

Heat and Mass Transfer

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Ignition and Wave Processes in Combustion of Solids

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Preface

In this book, the issues on the combustion of solids raised, which have not been considered in the earlier books “The Modes of Gaseous Combustion” (Springer, Heat and Mass Transfer 2016) and “Key Factors of Combustion, From Kinetics to Gas Dynamics” (Springer, Springer Aerospace Technology, 2017) where only gaseous combustion was the subject to review. It is clear that the problem of combustion of solid fuels makes the understanding of the process more complex as compared to gas combustion. Really, the equation of state in an analytical form is usually missing, therefore, in calculations, the question of finding of the closing equation for the corresponding system of the equations often arises. In addition, the gas–solid, liquid–solid and solid–solid systems possess their unique properties and laws; among them there are, e.g., phase transitions, the problems of stability of nanoparticles as well as flammability of coal–gas suspensions in coal mines, or the nature of solid–solid reactions etc. For instance, in the latter case the problem on the mechanism of the reactions between two different solid powders occurs due to very small diffusivities in solids. Really, in Ta + C system, the reaction rate is quite small, however, the reaction Ti + C proceeds at substantially higher velocities. Thus, the features of kinetic mechanisms in solid–solid reactions have been under discussion in the literature.

The book attempts to analyze the basic approaches to understanding of solid–solid and solid–gas combustion presented in contemporary literature. It focuses also on the application of classical combustion theory to ignition and flame propagation in solids and experimental investigation in the certain areas of filtration combustion, self-propagating high-temperature synthesis and nanopowders protection based generally on the works of the author and original works of his co-authors. The book may be useful for undergraduate and postgraduate students and researchers in the area of experimental studies of combustion.

In this book, contemporary results and achievements of Russian science in the area of combustion of solids are consistently set out for the first time. This applies in particular to theoretical works of one of the co-authors Boris S. Seplyarskii, whose investigations in the area of classical combustion theory form the ideological basis of the book. In addition, analytical formulas are presented in different areas of

combustion in solids (local ignition, filtration combustion, self-propagating high-temperature synthesis, combustion of gas suspensions), which have been already successfully used by Russian scientists for practical application.

The authors note that in the theoretical analysis, they tried to pay the main attention wherever possible to analytical consideration rather than to numerical calculations. It is evident that the development of an analytical approach is always followed by the creation of some ideology of understanding of the essence of a process using certain reasonable assumptions, which allow getting the solution of a complex problem in a rather simple and clear analytical form. Thus, the reader has an opportunity to understand the nature of the phenomenon, without penetrating into a particular architecture of algorithms of a calculation method.

The authors would also like to make the reader more familiar with virtually inaccessible works of Russian authors published up to 2017 in Russian.

It was shown that the problem on a local ignition of condensed substance comes down to the investigation of the dynamics of a reaction zone under condition of cooling of the ignition center with the inert environment; at the same time the power of a chemical heat source during the induction period can be considered approximately constant. The approximate analytical method was applied for analysis of the problem on a local chain-thermal explosion in the reaction of hydrogen oxidation in the presence of chemically active additive. The concept of an intermediate combustion wave with the maximum temperature equal to the initial temperature of the hot spot was introduced. It was shown that key parameters determining the critical size of a local source of ignition, are the temperature in the center of a local ignition zone; the quantity of the active centers of combustion created with the local source; and presence of active chemical additives in combustible gaseous mixture. Comparison to experimental data showed applicability of the developed approach for the analysis of critical conditions of a local ignition in combustible gas mixtures.

The concept of the wave mechanism of formation of a quasi-stationary zone of a chemical reaction was examined for determination of critical conditions and a delay time of ignition with heat losses. It was shown that the connection of the depth of burn-up and the velocity of an intermediate wave with the value of a heat loss coefficient determines the specifics of the ignition under nonadiabatic conditions. The wave theory of the ignition, which showed high efficiency when determining temporary characteristics of ignition in systems with the complex mechanism of chemical interaction (consecutive, parallel, independent reactions) was presented. On the basis of the wave mechanism of formation of a chemical reaction zone main characteristics of the ignition process were determined, namely the time of inert warming up, establishment and failure of a thermal balance; the physical meaning of these characteristics is also clarified. It was shown that the development of a heating process depends on a ratio of characteristic times of formation of a chemical reaction zone capable of independent propagation, and complete burn-out on a sample surface. Critical values of a heat loss coefficient were calculated. It was shown that critical ignition conditions coincide with limiting conditions of occurrence of an intermediate combustion wave ICW. The main characteristics of ignition process for a first-order reaction were determined. The results of numerical

calculations validated the main assumptions as well as the main conclusions of the approximate analysis. It was suggested to find the scale temperature (ignition temperature) from the equality of an external thermal flux to a heat flux from a reaction zone in an intermediate combustion wave, which maximum temperature is equal to ignition temperature. It was shown that at surface temperatures smaller than ignition temperatures, it is possible to consider warming up as inert one; the time of this stage makes the main part of a delay time of ignition τ_{ig} . It allows expressing τ_{ig} through the characteristics of an intermediate combustion wave. The analytical method of calculation of temporary characteristics of ignition of a porous body under conditions of a counter nonstationary gas filtration was created. It was found that the rate of heating of substance during ignition is close to the rate of heating of this substance with an intermediate wave of filtration combustion (IWFC) with the maximum temperature equal to ignition temperature. The analytical method of calculation of temporary characteristics of ignition of a porous sample with a stream of hot gas flowing into the substance (a cocurrent nonstationary filtration) was also suggested.

The convective mechanism of combustion was suggested for the explanation of an abnormally high combustion velocity found in combustion of “gasless” systems, titanium + soot, and also titanium + soot + polystyrene under conditions of one-dimensional filtration of impurity gases. The analysis of the available experimental and theoretical data showed that under conditions of impurity gas emission, the convective combustion mechanism can be provided by the movement of a melted layer of one of reagents under the influence of pressure difference of impurity gases. Physical and mathematical models of convective combustion of “gasless” systems were formulated. It was established that the realization of the accelerating combustion mode requires presence of the free volume, which is not occupied with a sample. It was shown that at an initial stage of combustion as well as at the value of free volume exceeding the sample volume, the velocity of the front and the pressure of gas increase are under the exponential law. Analytical expressions for calculation of the average velocity of convective combustion were obtained. An investigation of the model allowed explaining the distinctions in regularities of combustion of “gasless” systems under conditions of the counter, cocurrent and bilateral filtration of impurity gases. It was shown that depending on the organization of combustion process, the pressure difference of impurity gases can both accelerate, and slow down the penetration of the melt into an initial sample, changing thereby a combustion velocity. The estimates of the width of a warming up zone showed that impurity gas emission in the warming up zone occurs, first of all, at the expense of desorption of the gases and vapors, which are adsorbed on a surface of the particles of a fine component. By means of the new combustion model, the explanation of an increase in combustion velocity of “gasless” systems observed at thermal vacuum processing and reduction of diameter of initial samples was given. Based on the grounds of the convective-conductive theory of combustion (CCTC) of heterogeneous condensed systems it was offered to apply a method of pumping out a sample to control the synthesis. The regularities of combustion by the example of Ti – C powders under

conditions of artificially created pressure difference along the sample were investigated. It was shown that the removal of impurity gases in a warming up zone of the reaction front provides significant increase in the combustion velocity. It was established that preliminary thermovacuum processing TVP of initial mixes leads to an increase in combustion velocity for samples of bulk density. It was revealed that the presence of moisture does not practically influence on combustion regularities and phase structure of products of granulated Ti + 0.5C samples. It was found out that under conditions of Ar coflow the influence of humidity on the phase structure of reaction products decreases and combustion velocity of the powder sample increases. It was shown that the presence of moisture in the Ti + 0.5C powder sample has an impact on the phase structure of combustion products and practically has no influence on the combustion velocity of the sample without gas flow.

Thus, the available literature and experimental data confirm the applicability of the convective–conductive mechanism of combustion wave propagation in the fast-burning “gasless” systems containing a fusible reagent.

The analytical method of calculation of the critical size of the hot spot was created for greater values of a coefficient of heat exchange of particles and gas. By means of numerical calculations the functional dependence of the critical size of the hot spot on parameters following from the theory was validated; the range of applicability of approximate formulas was determined. Two mechanisms of the ignition of gas suspension by the hot spot were revealed for the first time:

- (a) ignition of gas suspension as ignition in quasi-homogeneous single-temperature medium;
- (b) ignition of particles in the center of the hot spot due to violation of thermal balance between the rate of heat allocation on a particle and heat dissipation into the gas.

It was shown that the value of the minimum energy of ignition does not practically depend on the mass concentration of particles in gas suspension at a constant value of initial temperature θ_{in} . The method of calculation of the critical size of the hot spot R_{cr} can be used for determination of R_{cr} for the complex mechanism of interaction of particles with an oxidizer (parallel, consecutive, independent reactions).

Various mechanisms of critical phenomena for the kinetic and diffusion modes of ignition at pulse energy supply were established. At greater values of a heat exchange coefficient Z (a kinetic ignition mode) the critical duration of an impulse is equal to the time of establishment of a zero gradient on a border: a heater–gas suspension. At small values of a heat exchange coefficient Z (a diffusion mode of an ignition) the critical duration of an impulse is less than τ_0 and it is found from the equality $\tau_1 = \tau_2$. Here τ_1 —the time of complete burning out of particles at $\xi = 0$, and τ_2 —the ignition time (a transition to the diffusion mode of a reaction) of particles at $\xi \rightarrow \xi_g + 0$. The expressions, allowing to determine necessary and sufficient conditions of the ignition of gas suspension by a heated body at pulse energy supply were obtained. Numerical calculations showed a possibility of

application of approximate formulas for determining of minimum duration of an impulse necessary for the ignition of gas suspension. By means of numerical calculations, it was established that the minimum time required to attain a high-temperature combustion mode is reached at $\tau_{\text{pul}} = \tau_0$. The investigations described allow calculating the minimum energy of ignition of hybrid gas suspension with a hot spot using the data on the kinetics and thermal effects of gas phase and heterogeneous reactions as well as on the amount of condensed phase in a unit of volume. The results of such calculation are necessary for the creation of safe conditions for carrying out technological processes, in which suspensions of combustible particles in gas containing oxidizer and small additives of combustible gas are formed. It was experimentally shown that at 650–750 °C coal gas suspension containing stoichiometric mixture of natural gas and air does not burn over surface coated with coal powder due to inhibiting effect of gases evolving during thermal treatment of coal powder. The ignition of the gas suspension can be promoted with small amounts of chemically active additive (e.g., dichlorosilane). Thus, we can conclude that the improved model of ignition of gas suspension of solid particles in a mix oxidizer—combustible gas must take into account inhibiting effect of gases evolving during thermal treatment of coal powder. The hydrocarbons (probably PAHs) arising in the ignition of HGS, on the one hand are flammable, and on the other hand have the inhibiting action on methane combustion, as it takes place in the process of inhibition of ignition of H₂–air mixes with small hydrocarbon additives. However, in the presence of small quantities of methane (lean mixtures) the ignition of volatiles evolved from coal, can provide the subsequent methane ignition, because the volatiles are hydrocarbons, probably, polycyclic aromatic hydrocarbons (PAH).

