

MODELING OF CATALYTIC REACTORS AS ELLIPTIC PROBLEMS WITH ESSENTIAL BORDER SINGULARITIES

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Abstract. *The modeling of catalytic reactors as sets of elliptic problems with boundary conditions of Dirichlet, Neumann, and mixed types, is studied. The main issue in the modelisation and solution procedure is the nonlinearity and presence of boundary singularities that are essential to these systems.*

After the introductory items, the main objective of this article is treated: the modeling of catalytic reactors as sets of elliptic problems with essential border singularities. A system of elliptic (stationary) advection-diffusion equations with boundary conditions of Dirichlet, Neumann and, also, of really demanding essential singular nonlinear Robin type is posed and an algorithm for their numerical solution is proposed.

This second set of examples are associated to problems drawn from Chemical Engineering (Simplified Catalytic Reactors) with the aim of providing reasonable solutions and acceptable a posteriori error estimates. The modeling and simulation of the reactor is also an issue in this article.

More research is still needed, in particular in the transient initialization modeling by parabolic equations, but the methods appear to be powerful and simple tools for obtaining accurate finite element solutions and error estimation and is able for adaptivity of meshes.

It is interesting to note that, including convex polygonal domains, the method is efficient and it appears to be not related to the order of the numerical algorithm.

1 INTRODUCTION

In this work several properties associated to the modeling of catalytic reactors as sets of elliptic problems with boundary conditions of Dirichlet, Neumann, and mixed types, are studied. The main issue in the modelisation and solution procedure is the nonlinearity and presence of boundary singularities that are essential to these systems. The focus of this work is in first place to study elliptic problems where the domains present essential border singularities in order to assess different types of error estimators. An illustrating example is treated first: the classical test problems based on variants of the Poisson equation with boundary conditions of Dirichlet, Neumann and Robin type.

Then, the main objective of this article is treated: the modeling of catalytic reactors as sets of elliptic problems with essential border singularities. A system of elliptic (stationary) advection-diffusion equations with boundary conditions of Dirichlet, Neumann and, also, of really demanding essential singular nonlinear Robin type is posed and an algorithm for their numerical solution is proposed.

This second set of examples are associated to problems drawn from Chemical Engineering (Simplified Catalytic Reactors) with the aim of providing reasonable solutions and acceptable a posteriori error estimates. The modeling and simulation of the reactor is also a critical issue in this article. In this sense generalizations of the model are proposed as well as the justification of the necessary simplifications that allow the reactor to be included in a more complex structure of chemical engineering reactors.

More research is still needed, in particular in the transient initialization modeling by parabolic equations, but the method appears to be a powerful and simple tool for obtaining accurate finite element solutions and error estimation and is able for adaptivity of meshes.

It is interesting to note that, including convex polygonal domains, the method is efficient and it appears to be not related to the order of the numerical algorithm.

When the singularities are created by the non conforming boundary conditions in a vertex of the polygonal domain the method is also efficient even in the nonlinear case.

1.1 Monolith converters

Monolith converters (i.e. with impermeable walls) have been thoroughly used in the last 25 years as afterburners of combustion engine exhausts and, e.g, for catalytic reactions in petroleum chemistry (see, for example the review of Cybousky¹, and the references therein).

The development objective is to meet clean-air standards established by the different countries in a relatively successful effort for pollution control.

The catalytic oxidation of hydrocarbons, nitrogen oxides, carbon monoxide and other contaminants of exhaust gases of automobiles is performed on the walls of thousands of (near parallel) passages of the monolith converter.

The physical characteristics of the industrial monoliths favors the process modelisation because of the uniformity of the flow, mass and heat transfer conditions across the monolith. So we will concentrate on a single passage model as a representative of the whole device.

One of the critical aspects of the class of converters addressed in this paper is the reduction of the so called cold-start emissions. By those we mean the amount of contaminants not converted during the initial low temperature performance of the device.

The control strategy is to raise the temperature with, e.g., an alternator driven heater. The simplest model for the results of the heater action is a ramp as defined in the article. So we obtain an one parameter boundary control problem (the control strategy then reduces to specify the time for pre-heating ending).

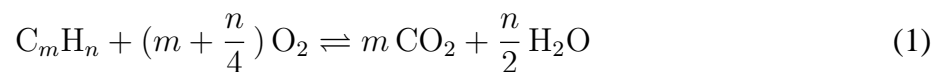
The main parts of this article related to monolith converters begin with the modeling of the problem in cylindrical coordinates introducing several simplifications. The statement of the boundary control problem follows, i.e. the inlet temperature raising and stabilization. The next step is to develop a finite element model of the variational (weak) equations. We set a double mesh algorithm in order to estimate the errors of approximation². Further model simplification and polynomial approximation of nonlinear terms in the heat balance equation is proposed. One of them is to represent the processes on the wall (catalytic) boundary by a global polynomial function of temperature and concentrations. A brief study of the stationary state equations (elliptic) and approximate solutions is performed in order to exemplify the reactor behavior. At this stage is necessary to specify the whole set of physical constants. Determination of inlet heating policies is necessary, resulting in a cold start heating process till an optimal desired temperature and then in approximations of heat and molar distributions. With an approximate initial temperature distribution we calculate the molar distributions of the reacting chemical species, and then we recalculate the temperatures in a stable process simulation. We then estimate the approximation errors in the case of the stationary state model.

When the objective is to study the regularity of solutions it is necessary to simplify the model because the substantive mathematics for the treatment of nonlinear systems of partial differential equations is lacking.

