Chemistry for Sustainable Development **16** (2008) 281–293

Numerical Simulation of Gas Combustion Processes and the Problem of Explosion Safety (Review)

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Abstract

An application of numerical methods to the studies on gas combustion processes has been considered including the tracer method employed in numerical simulation. Basing on the analysis of numerical data obtained, conclusions have been drawn concerning the problem of the explosion safety connected with the inhibition and the experimental determination of the rich flame propagation limit as well as the determination of the final pressure under self-ignition within a closed vessel.

Key words: fire and explosion safety, numerical simulation, combustion processes, inhibition, superadiabatic flame temperature, cold flames, tracer method, selective oxidation

INTRODUCTION

When the Institute of Chemical Kinetics and Combustion of the Siberian Branch of the USSR Academy of Sciences was founded in 1957, it was supposed, that one of the mainstreams of the Institute's activity will be presented by the studies on the processes of burning for the needs of chemical industry. Corresponding Member of the USSR AS A. A. Kowalskiy, the founder and the first director of the Institute, Academician of the USSR AS V. V. Voevodsky attached a great importance to this research field. In this connection the Institute took an active part in the fire and explosion proofing for a number of manufactures.

In particular, detailed studies were carried out concerning the safety problem for a large-scale formalin manufacture on the basis an oxide catalyst. Some results of these activities are presented in [1]. The authors concluded that the reliable solution of the fire and explosion safety problem should imply a close interaction of the experts in different fields such as chemists, technologists, power engineering specialists, designers, *etc*., which interaction should be carried out at a design stage, rather than after a routine accident. In addition, the authors of [1] emphasize that the solution of the explosion safety problem could be economically sound due to an increase in the productivity of an individual process vessel, improvement of the product quality, reduction of a process flowsheet for obtaining and purifying a product.

The solutions should always be based on a clear-cut understanding of the technological process itself and the laws of combustion processes. However, if everything is more or less obvious for technological processes, for combustion processes the situation is different. In spite of the fact that these processes were studied for a long time, many questions remain as yet unexplored using either experimental or theoretical methods. In this case numerical simulation could become a promising way to solve this problem.

Numerical studies of combustion processes always received much attention, which is connected with several factors. One of them is represents a complexity of such systems for experimental investigation, in particular of multicomponent systems consisting of several combustibles or oxidizers. Another important factor consists in the transience of processes. Numerical investigation with a detailed kinetics allows one to answer many questions insoluble by means of experimenting.

It is reasonable that the results of numerical simulation should be experimentally verified. On the other hand, there are experimental data those have not received reliable enough interpretation till now, and with the help of numerical research this problem could be solved. The present work demonstrates some examples of the successful application of numerical methods to the studies on self-ignition and flame propagation processes as well as shows some potentialities of these methods.

Numerical simulation is based on the application of blocks of chemical reactions, thermodynamic data, and the data concerning diffusion coefficients and properly a method for solving the set of equations those describe a real process. There are several modifications of such blocks presented in the literature those differ from each other by the number of reactions, by the number of species participating in the reactions, by reaction rate constants, by the values of thermodynamic quantities, by the data on diffusion coefficients. All these modifications have been optimized basing on numerous experimental data concerning normal flame propagation velocity, induction period (breakdown time) values and concentration profiles for primary, final and intermediate species. In this connection, the application of various modifications to particular conditions would be either their interpolation or extrapolation.

In the case of interpolation one could expect that the data obtained from numerical simulation would insignificantly differ from the data obtained by means of an experiment. However, in the case of extrapolation the data obtained from simulation can be out of all proportion to a real situation. Nevertheless, the use of numerical simulation in such a case can be also justified, since this promotes the development of the numerical simulation base itself due to supplementing it with new reactions or changing the values of parameters in corresponding blocks. The present work is devoted to considering some results of numerical simulation being of interest from the standpoint of knowledge concerning new aspects of already known phenomena such as self-ignition and laminar flame propagation as well as from the standpoint of explosion safety.

SELF-IGNITION PROCESSES

Chain explosion at high burnout level

There is an interesting result presented in [2–4] concerning the application of numerical simulation. The case in point is chain explosion during hydrogen oxidation at high burnout level. This result is not obvious; there were no corresponding theoretical or experimental data for the assumption concerning the possibility of chain explosion at almost full burnout of reagents. The simulation was carried out for isothermal conditions, the pressure value of 0.1 MPa and 70 % hydrogen-air mixture. Comparative analysis of elementary reactions rates has demonstrated that immediately prior to an abrupt increase in the rate of water formation the concentration hydrogen atoms could be presented by the equation

$$\frac{dH}{dt} \approx n_0 + [2K_2(O_2) - K_4(M)(O_2)$$
$$+ K_5(HO_2)](H)$$

where K_2 is the rate constant for reaction
$H + O_2 \rightarrow OH + O$;
K_5 is the rate constant for reaction
$H + HO_2 \rightarrow 2OH$;
K_4 is the rate constant for reaction
$H + O_2 + M \rightarrow HO_2 + M$;
n_0 is the chain initiation rate; M is the third particle.

The value of $\varphi' = 2K_2(O_2) - K_4(M)(O_2) + K_5(HO_2)$ represents the factor of branching in the presence of positive interaction between reaction chains. One can see that with water formation the concentration of molecular oxygen decreases. Due to this fact the value of the negative difference between the first and the second terms decreases and could become equal to the value of the third positive term. Thus, at certain values of O_2 and HO_2 concentration the branching factor value φ' can become positive. Indeed, the authors of [2] have demonstrated that as the reaction proceeds the branching factor taking into account a square-law branching reaction, becomes positive from negative reaching a maximum and decreasing then up to zero. In other words, the branching factor varies as water is formed, and there comes a moment when it becomes positive. Just this fact causes an abrupt increase in the rate of water formation. Depending on entry conditions the branching explosion could occur at different burnout levels. It should be noted that in poor hydrogen-air mixtures when there is a lot of molecular oxygen remaining among the products, the phenomenon of explosion at high conversion level values oughtn't to take place.

