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INFLUENCE OF HYDROCARBON ADDITIVES ON THE VELOCITY OF DETONATION WAVE AND DETONATION LIMITS IN LEAN MIXES BY THE EXAMPLE OF THE REACTION OF HYDROGEN OXIDATION

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ABSTRACT

The formalism of the one-dimensional detonation theory taking into account both thermal losses and the theory of branched chain processes was applied to hydrogen oxidation in the presence of hydrocarbon additive. It is shown that accounting for both reactions of termination of the active centers of combustion via molecules of hydrocarbon additive, and chain oxidation of hydrocarbon additive allows qualitative interpreting of the main features of the process. They are both passing of detonation velocity through a maximum at an increase in content of the additive in lean mix and the existence of two detonation limits on the concentration of the additive.

Keywords: One-dimensional, Chemical losses, Branched chain, Hydrogen, Hydrocarbon additive, Detonation.

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Contribution/ Originality

This study originates a new approximate analytical formula interpreting the main features of the detonation velocities and limits in lean hydrogen – air mixtures.

D – detonation velocity, cm/s;
D_0 – detonation velocity without losses, cm/s;
E – activation energy, erg/ mole;
f, g – kinetic factors of chain branching and chain termination;
H – sum of heat and chemical losses,
H′- enthalpy behind detonation wave, erg/ mole;
$k = C_p/C_V$, where C_p and C_V – heat capacities at constant pressure and constant volume correspondingly;
k_i - rate constants of elementary reactions, cm^3/s;
M – total pressure, cm^{-3};
p – total pressure of combustible mix, dyn/cm^2;
Q – thermal effect, erg/ mole;
q_1 - heat of reaction $2H_2 + O_2$, erg/ mole;
q_2 – heat of reaction of hydrocarbon oxidation, erg/ mole;
$[O_2]_0$ - initial concentration of oxidizer, cm^{-3};
R – universal gas constant, erg /(mole.grad);
T - temperature, ^oK;
T′(x) – temperature in the vicinity of detonation wave;

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t - time, s;

w – velocity of reaction products, cm/s;

v – volume of the mass unit, cm^3/g ;

x – nondimensional coordinate;

□□□ k□□□k - 1)(3 - k□□□

□□□□fraction of unreacted molecules of oxidizer;

□□□□□□k□□p□k□□□

□□□□□□□□□□□□

□ =q_1 (1+q_2k′ [RH]/k_2□□O_2]$_0q_1$) – heat of overall reaction, erg/mole;

□□□□rate of chemical reaction, molec/s;

□ - fuel fraction in the mix with air: □H_2 + 0.5(O_2 + 3.76N_2),

Indexes

'o' – initial state;

i = 0 – 6 - number of elementary reaction

1. INTRODUCTION

As is known, in subsonic flames flame front moves forward through the gas mixture; the reaction zone (chemical combustion) propagates through the medium by processes of diffusion of heat and mass. Another combustion mode, detonation is characterized by supersonic flame velocities, and substantial overpressures. The main mechanism of combustion propagation is considered as a pressure wave that compresses the initial gas ahead of the wave to a temperature, which is above thermal ignition temperature. The reaction zone is a self-driven shock wave where the reaction zone and the shock are coincident; the chemical reaction is initiated by the compressive heating caused by the shock wave.

Investigations within Zel'dovich - von Neumann – Döering (ZND) detonation theory, which allows analytical consideration (see below), can be conducted at several levels of detail [1, 2]. At the simplest level of adiabatic propagation and downstream chemical equilibrium, the detonation velocity can be simply determined without knowledge of chemical kinetics [1]. The predicted velocity agrees well with experimental observations for propagation under conditions far enough from detonation limits. Finite rate kinetics and the associated kinetic mechanisms are needed, however, in the study of certain aspects of detonation phenomena [2]. One is concerned with near-limit propagations leading to quenching of the detonation wave. The friction and heat losses at the wall of the detonation tube, or wave curvature are usually considered as a quenching agent. The simplest description of chemistry is that of a one-step irreversible reaction. Theories and detailed computations have been conducted on various aspects of detonation based on this assumption, and useful insights have been gained. At the same time, however, it is also recognized that such a simplification inherently cannot quantitatively describe many detonation responses of interest, especially in view of the sensitive Arrhenius nature of the reaction rate to temperature variations. Furthermore, any correlations of the experimental results with adjustable kinetic parameters such as the overall activation energy and reaction order are applicable only in limited ranges of the system and thermodynamic parameters. Moreover, in the use of one-step chemistry the influence of chain-branching–termination mechanisms that are invariably multistep in nature cannot be taken into account. A prominent example is the three explosion limits of the hydrogen/oxygen system, which shows that for a homogeneous mixture at a fixed temperature, increasing the system pressure from a lower pressure limit can render it to be explosive, nonexplosive, and explosive again. Another well-known example is the observation that ignition can be largely achieved via chain carriers (atoms and radicals) branching along with thermal feedback. Such a phenomenon again cannot be described by a one-step overall reaction. Thereby in Nickolai [3] a new term "chemical losses" was introduced, which allows

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accounting for termination of chain carriers and thus, enables one to consider the main features of branched-chain nature of kinetic mechanism.

