbooks. In both cases, we observe good precision of obtained results; deviations are small and only for the largest Thiele modulus values slightly exceed 5%.

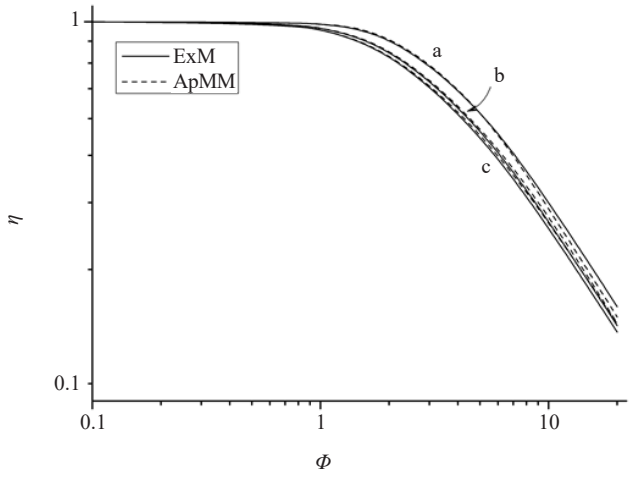

Figure 3. The comparison of effectiveness factor resulted from solution of ExM and ApMM for data given in [22] for Langmuir Hinshelwood-type kinetics. Results obtained for: $(a)\ R=\frac{1.5c}{1+0.5c}$, $(b)\ R=\frac{2c}{1+c}$, $(c)\ R=\frac{6c}{1+5c}$

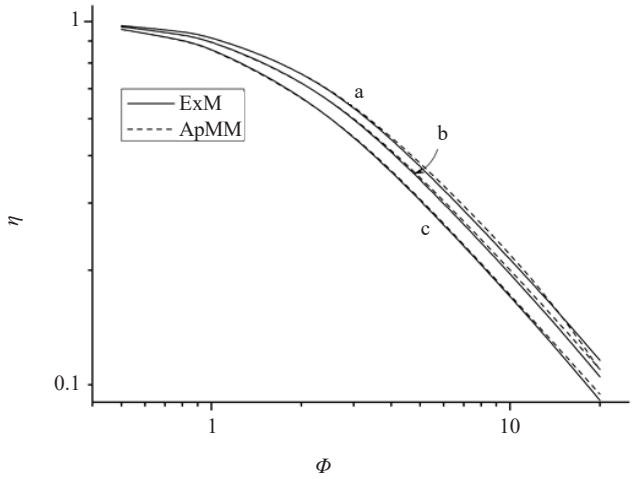

Figure 4. The comparison of effectiveness factor resulted from solution of ExM and ApMM for data given in [22] for the type of power-law kinetics. Results obtained for: (a) $R=c_1^{0.5}c_2$, (b) $R=c_1c_2$, (c) $R=c_1^2c_2$

Let us summarize the results presented. They indicate that the ApMM is a very convenient tool for the analysis of chemical or biochemical processes. The application of the proposed methods from different areas of chemistry and biochemistry (for more information, see [3], Introduction Section) proves that improved versions of the approximate model with an extended application range should find more numerous applications. The model has, in our opinion, one more important advantage. Despite the higher precision, the mathematical complexity of the solution does not change. The same type of issue is to be solved, that is, ordinary differential equation set for the unsteady state and algebraic equation set for the steady-state model version. The same procedures as for the GLDFM presented in [3] can be used.

We consider our presented approach as a first attempt, and the intended investigations are as follows:

• Extension of the model in the range of smaller D_R-values.

• The function that allows us to calculate the modified Thiele modulus value was based on numerical computations within a limited range of model parameters values, and next, using statistical techniques, the approximate function was determined; despite good statistical indicators, such procedure does not provide certainty of successful results of the ApMM model using. We will try to derive, based on theory, a function that better approximates the modified Thiele modulus value.

• The same reason as mentioned in the last bullet point makes application of the ApMM outside the investigated region is a bit risky; the solution to this issue is repeating the procedure in an extended investigation region. An alternative way is mentioned in the above point.

4. Conclusions

• The ApMM for diffusion with reaction processes in the mass and energy balances using the modified Thiele modulus hacs a wider applicability range than the GLDFM model.

• Despite the higher precision, the mathematical complexity of the solution does not change. The simplest numeric methods and the PC class computers can be employed.

• Valuable accuracy improvement is observed for fast processes inside porous pellets or biofilms that generate sharp concentration profiles, temperature profiles, or both.

• The modified Thiele modulus for the improved approximate model should be calculated from the derived using statistical procedure relationship (Equation (14)). It was determined for spherical geometry in the range $0 < \Phi < 20$ and $0 < D_R < 5$, and application outside there ranges is not recommended.

• Acceleration of calculations is noticeable.

Conflicts of interest

The authors declare no conflicts of interest.

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