The phenomenon of explosion at high burnout levels is possible due to the following two reactions. The first reaction yields HO_2, the second reaction due to interaction between HO_2 radical and H atom resulting in the formation two OH radicals. It was shown in [2–4] that at constant pressure this phenomenon exists within the range between two initial temperatures $T_{\min}$ and $T_{\max}$. At the temperature values lower than $T_{\min}$ the branching explosion is impossible, since $\varphi'_{\max} \le 0$. The upper bound of the region of two-stage non-steady state process is determined by the following conditions: φ' is always more than zero or $2K_2 \ge K_4M$.

Structure of the third self-ignition limit for hydrogen-air mixtures

The term self-ignition limit is usually taken to mean a set of entry conditions those result in spasmodic or abrupt transition from a slow mode of reaction to a fast, explosive mode. However, according to the continuity theorem for the solution of differential equations depending on entry conditions, there should be a transition region with respect to initial parameters with the change of reaction modes.

An attempt to prove the assumption that the third self-ignition limit for hydrogen-oxygen mixtures is of chain nature was undertaken in [5]. However, the estimation method chosen by the author of [5] appeared much less informative as compared to the method of numerical simulation taking into account a detailed kinetics. Indeed, the author of this work succeeded in demonstrating only that at pressure values about one atmosphere the limit is of chain nature. However, as early as in 1984 the character of the third limit, the nature of the limit structure determined and the changes connected with the increase in the initial temperature (or initial pressure) under the transition through the self-ignition limit have been described in [6]. As it follows from the analysis presented in [6], the transition region is characterized by an abrupt growth of the contributions of both square-law branching stage and the stages of square-law chain termination *via* the reactions such as

$H + HO_2 \rightarrow H_2 + O_2$

$H + HO_2 \rightarrow H_2O + O$

HO_2 radical participates in both reactions, a transformation chain such as

$H \rightarrow HO_2 \rightarrow H_2O_2 \rightarrow OH \rightarrow H$

taking place within a low temperature range.

In the transition region the transition to a shorter chain such as $H \rightarrow HO_2 \rightarrow OH \rightarrow H$ occurs.

Within the range of high temperatures the transition to a well-known chain for entirely branched reaction (during the induction period) such as $H \rightarrow (O, OH) \rightarrow 3H$ occurs.

The comparative analysis of the methods used in [5] and [6] has demonstrated that the numerical simulation with detailed kinetics is much more informative.

PROCESS OF FLAME PROPAGATION

Role of hydrogen atoms diffusion

There are diffusion fluxes of components occurring in the front of flame due to concentration gradients which fluxes could be directed both towards the initial mixture and towards reaction products. The maximal reactivity from this standpoint is exhibited by atomic and molecular hydrogen. The authors of [7] demonstrated that the velocity of flame propagation is to a considerable extent dependent on the diffusion coefficient of hydrogen atoms. The diffusion of hydrogen atoms into a low-temperature region should result in changing the conditions of a chain avalanche development, both in this region and in the region of high temperatures. This topic is in detail considered in [8].

The authors of [8] demonstrated that for 55 % hydrogen-air mixtures at pressure of 0.1 MPa and temperature of 300 K the profile for OH radical concentration demonstrates at least two maxima (Fig. 1, curve *1)*. The numerical data for the profile of OH radical presented in [9], allow one to conclude that in the flames

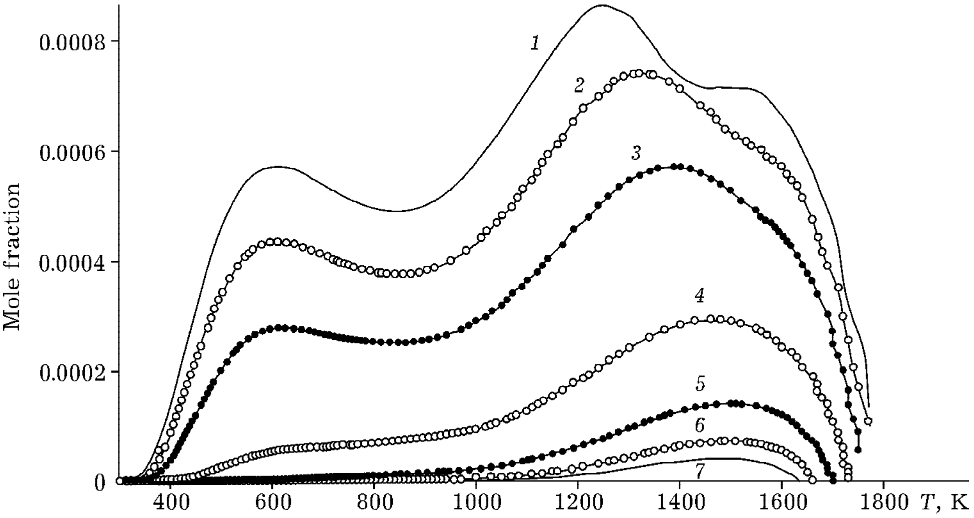

Fig. 1. Molar fraction profiles for OH radical in the flame front for the mixtures of 55 % H_2 + C_3H_8 + air (T_0 = 300 K, P_0= 0.1 MPa): *1* – with no C_3H_8 addition, *2–7* – with C_3H_8 addition, %: 0.1 (*2*), 0.2 (*3*), 0.4 (*4*), 0.6 (*5*), 0.8 (*6*), 1.0 (*7*).

of stoichiometric hydrogen-air mixtures the first maximum is much lower the than the second one. For rich mixtures the first maximum is much more pronounced being almost at the same level with the second one. In addition, the first maximum is exhibited in the low-temperature heating zone, rather than at high temperature values. The character of the profile for O and H atoms differs to a considerable extent from the character of the profile for OH radical. The increase in H and O atoms concentration occurs within a wide temperature range, the maxima being near the maximum flame temperature, and there is only one maximum for O and H atoms.

