

Modelling of Post Combustion Monolith Catalytic Reactor for the Carbon Monoxide Oxidation

Part III. Solving Methods

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Abstract

This third part of the work describes the methods used for solving the systems of differential-algebraic equations of the monolith converter model for the isothermal or adiabatic regimes. The simpler isothermal model is tighten to a single first order differential equation (ODE), which defines implicitly the derivative of the unknown, the concentration of key reactant, the carbon monoxide. However, this equation does not allow an obvious finding of the explicit expression for the derivative, as needed by classical numerical DE solvers (Runge-Kutta, Adams, etc.). Several approaches are then used in order to obtain the solution of isothermal model equation: 1 – its differentiation leading to an explicit second order ODE (with “stand-alone” second order derivative of the unknown), followed by numerical solving with common Runge-Kutta procedure, version for second order ODE; 2 – “Implicit RK-4” which consists of classical RK-4 completed at every step with a root finding algorithm for non-linear algebraic equations; 3 - solving the model algebraic equation for the unknown derivative using mainly Cardano formulae for third degree polynomials, followed by numerical solving with classical RK-4 of the first order explicit ODE thus obtained. The last two methods lead to identical solutions while the first method to a slightly different one, the differences being very small (about 10^{-5} %) and due to supplementary truncation error of the “two-fold” numerical integration in method 1. A procedure derived from method 2 is found to be effective for solving the equations of adiabatic converter model. Both models equations were written and solved with mentioned methods in MathCAD (the results will be given in Part IV [1]).

Key words: models, monolith, reactor, carbon monoxide, solving, numerical, methods.

Resolution of Isothermal Reactor Model Equations

The model of the steady-state isothermal monolithic reactor for carbon monoxide oxidation was detailed in the first part of the work [1]. As presented there, the model consists of a differential – algebraic system formed of:

- equations resulted from mass balance and relations describing mass transfer:

$$\Phi \cdot \frac{dg_{CO}}{dx} = \rho_f \cdot k_{fCO} \cdot a_v \cdot (g_{wCO} - g_{CO}) \quad (I-18a)$$

$$-\rho_f \cdot k_{fCO} \cdot a_v \cdot (g_{wCO} - g_{CO}) = R_{wCO} \cdot a_{cat} \quad (I-19a)$$

$$\Phi \cdot \frac{dg_{O2}}{dx} = \rho_f \cdot k_{fO2} \cdot a_v \cdot (g_{wO2} - g_{O2}) \quad (I-18b)$$

$$-\rho_f \cdot k_{fO_2} \cdot a_v \cdot (g_{wO_2} - g_{O_2}) = \frac{1}{2} R_{wCO} \cdot a_{cat} \quad (I-19b)$$

○ rate equation:

$$R_{wCO} = \frac{A \cdot \exp[-E_a/(R \cdot T_w)]}{(1 + Ka \cdot g_{wCO})^2} \cdot g_{wCO} \cdot g_{wO_2} \quad (III-1)$$

with:

$$Ka = B \cdot \exp\left(\frac{D}{R \cdot T_w}\right) \quad (I-17)$$

The meaning of symbols is the same as that given at the end of Part I [1]. Kinetic parameters A , E_a , B , D in the rate equation have constant, known values (Table I-1 in [1]).

Beside the previous main equations, isothermal model also contains: relations for the calculation of oxygen and carbon monoxide mass transfer coefficients, which were presented in Part II-B (equations II-37, [1]).

Based on the simplifying assumption E (see Part I), the invariability of diffusion coefficients on gas phase composition, it readily resulted from equations (II-37) that partial mass transfer coefficients, k_{fCO} , k_{fO_2} , are constant throughout the isothermal monolith. Assumptions E and F in Part I [1] and relation (II-19) [1] show that in isothermal regime the gas phase density, ρ_f , has a constant value too. Relations (II-43), (II-43a, b) and (II-41), (II-41a, b) [1] also specify which are the mentioned constant values mass transfer coefficients and gas phase density get respectively.

