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Simulation of multi-component mass diffusion pellet model using least squares spectral element method for steam methane reforming process

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Abstract

Mass based pellet model has been solved using least-squares formulation to describe the evolution of species composition, pressure, velocity, total concentration, mass diffusion flux in porous pellets for the steam methane reforming (SMR) process. The diffusion-reaction problems are computationally intensive, requiring efficient numerical methods for dealing with them. This paper presents formulation and algorithm of least-squares spectral element method (LS-SEM) for solving multicomponent mass diffusion pellet models. The mass diffusion flux is described according to the rigorous Maxwell Stefan model. The effectiveness factors have been calculated for the SMR process and compared with the literature data. The model evaluations revealed that the least-squares method is well suited for solving the multicomponent mass diffusion pellet models for the SMR process, achieving exponential convergence.

Keyword: SMR; Maxwell-Stefan model; mass based pellet model; LS-SEM

1. Introduction

The sustainable energy supply system of the future features electricity and hydrogen as the dominant energy carriers. Today, almost all hydrogen is produced via steam methane reforming of natural gas.

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Hence, the steam methane reforming is one of the important processes by the Norwegian gas industry for utilization of natural gas. Steam methane reforming (SMR) is a heterogeneous catalyzed process where methane and steam react over a nickel-based catalyst at high temperatures to produce synthesis gas which is basically a gas mixture of H_2, CO and CO_2. The two reformer reactions (I), and (II) and the water-gas shift reaction (III) are the most important reactions when methane is converted in the presence of steam to yield synthesis gas. The three main reactions in a SMR are represented by following equations [1]:

$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g) \qquad \Delta H_{298} = 206.2\,\text{kJ/mol} \tag{I}$$

$$CH_4(g) + 2H_2O(g) = CO_2(g) + 4H_2(g) \qquad \Delta H_{298} = 164.7\,\text{kJ/mol} \tag{II}$$

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \qquad \Delta H_{298} = -41.5\,\text{kJ/mol} \tag{III}$$

In this study the kinetic expressions were taken from literature. The reforming and shift reaction kinetics for the SMR process were obtained using Langmuir-Hinshelwood methodology by Xu and Froment [1].

Mathematical modeling of intraparticle mass- and heat transfer in porous pellet has been studied by many researchers. Elnashaie and Abashar [2] developed a mathematical model to study the phenomena of diffusion and chemical reactions in porous catalyst pellets for steam methane reforming process. They have compared the rigorous dusty gas model to the simpler Wilke-Bosanquet model. However, in their model they have taken the assumptions of steady state, negligible viscous flow and isothermal condition. We have focused a mass based pellet model with Maxwell-Stefan kinetics. Following established practice for heterogeneous catalytic reaction systems, the internal η - and overall Ω effectiveness factors were defined in our study [3].

In recent years, the work by Bochev [4] has shown the applicability of the least-squares spectral method (LSM) to solve engineering problem equations. Sporleder et al. [5] have solved fixed bed reactor model using the LS-SEM. Dorao and Jakobsen [6] applied least-squares method to solve population balance problems. This paper presents the formulation and the algorithm of the LS-SEM to solve the diffusion-reaction pellet model. The SMR is a very important process, known to be strongly diffusion limited. It has been studied extensively by many researchers and a variety of numerical methods applied to deal with the strong concentration gradients. Orthogonal collocation [7], in particular has been found to be an adequate method that is now routinely used in diffusion-reaction problems. But in this paper we have applied the LS-SEM method to solve the diffusion-reaction problem in a porous pellet to check the suitability of the method on the diffusion reaction problem.

The main goal of this paper is to check the suitability of LS-SEM for multicomponent mass diffusion pellet model.

2. Mathematical Model Formulation

In this study we have used a general model for the pellet in which the reactions take place on active sites within the porous body which represents an assembly of individual grains or channels. A mean pore diameter is assumed and the ratio between the porosity and tortuosity is used to characterize the fixed structure of the pellet. Possible pellet structural changes are not considered. Time dependent mass based pellet model, containing the multicomponent Maxwell-Stefan diffusion flux and including convection times have been given by Rout et. al. [8]. The initial- and boundary conditions given by Rout et. al. [8]

have been applied in the model equations. A system of non-dimensionalized model equations is used in the simulations.