Almost at the initial temperature in the flame front H atom yields HO_2 radical, and HO_2 radical mainly results in hydrogen peroxide formation. However, when the temperature slightly (20–30 K) increases the main role is played already by the square-law branching reaction resulting in fast growth of OH concentration. The reaction of H_2O_2 dissociation into 2OH also contributes to OH formation OH within the range of low temperatures in the heating zone.

Rich flame of 75 % hydrogen + 25 % oxygen mixtures stabilized in a porous torch was numerically studied and experimentally investigated in [10] at a pressure of 10.6 Torr. It follows from the experimental data obtained in this work that the concentration profile for OH radical exhibits two maxima. The authors of [10] concluded that in the low-temperature zone of the front the formation of water occurs as a result of the following three reactions:

chain termination reaction:

$H + O_2 + M \rightarrow HO_2 + M$

square-law branching reaction:

$H + HO_2 \rightarrow OH + OH$

chain propagation reaction:

$OH + H_2 \rightarrow H_2O + H$.

The first experimental maximum of OH radical concentration is reached within low-temperature region. This fact is in a good agreement with the results of [11] where a conclusion is drawn about the important role of the reaction of HO_2 radical formation in the low-temperature zone of rich H_2–O_2 mixture flames. However, according to the numerical calculations presented in [10] the two maxima should not present in the OH radical concentration profile. The data of numerical simulation from [8] indicate that the conclusions concerning the role of H atom diffusion of the square-law branching in low-temperature regions drawn in [10, 11], to all appearance, are valid not only for low, but also for higher pressures.

There is a profile of the classical branching factor, *i.e.* chain branching rate at unit concentration, in a flame front. It is obvious, that for low-temperature regions this factor is negative. The factor becomes positive only within a higher temperature region and at a certain temperature it can intersect zero mark. At this intersection point the value of chain branching rate is equal to the termination rate value. With further temperature increasing there could be a chain avalanche in the flame front.

In the flames of rich hydrogen-air mixtures the fast growth of OH radical concentration begins within low-temperature regions. Thus, there is a diffusion transfer of the origin of avalanche-like growth of reactive species concentration and, correspondingly, reactivity transfer from a high-temperature region into the low-temperature region of the flame front. The branching factor φ' becomes more than zero already at almost the temperature 30–40 K higher than the initial one.

Thus, within the framework of numerical simulation it was shown that the diffusion of hydrogen atoms into the low-temperature region within a hydrogen flame results in the formation of HO_2 radicals and an avalanche-like growth of OH radical concentration in the low-temperature zone of the front due to the reaction of square-law branching. The concentrations of H or O atoms demonstrate an increase within all the range of front temperature variation. There are no singularities in these dependences, the maximum of concentration being reached at the temperature value close to the maximum flame temperature.

To all appearance, due to the square-law branching within the low-temperature region, hydrogen flames exhibit propagation with the velocity values an order of magnitude higher than the normal hydrocarbon flame velocity.

It should be noted that these conclusions are of fundamental importance for understanding the phenomenon of superadiabatic temperatures of hydrocarbon flames as well as the processes of inhibition.

Nature of superadiabatic temperature of hydrocarbon flame

It is well known [12–16] that the maximal temperature in the rich hydrocarbon flame front can be higher than the adiabatic equilibrium temperature (Fig. 2). For the first time the hypothesis about the nature of this phenomenon has been stated by the author of [12, 13]. According to this hypothesis, molecular hydrogen is formed in rich hydrocarbon flames as a product that "diffuses from the zone of its formation with no free oxygen content into the oxidation zone of the flame where, in competition with carbon-containing components, it is oxidized faster than the latter". According to the data of [14, 15], the nature of superadiabatic flame temperature is caused by the features of the kinetic scheme for hydrocarbon oxidation. However, this viewpoint gives rise to doubts, since in this case it is difficult to explain the formation of water at early stages of chemical transformation. A possible validation of either hypothesis on the nature of the superadiabatic temperature effect could be provided by the data obtained from the studies on the origin of water formation in the low-temperature zone a flame. In the hypothesis by the author of [12, 13] the main role is attributed to molecular hydrogen diffusion. At the same time the diffusion of hydrogen atoms as well as their participation in the formation of water are not impossible. Numerical simulation allows one to answer this question. So, data analysis of the results of numerical simulation carried out for the flame of 10 % C_3H_8-air borderline mixture [16], has demonstrated that the general scheme of determining reactions within the range of 300–685 K may be expressed in the following form:

$$H + O_2 + M \rightarrow HO_2\,(+HO_2) \rightarrow H_2O_2\,(+M) \rightarrow 2OH(+C_3H_8) \rightarrow H_2O$$

At the temperature of 685 K the concentration of water in the flame front reaches the equilibrium value among the reaction products, whereas the most part of oxygen reacted is in water molecules rather than in CO and CO_2. After reaching the maximal temperature in the flame front the atoms of oxygen from water

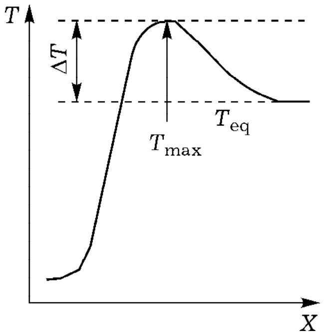

Fig. 2. Temperature profile in the front of rich hydrocarbon flame. X – coordinate, ΔT – superadiabatic temperature.

molecules are redistributed to form CO and CO_2 molecules. At the same time the concentration of molecular hydrogen increases.

