METHOD OF SPLINE-INTEGRATION: APPLICATION IN CHEMICAL KINETIC EQUATIONS

Ailton Durigon
University of Planalto Catarinensa - UNIPLAC,
Department of Exact and Technological Sciences
PoB 525, 88509-900, Lages, SC - Brazil
e-mail: ailton@uniplac.rct-sc.br

Abdulline A.L.
Kazan State Technical University - KSTU
Department of Engines
PoB 420111, Karl Marx Street, 10
e-mail: ala2000@mail.ru

Krioukov V.G., Iskhakova R.L
UNIJUÍ – Northwest Regional University of Rio Grande do Sul
Master Degree Program in Mathematical Modeling
PoB 560, 98700-000, Ijuí, RS – Brazil
São Francisco Street, 501
e-mail: kriukov@admijui.unijui.tche.br

Abstract. The work is dedicated to the solution of the chemical kinetic equations that are applied in the combustion process modeling, represented by ODE's that are complex and stiff. The θ-method with the transformation of ODE's in algebraic equations and the application of Newton-Rafson method are traditionally used for its solution. In this work the spline-integration method by the second power polynomials without correction (SK) and with correction (CK) is proposed instead of the θ-method. Its calculate algorithms are presented. The precision and computational volume indicators had been elaborated. The simulations for the reacting medias: "H_2+O_2" and "$Ar+C_2H_2+CH_4+NH_3$" had shown that the spline-integration method (in CK version) is at least in two times more economic than the θ -method. But SK version for the great integration intervals generates the oscillations in the solution increasing of computational volume.

Keywords:, mathematical modeling, stiff equations, spline-integration, combustion.

In the combustion process modeling, a important part belongs to the chemical kinetic equations that describe the substance transformations in the reacting medias (Oran & Boris, 1987). As a rule, these medias are complex and include many species (up to 100) between which occur hundreds chemical reactions. Therefore these equations (ODE's type) are sufficiently complicated. In order to solve it the universal (relatively of the reacting media) algorithms and software's (for example, Kee et all, 2000; Krioukov et all, 1997) with transformation of symbolic form of reactions in chemical kinetic equations are used. The modern computers easily solve these equations for one-dimensional problems. But simulation of the combustion processes in real units (combustion chambers, gas generators) demands as a rule two- or three- dimensional approaches. In this case the computational volume becomes gigantic.

For example, Blom & Verwer (2000) used only 26 species and 55 reactions (but in the 3D-approach) and had involved simultaneously the computational resources of several universities and research institutions for the modeling of the NO_x formation processes in the atmosphere. Therefore to search and to apply the new numerical methods (or known methods, but still not applied in the universal software's) in order to reduce the calculation volume is an important problem. It is know that the method of Gear (1971) or the θ-method (Pirumov & Kamzolov, 1966) is already used for the solution of the chemical kinetic equations during several decades. In present paper the method of spline-integration (Sallam, 2000) together with θ-method, applying them into the invariant software, are searched (Krioukov et all, 1977) for the conditions of adiabatic reactor. The chemical kinetic equations are presented in the exponential form:

$$\frac{d\gamma_i}{d\tau} = -e^{\gamma_i} \sum_j \nu_{ij}\Omega_j + \sum_q \sum_j \nu_{qj}\Omega_j \equiv f_{\gamma_i} ; \qquad \text{i, } q = 1, \ , n_s; \ \ j = 1,..., m_s; \qquad (1)$$

where: $\Omega_j = k_j \left(P / R_0 T \right)^{\overline{m}_j} \exp\left(-\sum_p n_{pj}\gamma_p \right)$; $\quad \gamma_i = \ln(r_i)$; P - pressure; R_0 - universal gas constant; τ - time; m_j - index of participation in reaction j of catalytic particle M ($m_j = 1$ if particle M participates in j-th reaction; $m_j = 0$ - in the absence of particle M); r_i - molar fraction of i-th species; v_{ij}, n_{pj} - stoichiometric coefficients of reactions; n_s – total substance number; m_s – total reaction number.

One of the equations (that describes the predominant species alteration) is substituted by the normalization relation:

$$F_z \equiv 1 - \sum_i e^{-\gamma_i} = 0 \tag{2}$$

Also the energy equation was enclosed in the model that is presented in this work by form:

$$F_T \equiv T - T_{ap} - \sum_q \left(I_p \mu_q - H_q^{ap} \right) r_q \bigg/ \sum_q C_{pq}^{ap} r_q = 0 \qquad q = 1, ..., n_s; \tag{3}$$

where I_p - mass enthalpy of the propellant; H_q^{ap}, C_{pq}^{ap} - the molar enthalpy and specific heat of reference of q-th species; T_{ap} - the reference temperature (Krioukov et all, 1997).

Then the system to compare the numerical methods composes for $(n_s - 1)$ ordinary differential equations and two algebraic equations. The unknown variables are γ_i and T.

2. Integration of the chemical kinetic equations

2.1 Description of θ-method and algorithm of solution

The system of ODE's (1) is stiff and can only be solved by implicit methods (Oran &Boris, 1987). The method of Gear (1971) is the most popular between them. In our model the method of Pirumov & Kamzolov (1966) or θ-method is used. In accordance with this method the Eq. (1) are presented in the form of finite differences:

$$\frac{\gamma_i^{n+1} - \gamma_i^n}{h} = s f_i(\gamma_i^n) + (1-s) f_i(\gamma_i^{n+1}) \tag{4}$$

where: n is step number; h – integration step; s – approximation parameter.