A model of the porous sample ignition was proposed, based on an assumption of a limiting role of the oxidizer diffusion in the ignition mechanism. It was shown that the ignition process can have a two-stage character. The duration of the stages was estimated by the methods of combustion theory. The applicability limits of the semi-infinite body model were determined. The role of the finite size of a sample in the ignition process was analyzed. The nonuniform surface mode of combustion of iron nanopowders and fingering patterns in combustion of nickel nanopowders in the absence of external flows was revealed for the first time. The method of estimation of the extent of passivation of Fe nanopowders with the use of a method of color high-speed filming was offered. It was experimentally established that both the dependencies of the period of a delay of ignition and quantity of the primary centers of combustion on the time of passivation can be used for estimation of the extent of passivation. On the basis of the experimental data, the approximate equation for estimation of the minimum time of complete passivation for the sample of arbitrary thickness was offered. By the method of X-ray phase analysis, it was established that 1 mm thick samples of iron nanopowder treated in a stream of 3% of air + Ar for the time interval more than 6 min contain only metallic iron. Therefore, the method of passivation suggested is rather effective. The effective means of stabilization of iron nanoparticles synthesized by the method of chemical

metallurgy by means of passivation in argon stream + 0.6% O₂ within 6–60 min was offered. It was established that at storage of iron nanopowder in a vessel equipped with the ground-in cover within 5 months in the ambient air any noticeable change of chemical composition of the powder was not observed. It was shown that nanoparticles form crystallites with a size $\sim 20\text{--}100$ nm. The results of Auger's method of spectroscopy are consistent with the fact that nanoparticles of iron contain an iron kernel and an oxide layer of 2–4 nm thick.

The average specific surface area of the passivated nanoparticles of iron determined by the BET method makes up to ~ 9.2 m²/g and does not practically depend on the time of passivation.

The effective method of stabilization of iron nanoparticles synthesized by the method of chemical metallurgy by means of passivation in the dry air at subzero temperatures was offered for the first time. It is experimentally shown that at a certain subzero temperature Fe nanoparticles do not ignite in dry air; however, passivation occurs and makes the particles stable at room temperature. It was shown that combustion modes at room temperature and subzero temperatures differ qualitatively. It was detected that both the content of oxides in the iron nanopowder sample after combustion and the maximum warming up decrease with a decrease in initial temperature. It was shown for the first time that the concepts of the classical macroscopic theory of a thermal explosion are quite applicable to nanoobjects.

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Chapter 2

The Theory of a Local Ignition

Abstract It is shown that the problem on a local ignition comes down to the analysis of the dynamics of a reaction zone under condition of cooling of the ignition center with the inert environment; at the same time the power of a chemical heat source during the induction period can be considered approximately constant. The approximate analytical method is applied for analysis of the problem on a local chain-thermal explosion in the reaction of hydrogen oxidation in the presence of chemically active additive. The concept of an intermediate combustion wave with the maximum temperature equal to the initial temperature of the hot spot is introduced. It is shown that key parameters defining the critical size of a local source of ignition, are the temperature in the center of a local ignition zone, the quantity of the active centers of combustion created with the local source, and presence of active chemical additives in a combustible gaseous mixture. Comparison to experimental data has shown the applicability of the developed approach for the analysis of critical conditions of a local ignition in combustible gas mixtures.

Keywords Local ignition center • Critical size • Hot spot • Adiabatic induction period • Heat losses • Thermal explosion • Approximate analytical • Numerical calculations

1 On the Theory of a Local Thermal Explosion

A problem on a local thermal explosion attracts attention for a long time because it is strongly associated with a problem of sensitivity of explosives to external non-thermal impacts. The most correct solution of a problem on a local ignition is obtained by A.G. Merzhanov with co-authors by numerical calculations [1]. In this paragraph, the generalized analysis of approximate methods of determination of a critical condition is given, the main features of the mechanism of a local thermal explosion are presented. The necessity of development of the approximate theory considering the revealed features of the mechanism of the process is highlighted.

In [2] the solution of a local problem on the basis of an asymptotic approach is obtained. The expressions for calculation of the critical value of Frank–Kamenetski parameter are derived. However, their application is connected with certain difficulties because of a complex form of equations.

In the present paragraph, a new approach to the solution of the problems on the local ignition, which allows obtaining considerably simple expressions for determination of critical conditions, is presented. In standard approximations and in the conventional dimensionless variables a thermal explosion of the flat Π -shaped center of a warming up (hot spot) in a reaction of a zero order is described by the equation

$$\begin{aligned} \partial\theta/\partial\tau &= \partial^2\theta/\partial\xi^2 + \exp\{\theta/(1+\beta\theta)\}, \\ \tau = 0, \theta = 0 &\text{ at } \xi \leq R_0, \theta = \theta_n \text{ at } \xi > R_0 \\ \xi = 0, \xi = \infty, \partial\theta/\partial\xi &= 0. \end{aligned} \quad (1.1)$$

Dimensionless variables and parameters:

$$\begin{aligned} \theta &= (T - T_0)E/RT_0^2, \\ \xi &= r\{\lambda RT_0^2/(Q\rho k_0 E) \exp(E/RT_0)\}^{-1/2} \\ \tau &= tQk_0 E/(cRT_0^2) \exp(-E/RT_0), \\ F_k &= Q\rho k_0 E/(\lambda RT_0^2) \exp(-E/RT_0) r_0^2 = R_0^2, \\ \beta &= RT_0/E, \quad \theta_n = (T_0 - T_n)E/RT_0^2, \end{aligned}$$

where T_0 —the temperature of an ignition center (hot spot), T_n —environment temperature, r_0 —radius of the center, t —time, E —activation energy, k_0 —a pre-exponential factor, Q —thermal effect of the reaction, λ —heat conductivity, c —thermal capacity, ρ —density.

The analysis of the results of a numerical calculation of a problem on a local ignition has revealed the following features of the process [1]:

1. The induction period of the thermal explosion in local ignition problems is a value of a unit order, i.e., of an order of the adiabatic induction period of a thermal explosion. The time of thermal relaxation of the ignition center is numerically equal to a value of F_k in chosen scales. The critical value of F_k parameter is 10–20 (depending on a geometrical form of the center). Therefore, a local ignition can be characterized by that the induction period of a local thermal explosion is much less than the time of thermal relaxation of the ignition center:

$$\tau_{\text{ind}} \ll \tau_T \quad (1.2)$$

It follows from the aforesaid that during the development of thermal explosion in the ignition center only the layer at a surface of the ignition center, in which all

temperature gradient is focused, is considerably cooled down; however, the substance in the central part of the center (hot spot) is not practically cooled.

2. Large variation in the initial temperature of the ignition center and the environment is characteristic of a local ignition ($\theta_n > 4$). At small values of θ_n the reaction is localized in separate centers, however, in this case the mechanism of the process significantly differs from the mechanism of a local thermal explosion, in particular, in the latter case induction periods of the thermal explosion in the center and in the environment are almost equal [3].

At large activation energy, chemical heat source is localized in a narrow temperature interval near the maximum temperature. Therefore, it is possible to allocate two zones in the ignition center similar to a combustion wave: (1) a reaction zone in the central part of the ignition center, where $\theta > -1$; 2) a zone of inert cooling at the surface border of an ignition center, where $\theta < -1$.

In the ignition center, practically, the whole of temperature gradient is concentrated in a zone of inert cooling. The environment surrounding the center is possible to be considered inert, as is shown in [1] because $\tau_{ad}(0) \ll \tau_{ad}(-\theta_n)$.

Thus, the problem on a local ignition has been reduced to the examination of the dynamics of a reaction zone in the center under conditions of cooling down with inert environment.

For establishment of a temperature profile in a reaction zone, we will estimate certain terms in the Eq. (1.1). According to the chosen scales, at initial stages of development of the process the change in dimensionless variables in a reaction zone makes

$$\Delta\theta_r \approx 1, \quad \Delta\xi_r \approx R_0 = (F_k)^{1/2}, \quad \partial^2\theta/\partial\xi^2 \approx 1/R_0^2 = 1/F_k$$

During the induction period, the power of a chemical heat source can be considered approximately constant and equal to the power at initial temperature [4]: $\exp\{\theta/(1 + \beta\theta)\} \approx 1$.

The estimation shows that at the initial stages of development of the process in the central region of the hot spot it is possible to neglect conductive heat losses in comparison with a heat source; temperature growth can be described by the equation of an adiabatic thermal explosion.

$$d\theta/d\tau = \exp\{\theta/(1 + \beta\theta)\}; \quad \tau = 0, \quad \theta = 0.$$

Therefore, as a characteristic time of a local ignition the adiabatic period of induction τ_{ad} should be taken, which is of a unit value in chosen scales: $\tau_{ad} = 1$

Eventually, the substance is being cooled down at a center surface, the border of a reaction zone moves to the center of a hot spot. If by the time $\tau = 1$ the size of the reaction zone in the center is that heat will not manage to be withdrawn; then there will be the ignition of the center.

The achievement of equality of the heat losses and thermal emission in a reaction zone by the time $\tau = 1$ is the critical condition. Therefore, we can estimate the critical size of a reaction zone $\Delta \xi_r^{\text{crit}}$;

$$\partial^2 \theta / \partial \xi^2 = \exp \{ \theta / (1 + \beta \theta) \}, 1 / \Delta \xi_r^{\text{crit}} \approx 1, \Delta \xi_r^{\text{crit}} \approx 1$$

The obtained value is near to the critical one for the vessel size in the thermal ignition theory of Frank–Kamenetskii. The results of calculation of F_k^{crit} from formulas (1.4) and (1.5) are shown in Table 1.

Thus, it is necessary for the ignition of the hot spot that during the induction period the size of a reaction zone did not become a subcritical one.