The intense reaction process at low temperatures (at almost initial temperature values in the heating zone) one could explain by the presence of profound H_2 and H diffusion fluxes. Indeed, the comparative analysis of the temperature values corresponding to the beginning of the formation of main products (H_2O, CO и CO_2) under the conditions of flame and self-ignition of propane-air mixtures at atmospheric pressure (the self-ignition temperature being about 750–900 K [17]) allows one to conclude that so considerable distinction is caused by diffusion fluxes of the lightest chemical transformation products into the heating zone.

The work [18] devoted to the studies on the nature of superadiabatic temperature of methane flames demonstrated that the diffusion of H atoms plays an important role in the occurrence of superadiabatic flame temperatures. Second, the diffusion of molecular hydrogen from the region of combustion products into the low-temperature zone does not result in the occurrence superadiabatic temperature effect.

Recurring to the hypothesis of the role of the diffusion of reactive combustion products in the formation of superadiabatic temperatures [12, 13], it should be noted that it is based on the two following ideas: first, the diffusion of an active participant of superequilibrium water formation and second, the participation of molecular hydrogen in this process. The reasons and studies stated in [12–14, 18] indicate that the role of diffusion can considerably contribute in the formation of superadiabatic temperatures; however H atom rather than H_2 operates as an active participant. Thus, it appeared that the hypothesis considered is valid only partly, but it is certainly useful. To all appearance, both chemical and diffusion mechanisms of superadiabatic temperature formation should be considered not as alternative and mutually exclusive hypotheses, but as two sides of an interesting phenomenon under discussion.

Inhibition of flame propagation process

Under the inhibition of hydrogen-air mixture flames the diffusion of hydrogen atoms into the heating zone also determines the inhibitor action efficiency. The authors of [8] presented OH radical concentration profiles for the flame of the mixture of 55 % H_2 with propylene additions and demonstrated that with increasing the amount of inhibitor the profile of OH concentration is deformed in the following manner: the first maximum decreases faster than the second one to disappear completely at propylene concentration of about 0.5–0.6 vol. %. At these concentration the normal flame velocity (S_u) three-fold decreases. To all appearance, it is connected with the fact that with an inhibitor added the value of $[HO_2]_{max}$ is reduced and the concentration of OH radical in the low-temperature region of a flame front decreases to a considerable extent. Against the background of the decrease in the value of the second maximum of OH concentration, its displacement towards the region of higher temperatures is observed.

The addition of propylene results in the reduction of maximal HO_2 and H_2O_2. concentration. At propylene concentration of 0.5–0.6 vol. % HO_2 and H_2O_2 maxima reach a minimum value and with the further increase in propylene concentration almost do not vary. These data to some extent confirm the hypothesis of the fact that the action of an inhibitor exhibits a saturation effect. In this case for achieving the saturation effect it is sufficient to add 0.5–0.6 vol. % of propylene into the initial mixture. Similar data were obtained using propane as an inhibitor of hydrogen flames (see Fig. 1). The analysis of numerical simulation data has demonstrated that, due to hydrogen atoms entering the zone of low temperature, the formation of HO_2 radicals, and then of H_2O_2 occurs. OH radicals are formed in the reactions of square-law branching and hydrogen peroxide dissociation. The OH radicals formed due to these reactions reacts with propane. This reaction is a first step in the transformation of propane molecules. It is just the heating zone (low-temperature zone) where chain termination occurs as the result of propane action as an inhibitor. The fraction of propane reacting with OH radicals could be as high as 40–50 %. Residuary propane reacts with H and O already within the region of high temperature (>1000 K).

The further transformations of an inhibitor added (propane, propylene) are also of a considerable interest. Propane (propylene) represents a combustible component, therefore addition to a rich mixture of 55 % of hydrogen with air should result in increasing the fuel excess coefficient and then the mixture composition would work for the boundary value. Hence, propane operates not only as an agent lowering the reactive species concentration, but also as an additional fuel source that is oxidized alongside with hydrogen. Reactive species taking part in the oxidation of propane are the same as those participating in the oxidation of hydrogen. The analysis of numerical data has demonstrated that within the flame front propane is consumed completely by the moment when the fraction of unexpended oxygen amounts to 50 %, and the fractions of H_2O, CO and CO_2 formed are at about 30–60 %. Thus, in rich hydrogen-air mixtures propane operates both as a chemical agent influencing the reduction of reactive species concentration due to increasing the chain termination rate, and as an additional fuel that causes the fuel excess coefficient to increase. With the increase in propane concentration its role as an additional fuel grows in proportion to its concentration, and the inhibition effect due to the reduction of reactive species concentration is limited to the inhibition level. Hence, at the concentration higher than 0.5 vol. % propane operates mainly as an additional fuel source that requires for a certain fraction of initial oxygen to be oxidized.

Tracer method in numerical simulation

The tracer method [19] has appeared effective enough for studying the mechanisms of chemical reactions. With the help of the kinetic tracer method developed last century by M. B. Neumann *et al.* it was possible to establish the sequence of transformations of some substances into others [19]. The essence of this method consists in adding either isotope-containing substance into reacting system during initial or another moment of time, which allows one to establish the sequence of chemical transformation stages for substances in the reaction as well as the transformation rates for the substances under investigation at various moments of time in the reaction course. Isotopes of either atom are used in the method.

Numerical simulation of combustion processes (flame propagation, self-ignition, *etc.*) allows one to use the tracer method as well, and the potentialities of the method in this case could appear of the same productivity. This method allows one to use as a label not only an isotope, but also a labeled atom with the same physical and chemical parameters as those for an unlabeled atom. A simple modification of the tracer method in numerical simulation was used, for example, in [20]. The authors of this work studied the role of CO_2 added into methane flame and demonstrated that CO_2 additive participates in the reactions and its role being not reduced to the role of an inert diluent. Two cases were considered, In the first case CO_2 species participated in corresponding reactions was added; in the second case the CO_2 species added was designated as FCO_2 and did not take part in the reactions. However, this variant of the method does not allow one to trace the fate of CO_2 species and to establish how, with what rate and what species were formed with the participation of atoms redistributed from CO_2 among other combustion products.