Attributing the value $s = 0,5$ we get the trapezoidal method. The scheme of Pirumov uses the value of $s = 0,4$ that allows to diminish the initial data errors. Considering the application of the Newton's method the Eq. (4) lead to the transcendental equations:

$$F_i^{n+1} \equiv \gamma_i^{n+1} - \gamma_i^n - h \left(s f_i(<\gamma_k^n>) + (1-s) f_i(<\gamma_k^{n+1}>) \right) = 0 \tag{5}$$

where: $\langle \gamma_k \rangle \equiv \gamma_1, \gamma_2, ..., \gamma_{n_s}$; $\gamma_i^n, \gamma_i^{n+1}$ are values of γ_i in beginning and in end of step h.

It is observed that the Eqs. (2, 3) already are ready to apply the Newton's method. The values γ_i^{n+1}, T^{n+1} are unknown in each integration step and are determined by the equations (with some null approach of $\gamma_i^{n+1,0}$, $T^{n+1,0}$):

$$\left[\frac{\partial F_i}{\partial x_k} \right] \Delta x_k^{m+1} = -F_i^m \qquad x = \gamma_i, T; \qquad i, k = 1, ..., (n_s + 1) \tag{6}$$

where m is iteration number.

During of integration the Jacobian calculated once is used for some steps (saving scheme) reducing the computational volume. In the algorithm are used the calculation indicators:
- the number of iterations (m_n) in the n-th step;

- the maximum difference between the iterations $\max_i \left| \Delta x_i^{m+1} / x_i^n \right|$;

- the maximum alteration of x_i in a step $\max_i \left| \left(x_i^{n+1} - x_i^n \right) / x_i^n \right|$;

- the number of steps (I_J) without recalculation of the Jacobian.
The control parameters of the integration step (and therefore of the volume and precision of calculations) are:
- the admissible alteration (Δ_x) of the unknowns to increase the step;
- the admissible error (ε_N) to conclude the iterations in step;
 - the admissible maximum number of iterations (m_p);
 - the admissible minimum number (J_2) of index I_J to increase the step;

- the admissible iteration number (m_a) to save the Jacobian.

The iterative process in a step is concluded: if $m_n > m_p$ or $\max_i \left| \Delta x_i^{m+1} / x_i^n \right| < \varepsilon_N$.

The Jacobian is recalculated in the *n*-th step if $m_n > m_a$.

The integration step increases: if $m_n \leq m_a$ and $\max_i \left| \Delta x_i^{m+1} / x_i^n \right| < \varepsilon_N$ and $I_J > J_2$ and $\max_i \left| \left(x_i^{n+1} - x_i^n \right) / x_i^n \right| \leq \Delta_x$.

The integration step diminishes: if $\max_i \left| \Delta x_i^{m+1} / x_i^n \right| > 3\varepsilon_N$ or $\max_i \left| \left(x_i^{n+1} - x_i^n \right) / x_i^n \right| > 3\Delta_x$.

In other cases the integration step is conserved.

For θ-method the following control parameters had been established: $\Delta_x = 0{,}005$; $\varepsilon_N = 10^{-5}$; $m_p = 12$; $J_2 = 3$; $m_a = 7$ that where chosen by the mathematical experiments (Krioukov et all, 1997), to know:

- the values $\Delta_x > 0{,}005$ causes the significant calculation errors, but if $\Delta_x < 0{,}005$ increases the calculation volume;

- the same effects had shown for $\varepsilon_N > 10^{-5}$ and $\varepsilon_N < 10^{-5}$. Besides for $\varepsilon_N > 10^{-5}$ the integration step size can oscillate increasing the calculation volume;

- the value m_p in interval $m_p = 8\ldots16$ not affect the calculation volume. But out of this interval, this volume rises because of increase of the calculations: of Jacobian ($m_p < 8$) or of right parts of the kinetic chemistry equations ($m_p > 16$). Therefore, the value $m_p = 12$ was chosen;

- the same reasons determine the choice of value m_a that does not influence in the calculation volume in the interval: $5 < m_a < 9$.

In the algorithm the analytical calculation of the derivatives of Jacobian is performed. In this case the iterative process is converged more quickly and the congealed Jacobian is used in a more number of integration steps than in version of numerical calculation of derivatives. Moreover, the analytical determination of derivatives for the exponential form of equations demands minor calculation volume. The partial derivatives of γ_k, T for the system (1-3) are:

$$\frac{\partial F_i}{\partial \gamma_k} = \delta_i^k + h \cdot (1-s) \left[e^{\gamma_i} \sum_j v_{ij} (\delta_i^k - n_{kj}) \Omega_j - \sum_p \sum_j v_{pj} n_{kj} \Omega_j \right] \quad i, k, p = 1, \ldots, n_s; \quad j = 1, \ldots, 2m_c; \qquad (7)$$

$$\frac{\partial F_z}{\partial \gamma_k} = e^{-\gamma_k} ; \qquad \frac{\partial F_T}{\partial T} = 1 ; \qquad (8)$$

$$\frac{\partial F_i}{\partial T} = h \cdot (1-s) \left[e^{\gamma_i} \sum_j v_{ij} \Omega_j \left(\frac{n_j - \overline{m}_j}{T} + \frac{E_j}{R_o T^2} \right) - \sum_p \sum_j v_{pj} \Omega_j \left(\frac{n_j - \overline{m}_j}{T} + \frac{E_j}{R_o T^2} \right) \right] \qquad (9)$$

$$\frac{\partial F_T}{\partial \gamma_k} = \left[\left(I_p \mu_k - H_k^{ap} \right) r_k - C_{pk}^{ap} r_k \left(T - T_{ap} \right) \right] / \sum_q C_{pq}^{ap} r_q = 0 \qquad k, q = 1, \ldots, n_s; \qquad (10)$$

where, δ_i^k - Kronecker symbol.

