

## DIFFERENTIAL QUADRATURE METHOD FOR SOME DIFFUSION-REACTION PROBLEMS

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In the paper, differential quadrature method (DQM) is used to find numerical solutions of reaction-diffusion equations with different boundary conditions. The DQM-method changes the reaction-diffusion equation (ordinary differential equation) into a system of algebraic equations. The obtained system is solved using built-in procedures of Maple®(Computer Algebra System-type program). Calculations were performed with Maple®program. The test problems include reaction-diffusion equation applied in heterogeneous catalysis. The method can be employed even in relatively hard tasks (e.g. ill-conditioned, free boundary problems).

**Keywords:** numerical algorithm, boundary value problem, reaction-diffusion equation

### 1. INTRODUCTION

Shooting methods, finite difference methods and orthogonal collocation methods are usually employed numerical approaches for solving chemical engineering boundary-value problems. The methods are well-known and their descriptions and applicability in chemical engineering are widely reported in research articles and textbooks, e.g. Davis (1984), Villadsen and Michelsen (1978). There are also available mathematical programs, both general mathematics software (Maple, Matlab, etc.) and simulating software (Comsol, Ansys, etc.) that are useful for solving engineering problems. However, there are problems, in which applicability of the mentioned methods/software is limited, inconvenient or both. The differential quadrature method (DQM) is a new numerical method which can be applied to a widened scope of our computation. Reaction-diffusion equation is a good illustration of potential problems to be solved. This type of equation is relatively often presented in literature, but mostly without practical applications. Typical illustrative examples for nonlinear problems are: (i) Meral and Tezer-Sezgin (2011) compared different boundary only and domain discretization methods in terms of accuracy of solutions and computational cost, (ii) Salah et al. (2014) looked for more efficient and more accurate solution methods by comparing results with the available analytical ones and computing the computational time, (iii) Jiwari et al. (2017) presented different types of patterns of nonlinear time dependent coupled reaction-diffusion models.

The aim of this work is to present advantages of DQM method as an alternative numerical method for the resolution of transport phenomena problems encountered in chemical engineering field. Writing a code for the method is rather a simple task. The DQM is precise and can be very helpful in relatively hard tasks. The paper provides illustrative examples of the application of the method. The examples have a physical meaning and appear in real processes relatively often.

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The DQM is conceptually close to the orthogonal collocation - both methods allow to reduce boundary value problem to a system of algebraic equations. So, we include a comparison of their performance.

## 2. PROBLEM FORMULATION

For one dimensional problems reaction diffusion equation is given by

$$\frac{d^2c}{dx^2} + \frac{\alpha}{x} \frac{dc}{dx} - \Phi^2 f(c) = 0 \quad (1)$$

For heterogeneous catalysis Eq. (1) describes mass-balance inside a catalyst pellet.  $f(c)$  is a kinetic rate equation, usually of the Langmuir-Hinshelwood type, power-law type etc.

For typical operating conditions, a solution usually must satisfy the following boundary conditions:

$$\left. \frac{dc}{dx} \right|_{x=0} = 0 \quad (2a)$$

$$c(1) = 1 \quad (2b)$$

Commonly applied numerical methods (shooting methods, finite difference methods, volume methods and orthogonal collocation methods) are efficient for diffusion-dominated systems, that is for small and medium values of  $\Phi$ . For systems with extremely fast reactions, strong diffusive effects, or both i.e. for high Thiele modulus values, the problem becomes ill-conditioned and as a result nonphysical oscillations in the solution or even lack of convergence can be observed.

If a dead zone in a pellet is formed, a solution must satisfy the following boundary conditions:

$$\left. \frac{dc}{dx} \right|_{x=x_0} = 0 \quad (3a)$$

$$c(x_0) = 0 \quad (3b)$$

$$c(1) = 1 \quad (3c)$$

If a dead zone in a pellet is present, the models: (i) Eq. (1) with boundary conditions (2a)–(2b) and (ii) Eq. (1) with boundary conditions (3a)–(3c) are complementary. The first model is valid for  $\Phi \leq \Phi_c$  while the second one for  $\Phi \geq \Phi_c$ , where  $\Phi_c$  is critical Thiele modulus. For  $\Phi = \Phi_c$  singularities can be observed (according to kinetic rate formula  $f(c)$ ). In that case numerical estimation of  $\Phi_c$  is a difficult task.