Therefore, the fact that the ignition and combustion of hydrogen- air and hydrocarbons-air mixes have branched chain nature [1, 2] significantly complicates the theoretical analysis of supersonic combustion [3] can be at least qualitatively taken into consideration. On the other side, because the approach considering only a single chemical reaction does not have any physical meaning, calculation algorithms in which the simplest kinetic schemes of the combustion process, allowing to describe the existence of the limits of ignition on pressure, for example, Liang and Bauwens [4] are being intensively developed.

We will consider this work before our analysis is presented. In Liang and Bauwens [4] for modeling hydrogen detonation the kinetic scheme, which describes all three limits of chain oxidation of hydrogen is offered. We will describe this work in more detail. Four elementary reactions were included in the scheme: chain initiation, chain branching and two reactions of chain termination, the first of which occurs on the wall, and the second one occurs in the volume, their rates make respectively r_I, r_B, r_W and r_G.

$R \rightarrow X$ (chain initiation)

$X + R \rightarrow P + 2X$ (chain branching)

$X \rightarrow P$ (termination on the wall)

$X + M + M \rightarrow P + 2M$ (termination in the volume),

where R is initial reagent, X – active radicals, P – end product, M is the third body. Mole fractions are $\square_1$ for R and $\square_2$ – for X. Nonviscous reactive flow in Liang and Bauwens [4] is described by Euler equations listed below.

$\partial\square\square/\partial t + \square\cdot(\square u) = 0$

$\partial(\square u\square\square/\partial t + \square\cdot(\square uu + p) = 0$

$\partial(\square e\square\square/\partial t + \square\cdot(\square eu + pu) = 0$

$\partial(\square\square_\square\square\square/\partial t + \square\cdot(\square\square\square_\square u) = \square(-r_I - r_B)$

$\partial(\square\square_\square\square\square/\partial t + \square\cdot(\square\square\square_\square u) = \square(r_I + r_B - r_W - r_G)$

$e = p/((\square-1)\square) + \frac{1}{2}\, u\cdot u - q; \quad q = (1-\square_\square\square\square\square\square_\square\square\square Q$

$p = \square T$

Nondimensional variables are: $\square$ - density, u - velocity , p - pressure, t - time, e – internal energy, T - temperature, $\square = Cp/Cv$, r_I – the rate of chain initiation, r_B – the rate of chain branching, r_W – the rate of chain termination on the wall, r_G – the rate of termolecular chain termination, Q – thermal effect.

Calculations showed that detonation cells become irregular if gas properties (temperature, pressure) behind a shock wave are close to an ignition limit. Quantitative comparison with experimental data was not carried out because the kinetic scheme is a generalized one.

It is obvious from above that the methods of numerical modeling in practice are not always available and ambiguous (see Introduction). In our opinion, for the solution of problems of explosion safety it is convenient to obtain simple analytical equations capturing the essence of the phenomenon; and which agree with experimental data. This problem is solved in this work with the use of results of Nickolai [3] on the basis of a formalism of ZND detonation theory taking into account the reduced kinetic scheme of hydrogen combustion in the presence of a small hydrocarbon additive. In Nickolai [3] on the basis of ZND detonation theory with allowance for the theory of branched chain processes by the example of the oxidation of hydrogen-rich mixtures in the presence of chemically active suppressant (inhibitor), it is shown that taking into account reactions of inhibitor with chain carriers leads to "chemical" losses in addition to heat losses. "Chemical" losses alone can provide the occurrence of concentration limit of detonation; the velocity of the combustion wave near the limit is supersonic. Theoretical estimates agreed qualitatively with the experimental data and numerical calculations on the inhibition of a developing detonation wave in H_2 –air mixtures with additives of propane–butane mixture (0.5÷4%) at a pressure of 1 atm.

Notice that in Nickolai [3] only rich H_2- air mixtures in the presence of a suppressant were considered.

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At atmospheric pressure, small hydrocarbon additives (further designated as RH) effectively influence on the velocities and concentration limits of detonation in the branched chain process of hydrogen oxidation [5]. Features of dependencies of these characteristics on the initial composition of a flammable mix have not been considered earlier. The present work is focused on this problem.

In this work, based on the results [3] the influence of active additive on the velocities and concentration limits of detonation in fuel lean mixes by the example of the reaction of hydrogen oxidation is considered. The work is aimed at qualitative interpretation of experimental data on detonation velocities in the lean hydrogen-air mixes in the presence of RH taking into account the reduced chemical mechanism of hydrogen combustion.

In rich hydrogen mixes, practically all oxygen atoms and OH radicals react with hydrogen, leading to development of chains and realization of branching [6] in reaction

$$H + O_2 \rightarrow O + OH$$

The role of the reverse reaction $O + OH \rightarrow H + O_2$ strongly increases in lean hydrogen mixes owing to deficiency of molecular hydrogen. Under these conditions, not all acts of a direct reaction provide branching but only these, after which chain propagation occurs:

$$O + H_2 \rightarrow OH + H\,, \quad OH + H_2 \rightarrow H_2O + H$$

At addition of RH to these mixes the reactions of oxygen atoms of and OH radicals with RH molecules competing with termination reactions [7] given below occur

$$O + OH \rightarrow H + O_2,\ OH + HO_2 \rightarrow H_2O + O_2 \text{ and } O + HO_2 \rightarrow OH + O_2$$

In spite of the fact that the radicals R formed in the reaction of RH with O and OH are low-active ones, they also develop chains to some extent, therefore, in the system under consideration hydrocarbon combustion is promoted by the active centers of the reaction of hydrogen combustion. Actually, in Rubtsov, et al. [8] the promotion of oxidation of propylene additives (1-2.7%) with hydrogen oxidation was observed. It was shown that the mixes containing 1-2.7% C_3H_6 with oxygen under conditions of Rubtsov, et al. [8] are not capable to ignite at a spark initiation without hydrogen. This means that the reaction

$$H + RH \rightarrow \text{termination}$$

in fuel lean mixes is not as effective as in rich ones, owing to the larger oxygen content. As a result, in the region of lean mixes the reactions of hydrogen oxidation and RH oxidation mutually accelerate each other. Really, in consent with Azatyan, et al. [9] the lower concentration limit of detonation at increase in concentration of RH increases, indicating a promotion of RH oxidation with the reaction of hydrogen oxidation.