A heat flux which is taken out of a reaction zone is greater than that heat flux, which chemical reaction can provide during the entire induction period. They are equal only under a critical condition. Therefore, we can find the law of the movement of the border of a reaction zone from the solution of a problem on cooling of an infinite plate with the infinite environment:

$$\theta = -(\theta/2) \left\{ \operatorname{erfc} \left[\frac{R_0 - \xi}{2\tau^{1/2}} \right] + \operatorname{erfc} \left[\frac{R_0 + \xi}{2\tau^{1/2}} \right] \right\} \quad (1.3)$$

Taking into account (1.2), we approximately describe a temperature profile in a zone of inert cooling with the first term of Eq. (1.3):

$$\theta = -(\theta_n/2) \left\{ \operatorname{erfc} \left[\frac{R_0 - \xi}{2\tau^{1/2}} \right] \right\}$$

Because the border of a reaction zone is the point, in which $\theta = -1$, we get the law of its movement:

$$2/\theta_n = \left\{ \operatorname{erfc} \left[\frac{R_0 - \Delta \xi_r}{2\tau^{1/2}} \right] \right\} \quad (1.4)$$

Under critical conditions at the moment $\tau = 1$ $\Delta \xi_r = \Delta \xi_r^{\text{crit}} \approx 1$ we obtain the expression for the critical size of the ignition center:

$$2/\theta_n = \operatorname{erfc} \{ (R_0^{\text{crit}} - 1)/2 \} = \operatorname{erfc} \{ (F_k^{\text{crit}})^{1/2} - 1 \} / 2 \} \quad (1.5)$$

Table 1 The results of calculation of F_k from formulas (1.4) and (1.5)

θ_H	$F_{k(1.4)}^{\text{crit}}$	$F_{k(1.5)}^{\text{crit}}$	ε (%)	θ_H	$F_{k(1.4)}^{\text{crit}}$	$F_{k(1.5)}^{\text{crit}}$	ε (%)
4	3.84	4.07	5.7	15	9.73	9.71	0.2
6	5.66	5.68	0.4	20	11.026	11.076	0.5
8	6.97	6.89	1.2	25	12.117	12.167	0.4
10	7.95	7.87	2.02				

The values of parameter F_k^{crit} calculated with the approximate formulas (1.4) and (1.5) with the approximate formula given in [1] are presented in Table 1:

$$F_k^{\text{crit}} = 2.66 (\ln \theta_n)^{1.3}$$

The comparison shows that the Eq. (1.4) obtained above describes with high precision the dependence of F_k^{crit} on θ_n in all reasonable intervals of change in θ_n .

The developed approach allows obtaining expression for F_k^{crit} in that case when the center and the environment have different thermophysical properties. Under these conditions, all main features of the mechanism of the process keep their meaning: the value induction period is of the order of unity, the time of thermal relaxation is much more than the induction period. Having allocated a reaction zone and an inert cooling one in the ignition center, we can find the law of the movement of the border between them using the solution of a problem on cooling of an inert infinite plate with the infinite environment with other thermophysical properties. The expression describing the temperature profile in a zone of inert cooling is similar to Eq. (1.3), only the multiplier $\theta_n/2$ in the right part is replaced by $\theta_n/(1+K)$, where $K = (\lambda_c \rho / \lambda_c \rho_c c_c)^{1/2}$ —the relation of thermal activities of the hot spot and of the environment.

For the critical value of F_k we get the expression:

$$(1+K)/\theta_n = \text{erfc} \left\{ \left[(F_k^{\text{crit}})^{1/2} - 1 \right] / 2 \right\}. \quad (1.6)$$

As is seen from (1.6) the value of F_k^{crit} does not depend on the overall temperature variation, but on the temperature difference in the center of the hot spot and on its surface, which makes $-\theta_n/(1+K)$.

As the area of change in $\text{erfc}(x)$ is in an interval [0; 1], the left part of Eq. (1.6) is less than unity $(1+K)/\theta_n < 1$. Physically, it means that within this approach the difference of temperatures in the hot spot, which makes $\theta_n/(1+K)$ cannot be less than one characteristic interval RT_0^2/E .

Degeneration of the local mechanism of thermal explosion happens when it is impossible to allocate reaction and inert cooling zones in the hot spot, i.e., it is impossible to neglect the reaction at the surface of a hot spot. As follows from the results of the numerical calculations [1] the degeneration occurs when the temperature difference in the hot spot is less than two characteristic intervals. Therefore, the fulfillment of the inequality

$$\theta_n/(1+K) > 2. \quad (1.7)$$

is necessary for the occurrence of a local thermal explosion.

Let us consider limiting cases.

- (1) Thermal activity of the environment is much more, than that of the hot spot, i.e., $K \ll 1$. The temperature of the surface of the hot spot is equal to

environmental temperature $-\theta_n$. Calculations showed that in spite of the fact that the temperature of the surface of the hot spot is much lower, than in case $K = 1$, the critical size of the hot spot increases slightly (no more than by 30%), i.e., even considerable improvement of heat exchange in the heated area with the environment does not significantly increase the critical size of the hot spot.

- (2) Thermal activity of the environment is much less, than that of the hot spot, i.e., in this case heat losses from the heated area are hindered, ignition of the hot spot occurs practically under adiabatic conditions, and the critical size of the heated area tends to zero. However, at greater values of K ($K \approx 10 - 15$) the inequality (1.7) is not fulfilled as the reasonable value of θ_n does not exceed 25. To determine the value of F_k^{crit} under these conditions, it is necessary to consider thermal emission from the chemical reaction in the entire heated area.

This method allowed getting dependencies of $F_k^{\text{crit}}(\theta_n)$ for the cylindrical and spherical ignition centers. In case of the cylindrical center, they have the following form:

$$2/\theta_n = -\frac{F_k^{\text{crit} 1/4}}{2^{1/4}} \left\{ \operatorname{erfc} \left[\left(F_k^{\text{crit}} \right)^{1/2} - 2^{1/2} / 2 \right]^2 \right\} + 1/8 \operatorname{ierfc} \left\{ \left[\left(F_k^{\text{crit}} \right)^{1/2} - 2^{1/2} \right] / 2 \right\} \left[\left(F_k^{\text{crit}} / 2 \right)^{1/2} + 3 \right] \quad (1.8)$$

And in case of the spherical hot spot

$$2/\theta_H = -\frac{2}{(3\pi)^{1/2}} \exp \left\{ - \left[\left(F_k^{\text{kp}} \right)^{1/2} - 3^{1/2} \right]^2 / 4 \right\} + \operatorname{erfc} \left\{ \left[\left(F_k^{\text{kp}} \right)^{1/2} - 3^{1/2} \right] / 2 \right\} \quad (1.9)$$

The comparison of the values obtained by means of (1.8) and (1.9) with numerical calculations [1] showed that the difference does not exceed 5% over all intervals of θ_n . When using in calculations only the first term in the right part of Eqs. (1.8) and (1.9) the difference does not exceed 20%.

We draw the following conclusions.

1. The method of approximate calculation of the critical size of the center of warming up (hot spot) based on splitting the heated area in a reaction zone and the inert cooling zone is developed.
2. It is shown that the critical size of the center is determined from a condition of equality of the heat losses and thermal emission in a reaction zone at the moment $\tau = \tau_{\text{ad}}$.
3. At the moment $\tau = \tau_{\text{ad}}$ the size of a reaction zone $\Delta \xi_r^{\text{crit}}$ has to be: $\Delta \xi_r^{\text{crit}} > 1$ for the flat center, $\Delta \xi_r^{\text{crit}} > \sqrt{2}$ for the cylindrical center, $\Delta \xi_r^{\text{crit}} > \sqrt{3}$ for the spherical center.

Otherwise the center is cooled down.

4. Comparison of the approximate analysis with the results of numerical calculations showed good agreement.
5. The proposed method allows determining the critical size of the center in case when the center and the environment have different thermophysical properties.

In the following section, on the basis of a numerical calculation the verification of the analytical expressions obtained in Sect. 1 is performed.

2 Nonstationary Ignition of a Hot Spot

A thermal explosion beginning in separate small volumes—the centers of ignition (hot spots) heated to high temperature is of very great importance for the condensed reactive substances. The similar centers are formed at mechanical impacts (shock or friction) on a chemically active agent. The analysis of a local ignition problem in a simple formulation is carried out in [1] by numerical calculation.

In Sect. 1, a thermal explosion of the flat Π -shaped center of a warming up (hot spot), in which the reaction of a zero order takes place is analytically considered [system of the Eq. (1.1)].

We remind that in Sect. 1 the method of the approximate analysis of critical conditions of a local ignition based on the assumption that a problem on a local ignition can be reduced to the examination of the dynamics of a reaction zone under conditions of cooling down the center with the inert environment; thus, the power of a chemical heat source during the induction period can be considered approximately constant and equal to unity in a dimensionless form:

$$\partial^2 \theta / \partial \xi^2 \approx 1/R_0^2 \ll 1, \quad \exp(\theta/(1 + \beta\theta)) \approx 1.$$

The estimation, which is carried out in Sect. 1 showed that at the initial stage of the development of the process in the central region of the hot spot it is possible to neglect conductive heat losses as compared to a heat source, and to describe temperature growth in the center of a hot spot with the equation of an adiabatic thermal explosion. Eventually, substance (we will further periodically use “a sample” instead) at a surface of the hot spot is cooled down, the border of a reaction zone moves to the center. If by the time $\tau = 1$ the width of a reaction zone is such that the heat from it cannot be withdrawn, there will be an ignition of the spot. The critical condition is the achievement of equality of the heat losses and thermal emission in a reaction zone by the time $\tau = 1$. Thus, it is necessary for the ignition of the center that during induction period the size of a reaction zone did not become subcritical. To determine the critical size of the hot spot it is necessary to find out, how a reaction zone width changes in time. From Sect. 1, we will recall the law of the movement of the border of a reaction zone from the solution of a problem on cooling of an inert infinite plate $2R_0$ thick with an infinite environment:

$$\theta(\xi, \tau) = -\frac{\theta_n}{2} \sum_{n=1}^{\infty} (-1)^n \left[\operatorname{erfc} \left(\frac{(2n-1)R_0 - \xi}{2\sqrt{\tau}} \right) + \operatorname{erfc} \left(\frac{(2n-1)R_0 + \xi}{2\sqrt{\tau}} \right) \right]$$

Taking into account that the induction time is much less than the time of thermal relaxation of the hot spot, the temperature profile in a zone of inert cooling is approximately described by the first term of a series:

$$\theta(\xi, \tau) = -\frac{\theta_n}{2} \operatorname{erfc} \left(\frac{R_0 - \xi}{2\sqrt{\tau}} \right)$$

Accepting as a boundary of a reaction zone a point, in which $\theta = -1$, we get the law of the movement of the boundary:

$$\frac{2}{\theta_n} = \operatorname{erfc} \left[\frac{R_0 - \Delta \xi_r}{2\sqrt{\tau}} \right]$$

Under critical conditions at $\tau = 1$ $\xi_r = \xi_r^{\text{crit}} \approx 1$. For R_0^{crit} we obtain the expression

$$2/\theta_n = \operatorname{erfc} \left((R_0^{\text{crit}} - 1)/2 \right) \quad (2.1)$$

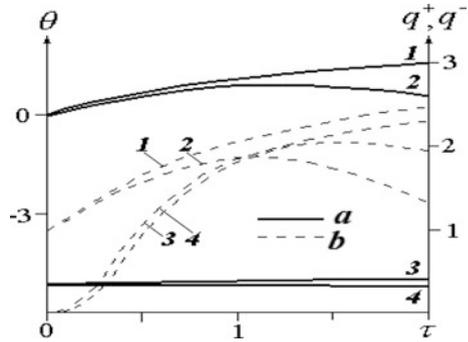
The critical size of the center calculated by this formula agrees well with the results of numerical calculations [1], the difference makes no more than 4% over the whole practically interesting interval of change in θ_n ($4 < \theta_n < 25$). Because earlier by means of the numerical analysis of the process the dynamics of its characteristic values was not examined, there was a necessity to compare conclusions and assumptions of the approximate approach theory with the results of numerical calculations.