3. The least-squares spectral method (LSM)

The basic idea in the LSM is to minimize the integral of the square of the residual over the computational domain. Consider the generalized formulation of an arbitrary set of partial differential equations and boundary conditions:

$$\mathrm{L}\mathbf{f} = \mathbf{g} \quad \text{in} \quad \Omega \tag{1}$$

$$\mathrm{B}\mathbf{f} = \mathbf{f}_\Gamma \quad \text{on} \quad \Gamma = \partial\Omega \tag{2}$$

In which Ω denotes the domain, $\partial\Omega$ indicates the boundaries of the domain and $\mathbf{f}$ is the unknown function. Here, we assume that L is a linear operator which corresponds to the system of equations and B is the boundary condition operator determining the problem domain.

Since the residual form of the equations (1) and (2) are $R_\Omega = \mathrm{L}\mathbf{f} - g$ and $R_\Gamma = \mathrm{B}\mathbf{f} - f_\Gamma$, the norm-equivalent functional may be written as

$$\mathrm{J}_N(\mathbf{f}_N) = \frac{1}{2}\int_\Omega \left(\mathrm{L}\mathbf{f}_N - \mathbf{g}\right)^2 d\Omega + \frac{1}{2}\int_\Gamma \left(\mathrm{B}\mathbf{f}_N - \mathbf{f}_\Gamma\right)^2 d\Gamma. \tag{3}$$

Furthermore, the function $\mathbf{f}(x)$ can be approximated by a truncated series expansion adopting nodal basis like,

$$\mathbf{f}(x) \approx \mathbf{f}_N(x) = \sum_{j=0}^{N} \mathbf{f}_j h_j(x) \tag{4}$$

where $\mathbf{f}_j$ is the basis coefficient associated with the basis function $\mathrm{h}_j(\mathrm{x})$. In nodal base, the basis functions consist of Lagrangian polynomials through Gauss-Labatto-Legendre (GLL) collocation points. Due to nodal basis property, the basis coefficient $\mathbf{f}_j$ is equal to the value of the discrete solution $\mathbf{f}_N(x)$ at the GLL points (nodes) x_j, i. e., $\mathbf{f}_j = \mathbf{f}(x_j)$

Introducing solution function expansion and minimizing the norm-equivalent functional, we found:

$$\frac{\partial}{\partial f_k}\frac{1}{2}\int_\Omega \left(\sum_{j=0}^{N} \mathbf{f}_j \mathrm{L}h_j - \mathbf{g}\right)^2 d\Omega + \frac{\partial}{\partial f_k}\frac{1}{2}\int_\Gamma \left(\sum_{j=0}^{N} \mathbf{f}_j \mathrm{B}h_j - \mathbf{f}_\Gamma\right)^2 d\Gamma = 0, \tag{5}$$

where $\Omega = [x_{min}, x_{max}] \times [y_{min}, y_{max}] \times [z_{min}, z_{max}]$ in three dimensional space. After differentiation, the equation (5) can be written as;

$$\int_\Omega \left(\sum_{j=0}^{N} \mathbf{f}_j \mathrm{L}h_j - \mathbf{g}\right) \mathrm{L}h_k d\Omega + \int_\Gamma \left(\sum_{j=0}^{N} \mathbf{f}_j \mathrm{B}h_j - \mathbf{f}_\Gamma\right) \mathrm{B}h_k d\Gamma = 0 \tag{6}$$

As our aim is to find the value of f_j, the equation (6) can be represented on the form,

$$\int_\Omega \sum_{j=0}^{N} \mathbf{f}_j \mathrm{L}h_j \mathrm{L}h_k d\Omega + \int_\Gamma \sum_{j=0}^{N} \mathbf{f}_j \mathrm{B}h_j \mathrm{B}h_k d\Gamma = \int_\Omega \mathbf{g}\mathrm{L}h_k d\Omega + \int_\Gamma \mathbf{f}_\Gamma \mathrm{B}h_k d\Gamma \tag{7}$$