In [21] we investigated the mixtures of CH_4 and hydrogen with air. The label was inserted in a hydrogen molecule, *i.e.* the flame propagation velocity and all the profiles were calculated for the mixtures such as $H^*H^*-CH_4-$air. In this case the H^* and H atoms were considered to be identical both physically and chemically. With the occurrence of a label at one of the components in the initial mixture a necessity arose to modify the GRI Mech-3 kinetic scheme [22] assumed as a basis. Among currently available full kinetic schemes for hydrocarbon oxidation, this scheme is the most suitable for studying the processes of combustion. The modification of this scheme consisted in the incorporation of new species those could be formed as the result of labeling the hydrogen atoms in the initial hydrogen molecule and, consequently, the incorporation of new reactions with their participation. New species were attributed with the properties corresponding to unlabelled species. Rate constants for the reactions with the participation of labeled species correspond to reaction rate constants for unlabelled species. In the case that the reaction of labeled species resulted in the formation of different products, we corrected for the rate constant of each forward reaction according to the reaction probability. The probability of either product formation due to a particular reaction was determined by the structure of the molecules participating in the reaction. For example, if the product is formed due to hydrogen atom abstraction out of CH_3H^* molecule the probability of the formation of a H^*-containing product is equal to 0.25 since all the H atoms in the CH_3H^* molecule are equivalent including H^*. The corresponding constant correction factor for such reaction is equal to 0.25.

The modification of the GRI Mech-3 kinetic scheme has resulted in a considerable increase in the number of reactions: instead of 325 reactions involving 53 species the modified kinetic scheme includes 2015 reactions with the participation of 131 species. The block of reactions involving nitrogen-containing components was not considered, since their concentrations are to a considerable extent low. In addition, the reactions with the participation of such species as C, C_3H_8 and C_3H_7 were not taken into account.

As against rate constants of forward reactions those were prescribed the rate constants of reverse reactions were automatically calculated within the framework of the software using the expression for the equilibrium constant. Within the software package [23, 24] the equilibrium constant the ith reaction K_{p_i} at constant pressure is defined as

$$K_{p_i} = \exp\left(\frac{\Delta S_i^0}{R} - \frac{\Delta H_i^0}{RT}\right)$$

Here ΔS_i^0 is the entropy change in the i-th reaction, ΔH_i^0 is the enthalpy change in the same reaction due to the transition from the initial reagents to products. The entropy and enthalpy of the k-th component are determined from the following formulae:

$$\frac{S_k^0}{R} = a_{1k}\ln T + a_{2k}T + a_{3k}\frac{T^2}{2} + a_{4k}\frac{T^3}{3} + a_{5k}\frac{T^4}{4} + a_{7k}$$

$$\frac{H_k^0}{RT} = a_{1k} + a_{2k}\frac{T}{2} + a_{3k}\frac{T^2}{3} + a_{4k}\frac{T^3}{4} + a_{5k}\frac{T^4}{5} + \frac{a_{6k}}{T}$$

The coefficients a_{jk} for two temperature regions are given in the thermodynamic database of GRI Mech-3 (14 values for the same reactant). With the label at H atom occurring it is necessary to introduce corrections in order to calculate rate constants for reverse reactions. The correction for changing the equilibrium constant was introduced into the value of coefficient $a_{7\kappa}$ in the expression for the entropy of the kth component (in the case when the label is present one needs to add the Napierian logarithm of the quantity describing the increase in the number of states for the kth component).

The analysis of numerical simulation data for the process of flame propagation in rich methane-hydrogen mixtures with air with a label at hydrogen molecule has demonstrated that oxygen is consumed mainly for the formation of water from hydrogen molecules and of hydrogen atoms from methane. The concentrations of CO and CO_2 are to a considerable extent lower than equilibrium values (Fig. 3). The formation of superequilibrium water amount among the products is caused by the phenomenon of superadiabatic temperatures. Moreover, the concentration of labeled water at the point corresponding to $T_{\max}$ appeared to be higher than its concentration in equilibrium products (see Fig. 3). On the basis of these data one may

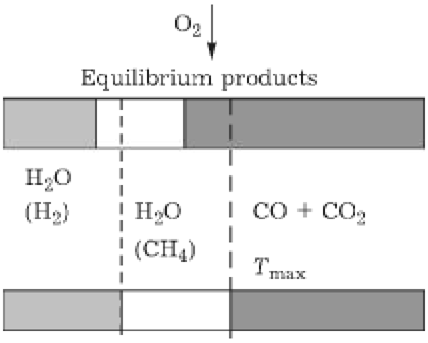

Fig. 3. Schematic diagram for the distribution of oxygen atoms in equilibrium products and in the flame of 21 % H_2 + 10.5 % CH_4 + air mixtures at the point with maximal temperature.

conclude that a selective, paramount oxidation of hydrogen can occur in complex multicomponent mixtures. The selectivity level depends on methane and hydrogen concentration ratio and on the remoteness of the mixture from the boundaries of a flame propagation region. The superadiabatic temperature phenomenon itself is determined by the contributions from all components.

The use of various variants of the label location in initial molecules allows one to determine, for example, the degree of participation of the added "inert" water in the reactions. It is commonly supposed that water, as well as CO_2 exhibits the properties of an inert diluent. However, it was shown in [20] that carbon dioxide takes an active part in the reactions under the conditions of flame propagation. Hence, the total effect of CO_2addition is not equivalent to the effect of inert dilution. Adding water with labeled hydrogen atoms into the mixture, one could trace the further transformations of this additive. Figure 4 demonstrates concentration profiles of some molecular components in the flame of 16 % H_2 + 8 % CH_4 + air mixture diluted with 10 % of H_2^*O .