Equation (1) with boundary conditions (3a)–(3c) is an example of free boundary problem. Finding a solution of a free boundary problem is usually a difficult task. The presented dead zone problem in heterogeneous catalysis is mathematically related to a nonlinear Stefan problem – it can be treated as its stationary version. It is worth noting that the most popular mathematical programs, such as Matlab, Maple, Mathematica and simulating programs (Comsol, Ansys) currently do not provide support of this type of calculations. Nevertheless, these programs are very useful – many authors implement their own algorithms (e.g. recently published Matlab's procedures given by Campo and Lacoa (2014), Johansson et al. (2014), Mitchell and Vynnycky (2014)).

## 3. MATHEMATICAL METHOD

The differential quadrature method is a numerical technique for solving differential equations. It was introduced by Bellman et al. (1972), but its improved version, useful for technical calculations, was

introduced over 20 years later by Chen (1996). The differential quadrature method (DQM) will be applied to approximate the solution of the mass-balance equation in a catalyst pellet, Eq. (1). Using this method, we approximate the derivatives of a function at any location by a linear summation of all the functional values at a finite number of grid points. First, we divide the domain into  $N$  grid points. The differential quadrature discretization of the first and the second derivatives at a point  $x_i$  is given by

$$c_x(x_i) = \sum_{j=1}^N a_{ij}c(x_j) \quad (4)$$

$$c_{xx}(x_i) = \sum_{j=1}^N b_{ij}c(x_j) \quad (5)$$

$a_{ij}$  and  $b_{ij}$  are the weighting coefficients. They can be calculated as follows (with the use of  $N^{th}$  degree polynomials):

$$M(x) = \prod_{k=1}^N (x - x_k) \quad (6)$$

$$M^{(1)}(x_i) = \prod_{\substack{k=1 \\ k \neq i}}^N (x_i - x_k) \quad (7)$$

and further

$$a_{ij} = \frac{M^{(1)}(x_i)}{(x_i - x_j) M^{(1)}(x_j)}; \quad k = 1, 2, \dots, N, \quad i \neq j \quad (8)$$

$$a_{ii} = - \sum_{\substack{j=1 \\ j \neq i}}^N a_{ij}; \quad i = 1, 2, \dots, N \quad (9)$$

$$b_{ij} = 2a_{ij} \left( a_{ii} - \frac{1}{x_i - x_j} \right); \quad i = 1, 2, \dots, N, \quad j = 1, 2, \dots, N, \quad i \neq j \quad (10)$$

$$b_{ii} = - \sum_{\substack{j=1 \\ j \neq i}}^N b_{ij}; \quad i = 1, 2, \dots, N \quad (11)$$

The weighting coefficients of the higher order derivatives can be found in Chen (1996). When the DQM approach is applied to the problem (1), one obtains

$$\sum_{j=1}^N b_{ij}c(x_j) + \frac{\alpha}{x_j} \sum_{j=1}^N a_{ij}c(x_j) - \Phi^2 f(c_j) = 0; \quad i = 1, 2, \dots, N, \quad j = 1, 2, \dots, N \quad (12)$$

The stability of the DQM depends on the distribution of grid points. Chen (1996) recommends Chebyshev-Gauss-Lobatto grid point distribution:

$$x_i = \frac{1}{2} \left( 1 - \cos \frac{[(i-1)\pi]}{N-1} \right); \quad i = 1, 2, \dots, N \quad (13)$$

However, for simplicity, in the present work a uniform grid point distribution was used:

$$x_i = \frac{i-1}{N-1}; \quad i = 1, 2, \dots, N \quad (14)$$

The tests show that in the considered case there were no significant differences in the results obtained.

