



Implementation of Galerkin and moments methods by Gaussian quadrature in advection–diffusion problems with chemical reactions



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ABSTRACT

This work presents a method to solve boundary value problems based on polynomial approximations and the application of the methods of moments and the Galerkin method. The weighted average residuals are evaluated by improved Gauss–Radau and Gauss–Lobatto quadratures, capable to exactly compute integrals of polynomials of degree $2n$ and $2n + 2$ (where n is the number of internal quadrature points), respectively. The proposed methodology was successfully applied to solve stationary and transient problems of mass and heat diffusion in a catalyst particle and of a tubular pseudo-homogeneous chemical reactor with axial advective and diffusive transports. Through the improvement of the usual procedures of numerical quadratures, it was possible to establish a direct connection between the residuals on internal discrete points and the residuals on the boundaries, allowing the method to exactly reproduce the moments and Galerkin methods when applied to linear problems.

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1. Introduction

The application of the method of weighted residuals (MWR) consists basically in the approximation of the dependent variables of the problem by expansions series of known functions (called trial functions) with coefficients to be determined. The replacement of this approximation in the differential equation gives rise to the residual function. Nullifying the weighted average residual functions in the problem domain, with appropriate weights, it is possible to determine the coefficients of the proposed trial functions. The distinction between the different methods originates from the choice of the weights to be used in the computation of the weighted average residual functions. The most widely used methods are: orthogonal collocation method (OCM), method of moments, Galerkin method, and least square method (Finlayson, 1972; Villadsen & Michelsen, 1978).

The selection of trial functions is of great importance to the success of the MWR, because this choice is directly related to the accuracy and the convergence of numerical solution (Finlayson, 1971, 1972; Finlayson & Scriven, 1966; Snyder, Spriggs, & Stewart, 1964). The use of orthogonal polynomials as trial functions has some advantages, such as the minimization of the residuals maximum magnitude (Villadsen & Stewart, 1967). Most applications of this technique use Lagrange polynomial approximation, taking as collocation points the roots of orthogonal polynomials: Finlayson (1971) used the roots of Legendre polynomial, McGowin and Perlmutter (1971) used the roots of the Chebyshev polynomial, and Secchi, Wada, and Tessaro (1999), Lefrève, Dochain, Azevedo, and Magnus (2000), Sousa and Mendes (2004), Barroso, Henrique, Sartori, and Freire (2006), Damak (2006), Solsvilk and Jakobsen (2012) used the roots of Jacobi polynomials. The use of orthogonal polynomials also extends to majority of the computer packages that make use of MWR, such as PDECOL (Sincovec & Madsen, 1979), that uses the Legendre polynomials, COLSYS (Ascher, Christiansen, & Russell, 1981), that uses the Gauss–Legendre polynomials, MWRTTools (Adomaitis, 2002; Chang, Adomaitis, & Lin, 1999), that uses the Jacobi polynomials, and PDECHEB (Berzins & Dew, 1991), that uses the Chebyshev polynomials.

Only few papers present criteria to justify the choice of the Jacobi polynomial parameters α and β . Lefrève et al. (2000) select the values of these parameters to minimize the error of numerical solution. Secchi et al. (1999) select the values of α and β that best approximate the weight of a characteristic function obtained by a self-adjoint form of the system. Solsvilk and Jakobsen (2012) applied orthogonal collocation, Galerkin, tau and least squares methods, using the Jacobi polynomial with different values of the parameters α and β , in order

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to investigate the influence of the node point distribution in the accuracy and in the condition number of the coefficients matrix. According to these authors the utilization of Legendre polynomial gives the best result in terms of accuracy and lowest condition number of the coefficients matrix.

The MWR is commonly applied to solve models described by partial differential equations systems and boundary value problems widely used in chemical engineering. Models of tubular reactors with axial dispersion were solved by: Grotch (1969), applying the Galerkin method, Finlayson (1971), applying the OCM, McGowin and Perlmutter (1971), applying the OCM and also the Galerkin method, and Lefèvre et al. (2000), applying the OCM. Problems of mass and heat diffusion in a catalyst particle were solved by: Villadsen and Stewart (1967), Villadsen and Michelsen (1978), and Dudukovic and Lamba (1978), applying the OCM, and Wedel, Michelsen, and Villadsen (1977), applying the OCM and the Galerkin method. Hanse (1971) applied the OCM to solve the dynamic and stationary model of a packed bed reactor. Sousa and Mendes (2004) applied the OCM in the resolution of a catalytic membrane reactors model. Secchi et al. (1999) applied the OCM in the radial discretization of a set of partial differential equations that describe the process of ultrafiltration of bovine serum albumin in hollow fiber membranes. Wang, Anthony, and Akgerman (2005) used the OCM in the solution of trickle bed and slurry reactors models for methanol production.

As reported by Finlayson and Scriven (1966), the accuracy of the numerical solution is more sensitive to changes in the trial function than with the type of MWR applied. Snyder et al. (1964) verified that the convergence of the Galerkin method increasing the number of expansion terms is faster when compared with the collocation method or the least squares method. Becker (1964) classifies the least squares method as the best criterion of weighting for the application of MWR. Although because of its difficulty for implementation the use of this methodology is considerably limited. Wedel et al. (1977) reported that the collocation method is easier to be applied than the Galerkin method, since the computational effort needed for integration is avoided, and the results did not show a significant difference. Solsvilk and Jakobsen (2012) reported that the error obtained applying the Galerkin, tau and orthogonal collocation methods using Jacobi polynomial with different values of the parameters α and β , differ insignificantly. In its turn, the condition number of the coefficients matrices is more sensitive to this change. According to these authors the application of the Galerkin and tau methods, using the Legendre polynomial roots as collocation point, present lower condition numbers than the application orthogonal collocation and least square methods. Furthermore, the selection of the parameters α and β is more critical for the Galerkin, tau and least square methods than for the OCM. It must be pointed out, that these results were obtained applying those methods to a very simple and linear example: reaction–diffusion equation of a catalyst having a slab geometry or spherical geometry with a first order reaction in steady state, considering the symmetry and Dirichlet boundary condition at the surface.

Since the development of WRMs, it is well known that the application of polynomial approximation in problems with advection dominance gives origin to unrealistic oscillation in the solution and is not recommended for this type of problems (Becker, 1964; Finlayson & Scriven, 1966; Grotch, 1969; McGowin & Perlmutter, 1971; Snyder et al., 1964; Wedel et al., 1977). For problems with advection dominance, it is more indicated the use of orthogonal collocation on finite elements (Carey & Finlayson, 1975; Sereno, Rodrigues, & Villadsen, 1991) or other families of methods, such as finite differences and finite volumes, which are out of the scope of this work.

The original form of the orthogonal collocation method may just reproduce the method of moments and Galerkin method in a limited number of problems, such as models of linear differential equations with symmetry and Dirichlet boundary conditions. In models with non-linear differential equations and Danckwerts boundary conditions, for example, the classical form of the orthogonal collocation method cannot be directly related with methods of weighted residuals (MWR).

The present work aims to develop a systematic procedure to solve boundary value problems, proposing polynomial approximations to the dependent variables that nullify the first n weighted average residues, where the corresponding integrals are evaluated by improved Gauss–Radau and Gauss–Lobatto quadratures, which are capable to exactly compute the integrals of polynomial functions up to degree $2n+1$ and $2n+2$, respectively. With this improvement in the quadrature formulas, the method exactly reproduces the methods of the moments and Galerkin when applied to linear problems.

The main advantage of this new methodology is related to the utilization of the same Jacobi polynomial for both moments and Galerkin methods, with the specificities of each method appearing only in the evaluation of the system discretization matrices. After the discretization, the procedure for solving the resulting algebraic or differential–algebraic system is the same for both methods.

In Section 2, a detailed explanation of the proposed methodology is presented through its application to two specific problems: with spatial symmetry and without spatial symmetry. The main advantage of this methodology is its generalized characteristic. In comparison with the classical orthogonal collocation method, this procedure approaches closely the method of moments and method of Galerkin with no additional computational cost. In Section 3, the proposed methodology is applied for testing and evaluation of typical chemical engineering examples: mass and heat diffusion in a catalyst particle, and tubular pseudo-homogeneous chemical reactor with axial advective and diffusive transports, considering in both cases isothermal and non isothermal, and stationary and transient models.

2. Methodology

Following the traditional procedure (Villadsen & Michelsen, 1978), the proposed methodology begins with polynomial approximations of the dependent variables and their replacement in the problem equations, generating the residuals expressions. In order to establish the necessary conditions to determine the polynomial coefficients, the null weighted residual averages are evaluated using a convenient quadrature method for computation of the integrals. The discretized system can be solved by any algebraic equations system solver for stationary problems or any differential–algebraic equations system solver for transient problems.

In order to introduce the proposed methodology, let us consider two types of partial differential equation models. In the first one, we consider a transient second-order boundary value problem with spatial symmetry for planar, cylindrical or spherical geometry. Example of this type of problem is the transient reaction–diffusion equation in a catalyst particle with different shapes (slab, cylindrical, spherical). This model can be described in a generic way as:

$$F\left(t, x, \phi(x, t), \frac{\partial \phi(x, t)}{\partial t}, \frac{\partial^2 \phi(x, t)}{\partial x^2} + \frac{s}{x} \frac{\partial \phi(x, t)}{\partial x}\right) = 0 \quad (1.1)$$

in the domain $0 \leq x < 1$ and $t > 0$

$$\text{BC}_1 : \left. \frac{\partial \phi(x, t)}{\partial x} \right|_{x=0} = 0 \quad (1.2)$$

$$\text{BC}_2 : \left(\lambda \frac{\partial \phi(x, t)}{\partial x} + \phi(x, t) \right) \Big|_{x=1} = \phi_{\text{bulk}}(t) \quad (1.3)$$

$$\text{IC} : H \left(t, x, \phi(x, t), \frac{\partial \phi(x, t)}{\partial t} \right) \Big|_{t=0} = 0 \quad (1.4)$$

where $s = 0, 1$ and 2 for planar, cylindrical and spherical geometry, respectively, and λ is a model parameter.

The symmetry of the profile, described by the first boundary condition, Eq. (1.2), suggests the change in the spatial variable x to $u = x^2$ transforming the original equations to:

$$F \left[t, u, \phi(u, t), \frac{\partial \phi(u, t)}{\partial t}, 4 \left(u \frac{\partial^2 \phi(u, t)}{\partial u^2} + \frac{s+1}{2} \frac{\partial \phi(u, t)}{\partial u} \right) \right] = 0 \quad (1.5)$$

$$\text{BC}_1 : \left. \frac{\partial \phi(u, t)}{\partial u} \right|_{u=0} : \text{finite} \quad (1.6)$$

$$\text{BC}_2 : \left(2\lambda \frac{\partial \phi(u, t)}{\partial u} + \phi(u, t) \right) \Big|_{u=1} = \phi_{\text{bulk}}(t) \quad (1.7)$$

$$\text{IC} : H \left(t, u, \phi(u, t), \frac{\partial \phi(u, t)}{\partial t} \right) \Big|_{t=0} = 0 \quad (1.8)$$

Applying a polynomial approximation of degree n in the independent variable u to the state variable $\phi(t, u)$ according to

$$\phi(u, t) \approx \phi^{(n)}(u, t) = \sum_{j=1}^{n+1} \ell_j(u) \phi_j(t) \quad (2)$$

where $\ell_j(u)$ is the j th Lagrange polynomial in u of degree n such that:

$$\ell_j(u) = \prod_{\substack{k=1 \\ k \neq j}}^{n+1} \frac{u - u_k}{u_j - u_k} \Rightarrow \ell_j(u_i) = \delta_{i,j} = \begin{cases} 1 & \text{when } i = j \\ 0 & \text{when } i \neq j \end{cases} : (\text{Krö necker } \delta \text{ function}) \quad (3)$$

$\phi_j(t) = \phi^{(n)}(u_j, t)$, and $0 < u_1 < u_2 < \dots < u_n < u_{n+1} = 1$ are the $n+1$ interpolation points.

