

## REDUCTION OF THE REACTIONS MECHANISM THROUGH THE METHOD OF “ENGAGEMENT”

**A. Patricia Spilimbergo, patspi@unijui.edu.br**  
**Gilmar de Oliveira Veloso, gilmar.veloso@unijui.edu.br**

UNIJUI - Northwest University of the State of Rio Grande do Sul, Department of Physics, Statistics and Mathematical, PoB. 560, zip code: 98.700-000, Ijuí – RS, Brazil

**Viktor G. Krioukov, vkrujkov@kai.ru**  
**Raisa L. Iskhakova, vkrujkov@kai.ru**

UETK –Kazan State University, Department of Engines of Automobiles, Mail Box 42011, K. Marx Street 10, Kazan, Russia

**Abstract.** *This work presents the problem of the reduction the reactions mechanisms in the combustion process. The “engagement” method, presented in previous works, was developed for an zone of the alterations of parameters of the reagent medium. Formation of the reduced mechanism is realized in the scheme of mixture ideal reactor. The numeric simulations were realized for the reagent medium “S + H + O + (N)”. It was obtained a reduced mechanism for the zone of the excess intervals of the oxidizer ( $\alpha_{ox}$ ), of the temperature (T) and of the pressure (P). The original mechanism was reduced in three times, without loss in the precision of the results.*

**Keywords:** *Combustion mechanisms, Chemical Reactions, Reduced Mechanism, Chemical kinetics.*

### 1. INTRODUCTION

A new problem in the chemical kinetics of the combustion is the mechanisms reduction of the reactions that describe complex reagents medium (Lindstedt and Maurice, 2000). These mechanisms can contain dozens of species and hundreds of reactions. The direct introduction of those mechanisms in two and three dimensional problem to require a great volume computational, that can just be developed in supercomputer (Blom and Verwer, 2000). At the same time is known that most of the reactions and species present little influence in the combustion processes and they cannot be considered. For instance, if a mechanism with 300 reactions and 30 species is reduced until 30 reactions and 10 species, the volume computational of the kinetic block is reduced approximately in 270 times.

Researchers are, a long time, reducing the mechanisms of reactions through the intuition and of the experience. But with the increase of the complexity of kinetic schemes, this procedure becomes little safe and increases the probability of errors committed. Due to that numerous works were published (Smooke, 1991; Kalamatinos *et al.*, 1998; Glaude *et al.*, 2000; Tiafeeng *et al.*, 2001; Peters and Kee, 1987), where several methods of reduction of the mechanisms are proposed. Among them they to become detached: the velocity analysis method (Glaude *et al.*, 2000; Peters and Kee, 1987); the PCA method (Kalamatinos *et al.*, 1998; Tiafeeng *et al.*, 2001); “intrinsic low-dimensional manifold method” - ILDM (Smooke, 1991).

In each one of those methods the origin mechanism (complete mechanism, that will be indicated as C-mechanism) is accomplished in two stages: the formation of the “base” mechanism (S-mechanism) and the elaboration of the reduced mechanism (R-mechanism).

The first stage is more difficult, because:

- it demands that firstly is executed the calculation for the C-mechanism in whole the interval of alteration of the parameters,  $\alpha_{ox}$ , T and P (in other words, the formation of a data base);
- it doesn't possess a clear algorithm and uses the researcher's intuition considerably.

Particularly, in the velocity analysis method (Glaude *et al.*, 2000; Peters and Kee, 1987), the S-mechanism is formed leaning in the intuitive evaluations of the reactions, for the pre-exponential coefficients and for the activation energy.

In the methods PCA and ILDM in the first stage clearer algorithms are used, and they are removed of the C-mechanism the reactions with velocity relatively small. But, the S-mechanism obtained by this approach is voluminous, because no species is excluded of the C-mechanism and the reduction difficulties happen in the second stage. The tool of the stage second is based on the proposals of “stationary concentrations” and “fast reactions”. This reduction technique is known a long time, but it demands a lot of perspicacity to avoid considerable errors in the final R-mechanism.

It is observed that the methods presented in Smooke (1991), Kalamatinos *et al.* (1998), Glaude *et al.* (2000), Tiafeeng *et al.* (2001) and Peters and Kee (1987), they are not guided for problems where, for instance, is necessary obligatorily to include in the R-mechanism a certain species, independently of the concentration. Such problems appear when is necessary to foresee, for instance, pollutant species. Like this, can be considered that the existent methods, for the reduction of a C-mechanism, need improvements.