2 BASIC MODEL

We model a single passage of the monolith.

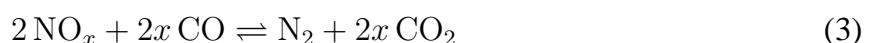
The hydrocarbon oxidation can be represented by



(e.g., for propane: $m = 3$, and $n = 8$), the carbon monoxide combustion



and the nitrogen oxides elimination



For simplicity we do not take into account the reactions for NO_x elimination.

The advection-diffusion molar balance for the chemical species i , $i = 1:s$, in the r reactions, reads^{3;4;5}

$$\nabla(D_i \rho \nabla Y_i) - \rho V \nabla Y_i - \sum_{j=1}^r \nu_{ij} R_{jH} = \frac{\partial(\rho Y_i)}{\partial t} \quad (4)$$

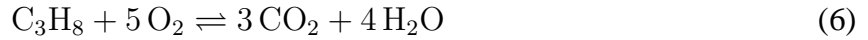
where Y_i denotes the molar fraction of species i , $\rho = P/R_g T$ is the density, T is the absolute temperature, R_g the ideal gas constant, and P the pressure (so we suppose negligible pressure drop); R_{jH} is the rate of the homogeneous (H) j^{th} reaction, and ν_{ij} the matrix of stoichiometric coefficients. The species diffusivities $D_i = D_i(T)$, are, in general temperature dependent. The advection term includes the velocity V of the air flux in the tube.

The heat balance reads^{3;4}

$$\frac{1}{\rho C_p} \nabla(K \nabla T) - V \nabla T - \sum_{i=1}^s \frac{M_i \Delta H_i}{\rho C_p} \sum_{j=1}^r \nu_{ij} R_{jH} = \frac{\partial T}{\partial t} \quad (5)$$

where the thermal diffusivity $K = K(T)$ is temperature dependent, M_i are the molecular weight, and ΔH_i the enthalpy of species i . The specific heat of the gas is C_p . So we have a system of problems similar to the called second boundary value problems⁶.

For example, in the case of the oxidation of propane with oxygen in air (1 atm), the reaction is



and the previous variables read: $Y_1 = Y_A$, molar fraction of propane, Y_O , molar fraction of oxygen, and the kinetics of homogeneous (H) and heterogeneous (p, wall) reactions are

$$R_{AH} = A_H e^{-\frac{E_H}{R_g T}} \left(\frac{P}{R_g T}\right)^2 Y_A Y_O \quad (7)$$

and

$$R_{Ap} = A_p e^{-\frac{E_p}{R_g T}} \frac{P}{R_g T} Y_A \quad (8)$$

where A_H and A_p are the preexponential (Arrhenius) factors, and E_H and E_p are the activation energies of the homogeneous and heterogeneous reactions

The cylindrical symmetry allows us to set boundary conditions in the four sides of a rectangular half section of the tube. In the inner side and the outlet side we pose natural (Neumann) conditions. On the wall side, where the catalytic reaction actually performs, is necessary to consider the heterogeneous reaction rates (faster than the homogeneous ones at operation temperatures) and the heat production (chemical reactions) and heat dissipation on the monolith. In the inlet side the conditions are essential (Dirichlet) and it is necessary to know the molar fractions and temperature of the gas.

2.1 Weak Formulation

We transform the conservation equations to cylindrical coordinates (r, φ, z) , and, based on the supposed radial symmetry we are only concerned with r and z . A further dimensional reduction leads to the variables η and ξ ($r = R\eta, z = L\xi$). The weak Galerkin formulation in the new variables $u = T$ and $w_i = Y_i, i = 1:s, s$ being the number of chemical species, is then set ($\psi \in H^1(\Omega)$ is a test function, Ω being the unit square, and H^1 the Sobolev space of distributions of square integrable as well as their first derivatives).

The boundary and initial conditions are, for $i = 1:s,$

$$w_i = Y_{i0}, u = T_0, \xi = 0 \text{ (inlet)} \quad (9)$$

$$\frac{\partial w_i}{\partial \xi} = 0, \frac{\partial u}{\partial \xi} = 0, \xi = 1 \text{ (outlet)} \quad (10)$$

$$\frac{\partial w_i}{\partial \eta} = 0, \frac{\partial u}{\partial \eta} = 0, \eta = 0 \text{ (center)} \quad (11)$$

$$-\frac{D_i}{R} \frac{\partial w_i}{\partial \eta} = \sum_{j=1}^r \nu_{ij} A_{jp} e^{-\frac{E_{jp}}{R_g u}} w_i, \frac{K}{R} \frac{\partial u}{\partial \eta} = Q(u, w_1, \dots, w_s), \eta = 1 \text{ (wall)} \quad (12)$$

$$w_i = Y_{i,ini}, u = T_{ini}, t = 0 \text{ (start)} \quad (13)$$

where $Q(u, w_1, \dots, w_s)$ models the heat balance in the wall.