One can see that almost 80 % of an "inert" water addition disappears, and water with one labeled hydrogen atom HH*O (54.7 % of initial labels in the products), hydrogen atom H* (6.7 %) as well as hydrogen HH* (19.08 %) appear in place of water with two labeled hydrogen atoms. The fraction of residuary water with two labeled hydrogen atoms amounts to 19.4 % with respect to the initial labeled water. Thus, labeled hydrogen atoms from the labeled water added mainly are transferred into the molecules of water with one label such as HH*O and into the molecules of hydrogen with one label such as HH*. The fraction of labeled hydrogen atoms in the molecules containing carbon atom is <1 %. From the data presented in Figure 4 one can see that the molecules of water added to rich hydrogen–methane mixtures actively participate in the reactions. Moreover, using these data one can determine how many labeled hydrogen atoms were redistributed from water molecules and what species were entered by them.

The authors of paper [20] devoted to the role of CO_2 in flames, mention only the fact that added CO_2 takes part in the reactions inasmuch as the authors considered only two variants: CO_2 either participates in the reactions, or does not participate. The numerical results for normal flame propagation velocities in these two cases appeared different. The addition of CO_2 results not only in exhibiting thermophysical effect connected with the variation of the

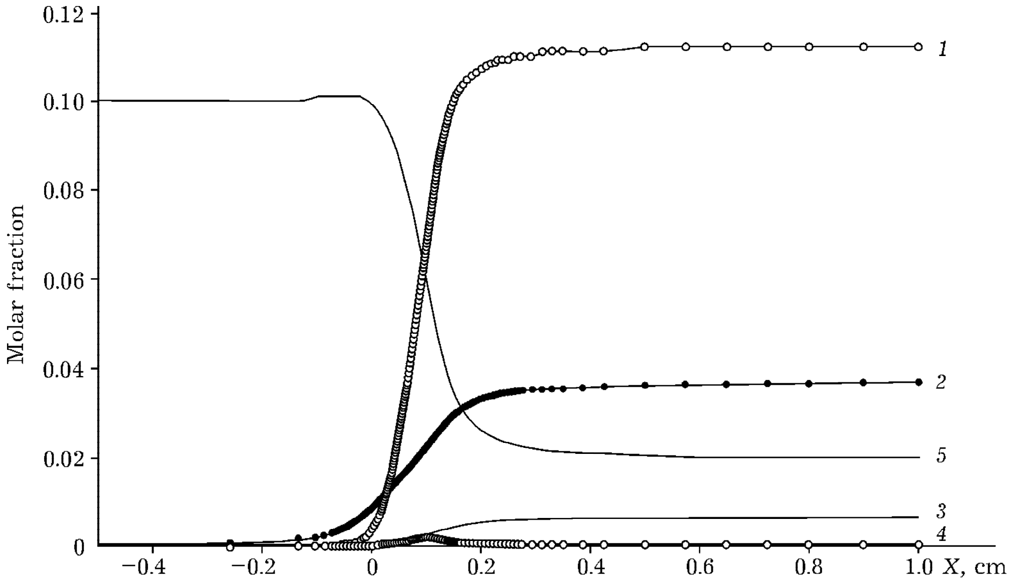

Fig. 4. Molar fraction profiles for transformation products with labeled hydrogen atom in the flame of (16 % H_2 + 8 % CH_4 + air) + 10 % H_2^*O mixture: *1* – HH*O, *2* – HH*, *3* – H*H*, *4* – CH_3H^*, *5* – H*H*O.

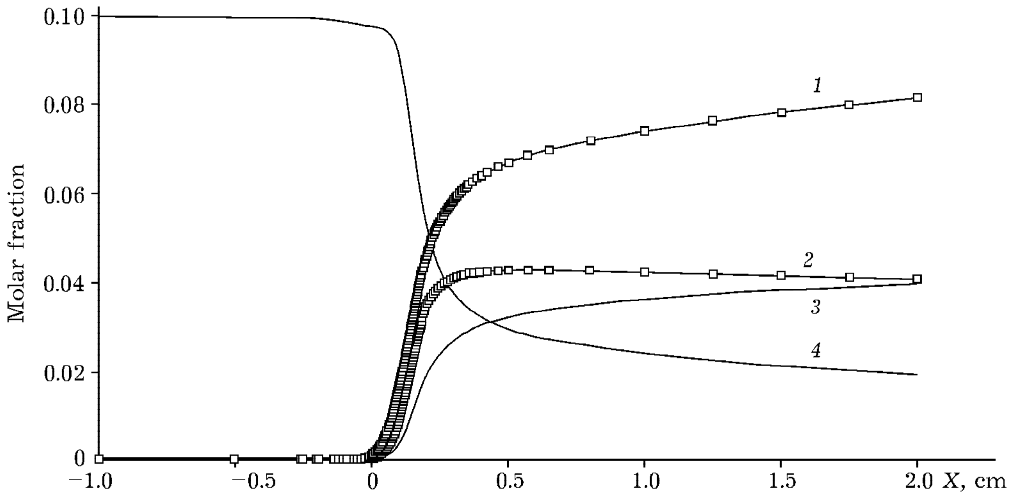

Fig. 5. Molar fraction profiles for transformation products with labeled oxygen atom in the flame of $(16\,\%\,H_2 + 8\,\%\,CH_4 + \text{air}) + 10\,\%\,CO_2^*$ mixture: *1* – H_2O^*, *2* – CO^*, *3* – COO^*, *4* – CO^*O^*.

thermal capacity and heat conductivity of the system, but also carbon dioxide actively participates in the reactions in flames. The use of a label at CO_2^* molecule has allowed the authors to trace the transfer of this label to other components as the result of the molecule taking part in the reactions. So, in products of a flame the labeled oxygen atoms in flames were distributed from product to product as it follows (Fig. 5): 14.5 % of the label remained at the initial CO_2^* molecule, 17.56 % of the label has been transferred to CO^* molecule, 20.78 % – to COO^* molecule, 47.14 % – to H_2O^* molecule.