The approximation proposed in Eq. (2), can also be represented by the form: $(4)\phi(u, t) \approx \phi^{(n)}(u, t) = \phi_{\text{bulk}}(t) + \sum_{j=1}^n a_j(t)[u^j - (1 +$

$$2j\lambda)] \text{ where } \mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} \in \mathfrak{R}^n.$$

Replacing the polynomial approximation $\phi^{(n)}(u, t)$, Eq. (2), in the model represented by Eq. (1.5), we obtain the residual of the approximation, defined by:

$$\mathbf{R}^{(n)}[u, \Phi(t)] = F \left[t, u, \phi^{(n)}(u, t), \frac{\partial \phi^{(n)}(u, t)}{\partial t}, 4 \left(u \frac{\partial^2 \phi^{(n)}(u, t)}{\partial u^2} + \frac{s+1}{2} \frac{\partial \phi^{(n)}(u, t)}{\partial u} \right) \right] \quad (5)$$

$$\text{where } \Phi(t) = \begin{pmatrix} \phi_1(t) \\ \phi_2(t) \\ \vdots \\ \phi_{n+1}(t) \end{pmatrix}.$$

The residual function expressed by Eq. (5) evaluates the quality of the approximation in every point of the domain: $0 \leq u \leq 1$.

In order to establish the necessary conditions to determine the numerical solution of the problem in the interpolation points, $\phi^{(n)}(u_j, t)$, we applied the concept of average value of a function to compute the first n average weighted residuals, as following:

$$\bar{\mathbf{R}}_j^{(n)}[\Phi(t)] = \left(\frac{s+1}{2} \right) \int_{u=0}^{u=1} u^{(s-1)/2} \omega_j(u) \mathbf{R}^{(n)}[u, \Phi(t)] du = 0, \quad \text{for } j = 1, 2, \dots, n, \quad (6)$$

where $\bar{\mathbf{R}}_j^{(n)}[\Phi(t)]$ is the j -th average weighted residual of the approximation and $\omega_j(u)$ is the j -th weight corresponding to the method of weighted residuals. In this work the method of moments and the Galerkin method were applied, resulting:

$$\text{Method of moments : } \omega_j(u) = u^{j-1} \quad \text{for } j = 1, 2, \dots, n \tag{7}$$

$$\text{Galerkin method : } \omega_j(u) = \frac{\partial \phi^{(n)}(u, t)}{\partial a_j} = u^j - (1 + 2j\lambda) \quad \text{for } j = 1, 2, \dots, n. \tag{8}$$

In the proposed methodology, the average weighted residuals, as defined by Eq. (6), are numerically calculated by Gauss-Radau quadrature procedure with the inclusion of upper bound point $u_{n+1} = 1$, resulting in:

$$\bar{\mathbf{R}}_j^{(n)}[\Phi(t)] \approx \sum_{k=1}^{n+1} \Omega_{j,k} \mathbf{R}_k^{(n)}(t) = 0, \quad \text{for } j = 1, 2, \dots, n \tag{9}$$

where $\mathbf{R}_k^{(n)}(t) = \mathbf{R}^{(n)}[u_k, \Phi(t)]$, $0 < u_1 < u_2 < \dots < u_n < 1$ are the n roots of the Jacobi polynomial $P_n^{(1, (s-1)/2)}(u)$, $u_{n+1} = 1$, $\Omega_{j,k} = H_k \cdot \omega_j(x_k)$ for $j = 1, 2, \dots, n$ and $k = 1, 2, \dots, n+1$ and H_k , for $k = 1, \dots, n+1$, are the Gauss-Radau quadrature weights given by $H_k = \left(\frac{s+1}{2}\right) \int_{u=0}^{u=1} u^{(s-1)/2} [\ell_k(u)]^2 du$. Eq. (9) is a linear system of algebraic equations that can be represented by the following matrix form:

$$\begin{bmatrix} \Omega_{1,1} \mathbf{R}_1^{(n)} & \dots & \Omega_{1,n} \mathbf{R}_n^{(n)} & \Omega_{1,n+1} \mathbf{R}_{n+1}^{(n)} \\ \Omega_{2,1} \mathbf{R}_1^{(n)} & \dots & \Omega_{2,n} \mathbf{R}_n^{(n)} & \Omega_{2,n+1} \mathbf{R}_{n+1}^{(n)} \\ \vdots & \ddots & \vdots & \vdots \\ \Omega_{n-1,1} \mathbf{R}_1^{(n)} & \dots & \Omega_{n-1,n} \mathbf{R}_n^{(n)} & \Omega_{n-1,n+1} \mathbf{R}_{n+1}^{(n)} \\ \Omega_{n,1} \mathbf{R}_1^{(n)} & \dots & \Omega_{n,n} \mathbf{R}_n^{(n)} & \Omega_{n,n+1} \mathbf{R}_{n+1}^{(n)} \end{bmatrix} = \mathbf{0} \tag{10}$$

This algebraic linear system can be solved according to:

$$\begin{bmatrix} \mathbf{R}_1^{(n)} \\ \vdots \\ \mathbf{R}_n^{(n)} \end{bmatrix} = \mathbf{V} \cdot \mathbf{R}_{n+1}^{(n)}, \quad \text{where } \mathbf{V} = \begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ V_{n-1} \\ V_n \end{bmatrix} = \mathbf{G}^{-1} \mathbf{P}, \quad \mathbf{G} = \begin{bmatrix} \Omega_{1,1} & \dots & \Omega_{1,n} \\ \Omega_{2,1} & \dots & \Omega_{2,n} \\ \vdots & \vdots & \vdots \\ \Omega_{n-1,1} & \dots & \Omega_{n-1,n} \\ \Omega_{n,1} & \dots & \Omega_{n,n} \end{bmatrix}, \quad \text{and } \mathbf{P} = \begin{bmatrix} \Omega_{1,n+1} \\ \Omega_{2,n+1} \\ \vdots \\ \Omega_{n-1,n+1} \\ \Omega_{n,n+1} \end{bmatrix} \tag{11}$$

The matrix \mathbf{G} is invertible when all quadrature points are different, which is always true for orthogonal polynomials, and due to the linearly independence of the residual weights; these two facts assure the full rank of matrix \mathbf{G} .

It is important to emphasize that Eq. (11) allows a unified procedure of the methods of moments, Galerkin and orthogonal collocation. The orthogonal collocation method can be obtained by setting the vector $\mathbf{V} = \mathbf{0}$, and when the method of moments or the Galerkin method are applied we must calculate the components of vector \mathbf{V} according to Eqs. (7) and (8), respectively, and the definition of the terms of matrix Ω . Besides, the proposed methodology connects the residual at the internal points to the residual at the upper boundary point.

The approximation for the dependent variables and its derivative can be described by the expressions (Villadsen & Michelsen, 1978):

$$\phi^{(n)}(u_i, t) = \phi_i(t) \tag{12.1}$$

$$\left. \frac{\partial \phi^{(n)}(u, t)}{\partial t} \right|_{u_i} = \frac{d\phi_i(t)}{dt} \tag{12.2}$$

$$\left. \frac{\partial \phi^{(n)}(u, t)}{\partial u} \right|_{u_i} = \sum_{j=1}^{n+1} \mathbf{A}_{i,j} \phi_j(t) \tag{12.3}$$

$$\left. \frac{\partial^2 \phi^{(n)}(u, t)}{\partial u^2} \right|_{u_i} = \sum_{j=1}^{n+1} \mathbf{B}_{i,j} \phi_j(t) \tag{12.4}$$

$$\left(u \frac{\partial^2 \phi^{(n)}(u, t)}{\partial u^2} + \frac{s+1}{2} \frac{\partial \phi^{(n)}(u, t)}{\partial u} \right) \Big|_{u_i} = \sum_{j=1}^{n+1} \mathbf{C}_{i,j} \phi_j(t) \tag{12.5}$$

where $\mathbf{C}_{i,j} = (u_i \mathbf{B}_{i,j} + \frac{s+1}{2} \mathbf{A}_{i,j})$.

Replacing in Eq. (9) the model described by Eq. (1), using the approximation presented in Eq. (12), gives rise to the following system of differential-algebraic equation (DAE):

$$F \left(t, u_i, \phi_i(t), \frac{d\phi_i(t)}{dt}, 4 \sum_{j=1}^{n+1} \mathbf{C}_{i,j} \phi_j(t) \right) = \mathbf{V}_i F \left(t, 1, \phi_{n+1}(t), \frac{d\phi_{n+1}(t)}{dt}, 4 \sum_{j=1}^{n+1} \mathbf{C}_{n+1,j} \phi_j(t) \right) \quad \text{for } i = 1, 2, \dots, n \quad (13.1)$$

$$\text{BC}_2 : 2\lambda \sum_{j=1}^{n+1} \mathbf{A}_{n+1,j} \phi_j(t) + \phi_{n+1}(t) = \phi_{\text{bulk}}(t) \quad (13.2)$$

$$\text{IC} : H \left(t, u_i, \phi_i(t), \frac{d\phi_i(t)}{dt} \right)_{t=0} = 0 \quad \text{for } i = 1, 2, \dots, n. \quad (13.3)$$

The steady-state version of this model can be obtained considering $(d\phi_i(t)/dt) = 0$ and $\phi_{\text{bulk}}(t) = \phi_{\text{bulk}} = \text{constant}$, transforming the DAE system of Eq. (13) into a system of non-linear algebraic equations:

$$F \left(u_i, \phi_i, 4 \sum_{j=1}^{n+1} \mathbf{C}_{i,j} \phi_j \right) = \mathbf{V}_i F \left(1, \phi_{n+1}, 4 \sum_{j=1}^{n+1} \mathbf{C}_{n+1,j} \phi_j \right) \quad \text{for } i = 1, 2, \dots, n \quad (14.1)$$

$$\text{BC}_2 : 2\lambda \sum_{j=1}^{n+1} \mathbf{A}_{n+1,j} \phi_j + \phi_{n+1} = \phi_{\text{bulk}}. \quad (14.2)$$

In the second type of problem, we consider a transient second-order boundary value problem without spatial symmetry. Example of this type of problem is the transient reaction–diffusion–advection equation in a tubular reactor. This model can be described in a generic way as:

$$F \left(t, x, \phi(x, t), \frac{\partial \phi(x, t)}{\partial t}, \frac{\partial \phi(x, t)}{\partial x}, \frac{\partial^2 \phi(x, t)}{\partial x^2} \right) = 0 \quad (15.1)$$

in the domain $0 < x < 1$ and $t > 0$

$$\text{BC}_1 : \left(-\lambda \frac{\partial \phi(x, t)}{\partial x} + \phi(x, t) \right)_{x=0} = \phi_{\text{feed}}(t) \quad (15.2)$$

$$\text{BC}_2 : \left. \frac{\partial \phi(x, t)}{\partial x} \right|_{x=1} = 0 \quad (15.3)$$

$$\text{IC} : H \left(t, x, \phi(x, t), \frac{\partial \phi(x, t)}{\partial t} \right)_{t=0} = 0 \quad (15.4)$$

Applying a polynomial approximation of degree $n + 1$ in the independent variable x to the state variable $\phi(t, x)$ according to

$$\phi(x, t) \cong \phi^{(n+1)}(x, t) = \sum_{j=0}^{n+1} \ell_j(x) \cdot \phi_j(t) \quad (16)$$

where $\ell_j(x)$ is the j -th Lagrange polynomial in x of degree $n + 1$ such that:

$$\ell_j(x) = \prod_{\substack{k=0 \\ k \neq j}}^{n+1} \frac{x - x_k}{x_j - x_k} \Rightarrow \ell_j(x_i) = \delta_{i,j} = \begin{cases} 1 & \text{when } i = j \\ 0 & \text{when } i \neq j \end{cases} \quad (17)$$

$\phi_j(t) = \phi^{(n+1)}(x_j, t)$, and $0 = x_0 < x_1 < x_2 < \dots < x_n < x_{n+1} = 1$ are the $n + 2$ interpolation points.