The numerical solution of the problem was performed on a nonuniform spatial grid for the implicit scheme on a four-point T-shaped template. Calculations were carried out over the whole practically interesting interval of θ_n . Illustrations were made for calculations at the following values of the parameters: $\theta_n = -10.5$, $\beta = 0.01$, $R_0^{\text{crit}} = 2.83$. The revealed features of process remain constant over the interval $4 < \theta_n < 25$.

Having compared the temperature value on a surface ($\xi = R_0$) of the chemically active hot spot and inert one of the characteristic size $R_0 \approx R_0^{\text{crit}}$ (Fig. 1), we see that during the development of the process on the surface of a hot spot, the temperature practically does not change and it is equal to a half of initial difference θ_n . Therefore, surface layers of a chemically active hot spot are cooled down as well as the inert one of the same characteristic size, and regularities of cooling differ little from the law of cooling down a semi-infinite body.

The dependence of temperature in the center of the hot spot on time for the spots with the size more and less than the critical one is almost linear to $\tau = 1$, the warming up at the moment $\tau = 1$ for $R_0 = 2.82$ is equal to 0.94, and for $R_0 = 2.87$

Fig. 1 Change in temperature in characteristic points of the hot spot (a) and thermal balance in the central part of the hot spot ($0 \leq \xi \leq 1$)(b). 1, 3 2.87; 2, 4 2.82; a 1, 2 the center of the hot spot, 3, 4 temperature of the surface of chemically active and inert center; b 1, 2 thermal emission, 3, 4 heat losses



is equal to 1.04. It allows drawing a conclusion that the estimation of the power of a chemical heat source based on the approximate theory is correct.

The border of a reaction zone in the hot spot is the point, which temperature is one characteristic interval less, than in the center of a hot spot. In the approximate theory, the border of a reaction zone was accepted as the point, where $\theta = -1$ on the temperature profiles corresponding to cooling down the inert spot. Apparently, dynamics of a point with $\theta = -1$ obtained from the solution of an inert problem reflects well the behavior of a reaction zone (Fig. 2).

At the moment $\tau = 1$ for the hot spot with $R_0 < R_0^{crit}$ we get $\xi_r = 0.95$ from the solution of an inert problem; $\xi_r = 0.98$ from the solution of an active problem; for $R_0 > R_0^{crit}$ at $\tau = 1$ we get $\xi_n = 1.02$ from an inert problem; $\xi_n = 1.01$ from an active problem. Thus, the critical size of a reaction zone in the approximate theory is determined correctly, and it is possible to find the size from the solution of an inert problem with good accuracy.

Let us consider the dynamics of thermal balance in a reaction zone. In Fig. 3 the change in the heat storage in a reaction zone is shown:

Fig. 2 Dependence of the size of a reaction zone on time. 1, 3 2.87; 2, 4 2.82; 1, 2 on cooling down the inert center; 3, 4 the solution of a problem for chemically active center

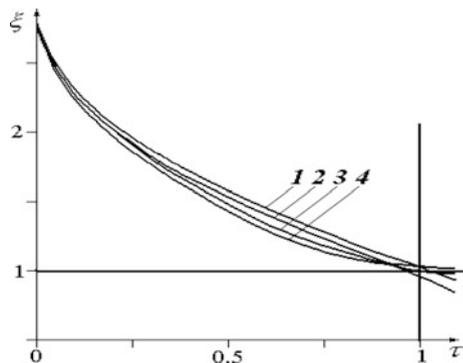
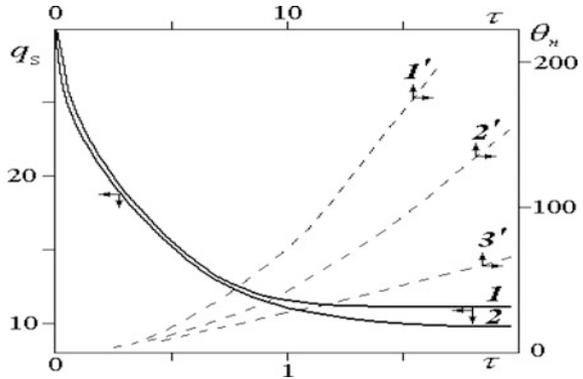


Fig. 3 Change in the heat storage in a reaction zone on time and temperature. $1-R_0 = 2.87$; $2-R_0 = 2.82$. $1'$ in a preheating zone of a stationary combustion wave; $2'$ in the vessel of the critical size of a problem on asymmetrical ignition; $3'$ in the center of the critical size (critical center)



$$q_s(\tau) = \int_0^{\xi_r} (\theta(\xi, \tau) + \theta_n) \partial \xi$$

For the center with $R_0 < R_0^{\text{crit}}$ the heat storage in a reaction zone monotonously decreases, i.e., the heat losses from a reaction zone are larger than thermal emission in it; the hot spot is cooled down. At $R_0 > R_0^{\text{crit}}$ heat storage till the moment $\tau = 1$ decreases, generally due to the reduction of the size of a zone, and then begins to grow. It means that at $\tau > 1$ thermal emission in a reaction zone is greater than heat losses; in the zone there is a heat storage leading to thermal explosion.

Especially, it can be demonstrated, comparing thermal emission and the heat losses in the central part of the hot spot with $\xi = 1$ (see Fig. 1):

$$q^+ = \int_0^1 \exp(\theta/(1 + \beta\theta)) d\xi, \quad q^- = \partial\theta/\partial\xi|_{\xi=1}.$$

At the beginning, at $\tau \ll 1$, the heat losses in this zone are small; the substance is heated up under adiabatic conditions. At $\tau = 1$, for $R_0 < R_0^{\text{crit}}$ the heat losses are larger than thermal emission, the hot spot is cooled down; at $R_0 > R_0^{\text{crit}}$ thermal emission in this zone is always greater than heat losses, the hot spot ignites.

Heat losses from a hot spot surface ($\partial\theta/\partial\xi|_{\xi=R_0}$) for spots with $R_0 < R_0^{\text{crit}}$ and $R_0 > R_0^{\text{crit}}$ are also almost identical for the whole time of the development of the process, but thermal emission significantly differs for the spots. In the hot spot with $R_0 > R_0^{\text{crit}}$ total thermal emission is always less than heat losses, and if the hot spot is supercritical, then the thermal emission at $\tau > 1$ becomes greater than heat losses, however, in a reaction zone the equality $q_r^+ = q_r^-$ is attained earlier at $\tau = 1$. It means that the substance layer at the surface of the hot spot does not give any noticeable contribution to total thermal emission, being an almost inert heat insulator of a zone of a chemical reaction.

Therefore, all assumptions made using the estimates based on the approximate theory were confirmed by the results of the numerical analysis.

A problem on degeneration of a local thermal explosion at small differences in initial temperature ($\theta_n < 4$) demands further discussion. In [1] the degeneration is associated with the influence of chemical reaction in the environment on the characteristics of the process. However, if one takes into account the fact that the characteristic time of a local ignition is the adiabatic induction period, then the warming up of the environment due to the chemical reaction at $\theta_n = -4$ during this time is a value of the order $\exp(-4) \ll 1$. This warming up is too small to influence on the ignition.

For the solution of this problem, let us compare initial heat storage in the hot spot of the critical size with heat storage in a stationary combustion wave at equal values of θ_n . (see Fig. 3). As is seen, at large θ_n the initial heat storage in the spot is much less than the heat storage in the preheating zone of the combustion wave. At $\theta_n \approx 4$ these become equal, therefore, at $\theta_n < 4$ the initial heat storage in the hot spot is enough for the occurrence of an intermediate combustion wave with the maximum temperature equal to the initial temperature of the hot spot. This conclusion was checked by the numerical calculation. The function of the thermal emission of the following form was used:

$$W = \begin{cases} \exp(\theta/(1 + \beta\theta)), & \theta \leq 0, \\ 0 & \theta > 0. \end{cases} \quad (2.2)$$

In Fig. 4, temperature profiles for critical centers, calculated by Eq. (2.1) for corresponding temperature differences are shown at different τ .

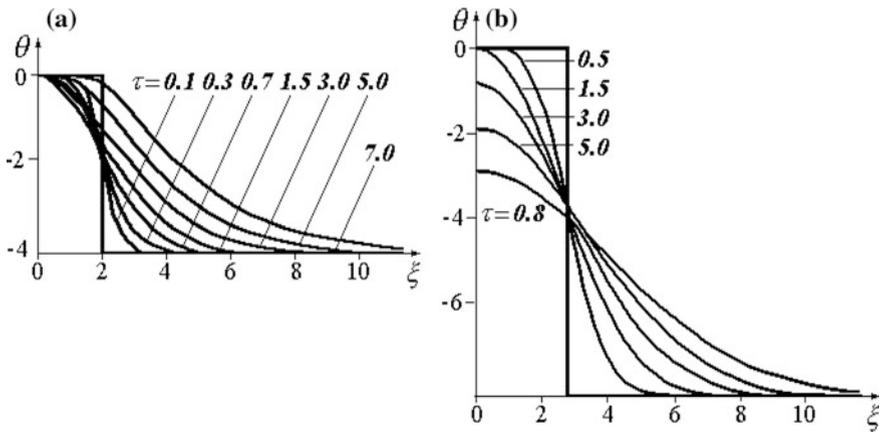


Fig. 4 Occurrence of an intermediate combustion wave from the hot spot of the critical size (a) and cooling down of the hot spot of the critical size (b) with the function of the thermal emission of type (2.2)

At $\theta_n = 4$ an intermediate combustion wave occurs, at $\theta_n = 8$ the hot spot is cooled down. The critical size of the hot spot with the thermal emission function of type (2.2) found at $\theta_n = 8$ showed that the initial heat storage in the hot spot under critical conditions is significantly less than heat storage in a preheating zone of a combustion wave. It becomes clear, if one takes into account that under critical conditions at the moment $\tau = 1$ the temperature profile in a zone of inert cooling is close to linear, but not to Michelson profile [4].