The condition of ignition of hydrogen-air mix takes the following form [10]:

$$2K[O_2]\,\square_0\square\square_0 = b\,k_6\,[O_2][M] + k_4$$

where K is the rate constant of the reaction $H + O_2 \rightarrow OH + O$, k_6 is the rate constant of the reaction $H + O_2 + M \rightarrow HO_2 + M$, k_4 is the rate constant of heterogeneous chain termination, $\square_1$ and $\square_2$ are the fractions of radicals OH and O atoms respectively, entering into the reactions of chain branching and chain propagation. The product $\square_0\square_0$ determines the fraction of branching events, b – the fraction of HO_2 radicals entering into the reactions of chain termination. It is evident from the meanings of $\square_0\square\square\square\square_0$ and b that in hydrogen-lean mixtures $\square_1$ and $\square_2$ noticeably decrease, though in rich mixtures $\square_0\square\cong\square\square_0 \cong 1$.

Therefore, in lean mixtures in the absence of active additives, the rate of branching decreases; in the presence of RH it becomes necessary to take into account the exothermic process of RH oxidation along with chain termination via RH molecules.

2. EXPERIMENTAL

Experiments were performed in a detonation tube [11] which consisted of four sections 14, 16, 64 and 83 mm in diameter connected with gradual diameter tapers. Previously prepared combustible mixes were maintained for several days for uniform hashing. The widest section of a pipe was filled with the mix containing an additive of RH.

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Three other sections were filled with easily detonating stoichiometric $2H_2 + O_2$ mix, which was ignited with a spark discharge. The detonation passed into a wider section where the detonation wave in the mix under investigation was formed. At certain concentrations of inhibitor, the detonation wave broke down to a shock wave and the combustion front that lagged behind a shock wave as it was earlier revealed in Azatyan, et al. [11]. As the limit concentration of inhibitor, we considered that one, at which the detonation wave occurred, but at small excess of this concentration, the detonation wave broke down. The velocities of a shock wave and detonation wave were registered with piezoelectric pressure gages; the velocity of flame front propagation was recorded with photo diodes, the signals from which were transferred to C9-8 digital oscilloscopes. The result of inhibitor action on the developed detonation was estimated from the values of velocities of shock wave fronts and flame fronts by a distance between them in the same sections of a detonation pipe. If the detonation wave occurred in the mix under investigation, then signals from a pressure gage and a photo diode in the same section of a pipe were recorded simultaneously (± 2 □s). The error in the measured velocity of a detonation wave in different sections of the pipe did not exceed ± 30 m/s. If the detonation mode was missing, the measured combustion velocity decreased, the signal of the pressure gage was registered earlier, than the photo diode signal (in the same section); at the same time, a value of the flame velocity was less than that of a shock wave. The velocity at one experimental point was the mean value of six measurements. The concentration of H_2 in hydrogen-air mixes made up 0÷45 % and that of inhibitor (propane - butane mix (1:1)) made up 0÷5 %. The dependence of a detonation wave velocity on the content of the inhibitor was measured at initial pressure 0.615 atm. Kinetic experiments on the initiated ignition of hydrogen-air mixes were performed in the stainless steel cylindrical reactor 10 cm in diameter and 20 cm long at atmospheric pressure. Initiation was provided with a spark discharge (0.91 J) in the center of the reactor at 293K. Light emission was registered by means of a photomultiplier, the pressure was registered by the piezoelectric gage; the signals were transferred to the electron beam memorable C9-16 oscilloscope.

3. DISCUSSION

The application of the formalism of the one-dimensional theory of detonation limits [12] to find out the conditions of detonation occurrence in the presence of RH, is justified only if energy losses via molecules of an active additive are taken into account [13]. As the experiment [11] shows the existence of a detonation limit on RH concentration, it is necessary to consider initially the propagation of a detonation wave with losses [3, 13]. One-dimensional propagation of a detonation wave with thermal losses is considered below; at the same time, the kinetics of chemical reaction unlike [12] is not described with a single Arrhenius reaction, but with a reduced mechanism of hydrogen oxidation [6]. We will follow the logic of a statement of this problem in Zel'dovich and Kompaneets [12] keeping the designations accepted in Zel'dovich and Kompaneets [12]. The equations of gas dynamics with the accounting of thermal losses have the form [12]:

$$D/v_o = (D-w)/v \; ; \; p-p_o = -D^2(v-v_o)/v_o^2; \; H'-H_o+1/2(p-p_o)(v_o+v) = -\int L dx \qquad (1)$$

v is the volume of mass unit, $D - w$ is the detonation wave velocity in a coordinate system fixed with the leading front of the detonation wave (D is the detonation velocity, w is the velocity of reaction products), p is pressure, H' is the enthalpy behind the detonation wave front, L is the function describing the heat losses, x is the coordinate, and the subscript '0' refers to the initial state. We will make some remarks on the function L describing thermal losses. In a turbulent flow, all transfer phenomena possess similarity. If any value, for example, J is transferred, then the coefficient of transfer is directly proportional to □J/4 (□ is density). For heat transfer, it is necessary to take the change of enthalpy □H upon transition to a wall temperature Tw instead of J. Then a heat flow through a unit of a surface g is proportional to □□H/4, and the losses referred to a unit of a cross section of a mass flow in a detonation wave will make L □ gz/d (z – pipe perimeter, d – pipe diameter) [12].