## 4. RESULTS

The DQM procedure was implemented by author in program Maple®. The resultant system of algebraic equations was solved using a built-in procedure for non-linear sets of algebraic equations. Recommendations of DQM-method will be presented for two mentioned problems. Firstly, a solution of Eq. (1) with boundary conditions (2a)–(2b) will be obtained. Let us assume a simple non-linear reaction rate

$$f_1(c) = c^2 \quad (15)$$

The problem is non-linear but it can easily be solved with the typical methods if the Thiele modulus is sufficiently small. If not – the problem becomes ill-conditioned and it requires the use of special methods of solution (e.g. orthogonal collocation method on finite element). Results are presented in Fig. 1.

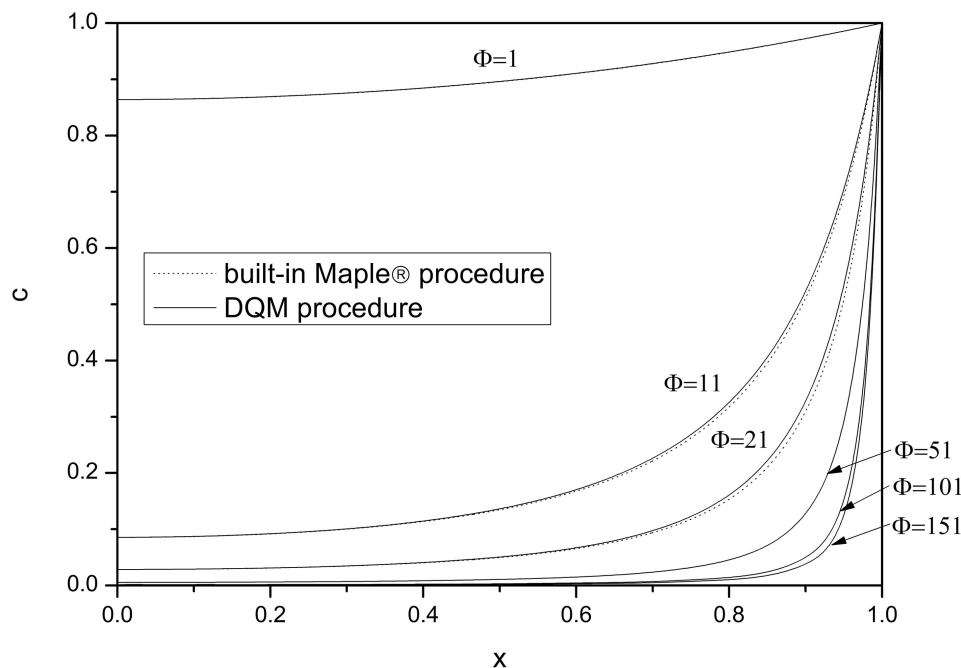


Fig. 1. Concentration vs. distance inside the pellet

The built-in Maple® procedure (mesh number = 8192) is able to solve Eq. (1) with a boundary condition (2) up to  $\Phi \approx 21$  (lack of convergence is reported by Maple for larger values of  $\Phi$ ), while the DQM-method (17 grid points) makes calculations possible up to  $\Phi \approx 160$ . Additionally, calculations using DQM-method were approx. 20 times faster. It follows that the DQM procedure is much better than the built-in Maple® procedure. The results obtained reveal that the tested method is fast enough and can be applied in a wide range of model parameter values. The number of grid points applied provided excellent precision of computation in the test performed. The number of grid points can be reduced for most practical applications. (They are usually characterized by a small or intermediate Thiele modulus value). This technique accelerates computations, while still producing sufficiently accurate concentration profiles.

A comparison with the orthogonal collocation method shows that both methods are of the same precision – the concentration profiles for Thiele moduli presented in Fig. 1 obtained by collocation method are almost identical – the sum of squared differences of effectiveness factor values is about  $2.5 \cdot 10^{-5}$ . In the tests performed, the DQM method generally was slightly faster than the orthogonal collocation method – an average time of computation was about 20% shorter. For comparison purposes, the discrete Chebyshev–Gauss–Lobatto orthogonal collocation method was used with the same number of grid points, i.e. 17. Chebyshev differentiation matrices were calculated according to Trefethen (2000).