For the increment $\left(\Delta x_n^{m+1} \right)$ calculation is used the preliminary LU-decomposition of Jacobian.

2.2 Method of spline-integration

In the method of spline-integration by quadratic polynomials the variables γ_i in each integration step ($\tau_n, \ldots, \tau_{n+1}$) are presented by expression:

$$\gamma_i^{n+1}(\tau) = \widetilde{a}_i^{n+1} + \widetilde{b}_i^{n+1} \tau + \widetilde{c}_i^{n+1} \tau^2 \qquad (11)$$

or normalizing:

$$\gamma_i^{n+1}(\overline{\tau}) = a_i^{n+1} + b_i^{n+1} \overline{\tau} + c_i^{n+1} \overline{\tau}^2 \qquad (12)$$

where: $\bar{\tau}=(\tau-\tau_n)/h_{n+1}$; $0\le\bar{\tau}\le1$; and $\gamma_i^{n+1}(0)=\gamma_i^n$; $\gamma_i^{n+1}(1)=\gamma_i^{n+1}$ - values of γ_i in beginning and end of the step; a_i^{n+1}, b_i^{n+1}, c_i^{n+1} - polynomial coefficients to determine.

The two versions of the method are analyzed in this work.

<u>SK - Integration without correction</u>. We admit that in the boundaries between steps the variables γ_i and its derivatives are equal:

$$a)\ \gamma_i^n(1)=\gamma_i^{n+1}(0);\qquad b)\ \frac{\partial\gamma_i^n(1)}{\partial\tau}=\frac{\partial\gamma_i^{n+1}(0)}{\partial\tau};\tag{13}$$

Using Eq. (13) we easily obtain:

$$a)\ a_i^{n+1}=a_i^n+b_i^n+c_i^n;\qquad b)\ b_i^{n+1}=\left(b_i^n+2c_i^n\right)\frac{h_{n+1}}{h_n};\tag{14}$$

i.e. beginning the calculation in the interval $(\tau_n,...,\tau_{n+1})$ the values a_i^{n+1}, b_i^{n+1} are known. Then in the resolution by the spline-integration method, only the coefficients c_i^{n+1} are unknown and the Eq. (1) can be written in the form:

$$\frac{d\left(a_i^{n+1}+b_i^{n+1}\bar{\tau}+c_i^{n+1}\bar{\tau}^2\right)}{d\bar{\tau}}=h_{n+1}f_i(<\gamma_k>)=h_{n+1}f_i(<a_k^{n+1}+b_k^{n+1}\bar{\tau}+c_k^{n+1}\bar{\tau}^2>)\tag{15}$$

where $h_{n+1}=\tau_{n+1}-\tau_n$; $i=1,...,n_s$ (except $i=z$). Accepting that the Eq. (15) will be satisfied in the points τ_{n+1} (i.e. $\bar{\tau}_{n+1}=1$), deriving its terms to the left and reducing the terms to the right, we obtain the system:

$$F_i^{n+1}\equiv b_i^{n+1}+2c_i^{n+1}-h_{n+1}f_i(<c_k^{n+1}>)=0\tag{16}$$

that is necessary to solve in each step together with the Eqs. (2,3). To solve the system of Eqs. (16), the Newton-Rafson method is also used and the partial derivatives are calculated for the Jacobian:

$$\frac{\partial F_i}{\partial c_k}=2\delta_i^k+h_{n+1}\left[e^{\gamma_i}\sum_j\nu_{ij}(\delta_i^k-n_{kj})\Omega_j-\sum_p\sum_j\nu_{pj}n_{kj}\Omega_j\right]\tag{17}$$

The remaining derivatives do not modify therefore $\partial\gamma_i/\partial c_k=\delta_i^k$. The initial values to integrate in the step $(n+1)$ are determined by formulas:

$$c_{i,0}^{n+1}=c_i^n\left(h_{n+1}/h_n\right)^2\tag{18}$$

going on the second derivative of interval $(\tau_{n-1},...,\tau_n)$ for interval $(\tau_n,...,\tau_{n+1})$.

<u>CK - Integration with the correction</u>. In this version after solution of the Eqs. (16) by SK-version and determination of the values b_i^{n+1}, c_i^{n+1}, γ_i^{n+1} the correction of coefficients b_i^{n+2} is accomplished. Instead of Eq. (14) are used the coefficients b_{ic}^{n+2} that calculate executing the interpolation for points γ_i^{n-1}, γ_i^n, γ_i^{n+1}. In this case we obtain:

$$b_{ic}^{n+2}=\left(q_i+2s_i\left(h_n+h_{n+1}\right)\right)/h_{n+2}\ .\tag{19}$$

where: $s_i=\left(\frac{h_n}{h_{n+1}}\left(\gamma_i^{n+1}-\gamma_i^n\right)-\gamma_i^n+\gamma_i^{n-1}\right)\!\!\bigg/\!\left(h_n^2+h_{n+1}h_n\right)$; $q_i=\left(\gamma_i^n-\gamma_i^{n-1}-s_ih_n^2\right)\!\big/h_n$.