The approximation proposed in Eq. (16) can also be represented by the form:

$$\phi(x, t) \approx \phi^{(n+1)}(x, t) = \phi_{\text{feed}}(t) + [\lambda a_2(t) - (1 + 2\lambda)a_1(t)] + (1 - x)^2 \sum_{j=1}^n a_j(t) x^{j-1} \quad (18)$$

which automatically satisfies both boundary conditions.

Replacing the polynomial approximation $\phi^{(n+1)}(x, t)$, Eq. (16), in the model represented by Eq. (15.1), we obtain the residual of the approximation defined by:

$$\mathbf{R}^{(n+1)}[x, \Phi(t)] = F \left[t, x, \phi^{(n+1)}(x, t), \frac{\partial \phi^{(n+1)}(x, t)}{\partial t}, \frac{\partial \phi^{(n+1)}(x, t)}{\partial x}, \frac{\partial^2 \phi^{(n+1)}(x, t)}{\partial x^2} \right] \quad (19)$$

where $\Phi(t) = \begin{pmatrix} \phi_0(t) \\ \phi_1(t) \\ \vdots \\ \phi_{n+1}(t) \end{pmatrix}$.

The residual function expressed by Eq. (19) evaluates the quality of the approximation in every point of the domain: $0 < x < 1$. In order to establish the necessary conditions to determine the numerical solution of the problem in the interpolation points, $\phi^{(n+1)}(x_j, t) = \phi_j(t)$, we applied the concept of average value of a function to compute the first n average weighted residuals, as following:

$$\bar{R}_j^{(n+1)}[\Phi(t)] = \int_{x=0}^{x=1} \omega_j(x) R^{(n+1)}[x, \Phi(t)] dx = 0, \quad \text{for } j = 1, 2, \dots, n \tag{20}$$

where $\bar{R}_j^{(n+1)}[\Phi(t)]$ is the j -th average weighted residual of the approximation and $\omega_j(x)$ is the j -th weight corresponding to the method of weighted residuals. The terms $\omega_j(x)$ presented in Eq. (20) are related with the method of weighted residuals applied to the numerical solution of the problem. In this work the method of moments and of Galerkin method were applied, resulting:

Method of moments : $\omega_j(x) = x^{j-1} \quad \text{for } j = 1, 2, \dots, n \tag{21}$

$$\text{Galerkin method : } \omega_j(x) = \frac{\partial \phi^{(n+1)}(x, t)}{\partial a_j} = (1-x)^2 x^{j-1} + \begin{cases} -(1+2\lambda) & \text{when } j = 1 \\ \lambda & \text{when } j = 2 \\ 0 & \text{when } j > 2 \end{cases} \quad \text{for } j = 1, 2, \dots, n. \tag{22}$$

In the proposed methodology, the average weighted residuals, as defined by Eq. (20), are numerically calculated by Gauss-Lobatto quadrature procedure with inclusion of both lower and upper bounds, $x_0 = 0$ and $x_{n+1} = 1$, resulting in:

$$\bar{R}_j^{(n+1)}[\Phi(t)] \approx \sum_{k=0}^{n+1} \Omega_{j,k} \cdot R_k^{(n+1)}(t) = 0, \quad \text{for } j = 1, \dots, n \tag{23}$$

where $R_k^{(n+1)}(t) = R^{(n+1)}[x_k, \Phi(t)]$, $0 < x_1 < x_2 < \dots < x_n < 1$ are the n roots of the Jacobi polynomial $P_n^{(1,1)}(x)$, $x_0 = 0$, $x_{n+1} = 1$, $\Omega_{j,k} = H_k \cdot \omega_j(x_k)$ for $j = 1, 2, \dots, n-1$ and $k = 0, 1, 2, \dots, n+1$, and H_k are the Gauss-Lobatto quadrature weights given by: $H_k = \int_{x=0}^{x=1} [\ell_k(x)]^2 dx$. For $j = n$, we have: $\Omega_{n,k} = H_k \cdot x_k^{n-1}$ when the method of moments is applied and $\Omega_{n,k} = H_k \cdot (1-x_k)^2 x_k^{n-1} + (C_n^{(1,1)})/p'_{nodal}(x_k)$ when the Galerkin method is applied (see Appendix A).

Eq. (23) is a linear system of algebraic equation that can be represented by the following matrix form:

$$\begin{bmatrix} \Omega_{0,0} R_0^{(n+1)} & \Omega_{0,1} R_1^{(n+1)} & \dots & \Omega_{0,n} R_n^{(n+1)} & \Omega_{0,n+1} R_{n+1}^{(n+1)} \\ \Omega_{1,0} R_0^{(n+1)} & \Omega_{1,1} R_1^{(n+1)} & \dots & \Omega_{1,n} R_n^{(n+1)} & \Omega_{1,n+1} R_{n+1}^{(n+1)} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \Omega_{n-1,0} R_0^{(n+1)} & \Omega_{n-1,1} R_1^{(n+1)} & \dots & \Omega_{n-1,n} R_n^{(n+1)} & \Omega_{n-1,n+1} R_{n+1}^{(n+1)} \\ \Omega_{n,0} R_0^{(n+1)} & \Omega_{n,1} R_1^{(n+1)} & \dots & \Omega_{n,n} R_n^{(n+1)} & \Omega_{n,n+1} R_{n+1}^{(n+1)} \end{bmatrix} = \mathbf{0} \tag{24}$$

Eq. (24) can be expressed in another form that relates the n residuals at internal points, $R_1^{(n+1)}, \dots, R_n^{(n+1)}$, with the residuals at the boundary points, $R_0^{(n+1)}$ and $R_{n+1}^{(n+1)}$, according to the expression:

$$\begin{bmatrix} \Omega_{0,1} & \dots & \Omega_{0,n} \\ \Omega_{1,1} & \dots & \Omega_{1,n} \\ \vdots & \vdots & \vdots \\ \Omega_{n-1,1} & \dots & \Omega_{n-1,n} \\ \Omega_{n,1} & \dots & \Omega_{n,n} \end{bmatrix} \begin{bmatrix} R_1^{(n+1)} \\ \vdots \\ R_n^{(n+1)} \end{bmatrix} = - \begin{bmatrix} \Omega_{0,0} & \Omega_{0,n+1} \\ \Omega_{1,0} & \Omega_{1,n+1} \\ \vdots & \vdots \\ \Omega_{n-1,0} & \Omega_{n-1,n+1} \\ \Omega_{n,0} & \Omega_{n,n+1} \end{bmatrix} \begin{bmatrix} R_0^{(n+1)} \\ \vdots \\ R_{n+1}^{(n+1)} \end{bmatrix}. \tag{25}$$

This algebraic linear system can be solved according to:

$$\begin{bmatrix} R_1^{(n+1)} \\ \vdots \\ R_n^{(n+1)} \end{bmatrix} = \mathbf{V}^{(1)} R_0^{(n+1)} + \mathbf{V}^{(2)} R_{n+1}^{(n+1)}, \quad \text{where } \mathbf{V} = [\mathbf{V}^{(1)} \quad \mathbf{V}^{(2)}] = \mathbf{G}^{-1} \mathbf{P}, \quad \mathbf{G} = \begin{bmatrix} \Omega_{0,1} & \dots & \Omega_{0,n} \\ \Omega_{1,1} & \dots & \Omega_{1,n} \\ \vdots & \vdots & \vdots \\ \Omega_{n-1,1} & \dots & \Omega_{n-1,n} \\ \Omega_{n,1} & \dots & \Omega_{n,n} \end{bmatrix} \quad \text{and } \mathbf{P} = - \begin{bmatrix} \Omega_{0,0} & \Omega_{0,n+1} \\ \Omega_{1,0} & \Omega_{1,n+1} \\ \vdots & \vdots \\ \Omega_{n-1,0} & \Omega_{n-1,n+1} \\ \Omega_{n,0} & \Omega_{n,n+1} \end{bmatrix}. \tag{26}$$

As already mentioned, this procedure allows a unified procedure of the methods of moments, Galerkin and orthogonal collocation. The orthogonal collocation method can be obtained by setting the matrix $\mathbf{V} = \mathbf{0}$, and when the method of moments or the Galerkin method are applied we must calculate the components of matrix \mathbf{V} according to Eqs. (21) and (22), respectively, and the definition of the terms of matrix Ω . Besides, the proposed methodology connects the residual at the internal points with the residuals at the boundary points.

The approximation for the dependent variables and its derivative can be described by the expressions (Villadsen & Michelsen, 1978):

$$\phi^{(n+1)}(x_i, t) = \phi_i(t) \quad (27.1)$$

$$\left. \frac{\partial \phi^{(n+1)}(x, t)}{\partial t} \right|_{x_i} = \frac{d\phi_i(t)}{dt} \quad (27.2)$$

$$\left. \frac{\partial \phi^{(n+1)}(x, t)}{\partial x} \right|_{x_i} = \sum_{j=0}^{n+1} \mathbf{A}_{i,j} \phi_j(t) \quad (27.3)$$

$$\left. \frac{\partial^2 \phi^{(n+1)}(x, t)}{\partial x^2} \right|_{x_i} = \sum_{j=0}^{n+1} \mathbf{B}_{i,j} \phi_j(t) \quad (27.4)$$

Replacing in Eq. (24) the model described by Eq. (15), using the approximation presented in Eq. (27), gives rise to the following system of differential-algebraic equation (DAE):

$$\begin{aligned} F \left(t, x_i, \phi_i(t), \frac{d\phi_i(t)}{dt}, \sum_{j=0}^{n+1} \mathbf{A}_{i,j} \phi_j(t), \sum_{j=0}^{n+1} \mathbf{B}_{i,j} \phi_j(t) \right) = \\ = \mathbf{V}_i^{(1)} F \left(t, 0, \phi_0(t), \frac{d\phi_0(t)}{dt}, \sum_{j=0}^{n+1} \mathbf{A}_{0,j} \phi_j(t), \sum_{j=0}^{n+1} \mathbf{B}_{0,j} \phi_j(t) \right) + \\ + \mathbf{V}_i^{(2)} F \left(t, 1, \phi_{n+1}(t), \frac{d\phi_{n+1}(t)}{dt}, \sum_{j=0}^{n+1} \mathbf{A}_{n+1,j} \phi_j(t), \sum_{j=0}^{n+1} \mathbf{B}_{n+1,j} \phi_j(t) \right) \end{aligned} \quad (28.1)$$

for $i = 1, 2, \dots, n$

$$\text{BC}_1 : -\lambda \sum_{j=1}^{n+1} \mathbf{A}_{0,j} \phi_j(t) + \phi_0(t) = \phi_{feed}(t) \quad \text{BC}_2 : \sum_{j=1}^{n+1} \mathbf{A}_{n+1,j} \phi_j(t) = 0 \quad (28.2)$$

$$\text{IC} : H \left(t, x_i, \phi_i(t), \frac{d\phi_i(t)}{dt} \right)_{t=0} = 0 \quad \text{for } i = 1, 2, \dots, n. \quad (28.3)$$