## 2. "ENGAGEMENT" METHOD

In the work Spilimbergo *et al.* (2006) the "engagement" method was proposed and was applied in a combustion regime (in a point) and was obtained the local mechanism (LS-mechanism). But, for the researchers that investigate two and three dimensional problems, are necessary correct mechanisms in a zone of  $\alpha_{ox}$ ,  $T$  and  $P$ , and not just in a point. In the present work, using the "engagement" method an algorithm of formation of the S-mechanism is proposed for an zone. As in Kalamatinos *et al.* (1998) the reduction of the C-mechanism is accomplished by the scheme of the ideal mixture reactor that is constituted by the equations:

1) of the chemical kinetics in the exponential form (Spilimbergo *et al.*, 2005):

$$\frac{d\gamma_i}{d\tau} = -e^{\gamma_i} \left( \sum_j v_{ij} \Omega_j + \frac{r_i^+ \mu_\Sigma}{\mu^+ \tau_p} \right) + \sum_q \sum_j v_{qj} \Omega_j + \sum_q \frac{r_q^+ \mu_\Sigma}{\mu^+ \tau_p} \quad i, p, q = 1, \dots, n_c; \quad j = 1, \dots, 2m_c \quad (1)$$

where:

$$\Omega_j = k_j \left( \frac{P}{R_o T} \right)^{\bar{m}_j} \exp \left( - \sum_p n_{pj} \gamma_p \right); \quad \bar{m}_j = m_j + \sum_p n_{pj} - 1; \quad \gamma_i = - \ln r_i; \quad (2)$$

$$\begin{aligned} v_{ij} &= v_{is}'' - v_{is}' ; \quad n_{ij} = v_{is}' ; \quad j = s ; \quad s = 1, \dots, m_c ; \\ v_{ij} &= v_{is}' - v_{is}'' ; \quad n_{ij} = v_{is}'' ; \quad j = s + m_c ; \quad s = 1, \dots, m_c ; \end{aligned} \quad (3)$$

$v_{is}'$ ,  $v_{is}''$  - estequiometric coefficients together of reversible reactions:

$$\sum_i v_{is}' B_i \Leftrightarrow \sum_i v_{is}'' B_i \quad (4)$$

being:  $s = 1, \dots, m_c$ ;  $B_i$  - symbol of the  $i$ -esima substance;  $m_j$  - participation index in the reaction  $j$  of the catalytic particle  $M$  ( $m_j = 1$ , if a particle  $M$  participate in the  $j$ -esima reaction and  $m_j = 0$  in an opposite way);  $k_j$  - velocity Constant of the  $j$ -esima reaction;  $r_i$ ,  $r_i^+$  - molars fractions of the  $i$ -esima specie in the reactor and reagents;  $n_c$ ,  $m_c$  - species number and reactions in the reagent medium;  $\tau_p$  - time of permanence;  $\mu_\Sigma = \sum_i r_i \mu_i$  - average molecular mass in the reactor;  $\mu_i$  - molecular mass of the  $i$ -esima specie;  $R_o$  - universal constant of the gas;  $\mu^+$  - average molecular mass of the reagents;

2) of the energy in integral form:

$$h = \sum_i H_i r_i / \sum_i \mu_i r_i \quad (5)$$

where  $h$  is the mass enthalpy and  $H_i$  is the molar enthalpy of the  $i$ -esima specie (that is function of the temperature).

In agreement with the "engagement" method, the initials data are: the mechanism indicator  $\zeta$  and the symbols:

- of the reagents (obligatorily);
- of the main combustion products (no obligatorily, because if their concentrations are considerable, these symbols will be included in the LS-mechanism automatically);
- of the species that are interesting for the researcher.

Like this, initially the LS-mechanism is just constituted by substances and any reaction. To follow some comments are presented on each block of the formation of the LS-mechanism algorithm.

B1. For each  $i$ -esima species that is included already in the LS-mechanism, all are considered of the reactions with this species.

B2. For these reactions are determined the maximum:

$$\Omega_{im} = \max \left[ \text{abs} \left( v_{ij} \Omega_j \right) \right] \quad j = 1, \dots, 2m_c; \quad (6)$$

$$\Omega_{id} = \max \left[ \text{abs} \left( v_{is} \left( \Omega_s - \Omega_{s+m_c} \right) \right) \right] \quad s = 1, \dots, m_c \quad (7)$$

where  $\Omega_{im}$  is the maximum value at the module among the portions is  $v_{ij}\Omega_j$  so much for the direct sense as for the inverse sense of the reactions with the  $i$ -esima species;  $\Omega_{id}$  is the maximum value at the module in the differences between the direct and inverse directions of these reactions.

B3. Among the reactions with the  $i$ -esima species is selected those that satisfy one of the inequalities:

$$abs(v_{ij}\Omega_j) \geq \zeta \Omega_{im} \quad j=1,\dots,2m_c \quad (8)$$

$$\Omega_{id} = \max [abs(v_{is}(\Omega_s - \Omega_{s+mc}))] \quad s=1,\dots,m_c \quad (9)$$

B4. Each reaction selected by the inequalities (8) and (9) is included in the LS-mechanism alternately, if no longer was included previously.

B5. Each species of each reaction selected by the block B3 is included also in the LS-mechanism, if no longer was included previously. Then in the LS-mechanism a species initially included, “engages” more some reactions and other species. Due to that, the proposed method is called “engagement” method.