In the next step, the solution of Eq. (1) with boundary conditions (4)–(6) will be discussed. It is the so-called “dead zone” problem. If a kinetic function is given in the form

$$f_2(c) = c^n \tag{16}$$

the “dead zone” appears if  $-1 < n < 1$  and Thiele modulus is sufficiently large, i.e. for  $\Phi > \Phi_c$ , where  $\Phi_c$  is the critical value of Thiele modulus. For  $\Phi < \Phi_c$  the reactant concentration in the center of the pellet is positive and a dead zone is absent; for  $\Phi = \Phi_c$  the concentration in the pellet center drops to zero and a dead zone is also absent (York et al., 2011). These two cases are out of our interest. For  $\Phi > \Phi_c$ , the reactant concentration is equal to 0 within the range  $(0, x_0)$ ; this range is the “dead zone” that appears in the pellet.  $x_0$  is an unknown coordinate of the end of the dead zone. As mentioned above, it is an example of a free boundary problem. Maple® currently do not provide support of this type of calculations and usefulness of the DQM-method will be presented on the basis of analytically obtained relation presented, e.g. by Andreev (2013).

$$\Phi_c = \sqrt{\frac{2}{1-n} \left( \frac{1+n}{1-n} + \alpha \right)} \tag{17}$$

If a kinetic equation is given by Eq. (16), the critical value of Thiele modulus is given by Eq. (20). The results obtained are presented in Table 1.

Table 1. Comparison of a critical value of the Thiele modulus obtained numerically with exact solution

$n$	$\Phi_{c,DQM}$	$\Phi_{c,an}$	$\delta, \%$	$n$	$\Phi_{c,DQM}$	$\Phi_{c,an}$	$\delta, \%$	$n$	$\Phi_{c,DQM}$	$\Phi_{c,an}$	$\delta, \%$
$\alpha = 0$				$\alpha = 1$				$\alpha = 2$			
0.75	7.48331	7.48331	0.0	0.75	8.00000	8.00000	0.0	0.75	8.48528	8.48528	0.0
0.50	3.4641	3.4641	0.0	0.50	4.00000	4.00000	0.0	0.50	4.47214	4.47214	0.0
0.25	2.10819	2.10819	0.0	0.25	2.66667	2.66667	0.0	0.25	3.12694	3.12694	0.0
0.00	1.41421	1.41421	0.0	0.00	2.00000	2.00000	0.0	0.00	2.44949	2.44949	0.0
-0.25	0.98086	0.9798	-0.1	-0.25	1.60800	1.60000	-0.5	-0.25	2.04561	2.03961	-0.3
-0.50	0.66867	0.66667	-0.3	-0.50	1.33883	1.33333	-0.4	-0.50	1.77383	1.76383	-0.6
-0.75	0.40706	0.40406	-0.7	-0.75	1.14996	1.14286	-0.6	-0.75	1.57692	1.56492	-0.7

For  $n \geq 0$  calculations are errorless while for  $n < 0$  the computed values of  $\Phi_{c,DQM}$  are not so accurate. The errors are not large for a specified tolerance – they are less than 1%. Also these tests demonstrate high accuracy of the applied quadrature method.

The last tests of the DQM method were made for real heterogeneous processes. Since the problems with dead zone need much effort we will focus on them. Firstly, a critical value of the Thiele modulus was computed. Methanol steam reforming over a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst will be considered as a practical example. Hydrogen production from hydrocarbon steam reforming is a cost-effective method of providing hydrogen; methanol steam reforming is a simple and efficient way of producing hydrogen on a small scale:



The kinetic equation, catalyst data and process data were reported by Lee et al. (2004). Catalyst properties, gas compositions and effective diffusivity of methanol and hydrogen are taken from that article. The authors

propose the following kinetic equation at atmospheric pressure and in the temperature range between 433 and 533 K:

$$-r_M = 2.19 \times 10^9 \cdot \exp\left(\frac{-103 \text{ [kJ/mol]}}{RT}\right) \cdot p_M^{0.564} \cdot (11.6 \text{ [kPa]} + p_H)^{-0.647}; \quad \left[\frac{\text{mol}}{\text{kg} \cdot \text{s}}\right] \quad (19)$$