The steady-state version of this model can be obtained considering $(d\phi_i(t)/dt) = 0$ and $\phi_{feed}(t) = \phi_{feed} = \text{constant}$, transforming the DAE system of Eq. (28) into a system of non-linear algebraic equations, Eq. (29).

$$F \left(x_i, \phi_i, \sum_{j=0}^{n+1} \mathbf{A}_{i,j} \phi_j, \sum_{j=0}^{n+1} \mathbf{B}_{i,j} \phi_j \right) = \mathbf{V}_i^{(1)} F \left(0, \phi_0, \sum_{j=0}^{n+1} \mathbf{A}_{0,j} \phi_j, \sum_{j=0}^{n+1} \mathbf{B}_{0,j} \phi_j \right) + \mathbf{V}_i^{(2)} F \left(1, \phi_{n+1}, \sum_{j=0}^{n+1} \mathbf{A}_{n+1,j} \phi_j, \sum_{j=0}^{n+1} \mathbf{B}_{n+1,j} \phi_j \right) \quad \text{for } i = 1, 2, \dots, n. \quad (29.1)$$

$$\text{BC}_1 : -\lambda \sum_{j=1}^{n+1} \mathbf{A}_{0,j} \phi_j + \phi_0 = \phi_{feed} \quad \text{BC}_2 : \sum_{j=1}^{n+1} \mathbf{A}_{n+1,j} \phi_j = 0 \quad (29.2)$$

The main advantage of the procedure proposed in this work is related to the possibility to develop a criterion for selecting the quadrature points and also to establish a direct connection between the residuals in the internal discrete points and the boundary residuals, allowing that the same Jacobi polynomial be used for the method of moments and for the Galerkin method. The specificity of each method appears only in the calculation of the discretization matrices of the system. Thus, the structure of the discretized equations is very similar to the structure generated by applying the classical form of the OCM. Note that by setting the vector $\mathbf{V} = \mathbf{0}$, the proposed procedure reduces to the classical OCM.

3. Selected problems for testing and evaluation

In order to test and evaluate the proposed methodology, two typical chemical engineering examples are solved: mass and heat balance in a catalyst particle with irreversible chemical reaction and tubular pseudo-homogeneous chemical reactor with axial advective and diffusive transports. Stationary and transient, isothermal and non-isothermal models will be considered. For stationary models the algebraic equations systems, resulting from the application of the discretization procedure, were solved by the Newton–Raphson method. For the transient models, where the application of the proposed methodology gives rise to a system of differential-algebraic equations, we use the computational code DASSL (Petzold, 1989).

In order to evaluate the performance of the method we use the mean square residual value, defined by the expression:

$$\bar{\mathbf{R}}(\mathbf{y}) = (s+1) \int_{x=0}^{x=1} x^s [\mathbf{R}^{(n)}(x, \mathbf{y})]^2 dx \quad (30)$$

3.1. Catalyst particle with irreversible chemical reaction

The unidirectional mass and energy balances in a catalyst particle at the unsteady state with geometry s ($s=0$ for plane, $s=1$ for cylindrical, and $s=2$ for spherical), in which there is an irreversible reaction of order m , described, in dimensionless form, by Eqs. (31)–(33).

$$\frac{\partial y(u, t)}{\partial t} - 4 \left(u \frac{\partial^2 y(u, t)}{\partial u^2} + \left(\frac{s+1}{2} \right) \frac{\partial y(u, t)}{\partial u} \right) + \Re[y(u, t), \theta(u, t)] = 0 \quad (31.1)$$

$$Le \frac{\partial \theta(u, t)}{\partial t} - 4 \left(u \frac{\partial^2 \theta(u, t)}{\partial u^2} + \left(\frac{s+1}{2} \right) \frac{\partial \theta(u, t)}{\partial u} \right) - \lambda \Re[y(u, t), \theta(u, t)] = 0 \quad (31.2)$$

where

$$\Re[y(u, t), \theta(u, t)] = \Phi^2 [y(u, t)]^m \exp \left[\gamma \left(1 - \frac{1}{\theta(u, t)} \right) \right] \quad (31.3)$$

subject to the following boundary conditions:

$$BC_1 : \left. \frac{\partial y(u, t)}{\partial u} \right|_{u=0} : \text{finite} \quad (32.1)$$

$$\left. \frac{\partial \theta(u, t)}{\partial u} \right|_{u=0} : \text{finite} \quad (32.2)$$

$$BC_2 : \left. \frac{2}{Sh} \frac{\partial y(u, t)}{\partial u} \right|_{u=1} + y(u, t) \Big|_{u=1} = y_{bulk}(t) \quad (32.3)$$

$$\left. \frac{2}{Nu} \frac{\partial \theta(u, t)}{\partial u} \right|_{u=1} + \theta(u, t) \Big|_{u=1} = \theta_{bulk}(t) \quad (32.4)$$

and to the following initial conditions:

$$y(u, t) \Big|_{t=0} = y_{initial}(u) \quad (33.1)$$

$$\theta(u, t) \Big|_{t=0} = \theta_{initial}(u) \quad (33.2)$$

in which the independent variables u ($u=x^2$ with x being the original spatial variable) and t are defined in the domain: $0 \leq u < 1$ e $t > 0$, Φ is the Thiele modulus, Le is the Lewis number, Sh is the Sherwood number, Nu is the Nusselt number, λ is the dimensionless heat of the reaction, γ is the dimensionless activation energy of the reaction and m is the reaction order.

The application of the procedure described in Section 2 results in the system of $2n$ differential equations and 2 algebraic equations, given by Eq. (34).

$$\begin{aligned} & \frac{dy_i(t)}{dt} - \sum_{j=1}^{n+1} \mathbf{C}_{i,j} y_j(t) + \Re[y_i(t), \theta_i(t)] - \mathbf{V}_i^{(y)} \left\{ \frac{dy_{n+1}(t)}{dt} - \sum_{j=1}^{n+1} \mathbf{C}_{n+1,j} y_j(t) + \Re[y_{n+1}(t), \theta_{n+1}(t)] \right\} = 0 \\ & Le \frac{d\theta_i(t)}{dt} - \sum_{j=1}^{n+1} \mathbf{C}_{i,j} \theta_j(t) - \lambda \Re[y_i(t), \theta_i(t)] - \\ & \mathbf{V}_i^{(\theta)} \left\{ Le \frac{d\theta_{n+1}(t)}{dt} - \sum_{j=1}^{n+1} \mathbf{C}_{n+1,j} \theta_j(t) - \lambda \Re[y_{n+1}(t), \theta_{n+1}(t)] \right\} = 0 \quad (34) \\ & \frac{2}{Sh} \sum_{j=1}^{n+1} \mathbf{A}_{n+1,j} y_j(t) + y_{n+1}(t) = y_{bulk}(t) \\ & \frac{2}{Nu} \sum_{j=1}^{n+1} \mathbf{A}_{n+1,j} \theta_j(t) + \theta_{n+1}(t) = \theta_{bulk}(t) \end{aligned}$$

where

$$\mathbf{C}_{i,j} = 4 \left(u_i \mathbf{B}_{i,j} + \frac{s+1}{2} \mathbf{A}_{i,j} \right)$$

$$\Re[y_i(t), \theta_i(t)] = \Phi^2 [y_i(t)]^m \exp \left[\gamma \left(1 - \frac{1}{\theta_i(t)} \right) \right].$$

Table 1
Mean square error, mean square residual and infinity-norm, considering the isothermal steady state problem for $m = 1, s = 2, Sh = 1$ and different values of Thiele modulus (Φ).

n	Method of moments			Galerkin method		
	$3 \int_0^1 x^2 [error(x)]^2 dx$	$3 \int_0^1 x^2 Res^2(x) dx$	$\ error(x)\ _\infty$	$3 \int_0^1 x^2 [error(x)]^2 dx$	$3 \int_0^1 x^2 Res^2(x) dx$	$\ error(x)\ _\infty$
$\Phi = 10$						
3	9.47×10^{-6}	2.88×10^{-2}	9.5×10^{-2}	5.09×10^{-6}	2.81×10^{-2}	5.68×10^{-2}
4	2.37×10^{-7}	1.14×10^{-3}	1.76×10^{-2}	1.02×10^{-7}	1.24×10^{-3}	9.73×10^{-3}
5	3.54×10^{-9}	2.65×10^{-5}	2.41×10^{-3}	1.37×10^{-9}	3.31×10^{-5}	1.28×10^{-3}
6	3.29×10^{-11}	3.77×10^{-7}	3.00×10^{-4}	1.20×10^{-11}	5.36×10^{-7}	1.85×10^{-4}
$\Phi = 20$						
3	7.55×10^{-5}	1.52	2.41×10^{-2}	5.04×10^{-5}	1.32	1.44×10^{-1}
4	8.41×10^{-6}	2.14×10^{-1}	9.49×10^{-2}	4.23×10^{-6}	1.90×10^{-1}	5.01×10^{-2}
5	7.54×10^{-7}	2.41×10^{-2}	3.24×10^{-2}	3.08×10^{-7}	2.32×10^{-2}	1.60×10^{-2}
6	5.01×10^{-8}	2.02×10^{-3}	9.31×10^{-3}	1.82×10^{-8}	2.20×10^{-3}	4.48×10^{-3}
7	2.45×10^{-9}	1.25×10^{-4}	2.26×10^{-3}	8.34×10^{-10}	1.55×10^{-4}	1.08×10^{-3}
8	8.89×10^{-11}	5.73×10^{-6}	4.69×10^{-4}	2.94×10^{-11}	8.07×10^{-6}	2.23×10^{-4}

The formulation presented here, Eq. (34), uses the same Jacobi polynomial, $P_n^{(1,(s-1)/2)}(u)$, for the methods of moments and Galerkin. The differences between the methods appear only in the computation of the components of the vectors $V^{(y)}$ and $V^{(\theta)}$.

Considering the specific case of isothermal and first order chemical reaction, the residue $R^{(n)}(u, y)$ is also a polynomial function in u with the same degree n of $y^{(n)}(u)$. Thus, the integrand of Eq. (6) is expressed as a polynomial in u of degree up to $2n - 1$, when the method of moments is applied, and of degree up to $2n$, when the method of Galerkin is applied. This makes possible to exactly evaluate the integral represented by Eq. (6) with Gauss-Radau quadrature, using the point $u_{n+1} = 1$ and n internal quadrature points, $0 < u_1 < u_2 < \dots < u_n < 1$, which are the roots of the Jacobi polynomial with $\alpha = 1$ and $\beta = (s - 1)/2$, i.e., $P_n^{(1,(s-1)/2)}(u)$.