The mass balance for species i ($i = 1:s$) leads to a set of equations that we omit for reasons of space, they lead to eqs. 29–38, and the heat balance to a set of equations that lead to eqs. 39–47, the last ones are included because they are approximated by polynomials in the sequel,

$$\frac{1}{R^2} \int_0^1 \int_0^1 \frac{R_g}{PC_p} \frac{\partial \psi}{\partial \eta} K(u) u \frac{\partial u}{\partial \eta} \eta d\eta d\xi \quad (14)$$

$$+ \frac{1}{R^2} \int_0^1 \int_0^1 \frac{R_g}{PC_p} \psi \frac{\partial u}{\partial \eta} K(u) \frac{\partial u}{\partial \eta} \eta d\eta d\xi \quad (15)$$

$$+ \frac{1}{L^2} \int_0^1 \int_0^1 \frac{R_g}{PC_p} \frac{\partial \psi}{\partial \xi} K(u) u \frac{\partial u}{\partial \xi} \eta d\eta d\xi \quad (16)$$

$$+ \frac{1}{L^2} \int_0^1 \int_0^1 \frac{R_g}{PC_p} \psi \frac{\partial u}{\partial \xi} K(u) \frac{\partial u}{\partial \xi} \eta d\eta d\xi \quad (17)$$

$$+ \frac{2}{L} \int_0^1 \int_0^1 \frac{\bar{V}_0}{T_0} \psi (1 - \eta^2) u \frac{\partial u}{\partial \xi} \eta d\eta d\xi \quad (18)$$

$$+ \sum_{i=1}^s \int_0^1 \int_0^1 \frac{PM_i \Delta H_i Y_O}{R_g C_p} \psi \sum_{j=1}^r \nu_{ij} A_{jH} e^{-\frac{E_{jH}}{R_g u}} \frac{1}{u} w_i \eta d\eta d\xi \quad (19)$$

$$+ \frac{1}{R} \int_0^1 \frac{R_g}{PC_p} \psi Q(u, w_1, \dots, w_s) d\xi \quad (20)$$

$$+ \frac{1}{L^2} \int_0^1 T_0 \psi K(u) \frac{\partial u}{\partial \xi} \eta d\eta \quad (21)$$

$$= - \int_0^1 \int_0^1 \psi \frac{\partial u}{\partial t} \eta d\eta d\xi \quad (22)$$

2.2 Inlet Control

We have reset the problem in the dimensionless domain of coordinates $(\xi, \eta) \in [0, 1] \times [0, 1]$ ($\xi = 0$, being the inlet, $\xi = 1$, the outlet, and $\eta = 1$, the wall side) and we may state the boundary control problem: to optimize the functional

$$J(v) = \int_0^{t_f} \int_0^1 \|CY(1, \eta, t)\|_\alpha^2 d\eta dt + \int_0^{t_f} \int_0^1 \|T(1, \eta, t) - T_{\text{ref}}^o(\eta)\|_\beta^2 d\eta dt \quad (23)$$

$$+ \int_0^{t_f} \int_0^1 \|T(0, \eta, t) - T_{\text{ref}}^i(\eta)\|_\gamma^2 d\eta dt \quad (24)$$

$$+ \int_0^{t_c} \|a(t)\|_\delta^2 dt \quad (25)$$

where $Y(1, \eta, t)$ is the vector of outlet molar fractions for each time t , $0 \leq t \leq t_f$, (t_f is the final time for evaluation), C is a weight matrix for the relative concentrations of outlet contaminants, $T_{\text{ref}}^o(\eta)$ is a reference outlet temperature distribution desirable for optimal performance of the converter, $T_{\text{ref}}^i(\eta)$ is a reference inlet temperature, here 750K, and, for simplicity, $v(t)$ is the temperature in the specification of the inlet Dirichlet boundary condition

$$T(0, \eta, t) = v(t), \quad 0 \leq \eta \leq 1, \quad 0 \leq t \leq t_f \quad (26)$$

i.e. $v(t) = T_{\text{ini}}$ from initial conditions. The function a represents the (alternator) preheating (see, e.g.,⁷). The norms in the functional J involve relative weights $(\alpha, \beta, \gamma, \delta)$ for the terms.

A simple —but realistic,— model for $v(t)$ is, in this problem, $v(t) = 300 + a(t)t$ where $\int_0^{t_c} a(t)t dt \leq C_1$ and $a(t) \leq C_2$, $0 \leq t \leq t_c$ for physical reasons (bounds C_1 and C_2), $[0, t_c]$ being the warm-up interval. Here for simplicity

$$v(t) = \begin{cases} 450 \frac{t}{t_c} + 300 & 0 \leq t \leq t_c \\ 750 & t > t_c \end{cases} \quad (27)$$

In this framework we look for the value of $t_c = \min\{C_1/225, t_c^*\}$ that optimizes the functional and the energy is bounded by the physical constants. Note that the third integral in the functional also contributes to a function of this parameter. The preheating policy is relevant in the startup process and must be taken into account for best simulation results.

2.3 Polynomial FEM

We state a polynomial finite element model in the dimensionless domain. A double mesh approach is adopted, the first coarser than the second, as a start for further extrapolation, domain decomposition, or mixture methods.

2.3.1 The elements

Let $\{K_m^H\}_{m=1}^M$ be a partition by rectangular elements of the domain $\Omega = [0, 1] \times [0, 1]$. Each one of the order H elements K_m^H is further divided in several, order h , rectangular subelements.

We define for each one of the rectangular elements K ^{8:9} of the two grids, the set of bilinear forms $B_1(K) = \{v: v \text{ is bilinear in } K, \text{ i.e. } v(x) = a_{00} + a_{10}x_1 + a_{01}x_2 + a_{11}x_1x_2, x \in K, a_{ij} \in \mathbb{R}, i, j = 0, 1\}$. A bilinear function $v \in B_1(K)$ is uniquely determined by its values $v(a^i)$, $i = 1, 2, 3, 4$, in the corners of the element, and that if K_1 and K_2 are two such elements with the common edge S and the functions $v_i \in B_1(K_i)$ are equal in the vertices of S , then $v_1 - v_2 = 0$ in S (because of $v_1 - v_2$ linearity in S).