### 3. ENLARGEMENT OF THE “ENGAGEMENT” METHOD

Being admitted that for some prescribed values of  $\alpha_{ox}$  (relationship among the reagents) and of the pressure  $P$ , is necessary to form the  $S_T$ -mechanism in an interval of the temperature  $[T_o(max),\dots,T_o(min)]$ , where  $T_o$  is the initial temperature of the reagent medium in the chemical equilibrium. With the entrance of the reagents and with the escape of the combustion products the temperature inside of the reactor is chanced for a stationary temperature  $T_f$ . This temperature depends on the permanence time ( $\tau_p$ ). If the  $\tau_p \rightarrow \infty$ , the value  $T_f \rightarrow T_o$ .

The figure 1 shows a alteration line of the  $T_f$ , with the decrease of the  $\tau_p$ , when  $T_o = \text{const}$ . With  $\tau_p = \tau_{ex}$ , the combustion is “stopped” and the temperature  $T$  suffers a fall down until the entrance temperature of the reagents. To each value of  $T_o$ , corresponds a value of  $\tau_{ex}$ . In the result it is formed an extinction line that separates the extinction zone (B) of the combustion zone (A)

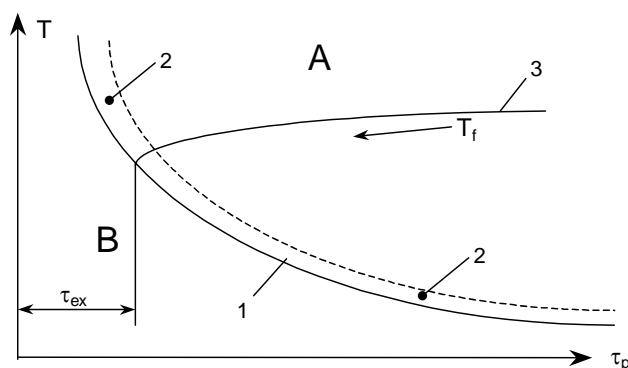


Figure 1.  $T_f$  dependence in function of the permanence time. 1 – extinction line; 2 – “Bordering” zone; 3 –  $T_f$  alteration in the zone A; A – combustion zone; B – extinction zone.

Initially to form the  $S_T$ -mechanism is necessary to realize a great amount calculation for the whole zone A, with the formation for each calculated point of a LS-mechanism and soon after, to couple all in a  $S_T$ -mechanism. But the amount of calculation can be reduced if these be realized in the “bordering” zone (zone 2) to the extinction line. The more if separates of this line, smaller becomes the volume of the LS-mechanism. For instance, in Spilimbergo *et al.* (2006), was shown that the LS-mechanism obtained for  $\alpha_{ox} = 1$ ,  $T_o = 1600 K$ ,  $P = 1 atm$  with  $\tau_p = 100\tau_{ex}$  was only constituted of 18 reactions. But if to admit that  $\tau_p = \tau_{ex}$ , in this case, the LS-mechanism will consider 24 reactions. This fact happens, because with the removal of the reagent system of the zone 2, this system approaches the chemical equilibrium. In this case, the direct and inverse velocity to remain the same and due to that the number of reactions is reduced to the number of species (according to the zone of “fast reactions” (Peters and Kee, 1987)). Due to that, to form  $S_T$ -mechanism in the whole zone A is necessary to realize calculations along the extinction line.

Being known only the character of this curves (the dependence  $\tau_{ex} = f(T_o)$  initially it is unknown) it can

intend the technique of formation of the  $S_T$ -mechanism, with  $\alpha_{ox}$  and  $P$  constant in the interval  $[T_o(max), \dots, T_o(min)]$ , described to follow:

- the interval is divided for  $n_T$  passage, with width  $\Delta T = (T_o(max), \dots, T_o(min)) / n_T$ . It is also chosen a step  $\delta\tau_p = \tau_{p,i+1} / \tau_{p,i}$  (for instance,  $\delta\tau_p = 1,1$ );
- it is chosen an initial point  $[T_o(max), \tau_{p,i} < \tau_{ex}]$ , inside of the zone B (Fig. 2) and realized a calculation for the C-mechanism, But this calculation doesn't reach the stationary state, because for  $T < 500 K$  the calculation of the composition evolution in the reactor is interrupted. The system returns for the initial state and the  $LS_T$ -mechanism is not formed.

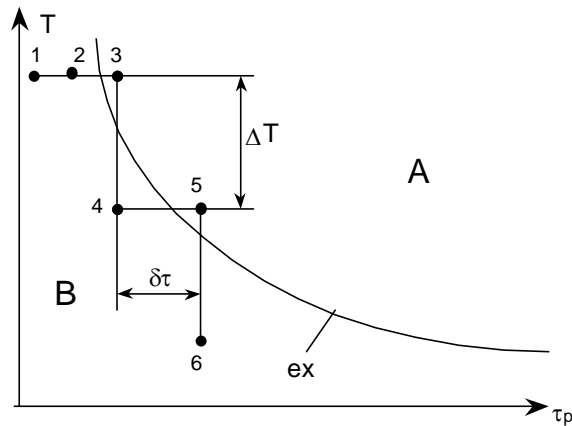


Figure 2. Points of the calculation for the  $S_T$ -mechanism formation.