The system of differential-algebraic equations (DAE) of the isothermal model has the unknowns CO and O₂ mass molar concentrations, g_{CO} , g_{wCO} , g_{O_2} and g_{wO_2} , and the following initial values:

$$g_{CO,O_2}(0) = (g_{CO,O_2})_0 \quad (I-21)$$

For an isothermal monolith the gas phase temperature, boundary layer and wall temperatures are the same and equal with that of the feed:

$$T = T_w = T_0 \quad (III-2)$$

The values of g_{CO0} , g_{O_20} , T_0 are known, corresponding to the given feed parameters CO, O₂ mass molar concentrations and temperature respectively (Tables II-2, II-1 [1]).

Feed mass flow, G , is also given and hence Φ , the total mass flux at the reactor inlet :

$$\Phi = G / A_s \quad (I-5)$$

Other data in the above DAE such as structural characteristics of the monolith, particularly A_s , a_v and a_{cat} , front cross sectional open surface area, washcoat external (“wetted”) specific surface and specific surface of active catalytic (platinum) sites, are known too (Tables I-1, II-1 in [1]).

The form of equations (I-18)...(I-19) allows elementary algebra manipulations leading to a simpler system of DAE, equivalent with the initial model. As suggested at the end of Part II [1], it is convenient that these operations have the purpose to express variables of the system as functions of key reactant concentration, $g_{CO}(x)$, since for physical properties and transfer coefficients the relations giving their dependence on CO conversion have already been established and, implicitly, the respective functions on CO current concentration $g_{CO}(x)$. Determination of relations expressing the functions on key reactant concentration $g_{CO}(x)$ is thus particularly needed for g_{wi} , $i = CO, O_2$, the mass molar concentrations in the boundary layer arising in the kinetic equation (III-1). All these relations are presented below. For the sake of equation writing simplification, notation omitting independent variable, x - e. g. g_{CO} instead of

$g_{CO}(x)$ -, will be preferred, excepting places where emphasize of mentioned variable dependence on axial coordinated will be sought.

From (I-18a) the next relation readily results:

$$g_{wCO} = g_{CO} + \frac{\Phi}{\rho_f \cdot k_{fCO} \cdot a_v} \cdot g'_{CO}(x) \quad (\text{III-3})$$

where $g'_{CO}(x) = dg_{CO}(x)/dx$. Considering the way for mass transfer coefficient k_{fCO} calculation through equations (II-37), (II-43), (II-43a, b) (see Annex to Part II [1]), relation (III-3) is then able to express boundary layer CO concentration g_{wCO} as a function of bulk gas phase CO concentration, g_{CO} , and properties of the same phase only.

Dividing equations (I-19a) and (I-19b) side by side and drawing out g_{wO_2} , the CO concentration in the boundary layer at catalyst surface, one obtains:

$$g_{wO_2} = g_{O_2} + \frac{1}{2} \cdot \frac{k_{fO_2}}{k_{fCO}} \cdot (g_{wCO} - g_{CO}) \quad (\text{III-4})$$

Substitution of the difference $(g_{wCO} - g_{CO})$ by its expression resulted from (I-18a) transforms (III-4) into:

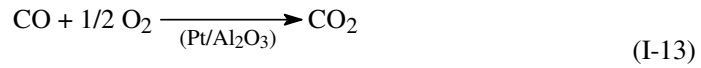
$$g_{wO_2} = g_{O_2} + \frac{1}{2} \cdot \frac{\Phi}{\rho_f \cdot k_{fO_2} \cdot a_v} \cdot g'_{CO}(x) \quad (\text{III-5})$$

The last relation redefines the oxygen concentration in the boundary layer as a function on variables characteristic to the gas phase alone, similarly with (III-3) in the case of CO.