By consideration of only thermal losses, the quantities p and v are linearly related [9] that allows obtaining the solution of (1) in an explicit form, enabling one to analyze its physical meaning. According to Zel'dovich and

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Kompaneets [12] we allocate a chemical fraction in enthalpy H ′ =k / (k-1)pv + □Q, assuming k = C_p/C_V identical before and behind a detonation front, neglecting both dependence of thermal capacity on temperature and initial pressure p_0, we obtain the expression [12]:

$$R(dT'(x)/dx) = \frac{Q(k-1)(vo - 2v(x))(\square - L/Q)}{k(v1 - v(x))} \quad (2)$$

where $v1$ = k/(k+1)/ v_0, T′(x) is temperature, R is the gas constant, □□ = d□□dx is the rate of a chemical reaction taken with the opposite sign (in the classical consideration [12] □□is described by the Arrhenius equation □□ = $Ae^{-\frac{E}{RT}}$). For a branched chain combustion process

$$\square \sim (f\text{-}g)\, n$$

where f-g is the difference between factors of branching and termination [6] n is the concentration of active centers taking part in chain branching.

Experimental dependence of the lower concentration limit of detonation on the concentration of RH is presented in Fig. 1a. In a point (1) hydrogen-air mix burns, it but it does not detonate. An increase in hydrogen content by 4% (point 2) also does not provide detonation; however, an increase in RH concentration by 1% (point 3) already provides a detonation mode. Therefore, though the rate or RH combustion is many factors of ten smaller than that of hydrogen, RH additive is many times more effective to cause detonation, than hydrogen additive.

As is clear from (2) thermal emission in reaction is Q□, and the value of dT′(x)/dx is proportional to Q(f-g) n – L; at the same time, the equality Q(f-g) n = L represents a condition of a chain thermal explosion [6] which accounts for branched chain nature of combustion. Thus, the realization of the chain thermal explosion as a consequence of a chain ignition is a necessary condition of detonation. At the same time, to provide combustion the condition of chain ignition f>g must be satisfied. The L value slightly changes with the change in the content of an additive; therefore, at other parameters being constant (except RH), the features of detonation wave propagation are determined by the f-g difference.

From (2) it is seen that if f-g> 0, but Q(f-g) n < L, then combustion occurs, but there is no detonation (point 1). At the same time, with the increase in RH concentration (in the direction to a point 3) both a factor g (velocity of chain termination via RH) and Q (as oxidation of RH is exothermic process) increase.

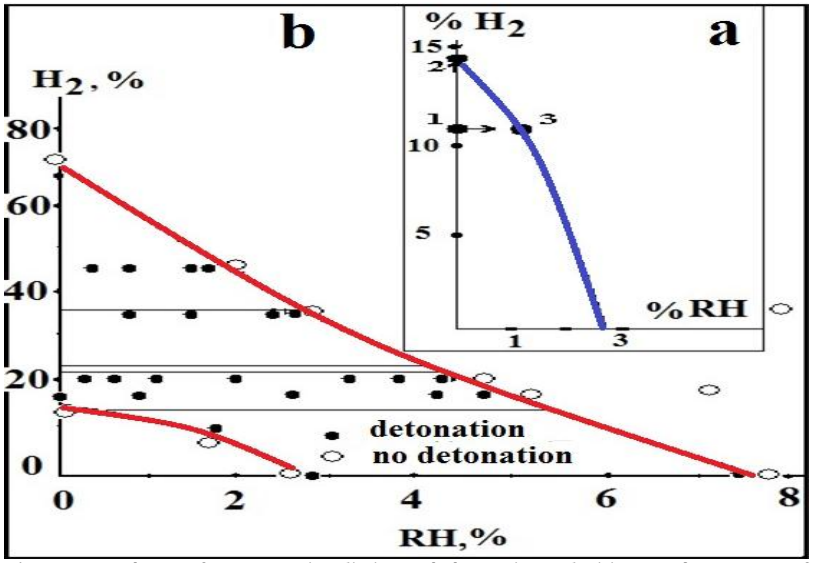

Fig-1. Dependence of concentration limits and detonation velocities on the content of hydrocarbon additive:

a) - dependence of the lower concentration limit of detonation on the content of RH;

b) – concentration region of stability of a detonation wave at 1 atm in mixes with various content of hydrocarbon [11] horizontal straight lines correspond to calculated concentrations in Fig. 3.

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Source: This work (a)

At small RH additives, acceleration of combustion is provided due to exothermic oxidation of RH, which is promoted by hydrogen oxidation. It is obvious that the increasing velocity of the combustion process provides an increase in thermal emission. With an increase in the content of RH additive, combustion process approaches the mode of chain thermal explosion. In this mode, detonation arises in a rather long pipe due to flame acceleration (point 3). At further growth of RH content a combustible mix due to increase in an f-g difference goes out of this mode (upon transition over the upper concentration limit of detonation), and then out of the ignition region (f<g), i.e. detonation ability of a lean mix goes through a maximum.