- the permanence time is increased ( $\tau_{p,2} = \delta\tau_p \cdot \tau_{p,1}$ ) and the calculation is repeated with the same  $T_o(max)$ . If the system continues in the zone B (point 2 in the Fig. 2), is determined  $\tau_{p,3} = \delta\tau_p \cdot \tau_{p,2}$  and again the same calculation is realized for the point 3;
- if the calculation reaches the stationary state (this means that the reagent system is in the combustion zone), the  $LS_3$ -mechanism is formed and it is determined the new value  $T_{o,1} = T_o(max) - \Delta T$ , and the system passes for the point 4;
- the calculation is realized in the point 4. If the stationary state be not reached, increases the permanence time  $\tau_4 = \delta\tau_p \cdot \tau_{p,3}$  and the system passes for the point 5. If in this point the stationary state is reached, is formed the  $LS_5$  -mechanism and also a version of the mechanisms  $S_T = LS_3 + LS_5$  and if determined the value  $T_{o,2} = T_{o,1} - \Delta T$ ;
- the calculation is realized for the point 6 and so forth until reaching the temperature  $T_o(min)$ , with the corresponding increase of the  $\tau_p$ . When the reagent system enters in a point of the combustion zone the  $S_T$  -mechanism is completed by the LS-mechanism formed in that point.

As result, for the prescribed values  $\alpha_{ox}$ ,  $P$ ,  $\zeta$  and for the temperatures  $[T_o(max), \dots, T_o(min)]$  is formed  $S_T(\alpha_{ox}, P, \zeta)$ -mechanism and also determined the extinction line. The scheme of this algorithm is presented in the Fig. 3.

It is observed that all of the calculations are realized with the use of the C-mechanism. Habitually the zone of the user's interest involves the intervals of the excess coefficient of the oxidizer  $[\alpha_{ox}(max), \dots, \alpha_{ox}(min)]$  and of the pressure  $[P(max), \dots, P(min)]$ . In this case is necessary to choose the widths  $\Delta\alpha_{ox}$  and  $\Delta P$  and to realize calculations (every time in the interval  $[T_o(max), \dots, T_o(min)]$ ) for the scheme presented in the Fig. 3. For each point  $\alpha_{ox,i}$ ,  $P_i$  is formed own  $S_T(\alpha_{ox}, P, \zeta)$ -mechanism. Then to obtain the GS( $\zeta$ )-mechanism is necessary to unite all the  $S_T$ -mechanisms.

To verify GS( $\zeta$ )-mechanism is necessary to repeat all of the calculations with  $\zeta = 0$ . In this case the applicative doesn't form the reduced mechanism, but it determines the extinction line. Therefore after the extinction lines they are compared obtained by the new calculations, with the lines obtained by the C-mechanism, if the results of the comparison don't satisfy the user is necessary to reduce the value of  $\zeta$  and to begin the work again.

When the GS-mechanism was already formed, it can go the creation of the RS-mechanism (in other words, to execute the second stage of the reduction). In this phase of the "stationary concentrations" mode is used. In the

way the equations of the chemical kinetics are considered presented by the molars fractions (Spilimbergo *et al.*, 2005):

$$\frac{1}{V} \cdot \frac{dn_i}{d\tau} = \sum_j v_{ij} W_j = \sum_j v_{ij} k_j \left( \frac{P}{R_o T} \right)^{m_j + \sum n_{pj}} \prod_p r_p^{n_{pj}} + \frac{r_i^+ P \mu_\Sigma}{\mu^+ \tau_p R_o T} - \frac{m^- r_i P}{M_v R_o T} \quad (10)$$