This statement can be expressed in the inner product form as,

$$\sum_{j=0}^{N}\mathbf{f}_j < \mathrm{L}h_j, \mathrm{L}h_k > + \sum_{j=0}^{N}\mathbf{f}_j < \mathrm{B}h_j, \mathrm{B}h_k > = < \mathbf{g}, \mathrm{L}h_k > + < \mathbf{f}_\Gamma, \mathrm{B}h_k > \quad (8)$$

In the matrix form, the equation 8 can be written on the form:

$$[A]_{kj}\mathbf{f} + [B]_{kj}\mathbf{f} = \mathrm{F}_k + \mathrm{F}_{\Gamma k} \quad (9)$$

$[A]_{kj} = < \mathrm{L}h_j, \mathrm{L}h_k >$, $[B]_{kj} = < \mathrm{B}h_j, \mathrm{B}h_k >$, $\mathrm{F}_k = < \mathbf{g}\mathrm{L}h_k >$ and $\mathrm{F}_{\Gamma k} = < \mathbf{f}_\Gamma, \mathrm{B}h_k >$. Moreover, the matrix $[\mathrm{A}]_{kj}$ from the equation 9 can then be expressed in the point wise form by the Gaussian quadrature rule:

$$[A]_{kj} \approx \sum_{i_q=0}^{P} w_{i_q}\mathrm{L}h_j(x_{i_q})\mathrm{L}h_k(x_{i_q}) = \sum_{i_q=0}^{P}[\mathrm{L}]_{i_q k}[\Lambda]_{i_q i_q}[\mathrm{L}]_{i_q j} = [\mathrm{L}]_k^T \Lambda [\mathrm{L}]_j \quad (10)$$

where the elements in the matrix L is defined as, $[\mathrm{L}]_{i_q j} = \mathrm{L}h_j(x_{i_q})$. Here, it is noted that w_{i_q} and x_{i_q} are the weights and points of quadrature [9], and Λ is the diagonal matrix containing weights of the quadrature. Hence, the matrix A can be written in the compact matrix form as:

$$A = \mathrm{L}^T \Lambda \mathrm{L} \quad (11)$$

Then, the source vector F_k from equation 9 can be written in the point wise form:

$$\mathrm{F}_k \approx \sum_{i_q=0}^{P} w_{i_q}\mathbf{g}(x_{i_q})\mathrm{L}h_k(x_{i_q}) = [\mathrm{L}]_k^T \Lambda \mathbf{g} \quad (12)$$

So, the vector F can be written in the compact matrix form as:

$$\mathrm{F} = \mathrm{L}^T \Lambda \mathbf{g} \quad (13)$$

3.2 Implementation of LSM to the mass based pellet model

Figure 1 illustrates the algorithm for solving the dynamic pellet model by using the LS-SEM. It starts with initial guess $\mathbf{f}^t$ at simulation time, $\mathrm{t} = 0$. Then, we have divided the whole computational domain into several sub-domains. Further, the non-linear flux expression demands a suitable linearization procedure. Hence, the Picard method is used to linearization procedure [10]. The Picard method, also known as successive approximation iteration, calculates the current value $\mathbf{f}^{k+1}$ from the previous value $\mathbf{f}^k$. $\mathbf{f}^{k+1} = G(\mathbf{f}^k)$, where G is a problem definition function which is the expression of the previous value of $\mathbf{f}^k$. Therefore, the initial guessed value of unknown $\mathbf{f}^k$ has been divided for different elements with linearization. So, the initial guessed value for each element is $\mathbf{f}_e^{t^k}$. Together with initial guessed vale of each element $\mathbf{f}_e^{t^k}$, the linearized operator $\mathrm{L}_e'(\mathbf{f}_e^{t^k})$ for each element with their corresponding source vector $g_e'(\mathbf{f}_e^{t^k})$ are calculated.