Fig. 2 illustrates the previously mentioned. In the Figure oscillograms of simultaneous registration of both integrated intensity of light emission and an increase in pressure during the initiated ignition of 15% H_2 - air mixtures in the presence of iso- C_4H_8 (isobutene) additives are shown. As is seen in the presence of > 1% additive (which itself does not burn under these conditions) the rate of hydrogen oxidation at first sharply increases, but then with an increase in RH concentration up to 4.8% decreases at an approach to an upper concentration limit of the inhibited ignition.

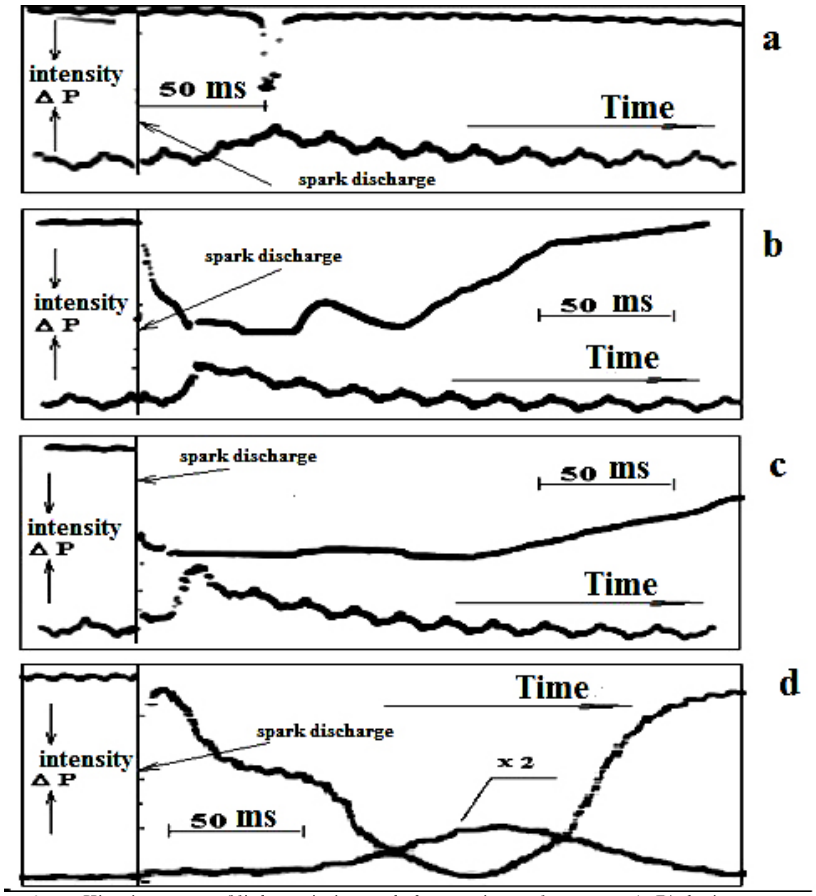

Fig-2. Kinetic curves of light emission and changes in total pressure (□P) during the initiated ignition of hydrogen - air mixes of in the presence of additives of iso – C_4H_8 at T_0 =298 K and atmospheric pressure.
a) – 15% H_2 + air, b) - 15% H_2 + air + 1% iso – C_4H_8, c)-15% H_2 + air + 2% iso – C_4H_8, d) - 15% H_2 + air + 4.8% iso – C_4H_8. At 6% iso – C_4H_8 there is no ignition.
Source: This work

As is also seen in Fig.2, the RH additives, which demonstrate a strong inhibiting action in stoichiometric and rich H_2 – air mixtures [11] are effective promoters in lean H_2 – air mixtures.

The rate of heat emission in the branched chain process of hydrogen combustion in the presence of RH takes the form (see Appendix):

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□□□

As is seen in Fig. 3, delay times of the initiated ignition differ approximately by a factor of ten. As the delay time is inversely proportional to a branching factor [6] which is approximately equal to $2k_2[O_2]_0$ (neglecting termolecular termination), therefore, at reduction of H_2 content in the mix it is possible to vary $k_2[O_2]_0$ by a factor of 10. The value of $q_2k'/k_2[O_2]_0q_1 \sim$ could be increased by about two orders at reduction of H_2 concentration in lean H_2-air mix by 10 ÷15%.

For an analysis of the solution of (5) we use also values Cp = 4R/m (m – is the average molecular weight of the gas mixture). R = 8.3.10^7 erg/mole.grad, E=22400.10^7 erg/mole [17] k=3/2,