In the first part of the work [1] it was shown that:

$$2 \cdot \frac{dg_{O_2}}{dx} = \frac{dg_{CO}}{dx} \quad (\text{I-20})$$

in agreement with the stoichiometry of the reaction (I-13)



Obvious integration of (I-20) leads to:

$$g_{O_2}(x) = \frac{1}{2} \cdot g_{CO}(x) + \text{const} \quad (\text{III-6})$$

The value of „const” is determined from the initial values assigned to the differential-algebraic system of the model, more precisely from the given feed composition (Tables II-1, II-2 [1]). The following relation between the mass molar concentrations of the two reactants in the gas phase is thus readily obtained:

$$g_{O_2}(x) = \frac{1}{2} \cdot g_{CO}(x) + \frac{\kappa}{2}, \text{ where } \kappa = 2 \cdot g_{O_20} - g_{CO0} \quad (\text{III-7})$$

One may notice that parameter κ is twice the feed O_2 excess with respect to the stoichiometric O_2 amount according reaction (I-13). Particularly, for the given monolith feed with composition specified in Table II-1: $\kappa = 0,1381542 \dots \text{mol} \cdot \text{kg}^{-1}$. With the use of (III-7) for g_{O_2} , relation (III-5) is able to compute g_{wO_2} , the mass molar concentration of oxygen in the boundary layer, depending only on parameters characteristic to the gas phase : g_{CO} , ρ_f and k_{fO_2} , the oxygen partial mass transfer coefficient.

Considering the already established relations described in Part II [1] for gas phase density ρ_f and k_{fCO, O_2} coefficients determination, it can be concluded that for CO and O_2 boundary layer concentrations, g_{wCO} and g_{wO_2} , arising in the kinetic law are now available expressions defining both of them as functions of a single variable, $g_{CO}(x)$, the key reactant concentration in the gas phase. Substitution of these expressions into the rate equation (III-1), use of (I-12a)

$$-\Phi \cdot \frac{dg_{CO}}{dx} = R_{WCO} \cdot a_{cat} \quad (I-12a)$$

and rearrangements of terms lead finally to the algebraic-differential equation:

$$F0 \cdot g_{CO}'(x) + \frac{\left(F1 \cdot g_{CO}'(x) + g_{CO}(x) \right) \cdot \left(F2 \cdot g_{CO}'(x) + g_{CO}(x) + \kappa \right)}{\left[1 + Ka \cdot \left(F1 \cdot g_{CO}'(x) + g_{CO}(x) \right) \right]^2} = 0 \quad (III-8)$$

where

$$F0 = 2 \cdot \frac{\Phi}{a_{cat} \cdot A \cdot \exp[-Ea/(R \cdot T_w)]} \quad (III-8a)$$

$$F1 = \frac{\Phi}{\rho_f \cdot k_{fCO} \cdot a_v} \quad (III-8b)$$

$$F2 = \frac{\Phi}{\rho_f \cdot k_{fO2} \cdot a_v} \quad (III-8c)$$

and Ka being given by (I-17).

In conclusion, the system of the (I-18), (I-19) and (III-1) DAE of the isothermal reactor is equivalent with the sole differential equation (III-8) having $g_{CO}(x)$ as unknown and the initial value (I-21) $g_{CO}(0) = g_{CO0}$.

Compared to the solving procedure used by the authors in a previous work (I-31), one of the advantages of reactor model equations reduction to a single DAE as described above is the possibility to foresee the solution type (unique or multiple, real or complex, singular, etc.) when model variables or data such as feed characteristics are modified. For example, the simulations carried out showed us that the use of the *same* model can be made for reactor feed with substoichiometric O_2 amounts ($O_2 / CO < 0.5 \text{ mol} / \text{mol}$) leading to right solutions which obey conditions (I-22), (I-23), (IV-2) [1]. Extension of model validity to this case is mainly due (and verified *a posteriori*) to the use of equations (III-7) and (III-5) within the model and for its resolution.