The concentration profiles of methanol and hydrogen inside a catalyst particle depend upon each other by the following mutual relation:

$$y_H - y_{H_s} = \frac{3D_{e,M}}{D_{e,H}} (y_{M_s} - y_M) \quad (20)$$

so that  $p_H$  can be removed from Eq. (19). As a result, the methanol concentration profile and the effectiveness factor can be determined from a single mass balance, Eq. (1), with boundary conditions (3a)–(3b). The Thiele modulus  $\Phi$  is defined by

$$\Phi^2 = L^2 \frac{(-r_M) \rho}{c_{M_s} \cdot D_{e,M}} \quad (21)$$

The results of calculations are presented in Table 2. They show that at higher temperature and for larger catalyst pellets dead zones may appear more readily. It agrees with the theory of diffusion-reaction processes because diffusion resistance grows within catalyst pellets.

Table 2. Critical Thiele modulus values for methanol steam reforming (the feed compositions are given by Lee et al. (2004))

	$\Phi_c$	$T$ [K]
feed comp. 30M45W125N $y_{M_s} = 15 \text{ mol\%}$ , $y_{H_s} = 0$ ; $d = 0.3 \text{ mm}$	6.2	528
feed comp. 30M45W125N $y_{M_s} = 15 \text{ mol\%}$ , $y_{H_s} = 0$ ; $d = 0.425 \text{ mm}$	6.1	513
feed comp. 30M60W100N10H $y_{M_s} = 15 \text{ mol\%}$ , $y_{H_s} = 5 \text{ mol\%}$ ; $d = 0.3 \text{ mm}$	5.9	531.5
feed comp. 30M60W100N10H $y_{M_s} = 15 \text{ mol\%}$ , $y_{H_s} = 5 \text{ mol\%}$ ; $d = 0.425 \text{ mm}$	5.9	516.5
feed comp. 30M60W110H $y_{M_s} = 15 \text{ mol\%}$ , $y_{H_s} = 55 \text{ mol\%}$ ; $d = 0.3 \text{ mm}$	dead zone is not observed for examined temperature range; extrapolated value of critical $\Phi_c = 5.3$ at 547.5 K	
feed comp. 30M60W110H $y_{M_s} = 15 \text{ mol\%}$ , $y_{H_s} = 55 \text{ mol\%}$ ; $d = 0.425 \text{ mm}$	5.2	531

The following observation is also of interest: values of the critical Thiele modulus are practically the same for the same gas compositions. It follows that  $\Phi_c$ -value is characteristic for the kinetic equation. The presented observation confirms conclusions drawn on the basis of theoretical considerations by Andreev (2013).

The last test was based on our own investigations. We examined a propene hydrogenation reaction carried out in a tubular reactor on a commercial nickel catalyst. A detailed description of experiments made was published by Szukiewicz et al. (2019). We determined the following kinetic equation:

$$r_p = 44400 p_p^{0.5} \exp\left(\frac{-26500}{RT}\right) \text{ [mol/(m}^3\text{s)]} \quad (22)$$

The reaction was carried out in isothermal conditions. Mass transfer resistances were neglected. It is easily to observe that under isothermal conditions the kinetic equation reduces to the form of Eq. (16) with  $n$  equal to 1/2. Investigations were conducted for a slab catalyst (catalyst pellet prepared as a disc with the diameter of 4.7 mm and thickness of 0.5 mm) and for a spherical catalyst pellet (catalyst pellet prepared as a sphere with the diameter of 4.6 mm). As was presented in Table 1, the calculated critical values of the Thiele modulus are equal to 3.4641 and 4.4721 for slab and sphere, respectively. Since the actual Thiele moduli are larger than their critical values we determined the effectiveness factors using Eq. (1) with boundary conditions (3). The selected results are presented in Table 3.