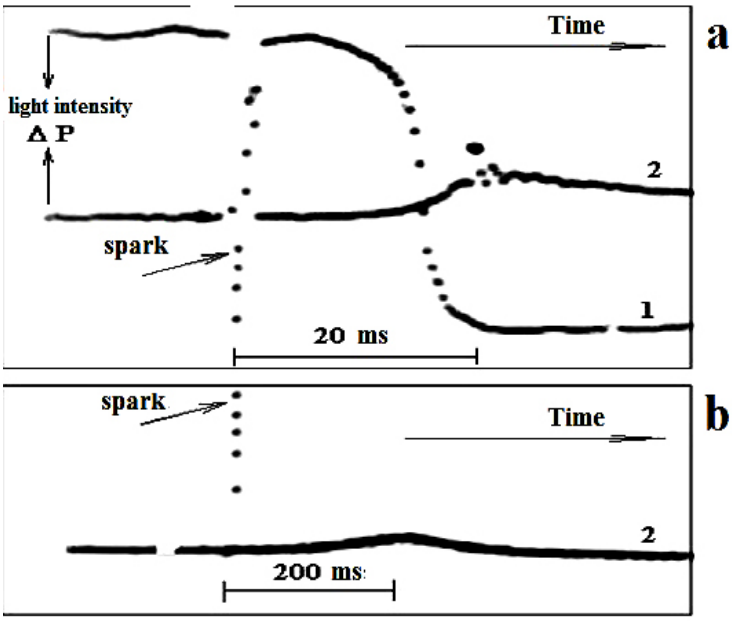

Fig-3. Kinetic curves of light emission (1) and changes in total pressure (2) during the initiated ignition of hydrogen-air mixes; 18% H_2 (a) and 10% H_2 (b) at T_0 =298 K and atmospheric pressure.

Source: This work

k_1=5.7.10^{-11} cm^3/molec.s (for propene [16]) k_0 = 4.10^{-11} cm^3/molec.s [16] k_6 = 6.47.10^{15}.(T/298)$^{-0.8}$ cm^3/mole^2.s [18]. T_0 value at the front of the detonation wave is taken as 1500K. The change of D_o in lean mixes was calculated from the data of Fig. 1a [19] in which the dependence of D_o on for H_2 – air mixtures is presented.

Equation (5) can be solved in explicit form using LambertW(x) function, which has the following definition: LambertW(x) + e$^{\text{LambertW(x)}}$ = x. For example, Fig. 4 (curve 1) shows a positive branch of the solution for = 1.23, at q_2 =0 and = 0 by the equation:

$$D = 0.65.10^{-5}\,[0.83.10^{21} + 0.30.10^{21}\,\text{LambertW}(-6.18\,X_o - 0.35)]^{1/2} \qquad (6)$$

In Fig. 4 a, b, experimental and calculated by the equation (5) dependencies of the velocities of a detonation wave normalized by D_o (for a given content of hydrogen) on RH concentration in lean hydrogen mixes are presented. These velocities are calculated for various hydrogen-air ratios in lean mixes taking into account the change of average molecular mass of gas mixture. At the same time, the reduction of an effective constant of the rate of chain branching as compared to the rate of termolecular chain termination (parameter was increased from 0 to 0.063 at an increase in hydrogen content), and to a rate of RH oxidation (parameter was increased from 0 to 130 at an increase in hydrogen content) was taken into account.

As is seen in Fig. 4, accounting for additional heat emission at the promoted oxidation of RH molecules along with a chain termination via RH, and termolecular chain termination as well allows qualitative explanation of experimental features. In other words, in consent with the initial equation (2) detonation velocity passes through a maximum with an increase in the concentration of an additive at hydrogen concentrations below stoichiometric ones. At further reduction of hydrogen content (curve 4 in Fig. 4b) the equation (5) describes the emergence of the

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lower concentration limit of detonation on RH concentration (designated by an arrow); that also agrees with experimental data.

Thus, the approach used in the present work allows qualitative description of the experimentally observed dependence of both the upper and lower detonation limits on RH additive in the mix. It is obvious that owing to the qualitative nature of the consideration performed any quantitative comparison of the calculations and experimental data cannot be quite correct.