We define the space V^H subspace of Sobolev space $H^1(\Omega)$: $V^H = \{v \in C^0(\bar{\Omega}): v|_K \in B_1(K), \forall K \in \{K_m^H\}_{m=1}^M\}$ In this framework the nodal values are global degrees of freedom.

In an analogous way we define the subspace V^h .

We look for the chemical species mass distribution (variables w_i) and the temperature distribution (variable u) represented by their respective values on the nodes. The grid is composed by an array of rectangles ($N_H \times N_K$ or $N_h \times N_k$) defined by axis sides adapted partitions.

2.3.2 The elementary matrices from mass balance

The bilinear test functions ψ let us represent function $w_i, i = 1:s$ and u as

$$w_i = \sum_{m=1}^M w_{im}(t)\psi_m, \quad i = 1:s, \quad u = \sum_{m=1}^M u_m(t)\psi_m \quad (28)$$

where M is the cardinal number of the set of nodes, and the coefficients $w_{im}(t), i = 1:s$ and $u_m(t)$ are dependent on time for each m .

We define the set I of nodal indexes as $I(m)$, with them the element K_m matrix for each chemical species $i, i = 1:s$, is

$$\sum_{\ell \in I} w_{i\ell} \int_{K_m} \frac{1}{R^2} \frac{\partial \psi_k}{\partial \eta} D_i(u) \frac{\partial \psi_\ell}{\partial \eta} \eta d\eta d\xi \quad (29)$$

$$+ \sum_{\ell \in I} w_{i\ell} \int_{K_m} \frac{1}{R^2} \psi_k \frac{1}{u} \frac{\partial u}{\partial \eta} D_i(u) \frac{\partial \psi_\ell}{\partial \eta} \eta d\eta d\xi \quad (30)$$

$$+ \sum_{\ell \in I} w_{i\ell} \int_{K_m} \frac{1}{L^2} \frac{\partial \psi_k}{\partial \xi} D_i(u) \frac{\partial \psi_\ell}{\partial \xi} \eta d\eta d\xi \quad (31)$$

$$+ \sum_{\ell \in I} w_{i\ell} \int_{K_m} \frac{1}{L^2} \psi_k \frac{1}{u} \frac{\partial u}{\partial \xi} D_i(u) \frac{\partial \psi_\ell}{\partial \xi} \eta d\eta d\xi \quad (32)$$

$$+ \sum_{\ell \in I} w_{i\ell} \int_{K_m} \frac{2\bar{V}_0}{LT_0} \psi_k u \frac{\partial \psi_\ell}{\partial \xi} (1 - \eta^2) \eta d\eta d\xi \quad (33)$$

$$+ \sum_{\ell \in I} w_{i\ell} \sum_{j=1}^r \nu_{ij} \int_{K_m} \frac{PY_O}{R_g} \psi_k A_{jH} \frac{1}{u} e^{-\frac{E_{jH}}{R_g u}} \psi_\ell \eta d\eta d\xi \quad (34)$$

$$+ \sum_{\ell \in \bar{I}} w_{i\ell} \sum_{j=1}^r \nu_{ij} \int_{K_m \cap \partial\Omega, \eta=1} \frac{1}{R} \psi_k A_{jp} e^{-\frac{E_{jp}}{R_g u}} \psi_\ell d\xi \quad (35)$$

$$+ \sum_{\ell \in \bar{I}} w_{i\ell} \int_{K_m \cap \partial\Omega, \xi=0} \frac{1}{L^2} \psi_k D_i(T_0) \frac{\partial \psi_\ell}{\partial \xi} \eta d\eta \quad (36)$$

$$+ \sum_{\ell \in I} w_{i\ell} \int_{K_m} \psi_k \psi_\ell \frac{1}{u} \frac{\partial u}{\partial t} \eta d\eta d\xi \quad (37)$$

$$+ \sum_{\ell \in I} w'_{i\ell} \int_{K_m} \psi_k \psi_\ell \eta d\eta d\xi = 0, \quad , k \in I \quad (38)$$

where \bar{I} stands for the border element index assignation.

2.3.3 The elementary matrices from heat balance

The several functions of temperature u appearing in the heat balance equation are approximated by polynomials. For example, in the case of propane oxidation, the function $(\exp(-E_H/(R_g u))/u) = (\exp(-13435/u)/u)$ from the sixth integral (homogeneous chemical reaction) is replaced (approximated) by $p(u) = (-4.754e-9 + 2.309e-11 u - 3.706e-14 u^2 + 1.966e-17 u^3)$ in an analogous way for the following functions of temperature we obtain approximations $p_1(u)$ for $K(u)u(\partial u/\partial \eta)/C_p, \dots, p_5(u)$ for $u(\partial u/\partial \xi), p_{5+j}(u)$ for $\Delta H_i \exp(-E_{jH}/R_g u)/(u C_p)$, for the r values of $j = 1:r$, $\tilde{p}_{r+6}(u)$ for $Q(u, w_1, \dots, w_s)/C_p, p_{r+7}(u)$ for $K(u)(\partial u/\partial \xi)$ (see equations 14-21). With them the variational heat balance element K_m equation reads

$$\int_{K_m} \frac{R_g}{R^2 P} \frac{\partial \psi_k}{\partial \eta} p_1(u) \eta d\eta d\xi \quad (39)$$