Several remarks on equation (III-8) are required:

- as shown in the end of Part II-B [1] based on assumptions E and F in Part I [1], constant values throughout the monolith can be admitted for both gas phase density ρ_f and partial mass transfer coefficients $k_{fCO, O2}$. Therefore parameters $F1$ and $F2$ have constant values for the whole reactor. Since $T_w = T = \text{const.}$, it easily results from (I-17) that $F0$ is constant too. Being more specific, gas phase density and mass transfer coefficients utilized for isothermal model solving are computed with relations (II-19), (II-41), (II-41b) and (II-37), (II-43), (II-43a, b), respectively (see also Annex to Part II-B [1]), and for the reference feed with parameters given in Table II-1 [1] have the following (approximate) values: $\rho_{fa} = 0.918767 \text{ kg} \cdot \text{m}^{-3}$, $k_{faCO} = 0.140908$ and $k_{faO2} = 0.142339 \text{ m} \cdot \text{s}^{-1}$. The corresponding values for $F0$, $F1$, $F2$ found from (III 8a - c) are (approximately): $F0 = 7.360707 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \cdot \text{m}_{reactor}$, $F1_a = 0.0193107 \text{ m}_{reactor}$, $F2_a = 0.0191166 \text{ m}_{reactor}$ and Ka value resulted from (I-17) is $Ka = 12.5073 \text{ kg} \cdot \text{mol}^{-1}$;
- referring to the relations for gas phase density ρ_f and mass transfer coefficients $k_{fCO, O2}$ determination, one may note that whatever the reactor regime (isothermal, adiabatic, isobaric, etc.) parameters $F1$ and $F2$ do not depend on pressure profile along the monolith. Since neither $F0$ is depending on pressure, the solution of equation (III-8), CO gas phase concentration $g_{CO}(x)$, and consequently the whole solution of the initial *model equations* used in the present work are invariable with the pressure inside or at the inlet of the monolith. Moreover, note that independence on pressure holds true even if pressure drop through the monolith channels is not negligible, i.e. when assumption F in Part I [1] is overruled;
- from the same two relations, (II-19) and (II-37) respectively, it results that the ratio between

parameters $F1$ and $F2$ depends neither on monolith temperature nor on its pressure;

d) the two terms (the second being the fraction) in the left hand side of equation (III-8) have units $[(g \text{ concentration})^2] = \text{mol}^2 \cdot \text{kg}^{-2}$.

To the knowledge of the author or of general textbooks concerned with differential equation solving and theory (see for example [2-4] [5a] [14, 15]), differential equation (DE) (III-8) does not have a form allowing a convenient analytical solution, even if independent argument x is missing or someone is appealing to previous b and c remarks. Neither more particular techniques such as variation of parameters or integral transforms do not prove to be effective for an analytical solution in the case of (III-8). Hence we have turned to numerical methods for differential equation solving in order to find out the solution of DE (III-8).

(Numerical) Methods Used for Solving the ODE of the Isothermal Reactor Model

By the Means of the Second Order Derivative of the Unknown, $g_{CO}''(x)$

Equation (III-8), which is equivalent to the isothermal converter model utilized in this work, can be regarded to as an algebraic equation of third degree in the derivative $g_{CO}'(x)$. Common versions of numerical methods for DE solving such as Runge-Kutta need DE to be written in a form with stand-alone highest order derivative of the unknown, but getting an explicit expression of the first order derivative $g_{CO}'(x)$ from (III-8) is yet cumbersome. However, considering that (III-8) is defining the first order derivative as an *implicit* function according to the relation of general form

$$F(x, g_{CO}(x), g_{CO}'(x)) = 0, \quad (\text{III-9})$$

where function F equals the left-hand side of (III-8) and using classical differentiation for the determination of implicitly defined functions (or partial differentiation of composite functions, see for example [5b], [12]), one can get the explicit expression for second order derivative, that is an analytic expression with separated $g_{CO}''(x)$, the second order derivative of the unknown, the carbon monoxide molar concentration in the gas phase. Details of this calculation and the final expression of $g_{CO}''(x)$ thus obtained will be presented in Part V (to be published).