Computation of system matrices $A_e'(\mathbf{f}_e^{t^k})$ and $\mathrm{F}_e'(\mathbf{f}_e^{t^k})$ are carried out for each element by the LS-SEM. We have assembled the matrices $A_e'(\mathbf{f}_e^{t^k})$ and $\mathrm{F}_e'(\mathbf{f}_e^{t^k})$ for each element into global system matrices for the whole computational domain, i.e., $A_{k+1}'(\mathbf{f}^{t^k})$ and $\mathrm{F}'(\mathbf{f}^{t^k})$. In the next step, we have solved the overall system matrices to get values of $\mathbf{f}^{t^{k+1}}$. We did update $\mathbf{f}^{t^k}$ with $\mathbf{f}^{t^{k+1}}$ until specified convergence criteria is reached. We have defined two convergence criteria like:

$$\varepsilon_{Residual} = \sqrt{\langle \mathrm{L}'(\mathbf{f}^{t^k})\mathbf{f}^{t^k} - g(\mathbf{f}^{t^k}), \mathrm{L}'(\mathbf{f}^{t^k})\mathbf{f}^{t^k} - g(\mathbf{f}^{t^k}) \rangle} \le 10^{-5} \quad (14)$$

$$\varepsilon_{iteration} = \sqrt{\mathbf{f}^{t^{k+1}} - \mathbf{f}^{t^k}, \mathbf{f}^{t^{k+1}} - \mathbf{f}^{t^k}} \leq 10^{-10} \tag{15}$$

The residual denotes a measure for the overall error obtained for the system of equations discretized by the least squares method. The iteration overall error denotes a measure of the difference in variable values between the second last- and the last preceding iterations. After we have received our specified convergence criteria, we went to next time step. We checked the current simulation time with the specified final simulation time, t_{final}. If both were not same, then, we did update $\mathbf{f}^t$ with $\mathbf{f}^{t+\Delta t}$.