$$+ \int_{K_m} \frac{R_g}{R^2 P} \psi_k p_2(u) \eta d\eta d\xi \quad (40)$$

$$+ \int_{K_m} \frac{R_g}{L^2 P} \frac{\partial \psi_k}{\partial \xi} p_3(u) \eta d\eta d\xi \quad (41)$$

$$+ \int_{K_m} \frac{R_g}{L^2 P} \psi_k p_4(u) \eta d\eta d\xi \tag{42}$$

$$+ \int_{K_m} \frac{2\bar{V}_0}{LT_0} \psi_k p_5(u) (1 - \eta^2) \eta d\eta d\xi \tag{43}$$

$$+ \sum_{i=1}^s \int_{K_m} \frac{PM_i Y_O}{R_g} \psi_k \sum_{j=1}^r \nu_{ij} A_{jH} p_{5+j}(u) w_i \eta d\eta d\xi \tag{44}$$

$$+ \int_{K_m \cap \partial\Omega, \eta=1} \frac{R_g}{RP} \psi_k \tilde{p}_{r+6}(u) d\xi \tag{45}$$

$$+ \int_{K_m \cap \partial\Omega, \xi=0} \frac{1}{L^2} \psi_k T_0 p_{r+7}(u) \eta d\eta \tag{46}$$

$$+ \sum_{\ell \in I} u'_\ell \int_{K_m} \psi_k \psi_\ell \eta d\eta d\xi = 0, \quad k \in I \tag{47}$$

Further algebraic manipulation leads to a sparse polynomial equation analogous to eqs 29–38. For example the first integral (q_j is the degree of polynomial p_j)

$$\int_{K_m} \frac{\partial \psi_k}{\partial \eta} \left(\sum_{i=0}^{q_1} c_i \left(\sum_{\ell \in I} \psi_\ell u_\ell \right)^i \right) \eta d\eta d\xi \tag{48}$$

is transformed to a polynomial in terms of the form $u^a = u_{\ell_1}^{a_1} u_{\ell_2}^{a_2} u_{\ell_3}^{a_3} u_{\ell_4}^{a_4}$, where $\ell_i \in I, i = 1:4$, and $a = (a_1, a_2, a_3, a_4) \in \mathbb{N}_0^4, |a| = \sum a_k$ being the monomial degree. Analogous polynomial equations are obtained for the other terms, their programming and resolution resulting easier than their formal statement. A *sparse system of polynomials* is a collection of polynomials of the general form

$$\sum_{a \in A_k} c_{k,a} u^a \tag{49}$$

where the A_k are fixed finite subsets of \mathbb{N}_0^4 .

The coefficients $c_{k,a}$ were the element integrals. The notation and solution methodology follows the lines set by Sturmfels¹⁰. The direct method (based in Gröbner basis) or the homotopy method were alternatively applied depending on the dimension of the whole problem.

2.4 Double mesh error estimation

The setting of a double mesh finite element approach leads to an estimation of local errors.

This estimation of errors is necessary to the development of an adaptive method (in the finite element model mesh), that leads to refinements in the approximation and the quasi-uniformization of the errors with minimal number of elements. In this case the adaptive mesh modification leads to a refinement of the rows of rectangles nearer to the wall.

2.5 Numerical complexity of the model and border singularities

The main difficulty with the model as stated is the numerical complexity with the polynomial representation of the highly nonlinear terms. That leads to the possible lack of stability in the main integration.

In order to assess the solutions regularity of these complex systems of differential equations, the border singularities, that are essential to the basic model, impose a new mathematical difficulty: the theory for this class of highly non linear systems with Robin boundary conditions and nonlinear singularities in the border is not developed enough in order to guarantee the correct posing of the problems and the convergence of the iterative methods that are necessary to deal with the complete problem.

It is possible to obtain numerical solutions and qualitatively estimate the errors of these solutions, but, the goal of proving convergence of the iterative method (adaptive) can only be tractable with models of these systems that are far more simple than those exposed so far.

In the next sections such simplified models are introduced and some results are drawn from them.

3 MATHEMATICAL FORMALIZATION AND SIMPLIFICATION OF THE MODEL

We extract from Kenig's book¹¹ (chapter on open problems): another interesting example of boundary value problems is the so called mixed Dirichlet–Neumann problem. Thus, consider a splitting $\partial\Omega = \bar{\Sigma}_1 \cup \bar{\Sigma}_2$ where Σ_i are Lipschitz subdomains of $\partial\Omega$, $\bar{\Sigma}_1 \cap \bar{\Sigma}_2 = \partial\Sigma_i$. We attempt to prescribe Dirichlet data f_1 on Σ_1 , and Neumann data f_2 on Σ_2 , i.e. solve

$$\Delta u = 0 \quad \text{in } \Omega \quad (50)$$

$$u|_{\Sigma_1} = f_1 \quad (51)$$

$$\frac{\partial u}{\partial \bar{N}}|_{\Sigma_2} = f_2 \quad (52)$$

When $f_2 \in L^2(\Sigma_2)$, and f_1 is the restriction to Σ_1 of a function $f_1 \in W_1^2(\Omega)$, it is possible to use the Lax–Milgram lemma to find a variational solution to 50–52 which belongs to $W_1^2(\Omega)$. If f_1 is the restriction of a function in $W_1^2(\partial\Omega)$ to Σ_1 , it might be reasonable to expect that $(\nabla u)^* \in L^2(\partial\Omega, d\sigma)$. Unfortunately, this can be false even when Ω is smooth.