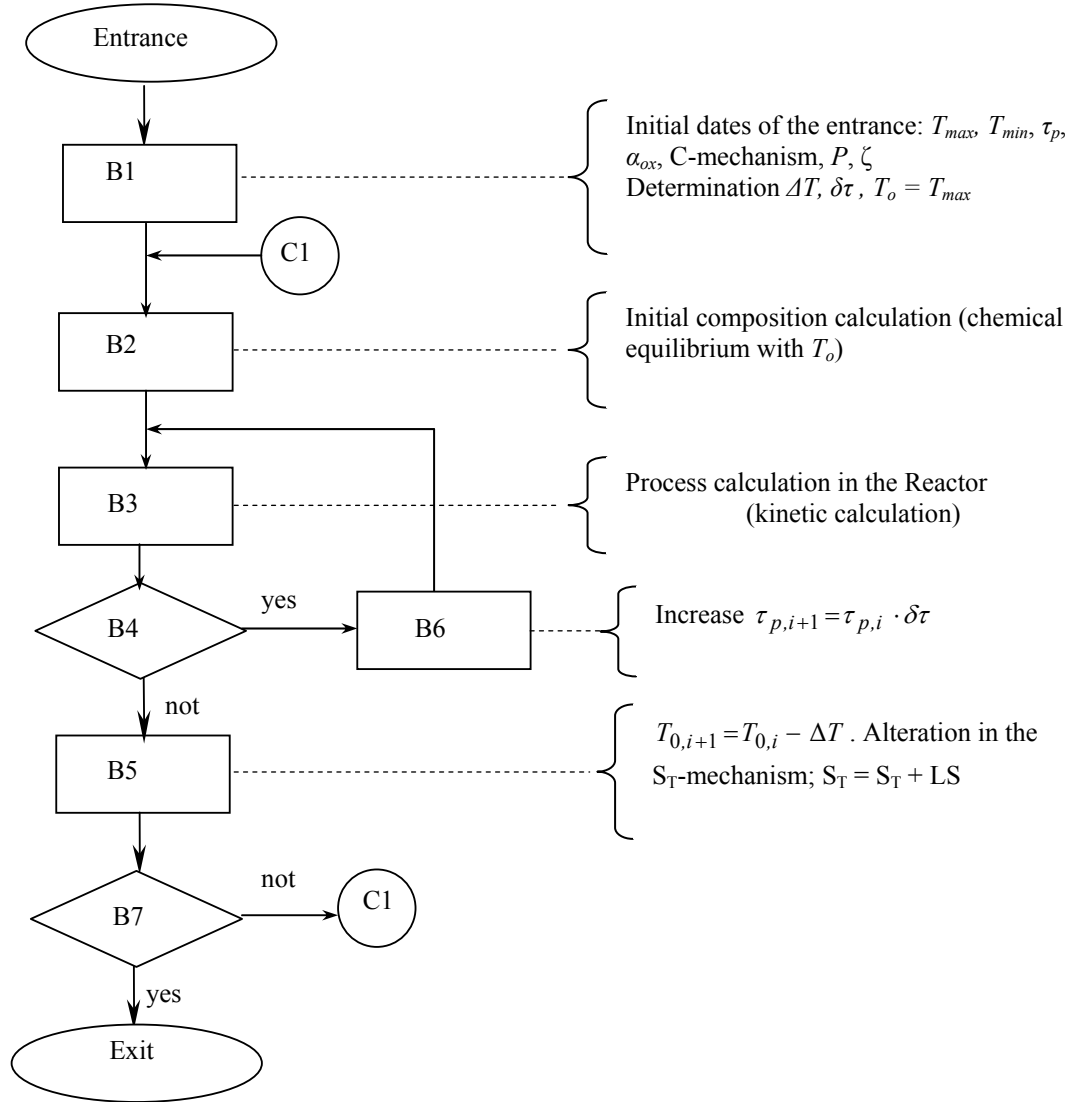


Figure 3. Algorithm formation scheme of the GS-mechanism. B4 - temperature in the reactor decreases even  $T < 500K$ ?; B7 - temperature  $T_{o,i} < T_o$  (min)?.

Then it is necessary to take into account the following suppositions:

- in the stationary regime the left part of equation (10) becomes null;
- for the intermediate species (that are not reagents) is had  $\frac{r_i^+ P \mu_\Sigma}{\mu^+ \tau_p R_o T} = 0$ ;
- if some intermediate species is small, then  $\frac{m^- r_i P}{M_v R_o T} \approx 0$ .

Then, can be concluding that:

$$\sum_j v_{ij} W_j^+ - \sum_j v_{ij} W_j^- \approx 0 \quad (11)$$

This means that the  $j$ -esima intermediate species is in chemical equilibrium with some species. Frequently is a

reaction  $z$  (the “fast reaction”) for which is correct the expression (12), in the GS-mechanism application zone:

$$v_{iz}W_z^+ \approx v_{iz}W_z^- \quad (12)$$

then, the can be excluded  $i$ -esima species and the “fast reaction” of the GS-mechanism. For instance, the “fast reaction” is considered:



the intermediate species of small concentration is “O”, then, using (12) one can write:

$$k_z^+ \left( \frac{P}{R_0 T} \right) \cdot r_{\text{OH}} \cdot r_{\text{H}} = k_z^- \left( \frac{P}{R_0 T} \right) \cdot r_{\text{H}_2} \cdot r_{\text{O}} \quad (14)$$

being obtained:

$$r_{\text{O}} = \frac{k_z^+ \cdot r_{\text{OH}} \cdot r_{\text{H}}}{k_z^- \cdot r_{\text{H}_2}} = K_z \frac{r_{\text{OH}} \cdot r_{\text{H}}}{r_{\text{H}_2}} \quad (15)$$

where  $K_z$  is the equilibrium constant of the  $z$ -esima reaction. Then is excluded of the GS-mechanism the reaction (13) and the species “O”, substituting in all of the chemical kinetics equations for the expression (15).

#### 4. GS-MECHANISM FORMATION FOR THE REAGENT MEDIUM “H + O + S + (N)”

The “engagement” method, for an zone, was implanted in the code RISTV. Simulations were realized for the reagent medium “H + O + S + (N)”, in the intervals:  $T_0 = 2000\text{K}, \dots, 1200\text{K}$ ;  $\alpha_{ox} = 1; \dots, 1,5$  and  $P = 1\text{atm}, \dots, 5\text{atm}$ .