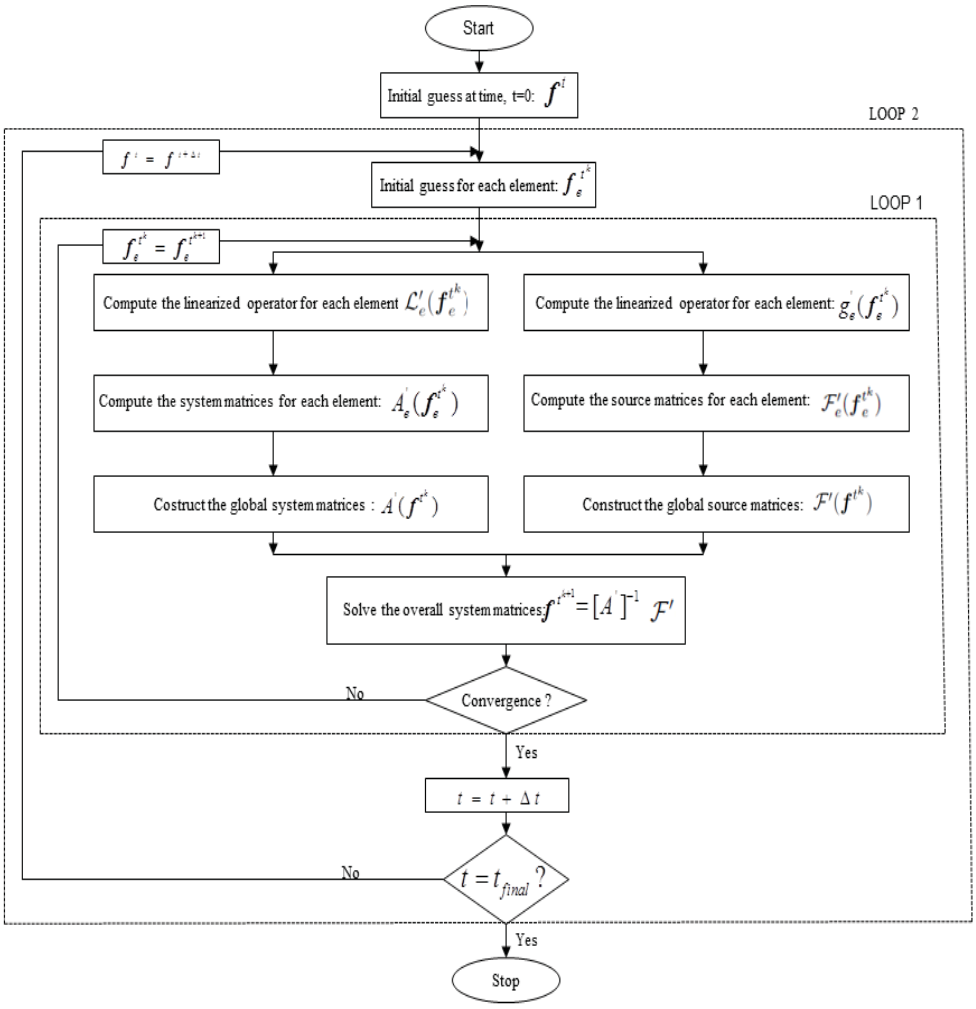


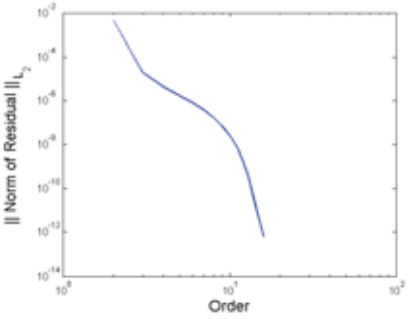
Fig. 1. Integration algorithm for solving the dynamic pellet model by using LS-SEM.

4. Results and Discussion

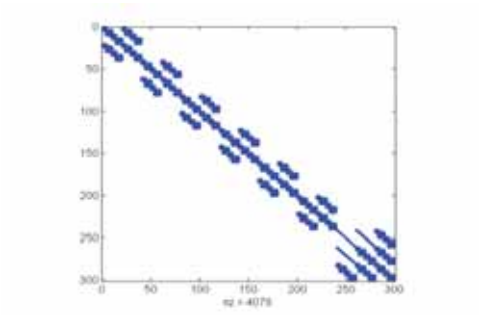
The mass based dynamic model describes the evolution of species mass fraction, pressure, density, temperature, gas velocity, mass diffusion flux, heat flux and convection for the SMR process.

The present paper focuses the algorithm of diffusion model using the LS-SEM and to check the suitability of the LS-SEM for solving diffusion-reaction problem.

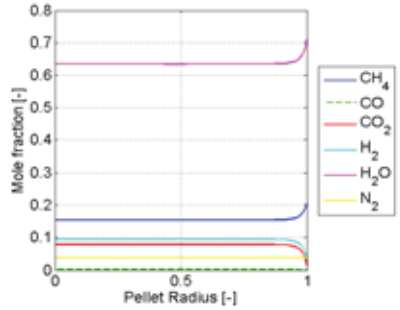
Figure 2(a) shows the dependence of the error with expansion order, N. It has been shown that the error is reduced with an exponential convergence rate. The norm of the residual, shown in the figure 2(a) decreases until reaching a point of limiting accuracy, close to numerical precision. The convergence rate is strongly affected by the capability of the solver, which allows for the attainment of more accurate results.