For isothermal and first order chemical reaction, the application of the method of moments results in a system of equations identical to that generated by the application of the classical OCM, using as collocation points the n roots of the Jacobi polynomial with $\alpha = 0$ and $\beta = (s - 1)/2$. The application of Galerkin method can only be reproduced by the classical OCM in the specific case of Dirichlet boundary condition, when $Sh \rightarrow \infty$. In this specific situation, the integration of the average weighted residue, Eq. (6), can be exactly evaluated by Gauss-Jacobi quadrature adopting as internal points of quadrature the n roots of $P_n^{(1,(s-1)/2)}(u)$. This is equivalent to impose that the residual function will be zero in the n roots of this Jacobi polynomial.

In order to evaluate the utilization of the mean square residue in the performance of the applied MWR, the proposed methodology was applied to the stationary and isothermal model. In Table 1, the mean square error, mean square residual and infinity-norm are compared considering the following parameters values: $m = 1, s = 2$ and different values of Thiele modulus (Φ).

Analyzing the values presented in Table 1, we verify that the two methods (moments and Galerkin) present similar performances. For all the cases the Galerkin method presents a better performance, but the difference is not significant. Comparing the values obtained by the mean square error, the mean square residual and the infinity-norm, it is possible to conclude that the value of the mean square residual can be used to evaluate the performance of the applied MWR. The values obtained show a good agreement between the mean square residual and the infinity-norm, indicating that large pointwise errors are properly weighted.

Analyzing Fig. 1, it is possible to note that the utilization of low number of quadrature points gives rise to solution with unrealistic oscillation. These oscillations occur due to the inability of polynomial approximations to describe severe gradients.

Comparing the results presented in Fig. 2, it is possible to observe that the increase of the Thiele module introduce steep gradients near the surface. In both cases the adaptability of the polynomial approximation, and consequently its accuracy, can be improved by increasing the number of quadrature points. It must be pointed out that increasing the number of quadrature points also increases the computational efforts. It is very important to consider this aspect, because in some cases it is more indicated the use of adaptive mesh, that allows increase the number of quadrature points in regions absolutely necessary, than increase the global points of quadrature.

In Fig. 3, it is possible to verify that the location of the points where the residual function is zero slightly changes with the value of Sh parameter, when the Galerkin method is applied. This feature indicates that the proposed methodology has a self-adaptive property, since the location of the points where the residual function is zero changes with the variation of model parameters.

For the non-isothermal and stationary case, the methodology was applied using 5 internal quadrature points considering the values of the parameters: $\Phi = 0.5, m = 1, s = 2, Sh = 66.5, Nu = 55.3, \gamma = 20$ and $\lambda = 0.6$ (Finlayson, 1972).

In this case, when the Galerkin method is applied, we observe that the points where the residual function for the mass balance equation is zero are not the same points where the residual function for the energy balance equation is zero (see Table 2). It is also observed that the location of the points where the residual functions are zero is different for the methods of moments and Galerkin (Figs. 4 and 5, respectively), indicating, once more, the adaptive feature presented by the proposed procedure.

Comparing the mean square residues shown in Table 3, we can see that the proposed methodology produces more accurate results than the application of the classical form of the OCM, especially if it takes into account the results obtained by the method of moments.

Table 2
Values where the residual functions are zero with the Galerkin method.

x	$Res_y(x) = 0$	$Res_\theta(x) = 0$
x_1	0.0628	0.0628
x_2	0.2358	0.2360
x_3	0.4766	0.4771
x_4	0.7259	0.7268
x_5	0.9233	0.9248

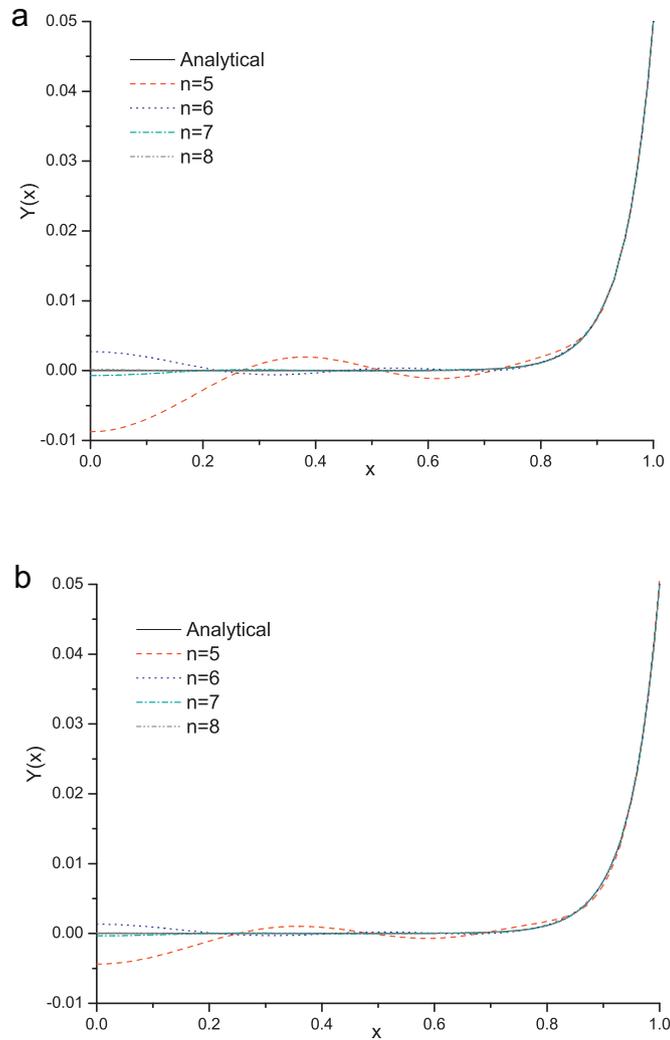


Fig. 1. Concentration profile in the stationary and isothermal model of catalyst particle, obtained by the application of methods of moments (a) and Galerkin (b) considering different internal points of quadrature and parameters $m = 1$, $s = 2$, $Sh = 1$ and $\Phi = 20$.

For the non-isothermal and transient case, the methodology was applied using 8 internal quadrature points, considering the values of the parameters: $\Phi = 0.5$, $m = 1$, $s = 2$, $Sh = 66.5$, $Nu = 55.3$, $\gamma = 20$, $\lambda = 0.6$, $Le = 0.9$, and $y_{bulk}(t) = \theta_{bulk}(t) = 1$ (Finlayson, 1972). The initial conditions are: $y_{initial}(u) = 0$ and $\theta_{initial}(u) = 1$. In Fig. 6, it is possible to observe that the point close to the upper boundary where the energy balance residual function is zero slightly changes with time. This fact was also observed for the residue function of the mass balance. This behavior is more clearly identified when the method of Galerkin is applied due to the residual weights parameter dependence, Eq. (8). When the method of moments is applied, the location of the points where the residual functions is zero is almost unchanged, changing only due to the non-linearity of the model equations. In this late method, these points remain very close to the collocation points when the classical form of the OCM is applied with collocation points properly selected as the n roots of the Jacobi polynomial with $\alpha = 0$ and $\beta = (s - 1)/2$, corresponding to the numerical computation of the integrals of the weighted residuals by pure Gaussian quadrature method, that does not include boundary points.

Table 3

Mean square residue of the classical orthogonal collocation, method of moments, and Galerkin method for the non-isothermal steady-state model, with $\Phi = 0.5$, $m = 1$, $s = 2$, $Sh = 66.5$, $Nu = 55.3$, $\gamma = 20$ and $\lambda = 0.6$.

n	Orthogonal collocation $P_n^{(0,0)}(u)$		Method of moments		Galerkin method	
	\bar{R}_y	\bar{R}_θ	\bar{R}_y	\bar{R}_θ	\bar{R}_y	\bar{R}_θ
3	6.15×10^{-2}	2.21×10^{-2}	1.59×10^{-2}	5.72×10^{-3}	2.87×10^{-2}	1.02×10^{-2}
4	1.61×10^{-3}	5.80×10^{-4}	4.65×10^{-4}	1.67×10^{-4}	7.85×10^{-4}	2.78×10^{-4}
5	3.04×10^{-5}	1.09×10^{-5}	7.44×10^{-6}	2.67×10^{-6}	1.33×10^{-5}	4.67×10^{-6}
6	4.60×10^{-7}	1.65×10^{-7}	9.42×10^{-8}	3.39×10^{-8}	1.79×10^{-7}	6.24×10^{-8}

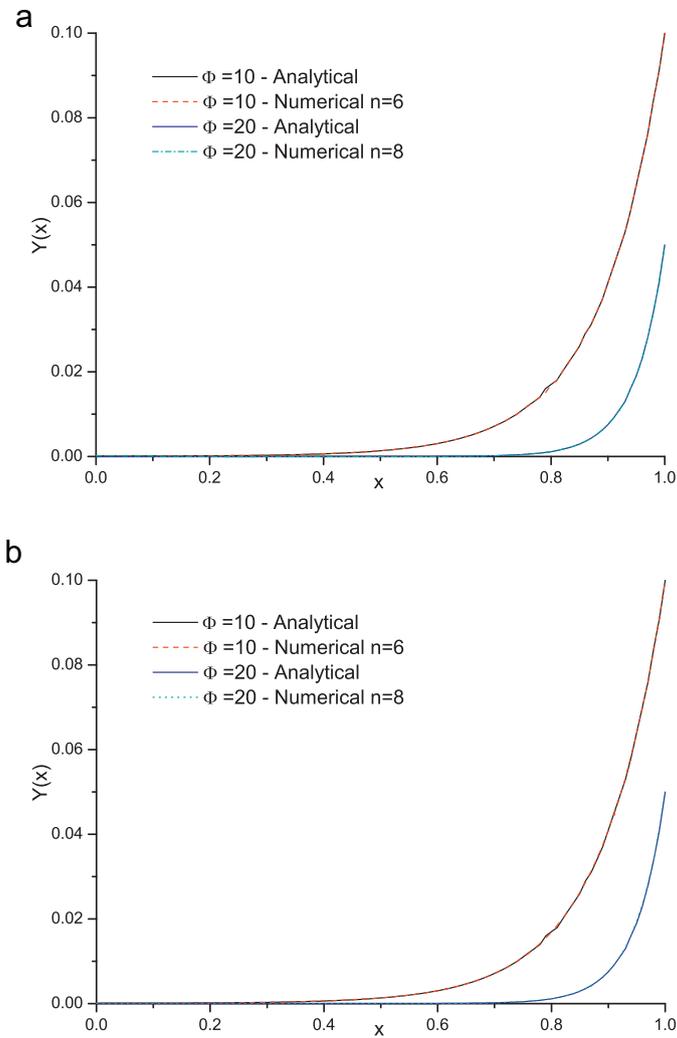


Fig. 2. Concentration profile for different ϕ in the stationary and isothermal model of catalyst particle, obtained by the application of the methods of moments (a) and Galerkin (b) with parameters $m = 1$, $s = 2$ and $Sh = 1$.