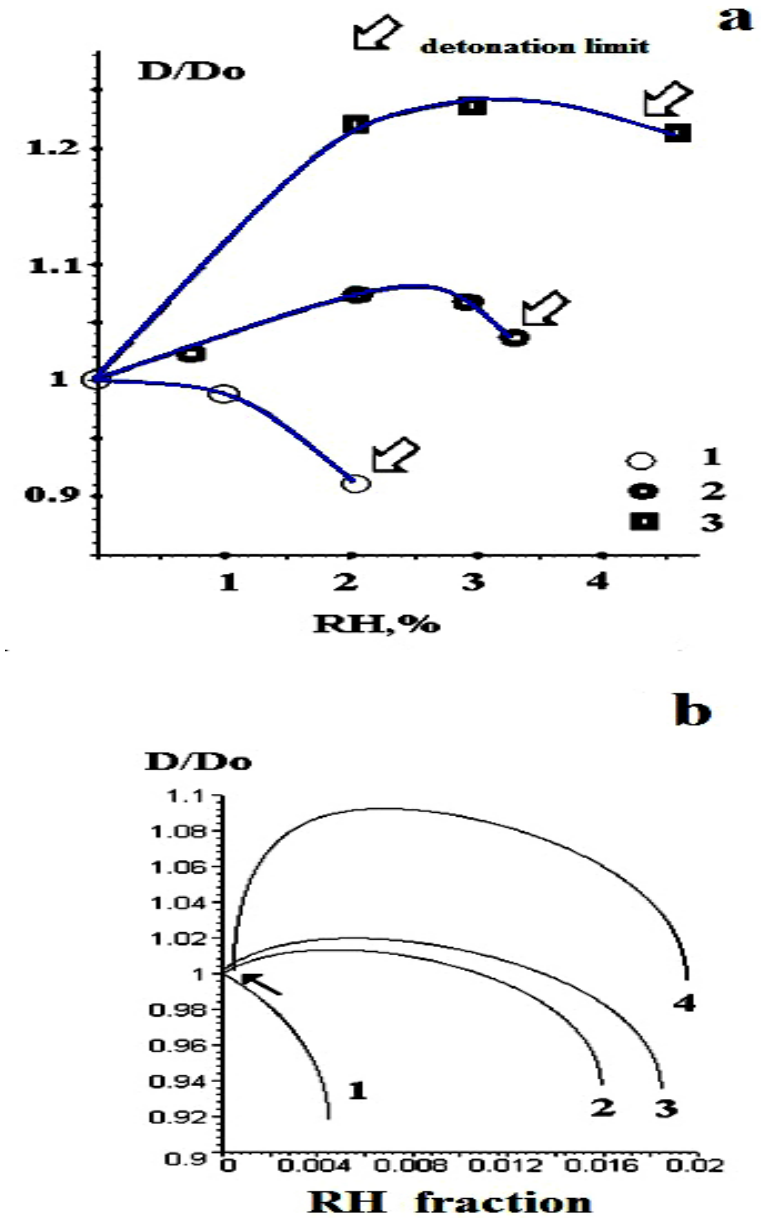

Fig-4.a. – dependence of normalized detonation velocities on the content of RH: 1 - 45% of H_2, 2 – 33% of H_2, 3 - 16% of H_2;
b) –qualitative calculation by the equation (5) for mixes
1 – 36% of H_2, □□□□□□□□0;
2 – 24% of H_2, □□□□□□□□□□□□□50;
3 - 21% of H_2, □□□□□□□□□□□□□□□□70;
4 – 14% of H_2, □□□□□□□□□□□□130.

The arrow specifies the lower limit of a detonation on RH (in the vicinity of the point 3 Fig. 1a)

As it is specified in the Introduction, numerical calculation can guarantee reliable results only if the reliability of all input parameters used in a rather wide range of entry conditions is provided as opposed to an analytical solution (if that can be obtained). However, the overestimation of opportunities of numerical modeling one can

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notice in certain researches, e.g. [18]. It should be noted that the numerical calculation does not provide information on physical meaning and uniqueness of the solution and owing to above mentioned, it is suitable only for the interpretation of already available experimental data, but it cannot be used for prediction of any new phenomena or regularities as it is made, e.g. in Bunev and Babkin [18]. In addition, accounting for hundreds of elementary reactions does not guarantee the reliability of the results of a calculation because the vast majority of rate constants and their temperature coefficients are insufficiently exact to draw trustworthy conclusions on the basis of calculations with such errors. For instance, in Bunev and Babkin [18] the inhibition via propene (RH) has a form

$$RH + H \rightarrow R + H_2,\ R + H \rightarrow R_1H + H_2,\ R_1H + H \rightarrow R_1 + H_2,$$

i.e. addition of H atom to an olefinic linkage [20] is not taken into account. Therefore, the results of Bunev and Babkin [18] cannot refer to propene. Thus, wrong interpretation of propene action depreciates the calculations performed in Bunev and Babkin [18].

We summarize shortly the results obtained. The formalism of the one-dimensional detonation theory taking into account both thermal losses and the theory of branched chain processes was applied to lean hydrogen oxidation in the presence of hydrocarbon additive. It is shown that accounting for both reactions of termination of the active centers of combustion via molecules of hydrocarbon additive, and chain oxidation of hydrocarbon additive allows qualitative interpreting of the main features of the process. They are both passing of detonation velocity through a maximum at an increase in content of the additive in a lean mix and the existence of two detonation limits on the concentration of the additive.

4. APPENDIX

Let the origin of coordinates be directly behind the shock wave front, and let the initial values at this point be $v=(k-1)/(k+1)v_0$ and □□□□□ Let us study the behavior of $T'(x)$ near the front, taking $v_1=(k-1)/(k+1)v_0$. Let us calculate the rate of chemical reaction in the lean mixture, taking into account the oxidation of RH in the presence of the excess of the oxidizer. The reactions of an active additive by the example of propane are taken into account as follows. Chain termination via propane molecules is the reaction:

$$H + C_3H_8 \rightarrow H_2 + C_3H_7 \qquad k_1$$

Notice that the rate constants of reactions of OH radicals and O atoms with RH are, as a rule, several times less than k_1 [21] under our conditions. Therefore, in view of the qualitative consideration of the problem, we confine ourselves with the reaction

$$H + C_3H_8 \rightarrow H_2 + C_3H_7$$

Low active radicals C_3H_7 (the rate of RH oxidation is markedly less than the rate of branched chain H_2 oxidation, e.g. [8] in the presence of excess O_2 can rather rapidly react with O_2 molecules. As a result, either RH molecules could be regenerated or RH is consumed in the oxidation process in the consequence of reactions, which is determined by an overall rate constant k_5:

$$C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \quad k_3 \quad \text{or} \quad C_3H_7 + O_2 \rightarrow C_3H_6O + OH \ (k_5)$$

The reaction rate in the line of k_5 is

$$k_1k_5[H][RH]/(k_3 + k_5) = k'\,[H][RH]$$

Because the detailed mechanism of hydrocarbon oxidation is under discussion (e.g.[18]) the result obtained is only a qualitative illustration of accounting for two paths of consumption of C_3H_7 radicals, causing either regeneration or oxidation of RH respectively. The reduction of the lower detonation limit with an increase in concentration of an RH additive can be explained by the competition between these two reaction ways. This is due to the progressive growth of heat release and occurrence of the overall reaction in the kinetic mode corresponding

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to DDT (deflagration to detonation transition), and the subsequent detonation failure due to chain termination via molecules of an additive at further increase in the concentration of RH.