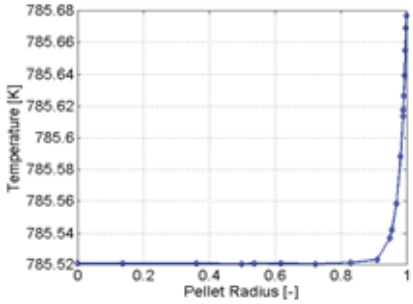
(a) Norm of the residual



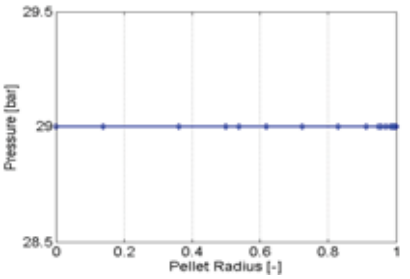
(b) Shape of the problem matrix



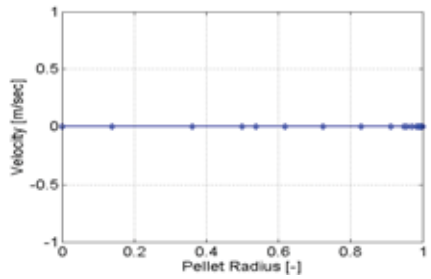
(c) Mass fractions



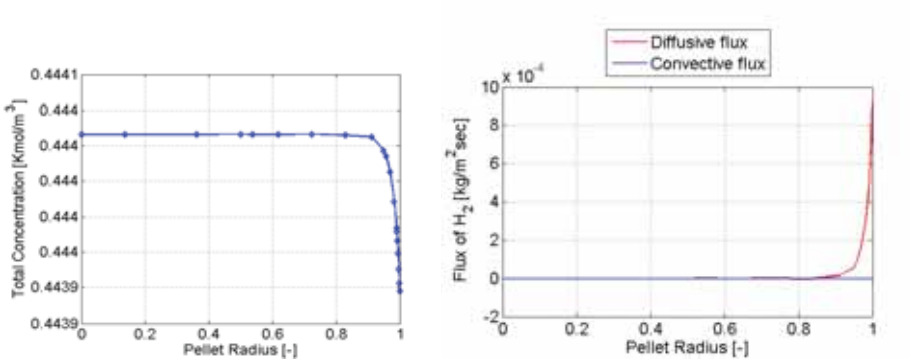
(d) Temperature



(e) Pressure



(f) Velocity



(g) Concentration (h) Flux

Fig. 2. The results of mass based Maxwell-Stefan model

The shape of the problem matrix has been shown in the figure 2(b). When the equations involve an identity operator, the choice of the search affects appreciably the fill-in of the problem matrix, the Lagrange polynomials evaluated at the GLL quadrature points yields zeros and ones. Figure 2(c) shows the steady-state mole fraction profiles of different components across the pellet for the SMR process. In the case of the SMR simulations, the temperature variation between the surface and the center of the pellet is less than 1K which has been shown in the figure 2(d), which are in agreement with the literature [11]. Hence, there is uniform temperature across the pellet. Figure 2(e) shows that there is no variation of pressure from the surface to the center of the catalyst. This validates the assumption of the mass based model as there is no mass formation near the pellet surface. Since there is no pressure gradient, there is no viscous flow and as a consequence no convective flux. As an illustration the convective flux of H_2 has been shown in figure 2(h). Figure 2(h) shows that close to external surface, the diffusion fluxes clearly dominate over the convective fluxes, hence neglecting the convective flux terms in the governing equations is a reasonable model approximation. Figure 2(g) shows that the density increases from the surface to the center as there is a net production of gases in the pellet.

Table 1. Internal and overall effectiveness factors for the SMR process

Reaction	η	Ω
I	0.01	0.0075
II	0.008	0.0033
III	0.07	-2.56

The internal effectiveness factors η and the overall effectiveness factors Ω for the reactions I, II and III have been given in table 1. Ω for the shift reaction is sensitive to the gas composition and it may change the sign at the catalyst surface [3]. The effectiveness factor for the shift reaction may tend towards infinity [3]. For the other two reactions the internal effectiveness factors are in the range of 0.01 to 0.001, which are in agreement with the literature values [12].

5. Conclusion

In this work, mass based mathematical model has been formulated for the SMR process and validated with literature data. The model results generally support the conventional model approximations like uniform temperature across the pellet as the temperature variation between the surface and the center of the pellet is less than 1K and constant pressure within the pellets. Moreover, the magnitude of the diffusion fluxes generally dominates over the convective fluxes.

The LSM is well suited for the solution of the pellet model equations, achieving exponential convergence in the method order. This method has been described and can be applied for the solution of the transport and reactions problems constituting a pellet model.

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