The DE with separated highest order (two) derivative was then numerically solved with the classical RK-4 (fourth order Runge-Kutta) procedure, version for DE of second order. Two initial values were of course needed, the first being (I-21a) already shown. The second is the value of first order derivative at $x = 0$, $g_{CO}'(0) = g_{COd0}$, where g_{COd0} is the root of the algebraic equation resulted from (III-8) or from (III-9) after $g_{CO}(x)$ was set $g_{CO}(0) = g_{CO0}$, according to the same (I-21a). For example, it was thus determined $g_{COd0} = -6,16425028... \text{ mol} \cdot \text{kg}^{-1} \cdot \text{m}^{-1}$ for the monolith reference feed with the parameters specified in Table II-1 [1].

The numerical solution of DE (III-8) computed in this manner is very close to those found with the next two procedures. Differences were small, below $10^{-5} \%$ for a step size $h = 0,001 \text{ m}$, and were attributed mainly to supplementary truncation of the repeated numerical integration.

“Implicit RK-4” Method (see also the Note at the end of this paper)

The implicit Runge-Kutta of fourth order procedure (abbreviated “Implicit RK-4” or “RK-4 I”) was established based on the signification which could be assigned to the ratios $\frac{k_{1j}}{h}$, $\frac{k_{2j}}{h}$, $\frac{k_{3j}}{h}$ and $\frac{k_{4j}}{h}$ in the classical RK-4 algorithm, where by k_{1j} , k_{2j} , k_{3j} and k_{4j} are often

designated intermediary increments of the approximated solution. The four ratios are corresponding to the values of the derivative in the end points of the three subintervals within $[x_j, x_{j+1}]$ step, values which are yet not known in the case of a DAE (or implicit DE). Hence, in addition to ordinary RK-4 algorithm, our „RK-4 I” procedure appeals four times at every j step to a root finding routine in order to numerically solve with respect to k_{1j} , k_{2j} , k_{3j} or k_{4j} the nonlinear algebraic equations resulted from (III-8) by the replacement of $g_{co}'(x)$ with $\frac{k_{1j}}{h}$, $\frac{k_{2j}}{h}$, $\frac{k_{3j}}{h}$ or $\frac{k_{4j}}{h}$ respectively. More details on “RK-4 I” method used for the numerical solving of DAE (III-8) will be found in Part V. Anyhow, the reader may consult for example references [6] [12] [13] on classical RK-4 algorithm. In Part V, “RK-4 I” results will also be compared to those obtained using an Euler procedure adapted to DAE or to those computed by the so-called “Euler-F”, a newly proposed effective procedure for DAE numerical solving.

Pontelides *et al.* [7] introduced the index criterion for DAE classification with respect to their complexity. They defined the DAE index as the minimum number of differentiations needed for the DAE conversion to a set of ODE or DE with separated highest order derivatives. Considering the two solving methods described, the initial system of DAE of the isothermal model can be ranged amongst those with index equal to 1.

Finding Out the Explicit Expression for $g_{co}'(x)$ from Algebraic Equation of Degree III in $g_{co}'(x)$

From DAE (III-8), of third degree in the derivative $g_{co}'(x)$, three explicit expressions of the first derivative can be found with the help of Cardano formulae. These general formulae for analytically finding the roots of the third degree polynomial equation are given for example in [8-11, 16] (or slightly erroneous in [12]). The three-resulted ODE of first order with stand-alone derivative were then numerically solved with classic RK-4 procedure. The real solution thus computed was identical with that given by method 2. Anyhow, DAE (III-8) and its solutions must further be checked for denominator zeroing or singular (particular) solutions. More details about the use of different methods for solving the model equations will be presented in Part V of the work.

Solving DAE System of Adiabatic Reactor Model

As established in Part II-A [1], the model of the adiabatic converter consists of a differential-algebraic system comprising:

- equations resulted from mass balance and mass transfer, which are the same (I-18a, b) and (I-19a, b) specified above;
- rate equations, (III-1) and (I-17). It was shown in the first paragraph that the group of the four equations (I-18a, b) and (I-19a, b) together with the kinetic equations which otherwise form the isothermal model are reducible to a single DAE, namely (III-8);
- equations issued from heat balance and thermal transfer relations, that is relations (II-5)...(II-7), (II-10)...(II-12) [1]. In Part II-A [1] it was proved that all these five relations are equivalent with only two equations, (II-10) and (II-12). Anyway, several reasonable groupings equivalent to both (II-10) and (II-12) are possible from all the (six) available heat relations. The choice of the two equations (II-10) and (II-12) is argued in the same part [1].