Combustion mechanism (C-mechanism), extracted of LEEDS (2000), contains 26 species and 118 reactions. The considered reagents were:  $\text{H}_2\text{S}$  (combustible) and “air” (oxidizer). Besides, the  $\text{N}_2$  was considered as inert species and the reduction indicators of the mechanism of reactions were considered in the interval  $\zeta = 0,1; \dots, 0,3$ . Some results of these simulations are presented below. In the table 1, the GS-mechanism reactions are shown (with indicator  $\zeta = 0,2$ ) that is constituted by 14 species: S,  $\text{S}_2$ , H,  $\text{H}_2$ , O,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , OH, HS,  $\text{H}_2\text{S}$ , SO,  $\text{SO}_2$ , HSO and  $\text{HS}_2$ .

Table 1. GS-mechanism for the medium “H + O + S + (N)”, generated with indicator  $\zeta = 0,2$ .

1R	$\text{H}_2\text{S} + \text{M} = \text{H}_2 + \text{S} + \text{M}$	16R	$\text{S}_2 + \text{O} = \text{SO} + \text{S}$
2R	$\text{H}_2\text{S} + \text{H} = \text{HS} + \text{H}_2$	17R	$\text{HS}_2 + \text{H} = \text{S}_2 + \text{H}_2$
3R	$\text{H}_2\text{S} + \text{O} = \text{HS} + \text{OH}$	18R	$\text{HS}_2 + \text{OH} = \text{S}_2 + \text{H}_2\text{O}$
4R	$\text{H}_2\text{S} + \text{OH} = \text{HS} + \text{H}_2\text{O}$	19R	$\text{HS}_2 + \text{S} = \text{S}_2 + \text{HS}$
5R	$\text{H}_2\text{S} + \text{S} = \text{HS} + \text{HS}$	20R	$\text{SO} + \text{OH} = \text{SO}_2 + \text{H}$
6R	$\text{H}_2\text{S} + \text{S} = \text{HS}_2 + \text{H}$	21R	$\text{SO} + \text{O}_2 = \text{SO}_2 + \text{O}$
7R	$\text{S} + \text{H}_2 = \text{HS} + \text{H}$	22R	$2\text{SO} = \text{SO}_2 + \text{S}$
8R	$\text{HS} + \text{O} = \text{SO} + \text{H}$	23R	$\text{HSO} + \text{O}_2 = \text{SO}_2 + \text{OH}$
9R	$\text{HS} + \text{OH} = \text{H}_2\text{O} + \text{S}$	24R	$\text{S} + \text{OH} = \text{HS} + \text{O}$
10R	$\text{HS} + \text{O}_2 = \text{HSO} + \text{O}$	25R	$\text{HS} + \text{O}_2 = \text{SO} + \text{OH}$
11R	$\text{S} + \text{OH} = \text{SO} + \text{H}$	26R	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$
12R	$\text{S} + \text{O}_2 = \text{SO} + \text{O}$	27R	$\text{H}_2 + \text{O} = \text{H} + \text{OH}$
13R	$2\text{HS} = \text{S}_2 + \text{H}_2$	28R	$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$
14R	$\text{HS} + \text{S} = \text{S}_2 + \text{H}$	29R	$\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$
15R	$\text{S}_2 + \text{H} + \text{M} = \text{HS}_2 + \text{M}$		

It is observed that this mechanism is constituted of 29 reactions and 14 species. The same calculations executed with indicator  $\zeta = 0,1$ , generated a GS-mechanism composed by 39 reactions and 15 species. Besides the reactions of the Table 1, in this GS-mechanism was also included the substance  $\text{HO}_2$  and the reactions that are shown in the Table 2.

Table 2. Reactions included in the GS-mechanism with  $\zeta = 0,1$ .

Reações		
$\text{S}_2 + \text{M} = 2\text{S} + \text{M}$	$\text{HSO} + \text{H} = \text{H}_2\text{O} + \text{S}$	$\text{HSO} + \text{OH} = \text{SO} + \text{H}_2\text{O}$
$\text{HS}_2 + \text{O} = \text{S}_2 + \text{OH}$	$\text{HSO} + \text{O} = \text{SO}_2 + \text{H}$	$\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$
$\text{HSO} + \text{H} = \text{HS} + \text{OH}$	$\text{HSO} + \text{O} = \text{SO}_2 + \text{H}$	$\text{H} + \text{O}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{H}_2\text{O}$
$\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$		

But, with  $\zeta = 0,3$ , it is obtained 22 reactions and 13 species and are excluded of the Table 1 the reactions 7R, 9R, 10R, 17R, 23R, 25R, 27R, besides the species HSO. With base in those results can be conclude that:

- it happens an essential reduction of the C-mechanism for the “engagement” method: the number of species is reduced in two times, while the number of reactions in four times;
- with the increase of the indicator value  $\zeta$ , the GS-mechanism generated is reduced mainly due to reduction of the number of reactions.

In the figures 4, 5 and 6 are presented the extinction lines for the conditions  $P = 1 \text{ atm}$ ;  $\alpha_{ox} = 1; 1,2; 1,5$ , obtained for several  $\zeta$ .