3.2. Tubular pseudo-homogeneous chemical reactor with axial advective and diffusive transports

The mass and energy balances in a fixed-bed reactor, in which an irreversible chemical reaction of order m occurs, are described by the following system of partial differential equations:

$$\frac{\partial y(x, t)}{\partial t} + \frac{\partial y(x, t)}{\partial x} - \frac{1}{Pe_m} \frac{\partial^2 y(x, t)}{\partial x^2} + \Re[y(x, t), \theta(x, t)] = 0 \quad (35.1)$$

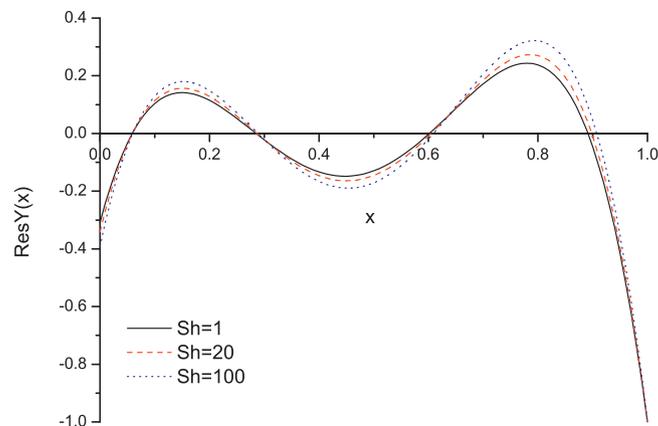


Fig. 3. Normalized residual in the catalyst particle considering steady-state isothermal model for different values of the parameter Sh applying the Galerkin method.

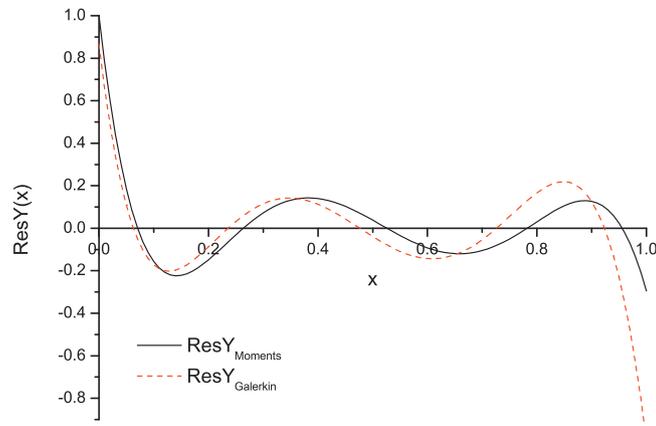


Fig. 4. Normalized residual of the non-isothermal steady-state mass balance equation in the catalyst particle when applying the moments and Galerkin methods.

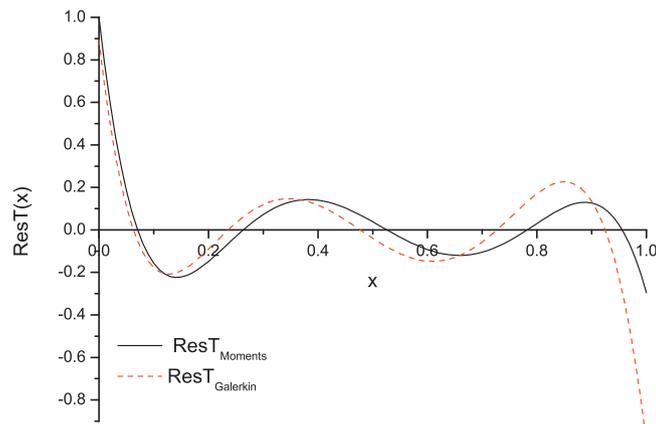


Fig. 5. Normalized residual of the non-isothermal steady-state energy balance equation in the catalyst particle when applying the moments and Galerkin methods.

$$\frac{\partial \theta(x, t)}{\partial t} + \frac{\partial \theta(x, t)}{\partial x} - \frac{1}{Pe_h} \frac{\partial^2 \theta(x, t)}{\partial x^2} - \lambda \mathfrak{N}[y(x, t), \theta(x, t)] = 0 \tag{35.2}$$

where

$$\mathfrak{N}[y(x, t), \theta(x, t)] = Da[y(x, t)]^m \exp \left[\gamma \left(1 - \frac{1}{\theta(x, t)} \right) \right] \tag{35.3}$$

subject to the following boundary conditions:

$$BC_1 : -\frac{1}{Pe_m} \frac{\partial y(x, t)}{\partial x} \Big|_{x=0} + y(x, t) \Big|_{x=0} = y_{feed}(t) \tag{36.1}$$

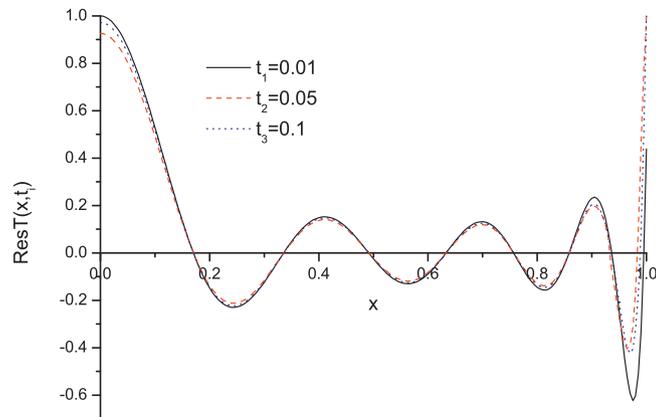


Fig. 6. Normalized residual of the non-isothermal and transient energy balance equation in the catalyst particle for different times when applying the Galerkin method.

Table 4
Concentration values at the inlet and outlet of the reactor for the stationary and isothermal case, obtained by Finlayson (1972) and by the application of the proposed procedure.

n	Finlayson (OCM)		Moments		Galerkin	
	y(0)	y(1)	y(0)	y(1)	y(0)	y(1)
<i>m</i> = 1, <i>Pe</i> = 15 and <i>Da</i> = 8						
4	0.7260629	0.0026254	0.7246852	0.0034243	0.7272829	0.0038743
6	0.7220846	0.0028608	0.7220526	0.0028642	0.7222041	0.0028928
8	0.7219910	0.0028617	0.7219909	0.0028617	0.7219981	0.0028632
Exact	0.7219898	0.0028617	–	–	–	–
<i>m</i> = 2, <i>Pe</i> = 1 and <i>Da</i> = 2						
3	0.6368092	0.4575999	0.6367842	0.4575887	0.6367910	0.4575923
6	0.6367841	0.4575887	0.6367841	0.4575887	0.6367841	0.4575887
FDM	0.6367841	0.4575887	–	–	–	–

$$-\frac{1}{Pe_h} \frac{\partial \theta(x, t)}{\partial x} \Big|_{x=0} + \theta(x, t) \Big|_{x=0} = \theta_{feed}(t) \quad (36.2)$$

$$BC_2 : \frac{1}{Pe_m} \frac{\partial y(x, t)}{\partial x} \Big|_{x=1} = 0 \quad (36.3)$$

$$\frac{1}{Pe_h} \frac{\partial \theta(x, t)}{\partial x} \Big|_{x=1} = 0 \quad (36.4)$$

and to the following initial conditions:

$$y(x, t) \Big|_{t=0} = y_{initial}(x) \quad (37.1)$$

$$\theta(x, t) \Big|_{t=0} = \theta_{initial}(x) \quad (37.2)$$

where the independent variables *x* and *t* are defined in the domain: $0 < x < 1$ and $t > 0$, *Da* is the Damköhler number, *Pe_m* is the Peclet mass number, *Pe_h* is the Peclet energy number, λ and γ are dimensionless parameters, and *m* is the reaction order.

Table 5
Mean square error and mean square residue, considering the isothermal steady state problem for *m* = 1, *Da* = 20 and different values of mass Peclet numbers (*Pe_m*).

n	Method of moments		Galerkin method	
	$\int_0^1 [error(x)]^2 dx$	$\int_0^1 Res^2(x) dx$	$\int_0^1 [error(x)]^2 dx$	$\int_0^1 Res^2(x) dx$
<i>Pe_m</i> = 0.1				
3	3.03×10^{-11}	1.52×10^{-5}	1.56×10^{-11}	1.54×10^{-5}
4	2.95×10^{-13}	4.24×10^{-7}	1.33×10^{-13}	4.43×10^{-7}
<i>Pe_m</i> = 1				
3	1.41×10^{-6}	1.20×10^{-2}	1.13×10^{-6}	1.72×10^{-2}
4	4.01×10^{-8}	9.70×10^{-4}	2.29×10^{-8}	1.00×10^{-3}
<i>Pe_m</i> = 10				
3	8.81×10^{-4}	1.05	8.18×10^{-4}	1.07
4	9.69×10^{-5}	1.71×10^{-1}	8.03×10^{-5}	1.80×10^{-1}
5	9.37×10^{-6}	2.33×10^{-2}	6.60×10^{-6}	2.55×10^{-2}
6	7.65×10^{-7}	2.60×10^{-3}	4.58×10^{-7}	2.98×10^{-3}
<i>Pe_m</i> = 100				
3	6.95×10^{-3}	4.74	5.98×10^{-3}	4.61
4	1.66×10^{-3}	1.33	1.41×10^{-3}	1.42
5	3.49×10^{-4}	3.29×10^{-1}	2.92×10^{-4}	3.90×10^{-1}
6	6.36×10^{-5}	7.02×10^{-2}	5.21×10^{-5}	9.24×10^{-2}
7	1.00×10^{-5}	1.29×10^{-2}	7.97×10^{-6}	1.86×10^{-2}
8	1.36×10^{-6}	2.05×10^{-2}	1.05×10^{-6}	3.19×10^{-3}

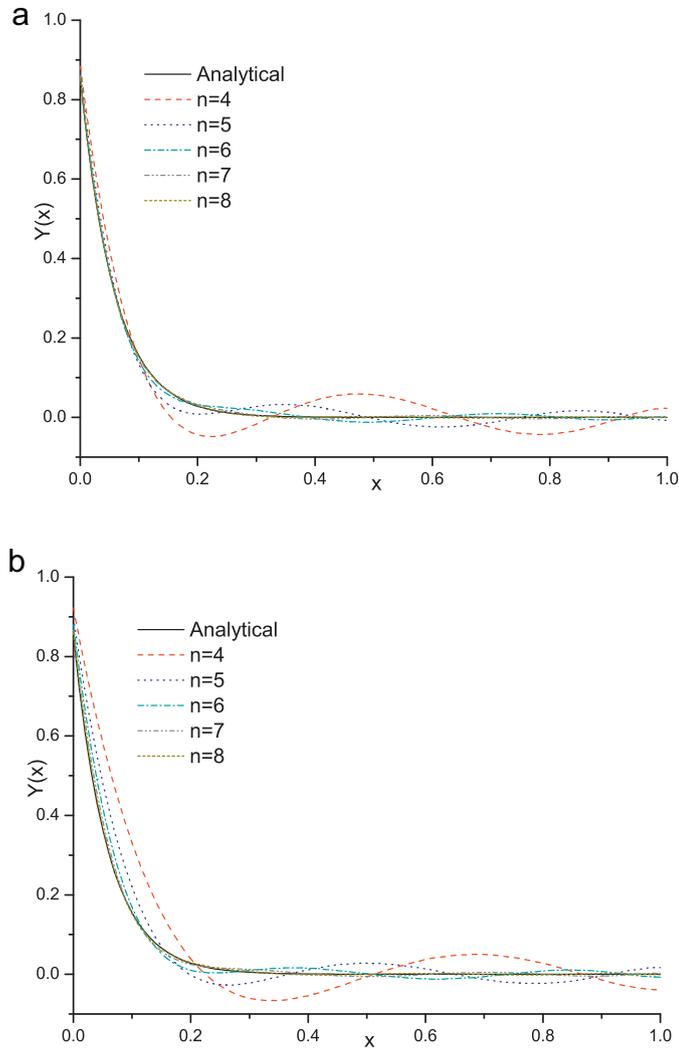


Fig. 7. Concentration profile in the stationary and isothermal model of the fixed-bed reactor, obtained by the application of the moments (a) and Galerkin (b) methods applying different internal points of quadrature and parameters $m = 1$, $Da = 20$ and $Pe_m = 100$.