Therefore, the model of the adiabatic monolith may be represented by the following basic equations:

$$F0(x) \cdot g_{CO}'(x) + \frac{\left(F1(x) \cdot g_{CO}'(x) + g_{CO}(x) \right) \cdot \left(F2(x) \cdot g_{CO}'(x) + g_{CO}(x) + \kappa \right)}{\left\{ 1 + B \cdot \exp[D/(R \cdot T_w(x))] \cdot \left(F1(x) \cdot g_{CO}'(x) + g_{CO}(x) \right) \right\}^2} = 0 \quad (\text{III-8})$$

$$T'(x) = \frac{\Delta H}{c_{pf}(x)} \cdot g_{CO}'(x) \quad (\text{II-10})$$

$$T_w(x) = T(x) + \frac{\Phi}{a_v \cdot \alpha(x)} \cdot g_{CO}'(x) \quad (\text{II-12})$$

to which are added the relations for the evaluation of physical properties and transfer coefficients. These last relations are briefly reminded downwards for the case of the adiabatic regime. Factors $F0(x)$, $F1(x)$ and $F2(x)$ are computed using (III-8a), (III-8b) and (III-8c), respectively.

The whole of the mentioned equations is setting a system of DAE with three unknowns $g_{CO}(x)$, $T(x)$ and $T_w(x)$ and the initial values

$$g_{CO}(0) = g_{CO0} \quad (\text{I-21})$$

$$T(0) = T_0 \quad (\text{II-9})$$

where g_{CO0} and T_0 are known parameters of the specified reactor feed (Tables II-1, II-2 [1]).

As established in the end of Part II-B [1], based on reactants great dilution (simplifying assumption E in Part I [1]), physical properties and transfer coefficients may be admitted independent on gas phase composition. Their values were approximated with those (designated by subscript a) for a mean gas phase composition, which in its turn was considered to correspond to 50% (0.5) conversion of the key reactant, the carbon monoxide. Subsequent use of assumption F ($p = p_0$, negligible pressure drop [1]) allowed determination of the mentioned mean-on-composition values with the next relations:

$$\rho_{fa}(T) = \rho_f(0.5, T, p_0) = \frac{P_0}{R \cdot T} \cdot Mm_f(0.5) \quad (\text{II-41})$$

$$k_{fi}(T) = k_{fi}(0.5, T, p_0), \quad i = \text{CO}, \text{O}_2 \quad (\text{II-43})$$

$$c_{pfa}(T) = c_{pf}(0.5, T) \quad (\text{II-42})$$

$$\alpha_a(T) = \alpha(0.5, T) \quad (\text{II-44})$$

where $\rho_f(0.5, T, p_0)$, $c_{pf}(0.5, T)$, $k_{fi}(0.5, T, p_0)$ and $\alpha(0.5, T)$ were further calculated with relations (II-19), (II-27), (II-37) and (II-40), respectively. Unlike the case of isothermal reactor, physical properties and transfer coefficients thus computed are *varying throughout the monolith channels in adiabatic regime* since they depend on gas phase temperature as suggested by the above five relations. The reader may also see example in Annex to Part II-B [1].

According to data given in Part II-A [1], the reaction enthalpy ΔH for CO oxidation (I-13) is considered to have a constant value, $\Delta H = \Delta H^o = -283750 \text{ J} \cdot \text{mol}^{-1}_{\text{CO}}$.