The value $c_{i,0}^{n+2}$ for the first iteration in step h_{n+2} is determined by Eq. (18) substituting n for $(n+1)$.

3. Numerical simulations

3.1. Reacting medias and the precision and computational volume indicators

To compare the spline-integration method and θ-method the two reacting medias had been established:
a)"O_2 and H_2" with species: H, H_2, O_2, HÒ, OH, HO_2 and 10 elementary reactions (LEEDS, 2000) occurred between them with the conditions: oxidizing excess coefficient $\alpha_{ox}=2,016$; $P=1$atm e $T_{in}=1000$K;

b) enriched air (60% of O_2 and 40% of N_2) and mixture C_2H_2 (10%) + CH_4 (80%) + NH_3 (10%) with 30 substances: N, N_2, NO, NO_2, NH, NH_2, NH_3, HNO, H, H_2, O, O_2, H_2O, O, CO, OH, HCO, H_2CO, HO_2, CO_2 among others and 121 elementary reactions (LEEDS, 2000) in conditions: $\alpha_{ox} = 1$; $P = 1$atm e $T_{in} = 1400$K.

In Figure (1) for the reacting media (b) are shown the temperature and the alteration of reagents O_2, N_2, C_2H_2, CH_4, NH_3 in the adiabatic conditions. At first the acetylene that is not steady is destroyed. As a result (until $\tau = 0{,}2$ms) the species O_2 slightly diminishes and increases T (less than 1700K) forming thus the intermediate substances H_2, H, CH_3, CH_2, etc (as products of pyrolysis C_2H_2). With the temperature increase the methane (in interval $\tau = 0{,}2...0{,}45$ms) starts to react with O_2 forming H_2O, CO and H_2. When the temperature is approached to ≈ 2100K the chained reaction mechanism becomes active and in a interval ($\tau = 0{,}45...0{,}55$ms) the temperature obtains its equilibrium value ($T \approx 3000$K).
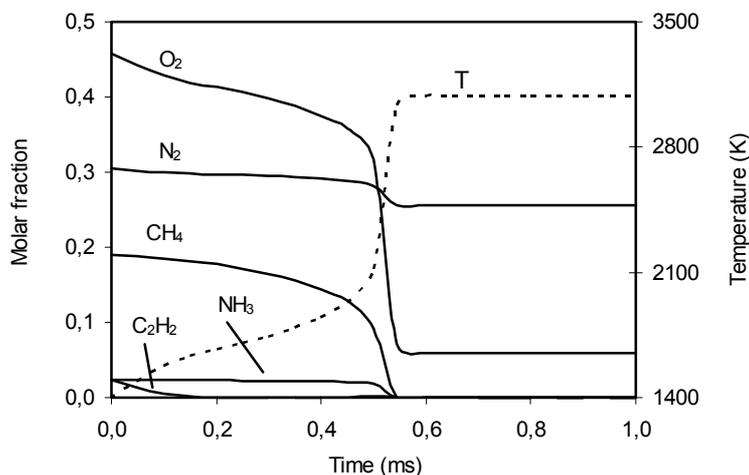
Figure 1. The alteration of species (O_2, N_2, NH_3, C_2H_2, CH_4) and of temperature by time.

In the preliminary simulations for the SK and CK schemes the best control integer parameters had been chosen: $m_p = 16$; $J_2 = 3$; $m_a = 9$. In comparison with the θ-method the values m_a and m_p had been increased because the values c_i are smaller than the values γ_i and high precision is necessary to determine them. Also for comparison of methods the two error indicators had been taken: the deviation from the equilibrium state (δ_m) and the atom conservation errors ($\delta r_i, \delta r_\Sigma$). The first indicator is determined by formula:

$$\delta_m = \frac{1}{n_s + 1}\left[\sum_i \left| r_i^d - r_i^e \right| + \left| T_d - T_e \right| \right] \tag{20}$$

where the superior indices denote: e - chemical equilibrium data and d – chemical kinetic data.

This indicator is applicable when it is known beforehand that the chemical equilibrium (what is certain for the reacting media "O_2+H_2") is established into the reacting system. The indicators for the atom conservation are more applicable. They are true for any closed reacting systems, therefore in the chemical reactions the atoms are not transformed. For each type of atoms the atom conservation indicator can be expressed by formula:

$$\delta r_i = \frac{\left| \left(\sum a_{ki} r_i^d + r_i^d \right) - \left(\sum a_{ki} r_i^e + r_i^e \right) \right|}{\left(\sum a_{ki} r_i^e + r_i^e \right)} \tag{21}$$

where a_{ki} is the number of k-th atom in i-th substance.

Also it is useful to introduce the total error indicator for atoms: $\delta r_\Sigma = \sum \delta r_i$. In general, the computational volume includes all the logical and arithmetical operations that are performed during calculation. But in our software are enclosed many operators and subroutines that are not linked with the numerical method and the use of indicators of type "total calculation time" there are not reflected advantages or imperfections of the numerical method. Therefore the indicators (more adjusted to the searched schemes) had been chosen that are correspond to the two fragments: calculation of direct parts of the chemical kinetic Eq. (1); calculation of the Jacobian.