We have seen that the catalytic reactor models are associated with partial differential equations and advection–diffusion systems with mixed boundary conditions. The chemical reactions are concentrated in boundary subsets (location of catalytic substances) with the consequence that there are numerical and mathematical singularities that have a profound effect in the solutions properties.

So, because the boundary singularities influence the process of error estimation (for adaptive algorithms) that are oriented by our group towards the mixed mesh methods for systems of equations, it is necessary to simplify the models towards a balanced equilibrium between the representation of the chemical problem and the ability of these methods to detect the singularities and to converge to the desired solution.

3.1 Monolith catalytic reactors revisited

Monolith reactors are particularly suitable for carrying out fast reactions in applications where space is at a premium, e.g., in car exhausts, fuel cell reforming.

Monolith reactors are divided into a number of channels. Reactions take place both in the fluid bulk and, primarily, on the catalyst-coated inner surfaces of the channels (see Fig. 1). Flow in the channels is laminar, and significant gradients in temperature and concentrations of reactants and products exist between the bulk fluid and the surface. Substantial heat transfer also takes place along the solid walls of the channels. When the thickness of walls is an issue there appear new porous flow additional PDE to the system of equations. In this work, thin walls are supposed.

The modelling of monolith reactors can be based on an understanding of the complex interactions between the reaction, mass and heat transfer and fluid flow phenomena. A first-principles approach appear in first approximation to be essential for predictive models that can quantify the effects of design and operating decisions on reactor performance. The effective utilization of such predictive models could lead to significant commercial benefits such as reduced time-to-market, better utilization of precious metal catalysts, higher efficiency of conversion, and better and more reliable reactor performance under a wide range of operating conditions. Paradoxically, from the mathematical point of view, instead, more simplified models are in order. The objective is to make tractable the regularity of solutions and *a posteriori* error estimation problem that are necessary to guarantee convergence of methods.

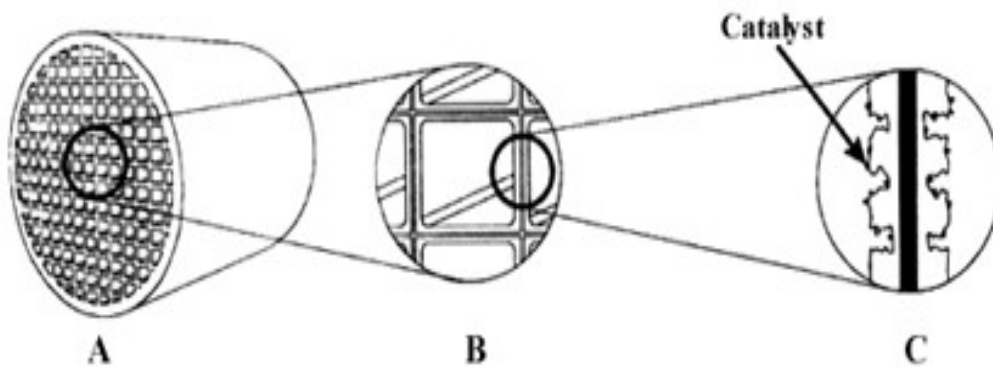


Figure 1: (A) Monolithic reactor, (B) Channel wall, (C) Porous ceramic (washcoat) with catalyst

The main issues are:

1. Catalytic reactor modeling
2. Parabolic evolution equations
3. Elliptic stationary state equations
 - (a) Geometry simplification

- (b) Only one species (system of two equations)
- (c) Linearization or polynomial modeling
- 4. *A posteriori* error estimation
- 5. Mixed mesh error estimation
- 6. Mesh refinement
- 7. Boundary control (temperature)

The models have to be able to represent the main industrial monoliths properties:

1. Flow and heat and mass transfer uniformity
2. Impermeable walls
3. Thousands of subparallel tubes in the monolith converter
4. Low pressure drop
5. Approximately cylindrical symmetry

So the basic dimensionless and simplified system of equations (stationary state) are:

- Concentration

$$-\nabla(f_1(u)\nabla w) + c_1 \frac{1}{u} \vec{v} \nabla w + F_1(u)w = 0 \quad (53)$$

- Temperature

$$-\nabla(u\nabla u) + c_2 \frac{1}{u} \vec{v} \nabla u + F_2(u)w = 0 \quad (54)$$

- Boundary condition on concentration

$$-\frac{\partial w}{\partial \eta} = G_1(u)w \quad (55)$$

- Boundary condition on temperature

$$-\frac{\partial u}{\partial \eta} = -G_2(u)w + G_3(u) \quad (56)$$

- Properties $f_1, F_1, F_2, G_1, G_2, G_3$ monotone increasing functions

The last properties of the model defining functions tell us that monotone operator properties are applicable, so one of the first steps towards solution regularity is completed.