The application of the tracer method in numerical simulation has allowed us to trace the level of interaction between the hydrogen oxidation scheme and the scheme of methane oxidation. It is an important point since it is connected with the question concerning the inhibition mechanism of flame propagation. The tracer method in numerical simulation allows one to exclude in part or completely the interaction of the two schemes, except for the thermal interaction. Figure 6 demonstrates temperature profiles in the flame of 21 % H_2 + 10.5 % CH_4 + air initial mixture for three variants of interaction between the two oxidation schemes. Under full interaction of the schemes the normal flame propagation velocity is equal to 10 cm/s, the temperature profile is stretched, the maximum temperature value for the flame

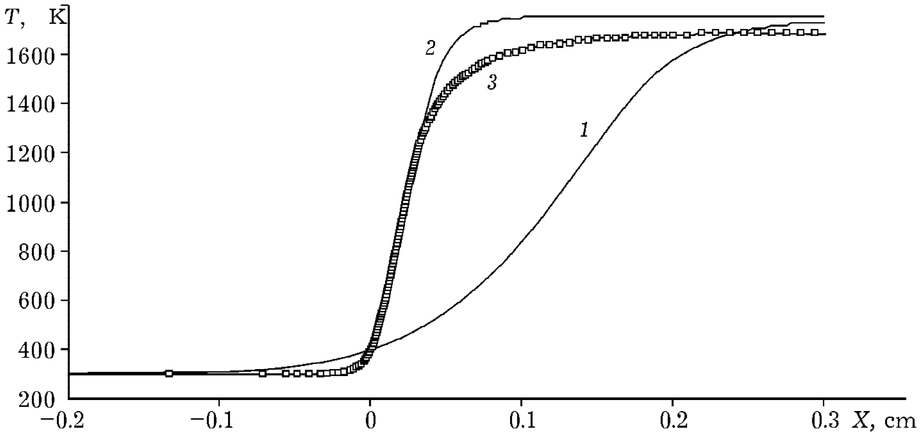

Fig. 6. Temperature profiles in the flame of 21 % H_2 + 10.5 % CH_4 + air mixture: *1* – full interaction of oxidation schemes, *2* – interaction of oxidation schemes only through O and O_2 as well as thermal interaction, *3* – only thermal interaction.

front amounting to 1749 K. In the case of imposing exclusion on the reactions between labeled and unlabeled species and proposing atomic and molecular oxygen to be common for the two oxidation schemes, the velocity of flame propagation exhibits an increase up to 54.4 cm/s, and the temperature profile becomes more abrupt. The maximum temperature would already amount to 1764 K, being 15 K higher than in the case of full interaction. Under full exclusion imposed on the interaction of the oxidation schemes, except for thermal interaction, the maximum temperature gradient in the flame front becomes even higher, the value of normal velocity being as high as 62.7 cm/s. In spite of the fact that imposing either exclusion results in reducing the concentrations of some components within isolated systems and in reducing the rates of corresponding reactions, the normal flame propagation velocity grows. To some extent the data presented demonstrate the range of methane effect on the process of flame propagation in hydrogen−air mixtures. It is evident that the methane added reacts with H, O, and OH species more actively as compared to molecular hydrogen. Just this is the fact determining the role of hydrocarbon as an inhibitor. It is enough “to isolate” the schemes of methane and hydrogen oxidation to make the reactivity of hydrogen in the presence of methane sharply increased. This fact indicates that the reactivity of hydrocarbons in the presence of hydrogen in non-isolated oxidation schemes is higher than the reactivity of hydrogen.

Thus, the tracer method offers outstanding possibilities in the field of numerical simulation as applied to studies on the processes of combustion. Using this method it can be possible to answer many questions connected with the features of flame propagation within complex multicomponent mixtures.

NUMERICAL SIMULATION OF COMBUSTION PROCESSES AND THE EXPLOSION SAFETY PROBLEM

The results of numerical simulation have raised some important issues connected with the problem of explosion safety. It is connected mainly with determining the rich flame propagation limit. It turned out, that a numerical solution exists for the mixtures with the combustible concentration exceeding an experimentally measured limit to a considerable extent. For example, in the case of dimethyl ether-air mixtures a numerical solution exists for 60 % CH_3OCH_3 mixtures, whereas the experimentally measured concentration limit makes amounts to only 26.7 % CH_3OCH_3. In the case of propane−air mixtures a numerical solution exists for 15 % propane concentration, whereas the experimental limit of concentration is as low as 10 % C_3H_8. A question arises: either the solutions for the mixtures beyond the limit represent a mistake of the numerical simulation connected with the uncertainty of the kinetic scheme for superrich mixtures ignoring any physical processes (for example, a radiation-caused heat loss from the flame front), or the experimental limit measurement is restricted by the experimenter’s ability and skill in the initiation of a combustion wave? May be, the last assumption is more correct. The fact is that according to the results of numerical simulation, as the concentration of combustible in the mixture increases the thickness of the flame zone grows. For example, for 10 % propane the thickness of flame front amounts to ~1 cm. For superrich dimethyl ether mixtures (80 % CH_3OCH_3, T_0 = 400 K) it can be as thick as 10 cm at a normal flame propagation velocity approximately equal to 0.7 mm/s. Unfortunately, the experimenters did not use such sources (or, perhaps, they did not raise a question concerning such sources) those would allow one to create great volumes of heated gases with the lifetime sufficient for the formation of a combustion wave. On the other hand, a considerable influence is exerted by the presence of gravitational field. At low values of normal flame propagation velocity under the conditions of the Earth’s gravitational field the centre of flame will be deformed and it can not be known whether the flame exist under such circumstances. So, under the conditions of weightlessness the rich limits obtained under terrestrial conditions could appear underestimated with corresponding consequences for space objects. The experience gained demonstrates [25] that incombustible (as it was considered earlier) mixtures with air can support flame propagation if the combustion wave is initiated by a volume ignition source.