The calculation of direct parts is fulfilled once in each step of integration and once in each iteration of the Newton's method. It is observed that for simple reacting systems of type (a) the computational volume of calculation of Jacobian (V_J) is smaller in comparison with the necessary volume for iteration (V_I). But for complex reacting systems the value V_J can be essentially more than V_I. Therefore we will evaluate in the numerical simulations the computational volume by means of two indicators that reflect the volumes V_I and V_J, to know: N_p - the sum of total number of iterations with number of the integration steps; N_J - the amount of calculation of Jacobian.

3.2. Comparison of the θ, SK and CK methods for reacting media "H₂ + O₂"

For this reacting media the θ-method and the methods of spline-integration: with correction (CK) and without correction (SK) and had been analyzed. The calculation precisions were evaluated by the deviation from the equilibrium state (δ_m) because this equilibrium is evident in the end of the combustion process. The influences of: admissible error (ε_N); admissible alteration (Δ_x) and integration interval (τ_f) on the values δ_m, N_p and N_J (being $\tau_f = 10^{-4}$ s, Δ_x (SK, CK) = 0,01, Δ_x (θ) = 0,005) had been determined in simulations. In the Figure (2) are shown the dependences $N_p = f(\varepsilon_N)$, $N_J = f(\varepsilon_N)$ for the three numerical schemes. For θ-method was chosen the parameter Δ_x (θ) = 0,005 because for $\Delta_x(θ) > 0,005$ the average error $\delta_m(θ)$ is inadmissible. The Table (1) showed that almost for all ε_N the errors δ_m had been constant.
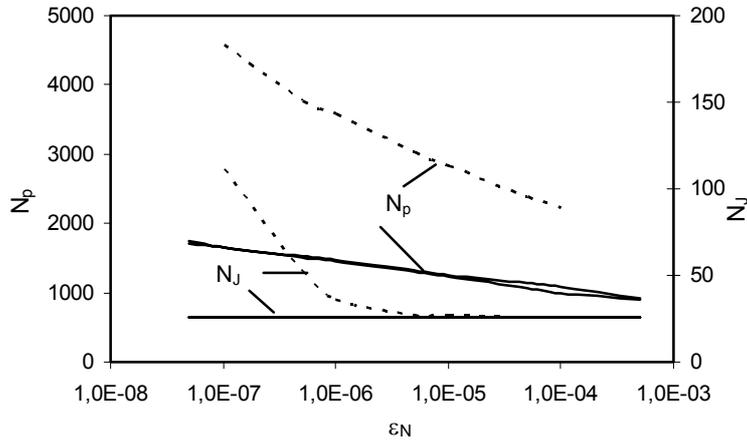
Figure 2. The computational volume in function of admissible error (— SK,CK; --- θ)

Table 1 - Influence of ε_N on the errors δ_m for the three numerical schemes.

Parameter ε_N	10^{-7}	$5 \cdot 10^{-7}$	10^{-6}	$5 \cdot 10^{-6}$	10^{-5}	$5 \cdot 10^{-5}$	10^{-4}
δ_m(SK).10^4	9,06	9,13	9,13	9,13	8,75	8,75	8,75
δ_m(CK).10^4	2,69	2,69	2,69	2,69	2,74	4,04	7,92
δ_m(θ).10^4	46,5	46,5	46,5	46,5	46,5	46,5	46,5

The CK scheme shows the minimum errors: $\delta_m(CK) \approx \delta_m(SK)/4 \approx \delta_m(θ)/15$. However for the great values ($\varepsilon_N = 10^{-4}$) $\delta_m(CK) \approx \delta_m(SK)$ is observed. The schemes SK and CK are more economic than the θ-method at least in two times (Fig.(2)). Indicators N_J are equal for the all schemes but in the high precision region for the θ-method the essential increase of N_J is observed. This effect is induced by necessity to accomplish greater number of iterations in the integration step (with posterior calculation of the Jacobian) than for the SK and CK schemes. The values $c_i \approx$ (0,001...0,01) $\ll \gamma_i$ and comparing the formula (7) with (17) it is observed that the Jacobian's for all methods are almost equal. Therefore the values $c_{i,0}^{n+1}$ assure of solution for less number of iterations. Considering relation $c_i \ll \gamma_i$ we choose for posterior simulations the values:

$$\varepsilon_N(θ) = \max_i \left| \left(\gamma_i^{n+1, m+1} - \gamma_i^{n+1, m} \right) / \gamma_i^n \right| = 10^{-5} \text{ for θ-method}$$

and $\varepsilon_N(SK, CK) = \max_i \left| \left(c_i^{n+1,m+1} - c_i^{n+1, m} \right) / \gamma_i^n \right| = 0,5 \cdot 10^{-6}$ for spline-integration schemes.

To determine the influence of parameter Δ_x on the errors δ_m the simulations with $\tau_f = 10^{-4}$s varying Δ_x in interval 0,.001... 0,08 had been accomplished. The errors (δ_m) and computational volumes for three schemes are shown in Tab. (2) and in Fig. (3).

Table 2 - Influence of parameter Δ_x on the errors δ_m for three numerical schemes.