Therefore, the critical size of the hot spot should be found from a condition of equality of initial heat storage in the hot spot to the heat storage in a vessel of the critical size of the problem on the asymmetrical ignition of Y.B. Zeldovich [4] (see Fig. 3, curve 2').

In the following section, verification of the analytical expressions obtained in the previous sections with the use of experimental results on combustion of hydrogen–air mixes in the presence of active additives obtained by a method of high-speed filming is carried out.

3 Initiation of a Hydrogen–Air Flame with a Hot Spot. Verification of the Theory

The knowledge of regularities of initiation of combustion processes provides the possibility of controlling combustion at its initial stages. It is obvious that conditions of initiation of a combustion wave depend on the size and shape of a reaction initial center created by an external local power source (e.g., a spark discharge) in the form of heat or chemically active particles. The action of initiators (spark, heating, introduction of the active centers or additives into a combustible mix) is based on the acceleration of chemical transformation both at the expense of an increase in gas temperature and of an increase in the number of active centers because the vast majority of gas-phase combustion processes has branched chain nature [6, 7]. Thus, control of a local ignition demands accounting for the changes in temperature of the hot spot and the quantity of active centers in it.

Dynamics of formation of the stationary flame front (FF) at spark ignition of gas mixture remains rather low-studied area of combustion physics [8–10]. One of the reasons is the difficulty of experimental investigation of ignition process, associated, first, with small times of stationary FF formation. A primary center of a spherical flame arising in a short period at a place of the spark discharge was experimentally observed in [11] by means of a photo register; the evolution of the center was not investigated. In [12] the frames of high-speed schlieren-filming of evolution of the primary combustion center are presented at the place of a spark discharge in stoichiometric propane–air mix. From the given shots, it follows that stationary FF occurs within very small delays (tens of microseconds). In [10] it was shown that the use of small chemically active additives in gas mixture allows increasing the values of ignition delays.

The paragraph is aimed at the examination of the problem on the ignition of gas combustible mix by a local source with both analytical and numerical methods. The so-called weak initiation, which does not provide any noticeable gas dynamic perturbations of the environment [12], is considered. The establishment of key parameters of the initiation process is carried out by the example of the model reaction of hydrogen oxidation at atmospheric pressure investigated by means of high-speed color cinematography.

Experiments were performed in the stainless steel reactor 25 cm long and 12 cm in diameter, supplied with removable covers and an optical quartz window 12 cm in diameter at an end face (Fig. 5). Electrodes of spark ignition (1.5 J) were placed in the center of the reactor. The distance between them was 0.5 mm. The previously prepared mixes 40% H₂ + 60% air + (0–2%) propene (C₃H₆) were used. For flame visualization, 2% of carbon tetrachloride (CCl₄) were added to the mixes. Speed filming of ignition dynamics and FF propagation was carried out from the end face of the reactor with a color high-speed digital camera Casio Exilim F1 Pro (frame frequency—1200 s⁻¹). The filming was turned on at an arbitrary moment before initiation. A video file was stored in computer memory and its time-lapse processing was performed. The pressure change in the course of combustion was recorded by means of a piezoelectric gage, synchronized with the discharge. Before each experiment the reactor was pumped out up to 10⁻² Torr with a fore vacuum pump 2NVR-5D. Gases H₂, C₃H₆ and liquid CCl₄ were chemically pure.

Influence of small chemical additive (propene, C₃H₆) on an ignition delay was investigated by the example of combustion of hydrogen in air at atmospheric

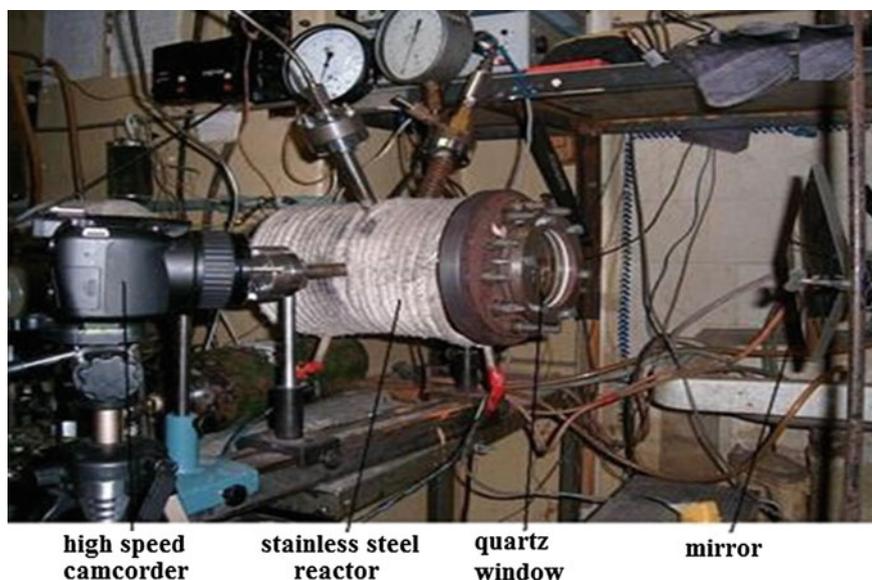


Fig. 5 Experimental installation

pressure. In Fig. 6a–d the results of high-speed filming of formation of a steady spherical flame front in 40% H_2 + 60% air mix illuminated with 2% of CCl_4 at 1 atm in the presence of 1, 1.5, and 2% of propene are shown.

We observed that without C_3H_6 additive, FF reaches the edges of an optical window already at the third shot after spark ignition. It means that the small propene additive (1–2%) leads to a considerable reduction of FF velocity. It should be noted that the additive of 2% of CCl_4 under these conditions is inert and it does not show noticeable action on hydrogen combustion in accordance with the results [8, 13]. FF occurrence in the presence of 2% of propene was observed not at once, but after six initiations by the spark discharge in this mix (Fig. 6d).

Figure 6c corresponds to three initiations by the spark discharge. As is seen, the primary center of combustion (the term “hot spot” is not good enough in this case, because it does not account for a chemical component of initiation) was formed, but it did not lead to flame propagation. From Fig. 6c, d, it is seen also that under conditions of three spark initiations the limit of flame initiation is observed at the

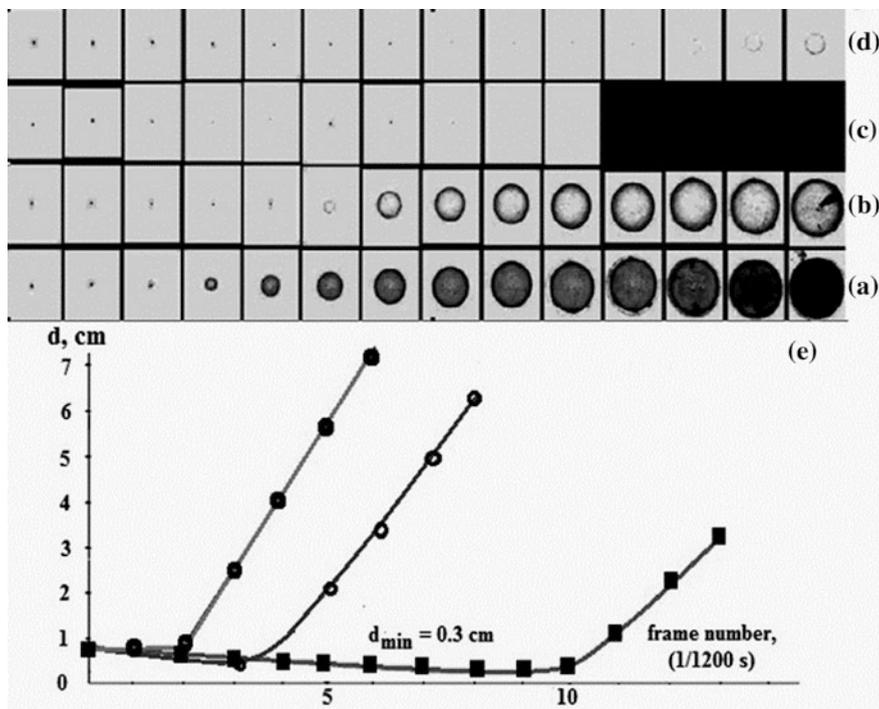


Fig. 6 Speed filming of a spherical flame front propagation in the H_2 —air mix at atmospheric pressure in the presence of propene. The flame front is illuminated by 2% CCl_4 additive. Speed of filming is 1200 frames/s. The first frames to the left in the picture are the first frames after spark discharge, **a** 1% of propene, **b** 1.5% of propene, **c** 2% of propene, the third initiation, **d** 2% of propene, the sixth initiation, **e** dependencies of the diameter of the flame zone on time for Fig. 6: **a** (points), **b** (circles), **d** (squares)

size of the primary combustion center much smaller than the reactor radius. Under these conditions, heat losses into reactor walls are missing. Therefore, an active chemical additive in the mix causes the observed limit of flame initiation. From Fig. 6e, in which experimental dependencies (see Fig. 6a–c) of the diameter of the flame zone on time are shown, it is possible to estimate the smallest diameter of the primary combustion center, which makes up ~ 0.3 cm.

The strong influence of small chemically active additive on the time and conditions of FF formation means that the evolution of the primary center is determined by not only the thermal effect of the reaction, but also by the chemical mechanism of interaction of the active centers of combustion (atoms and radicals) with the additive.