Another important result of the application of numerical simulation consists in data acquisition concerning superadiabatic temperatures those can be achieved under the conditions of self-ignition in the case when diffusion processes are absent. In rich combustible-oxidizer mixtures under self-ignition conditions the maximum temperature could be several hundreds degrees higher than the adiabatic equilibrium temperature value. The increase in pressure for a closed system is connected with the growth of temperature, therefore under the condition of superadiabatic temperature values pressure can appear higher as compared to the pressure calculated on the basis of the known heat of combustion.

It is interesting to note that according to the biblical plot about the Burning Bush (Book of Exodus 3: 2) this bush can exhibit a bright luminescence that could be mistaken for a flame. At the same time the bush does not burn, *i.e.* it is not scorched. According to the results of the experiments carried out in 1960 by Polish botanists [26], such bush named also "the bush of Moses" (Diptam, *Dictamnus Fraxinella*) really exhibits the property to flash. The authors of [26] observed a bush lighted up with a bluish-red flame. The energy was mainly evolved as light quanta. This feature is connected with the fact that this bush evolves ethers. When the weather is windless and sunny, ethers are abundantly accumulated in the bush itself, a cloud of ethers being formed around the bush to result in partly transforming into ether peroxides under light. By the way, peroxides represent highly reactive compounds those, in turn, can initiate reactions with a pronounced chemiluminescence. It is just this glow that is mistaken for a flame. Such a flame can exist for a long time enough. As a matter of principle, a fireball could be of the same nature. Thus, the mixtures of ethers with air exposed to light could represent a special hazard connected with the formation of peroxides those initiate cold flame, and then hot flame, too. The results of numerical simulation for the processes of flame propagation in the mixtures of methane or dimethyl ether with air and peroxide additions indicate that peroxides at sufficiently low concentration are capable to support propagation of cold flames with the temperature ranging within 800–1000 K (Fig. 7).

CONCLUSION

The analysis of numerical simulation results has demonstrated that, besides traditional data on normal flame propagation velocity values, concentration profiles of various components in reacting systems, induction periods, *etc.*, one can obtain the answers of many questions of

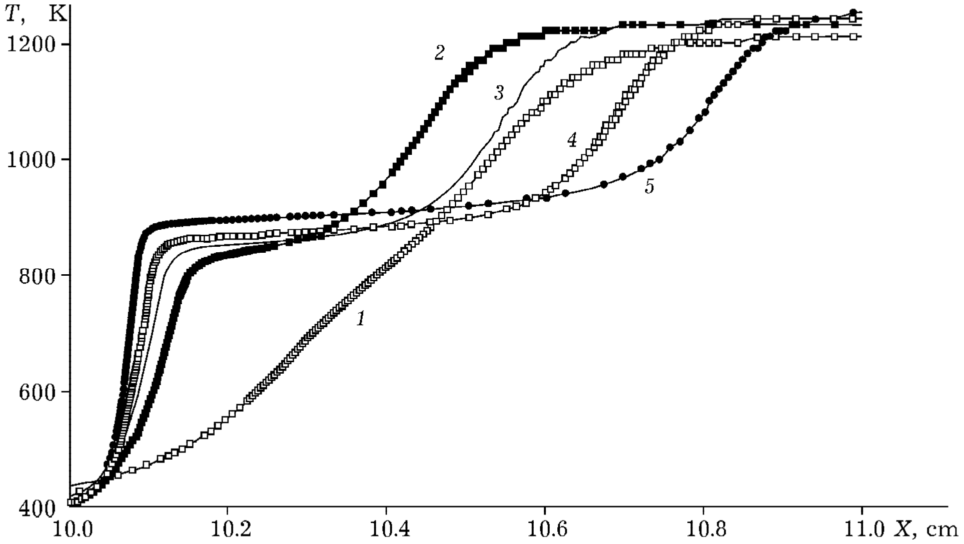

Fig. 7. Temperature profiles in the flame front for 30% CH_3OCH_3 + air mixture with various additions of ether peroxide: *1* – with no ether peroxide addition, *2–5* – with the addition of $CH_3OCH_2O_2H$, %: 1.5 (*2*), 2 (*3*), 2.5 (*4*), 3.5 (*5*).

interest from the standpoint of the knowledge of the nature of some phenomena in the field of combustion, the statement of new problems for experimental research as well as solving the problems of explosion safety.

Numerical simulation has allowed us to reveal some features of the inhibition process. So, it has been established that an inhibitor comes into play already at early stages of reagents transformation within the low-temperature zone of a flame front. An inhibitor appeared more reactive as compared to molecular hydrogen. This conclusion is not trivial at all, since earlier it was considered that hydrogen is the most reactive component. The numerical simulation has confirmed the conclusions that an inhibitor exhibits a limited ability in suppressing branching-chain processes, *i.e.* it possesses a certain level of inhibition. Moreover, with the use of numerical simulation it was demonstrated what a radical and in which place could an inhibitor react.

An important result was presented by the conclusion concerning the presence of selective oxidation in multicomponent systems drawn due to the use of the tracer method in numerical simulation. With the use of the tracer method a question has been solved concerning the transformations of seemingly inert water and carbonic gas added to gas mixtures.

One could consider establishing the nature of superadiabatic temperature values in hydrocarbon flames to be the most interesting result. It has been revealed that this phenomenon is based alongside with kinetic features on the diffusion of hydrogen atoms. The presence of superadiabatic temperatures results in a considerable extension of the flame propagation region which extension is important from the standpoint of explosion safety. The data obtained cast some suspicion on the reliability of experimentally obtained values for rich flame propagation limit, which is of fundamental importance for the explosion proofing of chemical technologies and, probably, of space objects.

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