Two comments on the system of DAE (III-8), (II-10) and (II-12) can be done :

- above remark b for the case of the isothermal model, the independence on pressure profile, remains valid, hence neither the solution of the adiabatic model equations is influenced by pressure (or particularly by monolith entrance pressure). Like in the isothermal reactor model again, the ratio $F1/F2$ depends neither on pressure nor on gas phase temperature T ;
- the adiabatic monolith factors $F0$, $F1$ and $F2$ in (III-8) are no more constant, but they are functions of channel axial coordinate x since bulk gas phase and boundary layer temperatures, T and T_w , are varying along the monolith. The three factors are depending on temperatures T or T_w in the following manner: $F0$ is varying with the wall temperature T_w according the exponential (III-8a); factors $F1$ and $F2$ are varying with the gas phase temperature T , being proportional to $T^{-3/4}$, as it can be quite readily deduced from the relations given for the

evaluation of gas phase density ρ_f and mass transfer coefficients k_{fCO,O_2} arising in (III-8b,c), namely the above (II-41) and both (II-43) and (II-37), respectively.

Because relation (II-12) is merely defining the boundary layer temperature T_w as a function on gas phase temperature T and on molar concentration g_{CO} , the foregoing system of the three equations (III-8)...(II-10)...(II-12) of adiabatic model may be considered equivalent to one with solely two DAE in the two unknowns $g_{CO}(x)$ and $T(x)$.

Solving with method 1, by the means of explicit expressions for the second order derivatives of the unknowns, $g_{CO}''(x)$ and $T''(x)$, may be in principle applied for the DAE system of the adiabatic reactor model too. But the unreasonably tedious calculus needed for the two second order derivatives makes this method completely impractical. Method 3, through determination of the (explicit) expressions of first order derivatives, $g_{CO}'(x)$ and $T'(x)$, is not usable since algebraic solving of the system (III-8)...(II-10)...(II-12) for the two unknowns $g_{CO}'(x)$ and $T'(x)$ is impossible (transcendental algebraic system, for which root finding using formulae with radicals is not possible).

Among all the three methods applied for the isothermal model, method 3 was therefore the only one that was usable for solving adiabatic model equations. More precisely, a version of "RK-4 I" adapted to a *system of first order DAE*, i.e. RK-4 method for system of first order differential equations whose derivatives are not separable, was applied for the latter model. The mentioned version has essentially the same algorithm, but a procedure for numerical solution finding of a system of two nonlinear equations is called for four times at each step instead the root finding routine for a single equation in one unknown. Details on potential application of method 1 or about advantages and issues of the "RK-4 I" version utilization for adiabatic model solving will be presented in Part V of the work (to be published).

Both models equations were written and solved in Mathcad. The same environment was also employed for carrying out part of algebraic symbolic computation.

Conclusions

Based on simplifying assumptions and using an algebraic computation path rationally chosen, all the initial equations of the isothermal converter model are reduced to a single ordinary differential equation (ODE) of first order with unknown the mass molar concentration $g_{CO}(x)$ of the key reactant, the carbon monoxide. From assumptions E (physical properties and transfer coefficients independent on the CO conversion) and F (negligible pressure drop) [1], it resulted that gas phase density and mass transfer coefficients arising in the mentioned ODE have constant values throughout the monolith channels in the isothermal regime. At the same time, the ODE of the isothermal model is an algebraic polynomial equation of degree III in the derivative of the unknown, $g_{CO}'(x)$. However, finding of an explicit expression for the derivative as needed by the classical routines for ODE numerical solving is not obvious and the ODE of the isothermal model may be thus regarded as defining implicitly the unknown's derivative.

Three methods are applied for isothermal model ODE solving :

1 – finding an explicit ODE with separated highest order (two) derivative of the unknown by differentiation of the isothermal model ODE. The second order ODE is then numerically solved using an RK-4 procedure.

2 – the method we called „RK-4 Implicit” (RK-4 I), which consists of a classic RK-4 completed with a root finding procedure for nonlinear algebraic equations applied four times every integration step ;

3 – solving analytically the algebraic equation of the isothermal model for the unknown the derivative of CO concentration using basically the Cardano formulae for the roots of third degree polynomial and subsequent numerical integration by common RK-4 procedure of the (three) first order explicit ODE resulted.