Table 3. Effectiveness factors and dead zone size for propene hydrogenation on nickel catalyst

No	$p_p$ [Pa]	$T$ [K]	$\Phi$	$\eta_{exp}$	$\eta_{calc}$	$\delta$ [%]	$x_0$
slab							
1	19200	403	7.99	0.135	0.138	-2.6	0.573
2	21600	393	6.86	0.158	0.163	-3.1	0.500
3	24000	413	8.35	0.132	0.133	0.0	0.591
sphere							
1	12000	353	54.25	0.0599	0.0669	-11.6	0.932
2	14000	333	60.99	0.0582	0.0559	3.9	0.944
3	16000	353	50.78	0.0645	0.0627	2.8	0.937

For both types of catalyst pellets agreement between calculated and determined values of the effectiveness factors is good despite the fact that the Thiele moduli varied in experiments in a very wide range. It confirms benefits of the DQM method.

Concentration profile inside the slab pellet can be evaluated theoretically (York et al., 2011). Hence for the operating conditions presented in Table 3, we can compare profiles calculated using the DQM method with those obtained theoretically. Results are presented in Fig. 2. The agreement between calculated and theoretical profiles is very good.

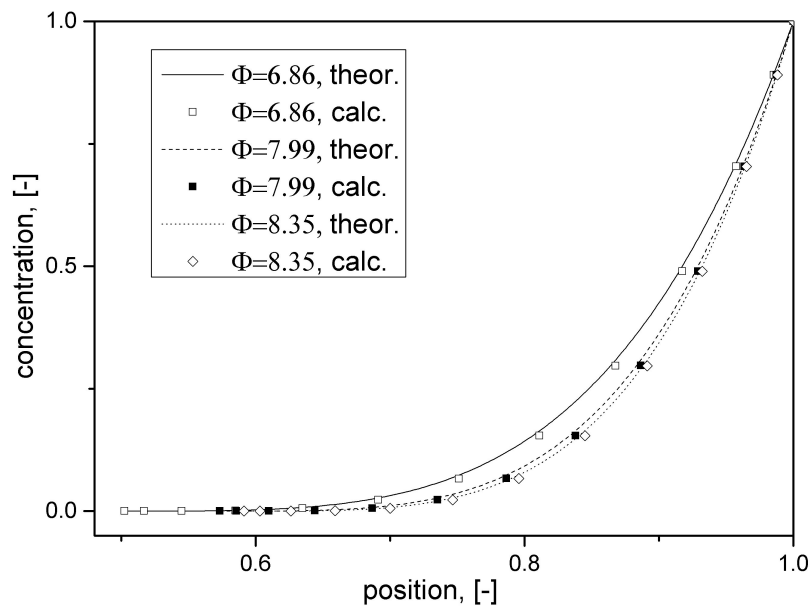


Fig. 2. Calculated and theoretical concentration profiles inside catalyst pellet

## 5. CONCLUSIONS

The following conclusions can be drawn from the presented results:

- the DQM method is “flexible” and effective – it can be used to produce results of high precision in a wide range of model parameter values, for free boundary problems and for real processes,
- the DQM algorithm can be easily implemented in CAS-type programs, e.g. Maple,
- its application range is wider than that of commonly used built-in procedures (in commercial programs)
- in the tests performed the DQM algorithm was slightly faster than the orthogonal collocation method.

*The financial support of the National Science Centre, Poland (Project 2015/17/B/ST8/03369) is gratefully acknowledged.*

## SYMBOLS

$c$	concentration, –
$D_e$	effective diffusivity, m <sup>2</sup> /s
$f(c)$	kinetic rate equation, –
$L$	radius of the catalyst particle, m
$p$	partial pressure, Pa
$p_p$	partial pressure of propylene, Pa
$R$	gas constant, mol/(J K)
$T$	temperature, K
$x$	distance, –
$y$	mole fraction, –

### *Greek symbols*

$\alpha$	geometry factor, – ( $\alpha = 0$ for slab, $\alpha = 1$ for cylindrical and $\alpha = 2$ for spherical geometry)
$\delta$	relative error, %
$\Phi$	Thiele modulus, –

### *Subscripts*

$H$	hydrogen
$M$	methanol

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*Received 03 December 2019*

*Received in revised form 11 February 2020*

*Accepted 13 February 2020*