The application of the procedure described in Section 2, results in the system of $2n$ differential equations and 4 algebraic equations, given by Eq. (38).

$$\begin{aligned}
 & \frac{dy_i}{dt} + \sum_{j=0}^{n+1} \mathbf{C}_{i,j}^{(y)} y_j + \mathfrak{N}[y_i, \theta_i] - \mathbf{V}_{i,0}^{(y)} \left[\frac{dy_0}{dt} + \sum_{j=0}^{n+1} \mathbf{C}_{0,j}^{(y)} y_j + \mathfrak{N}[y_0, \theta_0] \right] + \\
 & - \mathbf{V}_{i,1}^{(y)} \left[\frac{dy_{n+1}}{dt} + \sum_{j=0}^{n+1} \mathbf{C}_{n+1,j}^{(y)} y_j + \mathfrak{N}[y_{n+1}, \theta_{n+1}] \right] = 0 \\
 & \frac{d\theta_i}{dt} + \sum_{j=0}^{n+1} \mathbf{C}_{i,j}^{(\theta)} \theta_j - \lambda \mathfrak{N}[y_i, \theta_i] - \mathbf{V}_{i,0}^{(\theta)} \left[\frac{d\theta_0}{dt} + \sum_{j=0}^{n+1} \mathbf{C}_{0,j}^{(\theta)} \theta_j - \lambda \mathfrak{N}[y_0, \theta_0] \right] + \\
 & - \mathbf{V}_{i,1}^{(\theta)} \left[\frac{d\theta_{n+1}}{dt} + \sum_{j=0}^{n+1} \mathbf{C}_{n+1,j}^{(\theta)} \theta_j - \lambda \mathfrak{N}[y_{n+1}, \theta_{n+1}] \right] = 0 \\
 & - \frac{1}{Pe_m} \sum_{j=0}^{n+1} \mathbf{A}_{0,j} y_j + y_{n+1} = y_{feed}(t) \quad \frac{1}{Pe_m} \sum_{j=0}^{n+1} \mathbf{A}_{n+1,j} y_j = 0 \\
 & - \frac{1}{Pe_h} \sum_{j=0}^{n+1} \mathbf{A}_{0,j} \theta_j + \theta_{n+1} = \theta_{feed}(t) \quad \frac{1}{Pe_h} \sum_{j=0}^{n+1} \mathbf{A}_{n+1,j} \theta_j = 0
 \end{aligned} \tag{38}$$

where $\mathfrak{N}[y_i, \theta_i] = Da[y_i]^m \exp \left[\gamma \left(1 - \frac{1}{\theta_i} \right) \right]$ $\mathbf{C}_{i,j}^{(y)} = [\mathbf{A}_{i,j} - \frac{1}{Pe_m} \mathbf{B}_{i,j}]$ $\mathbf{C}_{i,j}^{(\theta)} = [\mathbf{A}_{i,j} - \frac{1}{Pe_h} \mathbf{B}_{i,j}]$.

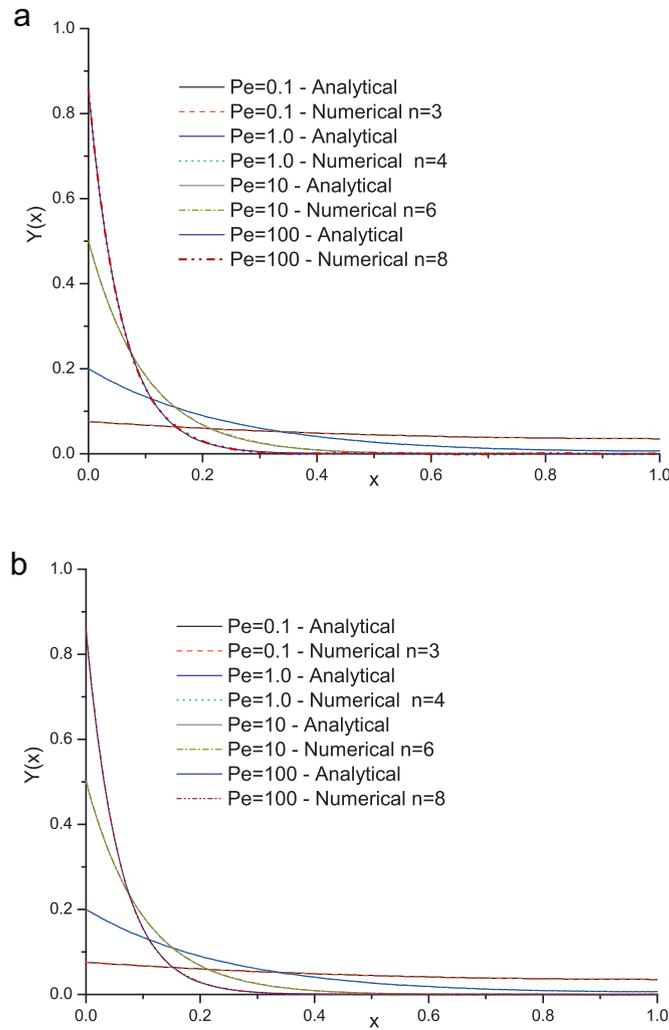


Fig. 8. Concentration profile for different Pe_m in the stationary and isothermal model of the fixed-bed reactor, obtained by the application of the moments (a) and Galerkin (b) with the parameters $m = 1$ and $Da = 20$.

The formulation given by Eq. (38) uses the same Jacobi polynomial, $P_n^{(1,1)}(x)$, for the method of moments and the Galerkin method. The differences between these methods only appear in the computation of the components of matrices $\mathbf{V}^{(y)}$ and $\mathbf{V}^{(\theta)}$.

Considering the specific case of isothermal and first order chemical reaction, the residual function $\mathbf{R}^{(n+1)}[x, y(t)]$ is also a polynomial function in x with the same degree $n + 1$ of $y^{(n+1)}(x, t)$. Thus, the integrand of the weighted average residuals of the approximation will be polynomials in x with degree up to $2n$, when applying the method of moments, and with degree up to $2n + 2$, when applying the Galerkin method. This makes possible to exactly evaluate the integral of the average weighted residuals by the improved Gauss-Lobatto quadrature (described in Appendix A), independent of the applied MWR. It is important to emphasize that, for this example, the application of the OCM, using as collocation points the roots of Jacobi polynomials with $\alpha = \beta = 0$, was unable to reproduce the methods of moments or Galerkin. This collocation procedure can be interpreted as a MWR using the Gauss-Jacobi quadrature method to compute the corresponding integrals of the method of moments. If the model equations are linear, this OCM and the method of moments will be almost equivalent, differing only in the last moment, when the Gauss-Jacobi quadrature method cannot compute exactly the corresponding integral.

The improvement in the Gauss-Lobatto quadrature formulas also enable the use of the same Jacobi polynomial, $P_n^{(1,1)}(x)$, for the methods of moments and Galerkin. In this case, the application of each method is specified in the computation of the components of matrices $\mathbf{V}^{(y)}$ and $\mathbf{V}^{(\theta)}$.

In order to compare the results of the proposed methodology with those obtained by Finlayson (1972) using OCM, the stationary and isothermal model was firstly solved, and the results for the reactor inlet and outlet concentrations are given in Table 4.

Analyzing the values presented in Table 4, it is observed that, for this linear problem, with $n = 4$ the proposed methodology presents numerical results closer to the analytical solution when compared to the results obtained by Finlayson (1972) applying the OCM, although for 6 points both methods are equivalent. For the nonlinear case ($m = 2$), with only 3 quadrature points, the numerical solution applying the method of moments is almost identical to the solution obtained by application of finite difference method (FDM) using 100 grids points (Finlayson, 1972). The increase in the number of quadrature points, from 3 to 6, does not change the solution obtained by applying the method of moments and produces some improvement in the solution obtained by the Galerkin method. These results indicate the superiority of the method of moments due to its simplicity and better convergence property when compared with the Galerkin method.

In order to evaluate the performance of the methodology in advective or diffusion dominated problem, the mean square of the error and residual were computed, considering the following parameters values: $m = 1$, $Da = 20$ and different values of Pe_m .

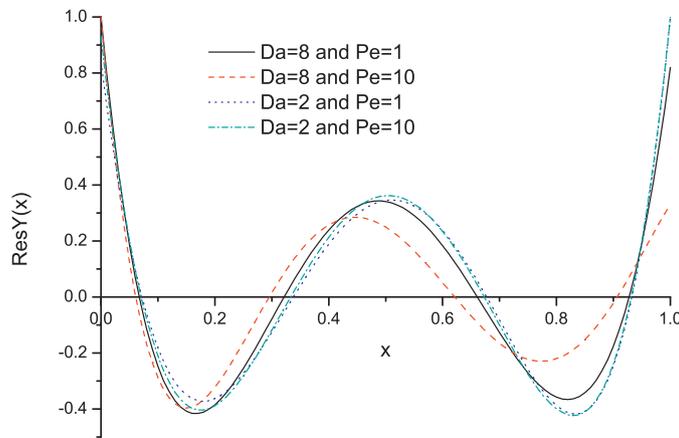


Fig. 9. Normalized residual of the non-isothermal steady-state mass balance in the fixed-bed reactor when applying the method of moments.

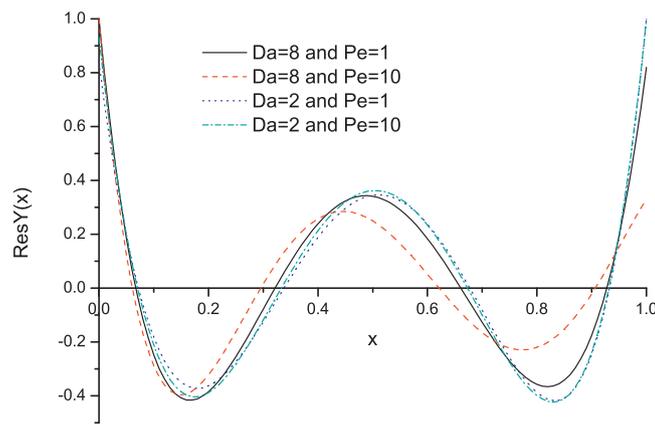


Fig. 10. Normalized residual of the non-isothermal steady-state mass balance in the fixed bed reactor when applying the Galerkin method.

Analyzing the values presented in Table 5, we verify that the two methods (moments and Galerkin) present similar performances. For all the cases, the Galerkin method presents a better performance, but the difference is not significant. Comparing the values obtained by the mean square error relative to the analytical solution and the mean square residual, it is possible to conclude that the value of the mean square residual can be used in evaluating the performance of the applied MWR.

Analyzing Fig. 7, it is possible to note that the utilization of low quadrature points gives rise to solution with unrealistic oscillation. Comparing the results presented in Fig. 8, it is possible to observe the increase in the gradient of the profiles due to the increase in the Pe_m number. These results confirm that the application of polynomial approximation gives better result for diffusive dominated problem. For advective dominated problem it was necessary to increase the quadrature points to maintain the accuracy of the numerical procedure. In cases in which is necessary to use high number of quadrature points is advisable the usage of adaptive meshes or the application of MWR on subdomains instead of global approximation methods.