Δ_x	0,001	0,002	0,005	0,01	0,02	0,04	0,08
δ_m(SK).10^4	3,25	3,44	4,63	9,13	28,7	73,7	137
δ_m(CK).10^4	3,04	3,01	2,71	2,69	6,89	10,88	82,2
δ_m(θ).10^4	10,6	18,7	46,2	94,9	210	446	604

For the equal values Δ_x all the schemes present the same computational volumes (for θ-method the indicators N_p and N_J are a little more). For small values of Δ_x the high computational volumes are observed and with the increase of Δ_x they diminish drastically. Table (2) shows that the same values Δ_x generate the very small errors δ_m for the schemes with the spline-integration (approximately in 40 times smaller than for θ-method). Fixing, for instant, the admissible value ($\delta_m = 0.5\%$) for all schemes obtain: $\Delta_x(\theta) = 0,005$; Δ_x (SK, CK) = 0,04. Then we conclude that for the SK and CK schemes the computational volumes are: $N_p \approx 1000$, $N_J = 30$ and for the θ-method: $N_p \approx 2800$, $N_J = 27$, i.e. in this case the spline-integration methods are more economic in 2,5 times.
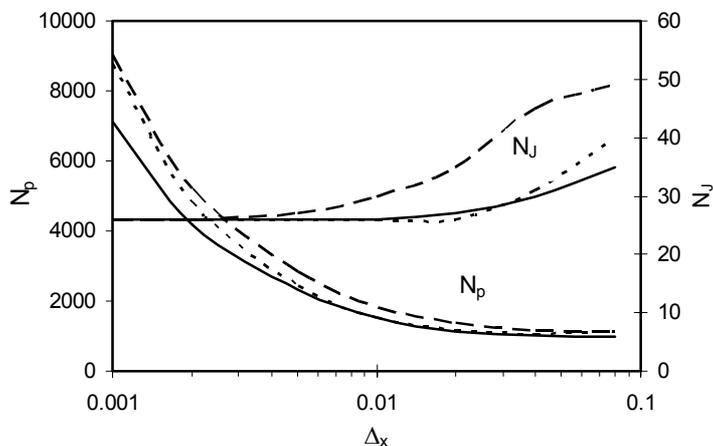
Figure 3. Alteration of computational volume in function of Δ_x (— CK; …SK; --- θ).

From practical point of view it is interesting to evaluate the influence of the integration interval on computational volume after the chemical equilibrium is reached. The results of these simulations for $\tau_f = 10^{-4}$s÷10^{-2}s (with $\varepsilon_N(\theta) = 10^{-5}$, ε_N (SK,CK)= 0,5 .10^{-6}, Δ_x (θ)= 0,005 and Δ_x (SK,CK)= 0,01) are presented in Fig. (4). Suddenly the SK scheme presented the unexpected results when starting with $\tau_f = 10^{-3}$s the essential increase of the indicator N_p(SK) is observed that for $\tau_f = 10^{-2}$s became more than $N_p(\theta)$ and moreover in 10 times increased value N_J (of 28 to 270).
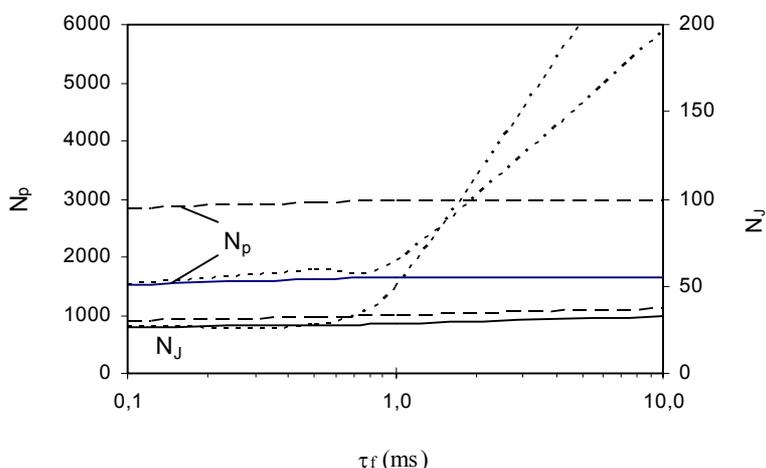
Figure 4. Alteration of computational volume in function of τ_f (— CK; … SK; --- θ).

The cause of this effect is oscillations that appear in SK scheme because of error in coefficients b_i when the reacting system reaches the chemical equilibrium state. In this case $b_i^{n+1} \neq 0$ although the reacting media composition must to be constant. Then the value c_i^{n+1} has to "compensate" the tendency to change the composition attributing the contrary signal to the signal of the coefficient b_i^{n+1}. As a result in the step end the derivative $d\gamma_i/d\tau$ (i.e. b_i^{n+2}) change its signal and then in step ($n+2$) the value c_i also change signal generating the sequence $c_i^{n+3} \approx -c_i^{n+2}$; $c_i^{n+4} \approx -c_i^{n+3}$ and etc., as shows Fig. (5). These oscillations prevent to increase integration step in SK scheme that leads to computational volume increase. The average errors δ_m remain constant with alteration τ_f being $\delta_m(SK) = 9\cdot10^{-4}$; $\delta_m(CK) = 2,7\cdot10^{-4}$ e $\delta_m(\theta) = 46\cdot10^{-4}$. Figure (4) shows that between the computational volumes of CK scheme and θ-method the relation is almost constant being $N_p(CK) \approx N_p(\theta)/2$.
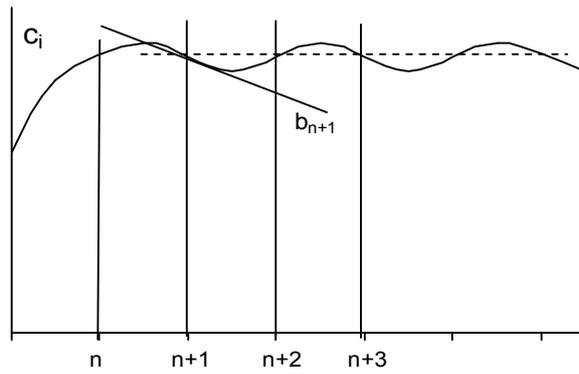
Figure 5. Alteration of variable c_i with the achievement of chemical equilibrium.