3.1.1 Modeled physicochemical processes

The main modeled processes are:

1. Catalytic reaction
2. Channel reaction
3. Mass and heat transference between gas and channel walls
4. Heat and mass convection in the gas
5. Heat conduction in the channel walls
6. Internal radiation heat exchange between walls
7. Heat exchange between walls and environment

3.1.2 Test problem (concentration)

A simplified test problem is included in this section in order to show a complete and analytic solution that can be used for comparison purposes. It also shows the simplest equation for this catalysis problem:

$$(b - \Delta)w = 0 \quad \text{in } \Omega \quad (57)$$

$$w = 1 \quad \text{in } \Gamma_1 \text{ (inlet)} \quad (58)$$

$$w_\eta + aw = 0 \quad \text{in } \Gamma_2 \text{ (top)} \quad (59)$$

$$w_\eta = 0 \quad \text{in } \Gamma_3 \text{ (outlet) and } \Gamma_4 \text{ (center)} \quad (60)$$

The solution can be stated as a series with the:

Eigenvalues from: $\lambda_k \sin \lambda_k = a \cos \lambda_k$, $\lambda_k : (k - 1)\pi + \varepsilon_k$, $\varepsilon_k \simeq \frac{a}{\lambda_k}$, $k > 4$
and

$$w(x, y) = \sum_{k \neq 0} \frac{2a \cos \lambda_k}{a \cos^2 \lambda_k + \lambda_k^2} \frac{\cosh \sqrt{b + \lambda_k^2}(L - x)}{\cosh \sqrt{b + \lambda_k^2}L} \cos \lambda_k \quad (61)$$

4 SYSTEMS OF ELLIPTIC EQUATIONS

In this section a slightly complex model is presented and solved. The main feature is that convergence of the coupled equations iterative scheme is obtained, associated to the error estimation needed to adaptivity and mesh refinement. Monolith catalytic reactors can be modelled by systems of partial differential equations as was stated in the previous section. These equations represent the mass and energy balances inside the reactor. The complete and detailed system, as shown, is so complex that several simplifications are in order for a mathematical study of the principal characteristics and properties of the original system.

The first simplifications (they are not essential but very convenient) lead to a system in two spatial dimensions (radial symmetric submodels) and only one species to be treated, so we have two equations one for the mass balance of this species and the other for the heat balance of the reactor.

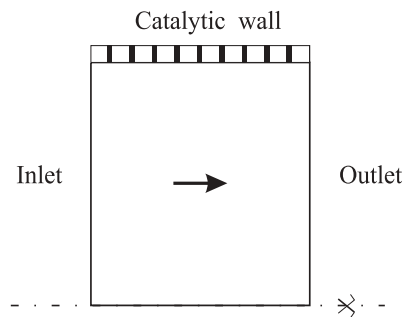


Figure 2: Schematics of the catalytic reactor domain.

The first steps in the mathematical analysis of the problem are towards the study of the equations in an uncoupled form. For them we perform determination of the ranges for the approximated solutions and study characteristics of the solutions, if they are monotonic, range of values of operation, etc. The goal is to consider the possibilities in the case of coupling of the equations.

In the domain where the problem is studied the catalytic substance is on one of the walls of the catalytic tube, in this case the upper wall (see Fig. 2). Here the main chemical reaction takes place. The heat transfer processes also are concentrated in this wall. The other portions of the boundary of the domain are the inlet where the values of the temperature and concentration are known, and the other two sides of the unit square where Neumann conditions are imposed.

The length of the reactor is variable. In our examples we take the dimensionless unitary distance for the sake of simplicity. The longer the reactor, the greater the amount of elimination reaction of the target species. The mean length of the reactor can be used as a design parameter.

The simplified equation that models the process: concentration w of a chemical species (e.g. propane) in a oxygen rich atmosphere is

$$-\Delta w + auw = 0 \quad (62)$$

where a is a parameter and u is the temperature of the domain (we take the unit square)
 The boundary condition on the catalytic boundary are

$$\partial w / \partial \eta + buw = 0 \tag{63}$$

where the symbol $\partial w / \partial \eta$ corresponds to the normal derivative of w and b is a parameter. The other boundary conditions are standard as was explained.

The simplified equation for the distribution of temperatures in our domain is

$$-\Delta u + cwu = 0 \tag{64}$$

where c is a parameter.

The Robin boundary conditions on the catalytic boundary are

$$\partial u / \partial \eta - d w u = -f(u) \tag{65}$$

where d es a parameter and $f(u)$ is a function of temperature u (heat transfer processes)

In order to solve this problem we use an iterative method. We start with a concentration distribution provided by the uncoupled equation. Then the heat equation is solved and the residues are studied in order to decide if the mesh has to be refined (near the singular vertex) so we obtain a new temperature distribution. The equation of concentrations is then solved (under the new temperature distribution) and the residues are calculated.

The new distributions are compared to the previous two and the process continues till an acceptable level of tolerance.

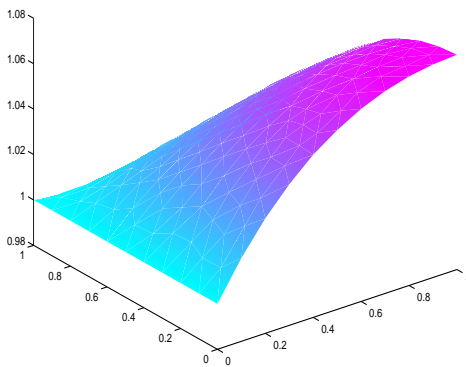


Figure 3: Temperature distribution.

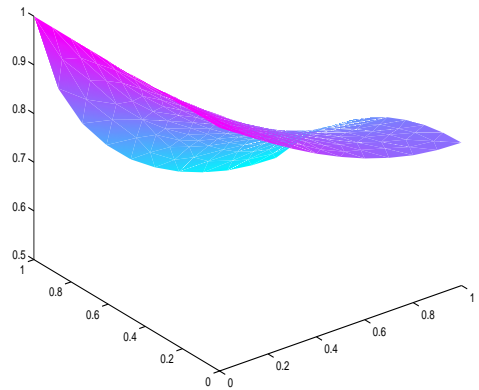


Figure 4: Concentration distribution.