Beside a DAE which is same with that of the model for isothermal regime, the adiabatic converter model contains two more equations derived from heat balance and transfer as well as relations giving the variation of physical properties and transfer coefficients with the temperature. Among all the three solving methods mentioned, only a method similar to the second proved to be effective in the case of the adiabatic model. According DAE classification proposed by Pontelides *et al.* [7], the models equations can therefore be placed among those with a complexity index equal to 1.

The use of the path followed by the algebraic manipulations reducing the number of equations can be extended to monolith models in which several reactions have to be considered. Thus every rate equation ought lead to a DAE similar to (III-8).

The results for the main distributed parameters characteristic to the steady state isothermal or adiabatic monolithic converter which were computed based on the two models will be presented in the next part [1].

Note

In the absence of other concise term available, we have employed „Implicit RK-4” (RK-4 I) as abbreviation for “RK-4 method for implicit DE” (*i.e.* DE with inseparable highest order derivative). It’s obvious that “RK-4 I” method we have used is still indeed a direct or open method, in a single step, like the classical RK-4 procedure. We have thus taken the liberty of considering there is no risk of confusion or contradiction between our “Implicit RK-4” naming and that of closed (multistep) methods such as Adams-Moulton or Gear which are often called “implicit” in the Anglo-American literature [12, 15].

Symbols

(see Parts I, II [1a, b] for the rest of notations)

$F0$ – factor in equation (III-8), $\text{mol}\cdot\text{kg}^{-1}\cdot m_{\text{reactor}}$

$F1, F2$ – coefficients in the same (III-8), m_{reactor}

F – (generic) function of three variables, in (III-9)

h – step size, m

j – step number or iteration

k_1, k_2, k_3, k_4 – intermediary increments of the (approximate) solution in the Runge-Kutta 4 procedure, $\text{mol}\cdot\text{kg}^{-1}_{\text{amstec}}$

N_{pas} – total number of steps

κ – integration constant, equation (III-7), $\text{mol}\cdot\text{kg}^{-1}_{\text{amstec}}$

„ ” „, (superscript) – 2nd order derivative (with respect to axial coordinate), $\frac{d^2}{dx^2}$

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(numbers of the form [I-*n*] or [II-*n*] in the present text are sending to reference „*n*” given in Part I or Part II respectively)

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Modelarea reactorului catalitic de postcombustie cu monolit pentru reacția de oxidare a monoxidului de carbon. Partea a III^a: Metode de rezolvare

Rezumat

În această parte a lucrării sunt prezentate metodele folosite la rezolvarea sistemelor de ecuații diferențial-algebrice ale modelelor reactorului. Modelul reactorului izoterm, mai simplu, poate fi restrâns la o singură ecuație diferențială ordinară (e.d.o.) de ordinul 1 ce definește implicit derivata necunoscută, concentrația reactantului cheie, monoxidul de carbon. Pentru rezolvarea ecuației modelului izoterm sunt folosite mai multe metode: 1 – obținerea unei e.d. explicite de ordin 2 prin derivarea implicită a ecuației modelului, urmată de integrarea numerică cu algoritm clasic Runge-Kutta (RK-4) în varianta pentru e.d. de ordin 2; 2 – metoda „RK-4 Implicit” ce constă din algoritm RK-4 clasic completat cu algoritm de determinare rădăcinii unei ecuații algebrice neliniare; 3 – explicitarea derivatei de ordinul 1 a necunoscută din ecuația modelului cu ajutorul formulelor Cardano pentru rădăcinile unei ecuații algebrice de gradul III, urmată de integrarea numerică cu algoritm clasic RK-4. Prin prima metodă se obține o soluție puțin diferită de cele rezultate cu ultimele două metode, diferențele fiind mici (10^{-5} %) și atribuite erorii de trunchiere suplimentare datorate integrării numerice de „două ori” pe care o implică metoda 1. Pentru determinarea soluției modelului adiabatic doar o metodă similară cu metoda 2 s-a dovedit a fi convenabilă. Ecuațiile celor două modele au fost scrise și rezolvate prin metodele menționate în platforma de calcul MathCAD (rezultate ce vor fi prezentate în Partea a IV^a [1]).