3.3. Comparison of the θ and CK methods for the reacting media: "Air enriched + (C_2H_2 + CH_4 + NH_3)"

The numerical simulations for this media had been performed only for θ-method and for the scheme with correction (CK), because SK method is not efficient because of oscillations in the solution. The calculation precision was tested through the atom conservation errors (δr_i, δr_Σ) because for the complex medias the deviation from the equilibrium state (δ_m) does not serve as indicating of precision. Three series of simulation had been realized, changing of admissible error (ε_N); admissible alteration (Δ_x) and integration interval (τ_f).

In Figure (6) the dependences $N_p = f(\varepsilon_N)$, $N_J = f(\varepsilon_N)$ (being $\tau_f = 10^{-4}$s, $\Delta_x(CK) = 0,01$, $\Delta_x(\theta) = 0,005$) are presented in interval $\varepsilon_N = 10^{-7}...10^{-4}$. It is verified that indicator N_J (θ) is bigger than N_J (CK) when error $\varepsilon_N \approx 10^{-7}$ but with the increase of value ε_N this difference diminishes. For the N_p - indicator is observed that with growth ε_N this indicator almost linearly diminishes in the both numerical schemes, leaving the ratio N_p (θ)/N_p (CK) ≈ 2. As seen, observed (Table (3)) that the ratio $\delta r_\Sigma(\theta)/\delta r_\Sigma(CK) \approx 3$ almost does not depend on value ε_N.
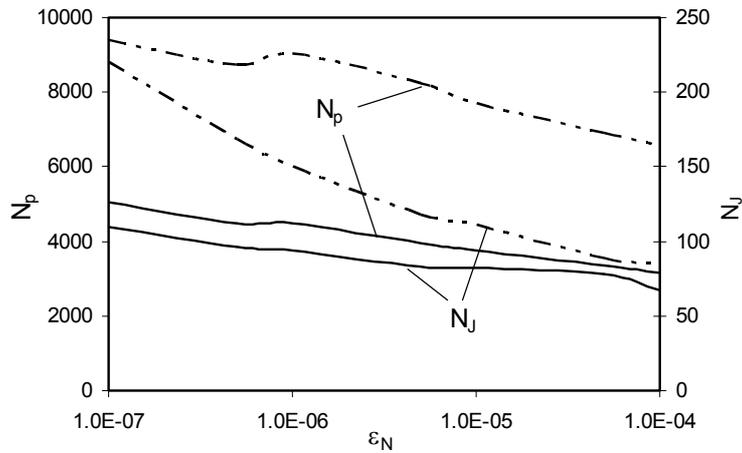
Figure 6: Computational volume in function of admissible error ε_N (—— CK, --- θ).
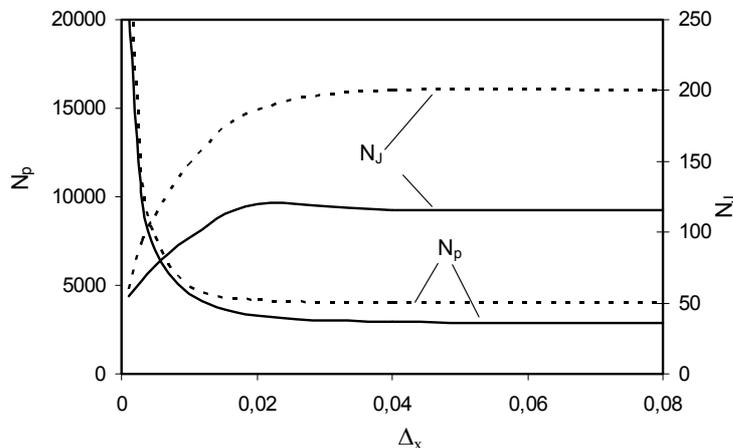
Figure 7. Alteration of computational volume in function of Δ_x (—— CK, --- θ).

Table 3 - Influence of the parameter (ε_N) on the errors δr_Σ for two numerical schemes.

Parameter ε_N	10^{-7}	5.10^{-7}	10^{-6}	5.10^{-6}	10^{-5}	5.10^{-5}	10^{-4}
$\delta r_\Sigma(\theta).10^3$	15,15	15,93	15,88	15,49	15,74	15,73	15,75
$\delta r_\Sigma(CK).10^3$	5,69	6,07	5,89	6,00	5,44	6,28	5,49