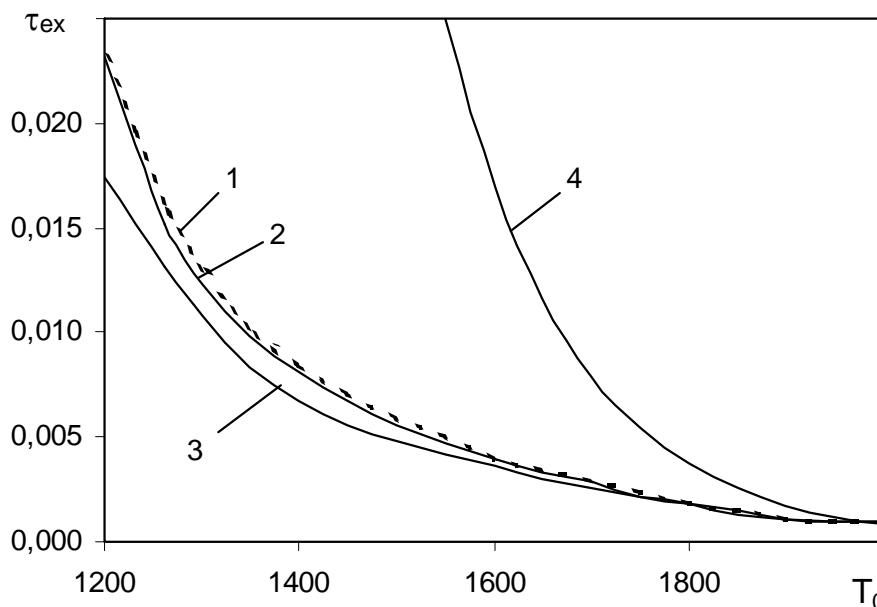


Figure 4. Extinction lines for  $\alpha_{ox} = 1$  and for different  $\zeta$ . 1 – C-mechanism; 2, 3, 4 – GS-mechanism; 2 – ( $\zeta = 0,1$ ); 3 – ( $\zeta = 0,2$ ); 4 – ( $\zeta = 0,3$ ).

Analyzing these figures can to detach:

- that the lines with  $\zeta = 0,1$  and  $\zeta = 0,2$  are close of the extinction line of the complete mechanism (C-mechanism);
- that the line with  $\zeta = 0,3$  is considerably different from the extinction line of the complete mechanism (C-mechanism).

This means (in agreement with Kalamatinos *et al.* (1998) and Tiafeeng *et al.* (2001)) that the mechanism GS ( $\zeta = 0,1$ ) and GS ( $\zeta = 0,2$ ) can be applied with safety in the whole zone of the prescribed intervals. But the mechanism GS ( $\zeta = 0,3$ ) is not safe and can probably only be applied in very distant zones of the extinction line. Therefore, to research or to form a R-mechanism is preferable to take into account the mechanism GS ( $\zeta = 0,2$ ), because it is very safe and exact.

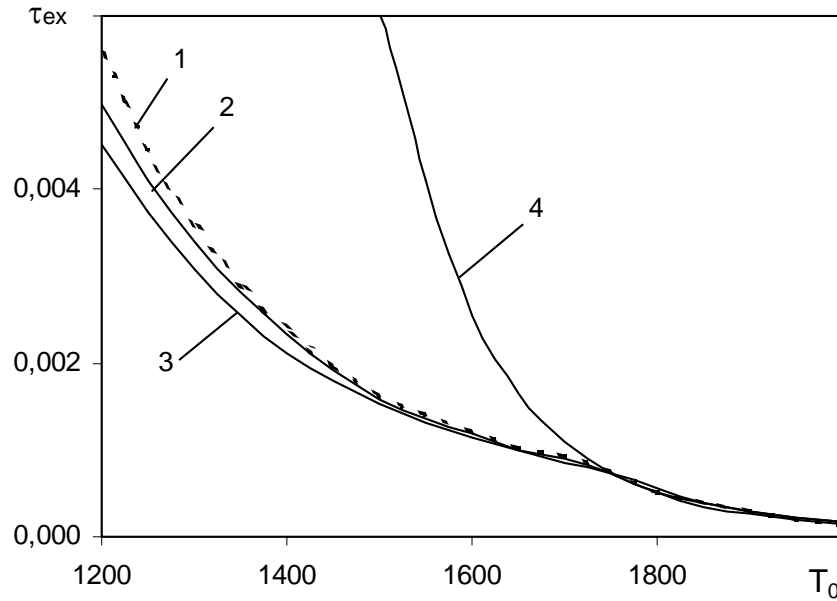


Figure 5. Extinction lines for  $\alpha_{ox} = 1,2$  and for different  $\zeta$ . 1 – C-mechanism; 2, 3, 4 – GS-mechanisms; 2 – ( $\zeta = 0,1$ ); 3 – ( $\zeta = 0,2$ ); 4 – ( $\zeta = 0,3$ ).