We show a numerical example of this process. The equations are

$$-\Delta u - 0.3wu = 0 \quad \text{in } [0, 1]^2 \tag{66}$$

with the boundary conditions $u = 1$ for all $0 < y < 1$ and $x = 0$, $\partial u / \partial \eta - 0.28wu = -0.3$ for all $0 < x < 1$ and $y = 1$, and homogeneous Neumann conditions in the other sides, and

$$-\Delta w = 0 \quad \text{in } [0, 1]^2 \quad (67)$$

with the boundary conditions $w = 1$ for all $0 < y < 1$ and $x = 0$, $\partial w / \partial \eta + uw = 0$ for all $0 < x < 1$ and $y = 1$, and also homogeneous Neumann conditions in the other two sides

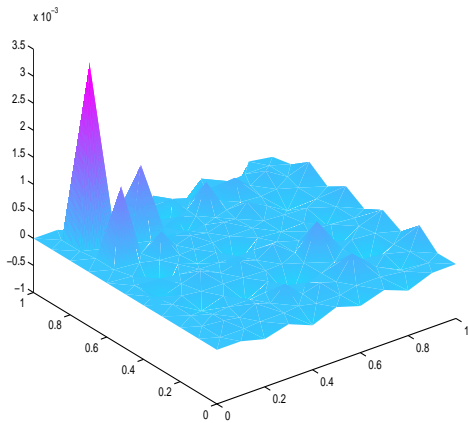


Figure 5: Residues corresponding to the concentrations.

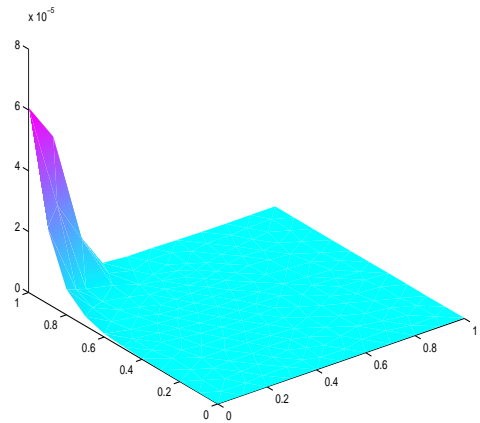


Figure 6: Zienkiewicz-Zhu errors for concentrations distribution.

In Fig. 3 we show the temperature distribution and in Fig. 4 the concentration distribution.

In Fig. 5 we show the residues corresponding to the concentrations. See that the residue map detects the singularity (due to the unmatching of the boundary conditions)

In Fig. 6 the Zienkiewicz-Zhu error estimation is shown, for the same estimation as Fig. 5 It is possible to see the general agreement of both estimations.

In Fig. 7 the concentrations distribution is shown for a problem similar to those treated precedently but with different boundary condition: the catalyst is located in the middle section of the wall (the initial and final section of the wall are inert because the active substance is not present there). The initial mesh is also shown in the plot. In this example the inlet condition is also changed with respect to the previous examples. Only in the inner part of the inlet the component that have to react in the tube is seeded. The conversion is greater on the catalyst wall but the efficiency of the whole process it is not completely effective. The level of conversion can be modified by the longitudinal enlargement of the tube and is one of the parameters that can be adjusted in order to comply with the conversion specification.

5 CONCLUSIONS

Different finite element models of monolith catalytic reactors are developed in this article. The initial ones are fully nonlinear and have to be linearized in order to obtain standard MEF models. Then, polynomial models are presented and those have proven useful for the approximation

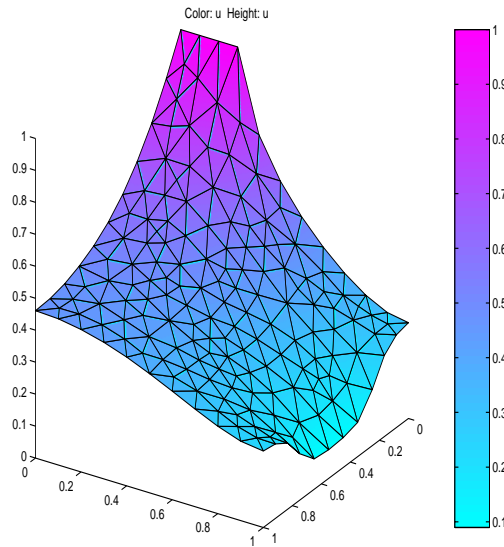


Figure 7: Concentration distribution. Other boundary condition.

of the concentrations and temperatures in the reactor, that are needed to calculate the level of efficiency of the dispositive. The application to these models for catalytic reactors of composite, or mixed, finite element mesh for elliptic problems with border singularities was treated. Two or more finite element meshes are allowed to share the problem domain. These component meshes have different intrinsic accuracies and are affected each by a weight or participation factor. The composite mesh has been used to estimate *a posteriori* discretization errors. A semiquantitative error estimator based in a double mesh algorithm has been proposed and we have shown elsewhere that the pattern of this *a posteriori* error is similar to the exact error (at least in the test problems). More research is still needed, but the composite mesh method appeared to be a powerful and simple tool for obtaining qualitative finite element error estimation and allow for adaptivity of meshes. In this case where the necessity is of border singularity detection the method is specially useful. When the singularities are created by the non conforming boundary conditions in a vertex of the polygonal domain the method is also efficient even in case of nonlinear methods.

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