To determine the influence of parameter Δ_x on the calculation errors and on computational volume the simulations had been accomplished with $\tau_f = 10^{-4}$, $\varepsilon_N(\theta) = 10^{-5}$ e $\varepsilon_N(CK) = 0,5.10^{-6}$ varying Δ_x in interval $0,001 \div 0,08$. In Figure (7) is shown the computational volume data for the both scheme. It is perceived that for small values ($\Delta_x < 0,01$) the both methods demand the great number of iterations (N_p) that quickly diminish with increase of indicator Δ_x, maintaining $N_p(CK)$ always less than $N_p(\theta)$. For the values $\Delta_x > 0.01$ the N_p is almost constant. It is observed that $N_J(\theta)$ is almost two times bigger than $N_J(CK)$ and, in the both schemes the value N_J grows until $\Delta_x \approx 0,02$ and later remains constant.
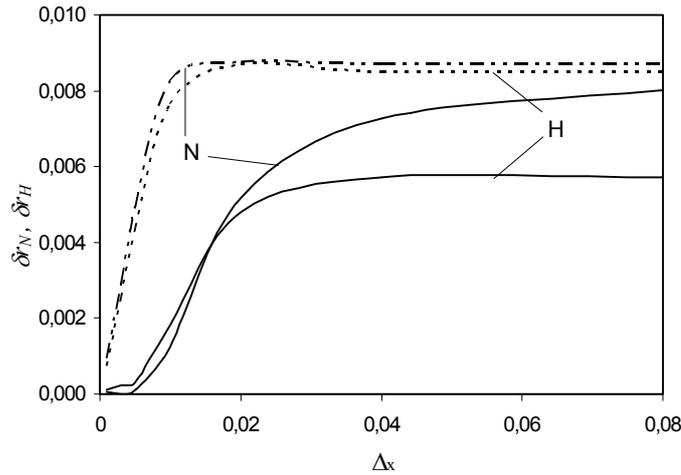
Figure 8. Variation of δr_N and δr_H in function of Δ_x (—— CK, ---θ).
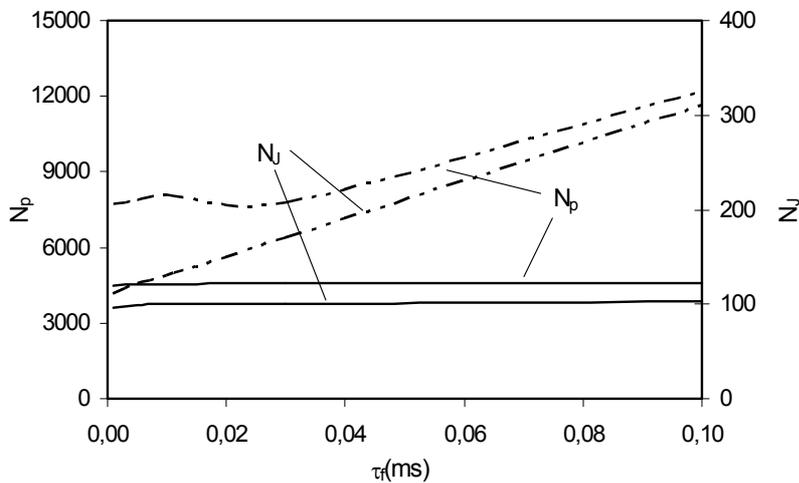
Figure 9. The computational volume in function of τ_f (—— CK, --- θ).

In Figure (8) are shown the alterations of the atom conservation errors δr_N and δr_H in function of Δ_x. For small Δ_x (until $\Delta_x < 0,005$) the difference between $\delta r_N(\theta), \delta r_H(\theta)$ and $\delta r_N(CK), \delta r_H(CK)$ is surprising. For example for $\Delta_x = 0,005$, the ratio $\delta r_N(\theta)/\delta r_N(CK) \approx 40$, showing a great advantage of the spline-integration method in this region. But with the increase of Δ_x this advantage is diminished. The same behavior is characteristic for the errors δr_O and δr_C e, also for the total error δr_Σ. As a rule for the scientific and practical necessities it is demanded to keep the value δr_Σ around 0,005. In this aspect we can mark that to get the ratio: $\delta r_\Sigma(\theta) \approx \delta r_\Sigma(CK) \approx 0,005$ the calculations would be performed with $\Delta_x \approx 0,003$ (for θ-method) and with $\Delta_x \approx 0,01$ (for CK scheme). In this case using Fig. (7) we determine the computational volumes: $N_p = 10000$, $N_J = 90$ (θ-method); $N_p = 4500$, $N_J = 90$ (scheme CK).

Also influence of the integration interval on computational volume and on the atom conservation errors was searched. The results of these simulations changing τ_f of 10^{-4} to 10^{-2} (with $\varepsilon_N(\theta) = 10^{-5}$, $\varepsilon_N(CK) = 0,5.10^{-6}$, $\Delta_x(\theta) = 0,005$

and $\Delta_x(CK)= 0,01$) are shown in Fig (9). It is verified that for CK scheme the total iteration number (N_p) and the number calculation of Jacobian (N_J) are kept almost constant in the interval τ_f. However for θ-method the values N_p and N_J grow linearly, thus showing the advantage of CK scheme. The difference between $N_p(\theta)$ and $N_p(CK)$ is increased of 2 times up to 3 times. For all the integration intervals the atom conservation errors are remained constant with ratio $\delta r_i(\theta)/\delta r_i(CK) \approx 2 \div 4$.

4. Conclusion

The two versions (SK and CK) of the spline-integration method had been implanted in software invariant "ERD" in order to compare with θ-method that traditionally are used in the codes of this type. The tests of three methods had been performed in conditions of adiabatic reactor for reacting medias "H_2+O_2" and "Air enriched + ($C_2H_2+CH_4+NH_3$)" in large intervals: of admissible errors ε_N; of admissible alteration Δ_x; of permanence time τ_f. The numerical simulations for the both reacting medias were shown that:
- scheme CK demands less the computational volume than the θ-method at least in two times (and with the essentially high precision);
- scheme SK (in general being better than θ-method) has the significant oscillations for great τ_f that leads to drastic growth of computational volume.

5. Acknowledgement

6. References

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