Before performing analysis of the process of a local ignition of hydrogen–air mix, it is important to remind a reader the features of development of the primary center by the example of a problem on the local thermal explosion of a flat Π -shaped warming-up center in which a zero-order chemical reaction occurs. According to [2, 3] the problem is described by the equation, see also Sect. 1:

$$\begin{aligned} \partial\theta/\partial\tau &= \partial^2\theta/\partial\xi^2 + \exp\{(1 + \beta\theta)\} \\ \tau &= 0, \quad \theta = 0 \quad \text{at} \quad \xi \leq R_0, \quad \theta = -\theta_H \quad \text{at} \quad \xi R_0 \\ \xi &= 0, \quad \xi = \infty, \quad \partial\theta/\partial\xi = 0. \end{aligned} \quad (3.1)$$

where $\theta = (T - T_0)E/RT_0^2$, $\xi = r\{\lambda RT_0^2/(Q\rho k_a E) \exp(E/RT_0)\}^{-0.5}$, $\tau = tQk_a E/(cRT_0^2) \exp(-E/RT_0)$, $R_0^2 = F_k = Q\rho k_a E/(\lambda RT_0^2) \exp(-E/RT_0)r_0^2 = r_0^2/at_{\text{del}}$, $\theta_n = (T_H - T_0)E/RT_0^2$.

Here, T_0 is the initial temperature of the center, T_n —environment temperature, r_0 —the initial size of the center, t —time, E , k_a , Q —energy of activation, a preexponential factor and the thermal effect of a zero order reaction, respectively, λ —heat conductivity, C —thermal capacity, ρ —density, a —heat diffusivity, t_{del} —the delay period of ignition.

The analysis of the results of numerical investigation of the problem leads to the following conclusions (see Sect. 1):

1. The dimensionless delay period of thermal explosion has an order of unit, i.e., an order of the adiabatic delay period of a thermal explosion. The time of thermal relaxation of the primary center is equal to the F_k value in the scales chosen. Therefore, for a local ignition t_{del} is much less than the time of thermal relaxation of the primary center τ_T :

$$\tau_{\text{del}} \ll \tau_T$$

It means that during development of the thermal explosion in the primary center only the layer at the surface of the center (in which the whole temperature gradient

is concentrated) is considerably cooled down, and the substance in the central part of the center is not practically cooled.

2. For a local ignition, initial temperatures in the center and in its environment are markedly different ($\theta_n > 4$). Therefore, at high activation energy a heat source is localized in a narrow temperature interval in the vicinity of the maximum temperature. Thus, it is possible to allocate two zones in the center: (1) a reaction zone, where $\theta > -1$, in the central part of the primary center; (2) a zone of inert cooling, where $\theta < -1$, settling down at a border of the surface of the primary center ($\theta = (T - T_0)E/RT_0^2$), T_0 is the temperature of the center.

Eventually, the substance cools down at the primary center surface and the border of the reaction zone moves to the middle of the center. Therefore, critical condition is the equality of heat losses and thermal emission in the reaction zone by the time of the termination of the delay period. From here, we will estimate the critical size of the reaction zone $\Delta\xi_p^{cr}$:

$$\partial^2\theta/\partial\xi^2 = \exp\{\theta/(1 + \beta\theta)\}; \quad 1/(\Delta\xi_p^{cr})^2 \approx 1, \quad \Delta\xi_p^{cr} \approx 1.$$

Thus, for ignition of the center it is necessary that the size of the reaction zone exceeds the critical one during the delay period.

The heat flux, which comes out from the reaction zone, is more than the thermal flux which chemical reaction can provide during a delay period. They become equal only under critical conditions at the moment of the termination of the delay period. Therefore, the law of movement of the border of a reaction zone can be found from the solution of a problem on plate cooling in an infinite environment [2, 3], see also Sects. 1 and 2:

$$\theta = -(\theta_n/2) \left\{ \operatorname{erfc} \left[\frac{R_0 - \xi}{2\tau^{0.5}} \right] + \operatorname{erfc} \left[\frac{R_0 + \xi}{2\tau^{0.5}} \right] \right\} \quad (3.2)$$

The temperature profile in a zone of inert cooling is approximately described by the first term of the expression (3.2) [14]:

$$\theta = -(\theta_n/2) \left\{ \operatorname{erfc} \left[\frac{R_0 - \xi}{2\tau^{0.5}} \right] \right\}$$

As the border of the reaction zone is the point in which $\theta = -1$, we get the law of its movement:

$$2/\theta_n = \left\{ \operatorname{erfc} \left[\frac{R_0 - \Delta\xi_p^{cr}}{2\tau^{0.5}} \right] \right\} \quad (3.3)$$

If the independent calculation or the definition of the adiabatic delay period in the primary center of exothermic self-accelerated reaction (for example, a branched

chain reaction) is possible, the use of the Eq. (3.3) will allow calculating the primary center radius R_0^{cr} . According to [2, 3] adiabatic delay period is related to the critical size of a reaction zone by a ratio $\Delta \zeta_p^{\text{cr}} = \sqrt{\tau_{\text{del}}}$ because under critical conditions at the time of $\tau = 1$ $\Delta \zeta_p = \Delta \zeta_p^{\text{cr}} \approx 1$ [3]. Then, the expression for the critical size of the primary center takes the form:

$$2/\theta_n = \left\{ \operatorname{erfc} \left[\frac{R_0^{\text{cr}} - \tau_{\text{del}}^{0.5}}{2\tau_{\text{del}}^{0.5}} \right] \right\}$$

in which $\theta_n = (T_0 - T_n)E/RT_0^2$, then we get:

$$2/\theta_n = \operatorname{erfc} \frac{R_0^{\text{cr}} - 1}{2} = \operatorname{erfc} \left[\frac{(F_k)^{1/2} - 1}{2} \right] = \operatorname{erfc} \left[\frac{r_0^{\text{cr}}/a\sqrt{t_{\text{del}}} - 1}{2} \right] \quad (3.4)$$

Thus, the value of the adiabatic delay period t_{del} is one of the key parameters of the process of a local ignition. The marked influence of small chemically active additive on the time of FF formation (see Fig. 6) according to Eq. (3.4) means that the additive has a strong impact on the value of t_{del} .

We will illustrate the influence of the chemical mechanism of combustion reaction on critical conditions of a local ignition by the example of the branched chain process of hydrogen oxidation, which is considered to be well known [6, 8, 9].

To describe hydrogen oxidation, let us take into account only the main stages of the process of chemical transformation: chain origination $\text{H}_2 + \text{O}_2 \rightarrow 2\text{OH}$ (k_0), chain propagation (k_1, k_3) and chain branching (k_2), termolecular chain termination (k_6, k_{11}), termination of a hydrogen atom on the additive in the reaction $\text{H} + \text{In} \rightarrow \text{products}$ (k_5) [10]. For the sake of simplicity, nonlinear reactions of chain propagation and chain branching during the delay period are ignored [8, 9]. In a chain unit of hydrogen oxidation $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ (k_1), $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ (k_2), $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ (k_3) heat is not practically released [6]. Here, k_i are velocity constants of the corresponding reactions. The heat of the reaction is released in recombination of the active centers. In rich mixes, these are hydrogen atoms, which concentration markedly exceeds concentrations of atoms O and radicals OH [6]. Atoms of hydrogen recombine with each other and with the molecules of oxidizer with participation of the third particle M with thermal effects Q_2 and Q_1 , respectively, in the following reactions:



We will qualitatively analyze the influence of various factors (initial gas temperature, initial concentration of hydrogen atoms, and concentration of additive) on the delay period of the thermal ignition of stoichiometric hydrogen–oxygen mix. The system of the equations describing an adiabatic process of thermal ignition is analyzed in dimensionless variables. The characteristic time scale was chosen as

$t_0 = 1/(k_2^0 [\text{O}_2]_0)$, where k_2^0 is the preexponential factor of the reaction (2). In the chosen scale 1 s corresponds approximately to $\sim 10^5$ dimensionless units along the τ axis in Fig. 7. Dimensionless variables and parameters were defined as follows: $\tau = t/t_0$, $Y_0, Y_1, Y_3 = [\text{concentration of atoms of hydrogen, molecular oxygen, and an additive, respectively}]/[\text{initial concentration of molecular oxygen}]$, T —temperature (K)

$$\begin{aligned} dY_0/d\tau &= 3k_0/k_2^0 + 2\exp(-8380/T)Y_0Y_1 - k_5/k_2^0Y_0Y_3 - k_6/k_2^0MY_0Y_1 - k_{11}/k_2^0(Y_0)^2M \\ dY_1/d\tau &= -3k_0/k_2^0 - \exp(-8380/T)Y_0Y_1 - k_6/k_2^0MY_0Y_1 \\ dT/d\tau &= 1/(C_p\rho)[Q_1k_6/k_2^0MY_0Y_1 + Q_2k_{11}/k_2^0(Y_0)^2M] \\ dY_3/d\tau &= -k_5/k_2^0Y_0Y_3 \end{aligned} \quad (3.5)$$

The equations of the set (3.5) were integrated using a fourth order Runge–Kutta method with an adaptive step of integration and the following initial conditions, $Y_0 = 1$, $Y_1 = 1$, $Y_3 = 0-0.03$, $T_0 = 1000$ (K) is the measured temperature value in gas in a zone of spark ignition [15]. The values of other parameters were the following: $\rho = 10^{-3}$ g/cm³ [16], $C_p = 0.88$ kcal/g grad [16], $M = 750 \times 10^{19}/T_0$ cm⁻³ (atmospheric pressure), $k_2 = k_2^0\exp(-8380/T)$ cm³/mol s = $0.30 \times 10^{-9}\exp(-8380/T)$ cm³/mol s [17], $k_{11} = 0.14 \times 10^{-31}(T/300)^{-0.4}$ cm⁶/mol² s [18], $k_6 = 10^{-32}$ cm⁶/mol² s [19], $k_5 = 10^{-11}\exp(-1500/T)$ cm³/mol s [13, 20], $k_0 = 0.33 \times 10^{-9}\exp(-22,000/T)$ cm³/mol s [21], $Q_1 = 45$ kcal/mol [6], $Q_2 = 100$ kcal/mol [6], $[\text{O}_2]_0 = 760(0.13 \times 10^{19}/T_0)$ cm³.

The results of calculations are presented in Fig. 7.

To estimate of the value of temperature increase at the expense of recombination of hydrogen atoms introduced into an initial mix, the calculation for lack of chain branching ($k_2 = 0$, the reaction of hydrogen oxidation does not occur, Fig. 7a, b) was carried out. It follows from the calculations that due to the heat, which is released in recombination of hydrogen atoms introduced into initial mix, the temperature of gas mix increases (Fig. 7a). The additive of propene to the same mix leads to a reduction of the maximum temperature (Fig. 7b). An influence of propene for the lack of the branching reaction shows itself as warming-up reduction. This is reached at the expense of smaller thermal emission in the reaction of the active center with propene in comparison with recombination of hydrogen atoms with each other and with oxygen molecules.