In Figs. 9 and 10, we can see that it is possible to observe that the point close to the upper the residual function is zero varies with the value of the parameters Pe and Da for the methods of moments and Galerkin.

Table 6

Concentration values at the inlet and the outlet of the reactor in the stationary and non-isothermal case, obtained by Finlayson (1972) and by the application of the proposed procedure.

n	Finlayson (OCM)		Moments		Galerkin	
	y(0)	y(1)	y(0)	y(1)	y(0)	y(1)
1	0.62609	0.25217	0.60847	0.21693	0.61376	0.22753
3	0.58031	0.23537	0.58016	0.23528	0.58032	0.23527
6	0.58006	0.23528	0.58006	0.23528	0.58006	0.23528

n	Finlayson (OCM)		Moments		Galerkin	
	$\theta(0)$	$\theta(1)$	$\theta(0)$	$\theta(1)$	$\theta(0)$	$\theta(1)$
1	1.02094	1.04188	1.02193	1.04385	1.02163	1.04326
3	1.02350	1.04282	1.02351	1.04282	1.02350	1.04283
6	1.02352	1.04282	1.02352	1.04282	1.02352	1.04282

Table 7

Values where the residual function is zero.

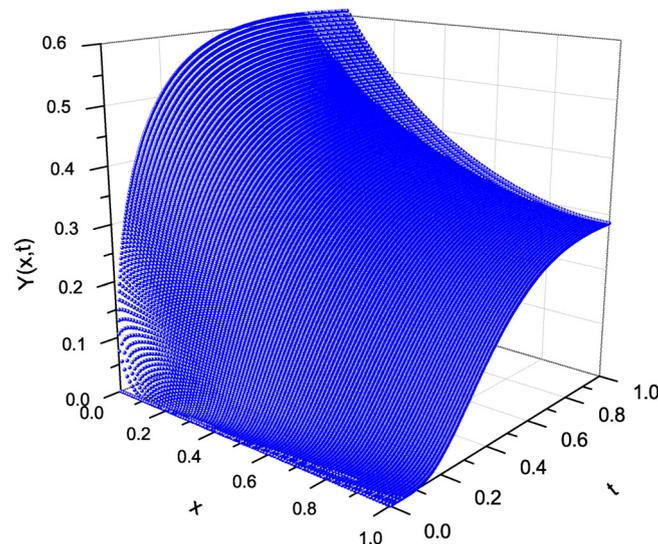
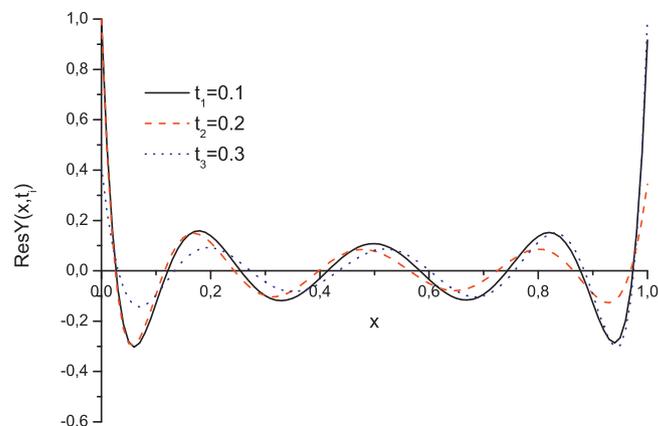
x	Moments		Galerkin	
	$Res_y(x)=0$	$Res_\theta(x)=0$	$Res_y(x)=0$	$Res_\theta(x)=0$
x_1	0.0012	0.0244	0.0905	0.0318
x_2	0.0598	0.1226	0.2132	0.1442
x_3	0.1830	0.2816	0.3692	0.2992
x_4	0.3527	0.4781	0.5447	0.4810
x_5	0.5455	0.6816	0.7177	0.6678
x_6	0.7328	0.8572	0.8652	0.8356
x_7	0.8849	0.9709	0.9711	0.9629

In Table 6, the values of concentration in the input and the output of the reactor for the non-isothermal and stationary case are compared with the results obtained by Finlayson (1972), using the parameters values: $Da = 3.36$, $m = 2$, $Pe_m = Pe_h = 2$, $\gamma = 17.6$ and $\lambda = 0.056$. The results in Table 6 show that the three methods are equivalent, but the method of moments is slightly superior to OCM and Galerkin method.

Comparing the points where the residual function is zero (collocation points) for the methods of moments and Galerkin, considering the same set of parameters used in the previous case (except the value of Pe_m that is now equal to 8), presented in Table 7, it can be observed that their location is not the same for the method of moments and the Galerkin method, and they are not the same for mass and energy balances. This is a new feature of the proposed methodology when compared with the classical orthogonal collocation method, where the locations of the collocation points are fixed and are the same for all discretized variables.

For the non-isothermal and transient case, the methodology was applied using 8 internal quadrature points and considering the same set of parameters used in Table 6 (Finlayson, 1972). We consider the start-up of the reactor, i.e., $y_{initial}(x) = 0$ and $\theta_{initial}(x) = 1$.

Fig. 11 presents the concentration profile of the reactor for the application of 8 internal points of quadrature. Small oscillations were observed at the beginning of the integration. These oscillations are related to the suddenly change in the flat initial profile of the problem that can hardly be well approximated by polynomial functions without a mesh refinement.

**Fig. 11.** Concentration profile in the transient and non-isothermal fixed-bed reactor, obtained by the application of the Galerkin method with 8 internal points of quadrature.**Fig. 12.** Normalized residual of the mass balance in the fixed-bed reactor at different times for non-isothermal transient model when applying the Galerkin method.

Another interesting characteristic of the proposed methods is the dynamical location of the collocation points, as can be observed in Fig. 12. This figure shows the dynamic profiles of the normalized residual function of the mass balance during the start-up of a fixed-bed reactor when the Galerkin method was applied. Similar behavior was observed when the method of moments was applied.

In this application the adaptive nature of both methods can be more clearly visualized. This adaptability is a consequence of the dependence of the residuals at the internal points to the value of the residuals at both boundaries.

4. Conclusion

One of the greatest challenges for the application of the orthogonal collocation is the appropriate selection of the orthogonal polynomial that ensures null average weighted residuals, which is null only in very simple and unrealistic examples. The selection of the orthogonal polynomial is directly related with the accuracy of the discretization procedure, since the accuracy of the methodology depends on the location of the collocation points in the problem domain that are the roots of the orthogonal polynomial.

The most notable aspect of the proposed procedures is that, by improvements in the usual procedures of numerical quadrature, it was possible to establish a direct connection between the residuals at the internal discrete points with the residuals at the boundaries. This aspect improve the usual method of polynomial approximation, since the structure of the resulting discretized equations are similar to the equations that results from applying the classical form of the orthogonal collocation method, based on criteria of average weighted residuals.

This work demonstrated that the implementation of the OCM, using as collocation points the roots of Jacobi polynomials, to solve the reaction-diffusion problem in a catalyst particle and the fixed-bed reactor model, considering in both cases isothermal operation and first order reaction, is unable to reproduce the methods of moments and Galerkin. This aspect contributed in favor of the proposed methodology, since the procedure developed was able to closely approach the method of moments and the Galerkin method in a simple way, where it is only necessary to identify the roots of Jacobi polynomials and the weights of the corresponding quadrature.

The results also showed that the procedure of discretization presents an adaptation to model parameter variations and also change with the type of the boundary conditions. This behavior is more clearly identified in problems with no axial symmetry. Moreover, we verify that the points where the residue function nullify, for distinct dependent variables, are not the same, as well as there are mobility of these points in transient problems. It is important to emphasize that in the classical form of the OCM, the collocation points do not present any mobility and are independent of the model parameters and boundary conditions.

The observed oscillations in some examples are characteristics of application of polynomial approximation in problems that presents high gradients. This unrealistic oscillation is not caused by the proposed procedure and appears in applications of the orthogonal collocation, moments and Galerkin methods. For this particular situation, the increase of collocation points is not the best alternative to improve the quality of solution. In this case is advisable the utilization of adaptive mesh procedure or the application of the MWR on subdomains.

Appendix A. Improved Gauss-Lobatto quadrature method

$$\int_0^1 (1-x)^\alpha x^\beta f(x) dx \cong \sum_{k=0}^{n+1} H_k f(x_k) + \frac{1}{(2n+2)!} \left. \frac{d^{2n+2} f(t)}{dt^{2n+2}} \right|_{t=\xi} C_n^{(1+\alpha, \beta+1)}$$

where the abscissas of the quadrature are $x_0=0$, $x_{n+1}=1$ and $0 < x_1 < x_2 < \dots < x_n < 1$ are the n roots of the Jacobi polynomial $p_n^{(\alpha+1, \beta+1)}(x)$, $H_k = \int_{x=0}^{x=1} [\ell_k(x)]^2 dx$ for $k=0, 1, \dots, n+1$ are the quadrature weights, and:

$$C_n^{(\alpha+1, \beta+1)} = \int_0^1 (1-x)^{1+\alpha} x^{1+\beta} [p_n^{(1+\alpha, 1+\beta)}(x)]^2 dx.$$

When $f(x)$ is a polynomial function of x of degree less or equal to $2n+2$, we have: $\frac{1}{(2n+2)!} \left. \frac{d^{2n+2} f(t)}{dt^{2n+2}} \right|_{t=\xi} = a_{2n+2}$, where a_{2n+2} is the $(2n+2)$ th coefficient of the polynomial, and the integral:

$$\int_0^1 (1-x)^\alpha x^\beta f(x) dx = \sum_{k=0}^{n+1} H_k f(x_k) + a_{2n+2} C_n^{(1+\alpha, \beta+1)}$$

can be exactly computed.

In particular, to calculate the n th weighted residual in Galerkin method in the second type of problem, Eq. (15.1), and considering the Lagrange interpolation of the residual: $\mathbf{R}^{(n+1)}(x) \cong \sum_{k=0}^{n+1} \ell_k(x) \cdot \mathbf{R}^{(n+1)}(x_k)$, we have:

$$\bar{\mathbf{R}}_n^{(n+1)} = \int_{x=0}^{x=1} (1-x)^2 \cdot x^{n-1} \cdot \mathbf{R}^{(n+1)}(x) dx.$$

Identifying that the function $(1-x)^2 \cdot x^{n-1} \cdot \mathbf{R}^{(n+1)}(x)$ is a polynomial function of degree $2n+2$ with the $(2n+2)$ th coefficient equal to:

$$\sum_{k=0}^{n+1} \frac{1}{p'_{nodal}(x_k)} \cdot \mathbf{R}^{(n+1)}(x_k),$$

where $p_{nodal}(x) = \prod_{i=0}^{n+1} (x - x_i)$, we can calculate $\bar{\mathbf{R}}_n^{(n+1)}$ through the improved Gauss-Lobatto quadrature procedure, resulting in:

$$\bar{\mathbf{R}}_n^{(n+1)} = \sum_{k=0}^{n+1} \left[H_k(1 - x_k)^2 \cdot x_k^{n-1} + \frac{C_n^{(1,1)}}{p'_{nodal}(x_k)} \right] \cdot \mathbf{R}^{(n+1)}(x_k).$$

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