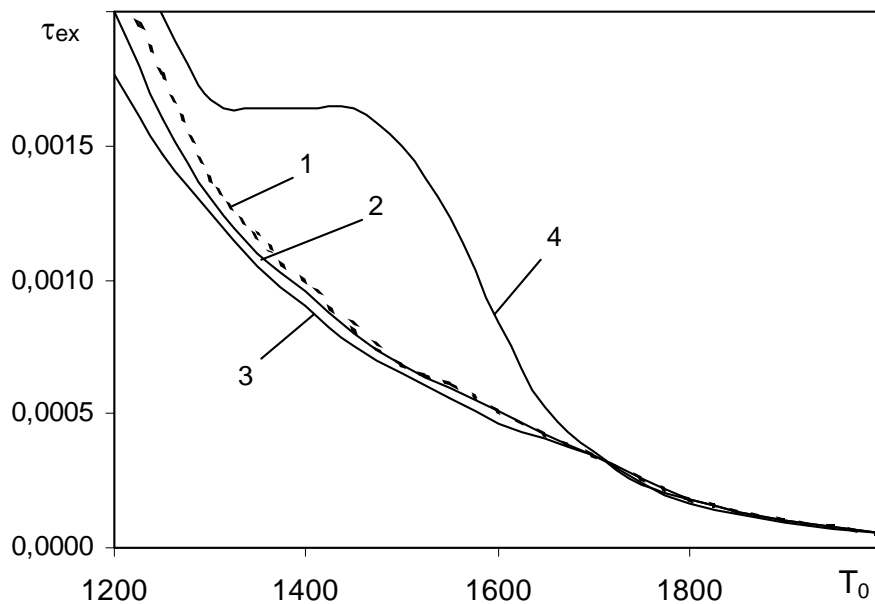


Figure 6. Extinction lines for  $\alpha_{ox} = 1,5$  and for different  $\zeta$ . 1 – C-mechanism; 2, 3, 4 – GS-mechanisms; 2 – ( $\zeta = 0,1$ ); 3 – ( $\zeta = 0,2$ ); 4 – ( $\zeta = 0,3$ ).

## 5. CONCLUSION

- The “engagement” method (presented in Spilimbergo *et al.* (2006)), to reduce complex mechanisms of chemical reactions, was developed with the objective of being applied in a zone formed by the pre-determined intervals of  $\alpha_{ox}$ ,  $P$  and  $T$ . The formation algorithm of the GS-mechanism, is based on the creation of  $S_T$ -mechanisms, in the close zones the extinction lines.
- The developed approach, was applied to form GS-mechanisms for the reagent medium “S + O + H + (N)” in the intervals of  $T_o = 1200K, \dots, 2000K$ ;  $\alpha_{ox} = 1; \dots; 1,5$  and  $P = 1atm, \dots, 5atm$ ; with different values of the indicator.
- The use of the “engagement” method, for the prescribed zone, using the C-mechanism (118 reactions and 26 species), the species number reduced in two times and the reações number in three the quattros times. For subsequent



application, the GS-mechanism with  $\zeta = 0,2$  is recommended because is only constituted by 14 species and 29 reactions and at the same time it presents a good precision.

## 6. REFERENCES

- Blom, J. G. and Verwer, J. G., 2000, "A comparison of integration methods for atmospheric transport-chemistry problems", *Journal of Computational and Applied Mathematics*, Vol. 126, pp. 381 – 386.
- Glaude, P. A., Battin-Leclerc, F., Fournet, R. *et al.*, 2000, "Construction and simplification of a model for the oxidation of alkanes", *Combustion and Flame*, Vol. 122, pp. 451 – 462.
- Kalamatianos, S., Park, Y. K. and Vlachos, D. G., 1998, "Two-parameter continuation algorithms for sensitivity analysis, parametric dependence, reduced mechanisms and stability criteria of ignition and extinction", *Combustion and Flame*, Vol. 112, pp. 45 – 61.
- LEEDS – Reaction Kinetics Database, Scholl of Chemistry, University of Leeds, 2000.
- Lindstedt, R. P. and Maurice, L. Q., 2000, "Detailed chemical-kinetic model for aviation fuels", *Journal of Propulsion and Power*, Vol. 16, pp. 187 – 195.
- Peters, N. and Kee, R. J., 1987, "The computation stretched laminar methane-air diffusion flames using a reduced four-step mechanism", *Combustion and Flame*, Vol. 68, pp. 17 – 29.
- Smooke, M. D., 1991, "Reduced kinetic mechanisms and asymptotic approximations for methane-air flame", Springer-Verlang eds, Berlin.
- Spilimbergo, A. P., Kriukov, V. G., Iskhakova, R. L. and Veloso, G. O., 2006, "Simulação numérica e otimização do mecanismo de reações do sistema reagente "S + O + H + (N)". Abstract of the XXIX Congresso Nacional de Matemática Aplicada e Computacional - CNMAC, Campinas, SP, 1 CD-ROOM.
- Spilimbergo, A. P., Kriukov, V. G. and Iskhakova, R. L., 2005, "Análise de Sensibilidade do mecanismo de reações usando o modelo do reator de mistura ideal", *Proceedings of the XXVI Iberian Latin American Congress on Computational Methods in Engineering - CILAMCE*, Guarapari, ES, pp. 1 – 14.

## 7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.