From Fig. 7c, in which the dependencies on time of concentrations of hydrogen atoms, oxygen, and propene ($k_2 \neq 0$) molecules are given for the absence and in the presence of propene, it is seen that propene additive provides an increase in τ_{del} . The delay period was estimated as the time of achievement of maximum concentration of hydrogen atoms.

Let us apply the results obtained to the explanation of influence of active chemical additives on the process of spark initiation. As in the area of discharge not only temperature increases, but also a super equilibrium concentration of active particles [12] is attained, then at the expense of their recombination (after discharge), the temperature will additionally increase, and τ_{del} will respectively

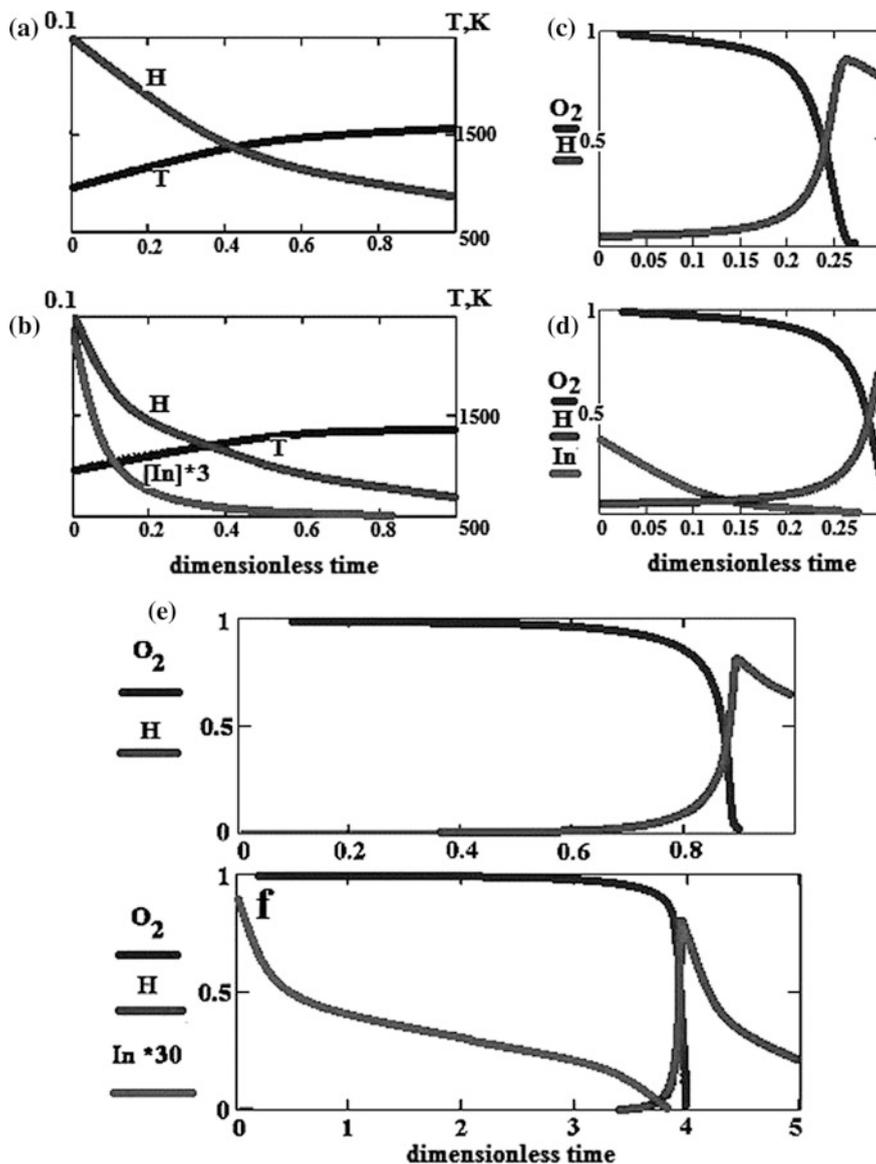


Fig. 7 Calculated dependencies of concentration of hydrogen atoms, molecular oxygen, temperature and additive at initiated combustion of hydrogen in air at atmospheric pressure. **a** $k_2 = 0$, the additive in the mix is missing; **b** $k_2 = 0$, concentration of additive in the mix is 3%; **c** the additive in the mix is missing, dimensionless concentration $[H]_0 = 0.1$; **d** concentration of additive in the mix is 3%, dimensionless concentration $[H]_0 = 0.1$; **e** the additive in the mix is missing, dimensionless concentration $[H]_0 = 0.017$; **f** the concentration of the additive in the mix is 3%, dimensionless concentration $[H]_0 = 0.017$

decrease (see Fig. 7c—calculation for dimensionless initial concentration of atoms of hydrogen 0.1, Fig. 7d—0.017).

Propene additives lead, on the contrary, to an increase in τ_{del} ; as the active centers of combustion, including those formed at an initiating impulse, are terminated on propene molecules and do not lead to chain branching until propene is consumed. In addition, influence of propene on the τ_{del} value shows itself also in a longer lifetime of the primary ignition center (Fig. 6a). Notice that the speed filming allows observing the behavior of a primary center directly before the chain explosion.

It is necessary to tell apart two cases. If the initial concentration of active particles is more than the concentration of the additive, the additive is quickly consumed due to interaction with these active particles and has no impact on the further development of ignition process. In this case, τ_{del} slightly depends on the additive concentration (see Fig. 7d) and is determined by the time of the development of ignition process without an additive.

If the initial concentration of active particles is less than the concentration of the additive, the delay period strongly depends on the concentration of the additive (see Fig. 7d, e). This result is a consequence of slow consumption of the additive in the reaction of chain origination.

It is known from literature data that the velocity of oxidation reaction is a sharp function of initial temperature [6–9, 12]. Such dependence is determined by the high activation energy of the chain branching reaction. This fact is a necessary condition of occurrence of critical phenomena of a local ignition and application of the approach developed above for their calculation. To estimate the critical size of the primary center (hot spot), we can use the analytical expression for τ_{del} in the hydrogen–air mix, obtained in the Appendix (Eq. 3.11).

Let us substitute the following values of parameters into the Eq. (3.4) for the critical size of the primary ignition center: $T_n = 300$ K, $E = 16.7$ kcal/mole, $a = 0.8$ cm²/s (for rich H₂-air mix [16]). Its solution for t_{del} is:

$$t_{\text{del}} = \frac{1.56(r_0^{\text{cr}})^2}{1 + 2\Omega^2} \quad (3.6)$$

where Ω is the root of the equation— $4175T_0 \operatorname{erfc} \Omega + 1,252,500 \operatorname{erfc} \Omega + T_0^2 = 0$, and T_0 is the temperature of the primary center. Dependencies of τ_{del} on the critical radius of the primary center for temperatures of the center 800, 1000, 1500, 2000 K, calculated by Eq. (3.6), are shown in Fig. 8.

Let us apply the obtained results to estimate the value of initial concentration of hydrogen atoms in the primary center. We will use for this purpose both the experimental data shown in Fig. 6e, and expressions for calculation of τ_{del} , obtained in the Appendix (Eqs. 3.9 and 3.11), which describe well experimental data from the literature. Experimental values of t_{del} given in Fig. 9 are taken from [22] and calculated by Eq. (3.11).

Fig. 8 Values of the critical radius calculated by Eq. (3.6) depending on the delay period τ_{del} for various temperatures of the primary center:
 1 800 K, 2 1000 K,
 3 1500 K, 4 2000 K

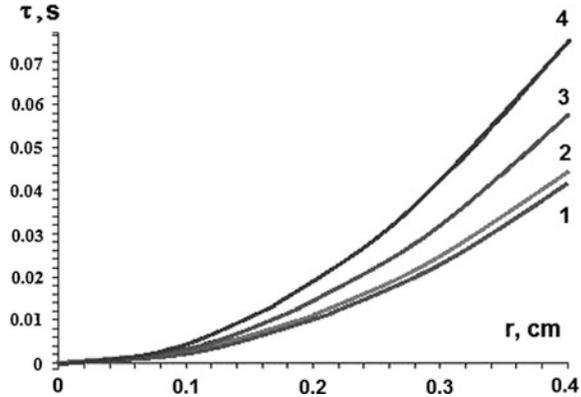
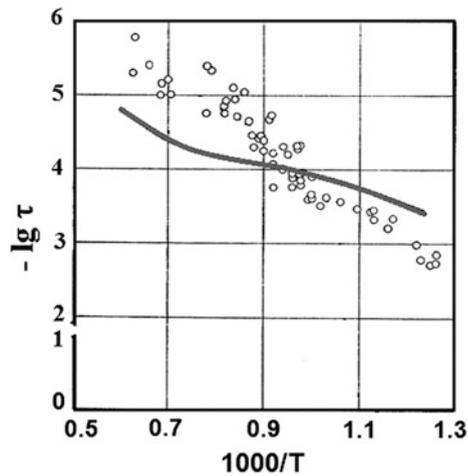


Fig. 9 Comparison of experimental data [22] for the periods of a delay (points) for the mix $H_2 + O_2$ (1:1, 1 atm) and calculated delay periods by Eq. (3.11) (a continuous curve) for $[H]_0 = 0$, $ln_0 = 0$, $O_2 = 750 \times 10^{19}/(2 T_0)$ cm^{-3} , other parameters are specified in the text



As is seen, the results of calculations by Eq. (3.11) for temperatures <1500 K adequately agree with experimental data [22] even for the mix $H_2:O_2 = 1:1$.

The smallest diameter of the primary center, from which a combustion wave develops, makes up 0.3 cm according to Fig. 6e. The value of $\tau_{del} \approx 0.02$ s at $T_0 = 1000$ K (experimental value of gas temperature in spark ignition zone [15]) corresponds to its critical radius according to Fig. 8. On the other hand, the delay period τ_{del} can be calculated directly by Eq. (3.9) for various initial concentrations of hydrogen atoms and $ln = 2\%$. The results of the calculations are shown in Fig. 10a. In this case, the delay period was considered as the time interval for which the warming up of a mix becomes equal to a characteristic interval $\frac{RT_0^2}{E}$. This interval for $E = 16.7$ kcal/mole and $T_0 = 1000$ K equals 120° . As follows from Fig. 10a the delay period ($t_{del} = 0.02$ c) corresponds to the initial concentration of hydrogen atoms $\sim 7 \times 10^{17} cm^3$, i.e., the value has a reasonable order. This result is

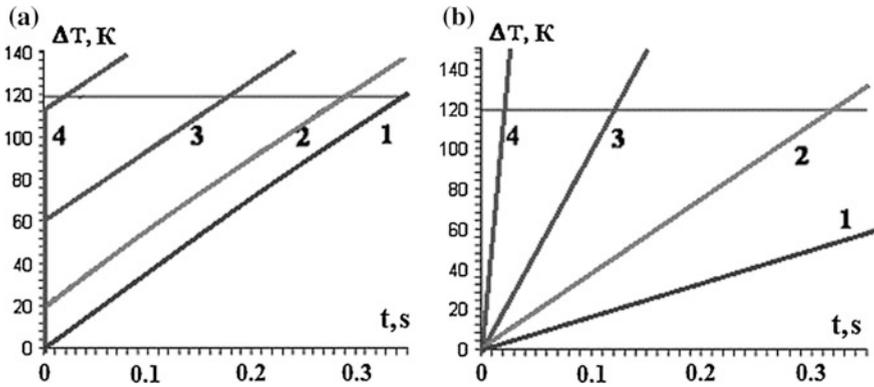


Fig. 10 The calculated values of the delay period from crossing of the graphics of the Eq. (3.9) and a straight line of $\frac{RT_0^2}{E} \cong 120$ a for various values $[H]_0$ at a given concentration of additive of $In = 2\%$, 1 $[H]_0 = 0$, 2 $[H]_0 = 10^{17} \text{ cm}^3$, 3 $[H]_0 = 3 \times 10^{17} \text{ cm}^3$, 4 $[H]_0 = 7 \times 10^{17} \text{ cm}^3$

evidence that the approach developed in Sects. 1 and 2 is applicable for the analysis of critical conditions of a local ignition.

As is seen in Fig. 10a, it is possible to allocate two stages at initial concentration of hydrogen atoms more than 10^{16} cm^3 in the course of warming up: the fast stage when the velocity of heat release is determined by recombination with the participation of hydrogen atoms in initial mix, and the slow one, related to heat release in the reaction of hydrogen oxidation.

For investigation of influence of initial concentration of additive on the critical size of the primary center and, respectively, on the value of critical energy of ignition, the calculation of change in a warming up in time by the Eq. (3.9) was carried out at various initial concentrations of additive (In) and given concentration of hydrogen atoms $[H]_0 = 10^{14} \text{ cm}^3$. Concentration of the additive was chosen in such a way that the inequality $[In] > [H]_0$ was fulfilled. The results of these calculations are shown in Fig. 10b. As well as for Fig. 10a t_{del} was considered as the time interval, for which the warming up of a mix becomes equal to one characteristic interval.

As is seen in Fig. 10b, an increase in concentration of an additive from 0.5 to 1% leads to an increase in t_{del} from 0.02 to 0.12 s, and from 1 to 2% from 0.12 to 0.32 s. However, such small amounts of additive (from 0.5 to 2%) correspond to the change in the critical size of the center and respectively, the minimum energy of ignition by ~ 6.25 times.

We summarize shortly the results obtained.

An approximate analytical method suggested in Sects. 1 and 2 is applied for the analysis of the problem on a local chain-thermal explosion by the example of the branched chain reaction of hydrogen oxidation in the presence of chemically active additive. It is shown that key parameters defining the critical size of the primary center of ignition, are the temperature in the local ignition center; the quantity of the

active centers of combustion created with the local source; and the presence of active chemical additives in combustible mixture. Comparison to the experiment has shown applicability of the developed approach for the analysis of critical conditions of a local ignition in combustible gas mixtures.

4 Conclusions

It is shown that the problem on a local ignition comes down to the investigation of the dynamics of a reaction zone under condition of cooling of the ignition center with the inert environment; at the same time, the power of a chemical heat source during the induction period can be considered approximately constant. The method of approximate calculation of the critical size of the center of warming up (hot spot) based on splitting the heated area in a reaction zone and the inert cooling zone is suggested. It is shown that the critical size of the center is determined from a condition of equality of the heat losses and thermal emission in a reaction zone at the moment $\tau = \tau_{\text{ad}}$ (adiabatic induction period). The method allows determining the critical size of the center in case when the center and the environment have different thermophysical properties. The concept of an intermediate combustion wave with the maximum temperature equal to the initial temperature of the hot spot is introduced. The approximate analytical method is applied for the analysis of the problem on a local chain-thermal explosion in reaction of hydrogen oxidation in the presence of chemically active additive. It is shown that key parameters defining the critical size of a local source of ignition, are the temperature in the center of a local ignition zone, the quantity of the active centers of combustion created with the local source, and presence of active chemical additives in combustible gas mixture. Comparison to experimental data has shown applicability of the developed approach for the analysis of critical conditions of a local ignition in combustible gas mixtures.

Appendix

Analytical determination of τ_{del} of hydrogen–air mix at atmospheric pressure.

We consider the branched chain mechanism of hydrogen oxidation, described above. We neglect the consumption of initial reagents during τ_{del} . Then we have:

$$\begin{aligned} \frac{dH(t)}{dt} &= I_0 + I_1 H(t) - 2k_{11} MH(t)^2 \\ C_p \rho \frac{dT(t)}{dt} &= Q_1 k_6 O_{20} MH(t) + Q_2 k_{11} MH(t)^2 \end{aligned} \quad (3.7)$$

where $l_0 = k_7 H_{20} O_{20}$ и $l_1 = 2k_2 O_{20} - k_5 I n_0 - k_6 O_{20} M$, H_{20} , O_{20} и $I n_0$ —initial concentration of initial reagents and an additive, C_p is molar thermal capacity at a constant pressure, ρ —density. In the first equation of the system (3.7) we put $H(t) = \frac{1}{k_{11} M y(t)^2} \frac{dy(t)}{dt}$, then we get:

$$\frac{d^2 y(t)}{dt^2} = l_0 k_{11} M y(t) + l_1 \frac{dy(t)}{dt}$$

Its solution under initial condition $H(0) = H_0$ (the local source generates only hydrogen atoms) is: $H(t) = \frac{-\xi_1 \exp(\xi_1 t) m + n \xi_2 \exp(\xi_2 t)}{k_{11} M (-\exp(\xi_1 t) m + n \exp(\xi_2 t))}$ where $\xi_1 = \frac{1}{2} l_1 + \sqrt{l_1^2 + 4k_{11} M l_0}$, $\xi_2 = \frac{1}{2} l_1 - \sqrt{l_1^2 + 4k_{11} M l_0}$, $m = \xi_1 - k_{11} H_0 M$, $n = \xi_2 - k_{11} H_0 M$.

Integration of the second equation of the set for $T(0) = T_0$ gives:

$$T(t) = T_0 + \left(\frac{(\xi_1 + \xi_2)\beta}{2\xi_1^2 \xi_2^2} + \frac{Q_1 k_6 O_2}{k_{11} M \rho C_p} \right) \ln \left(\frac{-\exp(\xi_1 t) m + n \exp(\xi_2 t)}{n - m} \right) - \frac{\beta t}{2\xi_1 \xi_2} - \frac{\beta m n (\xi_1 - \xi_2) (\exp(\xi_1 t) + \exp(\xi_2 t))}{2(n - m) \xi_1^2 \xi_2^2 (-\exp(\xi_1 t) m + n \exp(\xi_2 t))} \quad \text{where } \beta = \frac{Q_2}{C_p \rho k_{11} M} \quad (3.8)$$

According to [23] we will consider that the delay period expires when self-heating exceeds one characteristic interval, namely $\Delta T = T(t) - T_0 = \frac{RT_0^2}{E}$. We consider the activation energy of the linear branching reaction (k_2 , a limiting stage) as the activation energy.

During the delay period, it is possible to neglect concentration of accumulated hydrogen atoms. In addition, direct calculation shows that it is possible to ignore also the term $\frac{\beta t}{2\xi_1 \xi_2}$. The Eq. (3.5) after substituting the values ξ_1 and ξ_2 takes a form:

$$\frac{RT_0^2}{E} = \Delta T = \left(\frac{\beta l_1}{2k_{11}^2 M^2 l_0^2} + \frac{Q_1 k_6 O_2}{k_{11} M \rho C_p} \right) \ln \left(\frac{-\exp \left(\left(l_1 + \frac{k_{11} M l_0}{l_1} \right) t \right) (-\xi_2 + k_{11} H_0 M) + (-\xi_1 + k_{11} H_0 M) \exp(\xi_2 t)}{\left(l_1 + \frac{2k_{11} M l_0}{l_1} \right)} \right) \quad (3.9)$$

We simplify the Eq. (3.9) to get the equation for the delay period in an explicit form:

$$\frac{RT_0^2}{E} = \Delta T = \left(\frac{\beta l_1}{2k_{11}^2 M^2 l_0^2} + \frac{Q_1 k_6 O_2}{k_{11} M \rho C_p} \right) \ln \left(\frac{\exp(l_1 t) k_{11} M (H_0 l_1 + l_0)}{l_1^2} + 1 - \frac{k_{11} M H_0}{l_1} - \frac{k_{11} M l_0 t}{l_1} \right) \quad (3.10)$$

Further, we will calculate the value RT_0^2/E for the given conditions ($T_0 = 1000$ K, $E = 16.7$ kcal/mol): $RT_0^2/E \approx 120$. The point of intersection of the dependence (3.11) with a line $y = 120$ also will give the required value of the delay period τ_{del} (Fig. 10a, b). As is seen the value of the delay period depends both on the amount of the active centers introduced into a gas mixture at initiation and on the concentration of additive in the gas mixture. We solve the Eq. (3.10) for t , substituting $\frac{RT_0^2}{E}$ instead of ΔT . Then by definition $t = \tau_{\text{del}}$ the value of the delay period. We get:

$$\tau_{\text{del}} = \frac{1}{k_{11}Ml_0l_1} \left(\text{LambertW} \left(-\frac{H_0l_1 + l_0}{l_0} \exp \left(\frac{-l_1 \left(l_1 \exp \left(\frac{RT_0^2}{E\alpha} \right) - l_1 - k_{11}MH_0 \right)}{k_{11}Ml_0} \right) \right) \right) \times k_{11}Ml_0 + l_1^2 \left(\exp \left(\frac{RT_0^2}{E\alpha} \right) - 1 \right) + k_{11}MH_0l_1 \quad (3.11)$$

In the Eq. (3.11) $\text{LambertW}(x) + \exp(\text{LambertW}(x)) = x$ by definition,

$$\alpha = \left(\frac{\beta l_1}{2k_{11}^2 M^2 l_0^2} + \frac{Q_1 k_6 O_2}{k_{11} M \rho C_p} \right)$$

It is easy to show that the results of the calculation by Eqs. (3.9)–(3.11) practically coincide.

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