Let n(t), $O_2(t)$ be the ratios of concentrations of H atoms and O_2 molecules, respectively to the initial concentration $[O_2]_0$ of molecular oxygen; $[RH]$ is the hydrocarbon concentration; k_1, $k_2 = K\square_{\square}\square_{\square}$, k_6 – rate constants of reactions of H atoms with hydrocarbon, O_2 and termolecular termination correspondingly, k′ is an effective rate constant of C_3H_7 radical with O_2. Thus, C_3H_7 concentration is determined from a quasi-stationary condition:

$$[C_3H_7]=k_1\, n(t)\, [RH]/\{(k_3+ k_5)[O_2(t)][O_2]_o\}$$

Based on the simple mechanism of hydrogen oxidation [6] with allowance for the reaction $H + C_3H_8 \rightarrow H_2 + C_3H_7$, neglecting chain initiation we obtain:

$$dn(t)/dt = n(t)(2k_2\,[O_2(t)][O_2]_o - k_6\,[O_2(t)][O_2]_o.\, M - (k_1 - k')[RH]);$$

$$dO_2(t)/dt = -k_2 n\,(t)[O_2(t)][O_2]_o - k_1\,[RH] - k_6\,[O_2(t)][O_2]_o\, M$$

Let us divide the first equation by the second one to eliminate t and then denote (by definition) $[O_2] = \beta$. Further, the behavior of all the parameters is considered only near the shock wave front where the extent, to which the reaction proceeds is considerably small. Therefore, the result should be integrated with allowance for $n(\beta] = 1) = 0$ at constant temperature within a narrow zone near the front:

$$n(\square)=(1-\square)(2k_2-k_6M)/(k_2+k_6M)(k_1-k')[RH]\ln(1-k_2[O_2]_o(1-\square\square\square\square k_2[O_2]_o+k'[RH])/((k_2+k_6M)[O_2]_o)$$

With allowance for qualitative nature of the consideration, we omit the terms including k′. Assuming $\ln\square\square\square\square\approx\square\square\square\square\square\square\square$ we get:

$$n(\square) = 2(1-\square)(2k_2-k_6M)/(k_2+k_6M)\square\ k_1')[RH](k_2[O_2]_o(k_2+k_6M)\square\square\square\square\square\square \qquad (7)$$

Let us write the rate of heat release as $\square_1 = -k_2\square\square O_2]_0\, n(\square)q_1$, where q_1 is the thermal effect of the reaction of hydrogen oxidation; the rate of heat release in the process of RH oxidation is $\square_2 = -\,k'\,\square RH]n(\square\square q_2$, where q_2 is the corresponding thermal effect. We use (7), representing the overall heat release as $Q\square\square\square\square\square_{\square}\square\square\square\square_{\square}\square$ Thus, the promotion of RH oxidation with the process of H_2 oxidation is taken into account. We divide both parts of (7) by $[O_2]_o$, evaluating k_0 in $k_2 = k_0 e^{(-E/RT)}$. We ignore the temperature dependence of the rate constant of inhibition reaction, because activation energies of H atom interaction with hydrocarbons or halogenated ones are << E, see above. Then we get the equation (3):

$$Q\square = -q_1\left(1+\frac{q_2k'[RH]/k_2\square\square O_2]_o q_1}{2\square\square\square\square\square\square\square\square\square O_2]_o\square k_0 e^{-E/RT} - k_1[RH]/\square\square\square - k_6M[O_2]_o(1-\square)}\right) \qquad (3)$$

$$[O_2]_o\, k_0(1 + k_6M / k_0\, e^{-E/RT})$$

Let us substitute $Q\square$ into (2) and use the expansion $1/(1+x) \approx 1-x$ for small x (x<0.3) in the denominator; we divide both parts of the equation by c, where $c = D-w$ is the speed of sound in reaction products [12] and define $k_6M / k_0 = \square\square$ and $e^{-E/RT} = \square_{\square}$,

$$\square\square\square\square\square\square\square\square\square\square\square\square O_2]_o k_0\square - k_1[RH]/\square\square\square - k_6M[O_2]_o(1-\square\square_{\square}\square\square$$

$$R\,\frac{dT'(x)}{dx} = \frac{\square(k-1)[v_o - 2(k-1)v_o/(k+1)]\square\square/c(1-\square\square\square) - Lc/\square\square]}{[O_2]_o k_0\, k(kv_o/(k+1) - (k-1)v_o/(k+1))} \qquad (8)$$

The behavior of $Q\square$ is considered in the vicinity of the shock wave front. We use the expansion $E/(RT'(x)) = E/(RT_o) - E((T'(x)) - T_o)/(RT_o^2)$. Let in (8) $T'(x) - T_o = T(x)$, $\square\square\square\square\square\square\square\square\square\square\square\square$ $\square = k^{-1}(k-1)(3-k)\square\square$ and $f_o = e^{(-E/RT_o)}$, $\square = k_0[O_2]_o) - k_6\square\square\square\ M/k_0$:

$$R\,\frac{dT(x\square}{dx} = \square\square(2f_o\ \square\square\square\square e^{\square E(T(x)/(RT_o^2)} - \square^{\square\square\square}\square\square k_1[RH]/(\square)/c\,(1-\square/e^{-E/RT}) - cL] \qquad (9)$$

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We define H=□□□□□k$_1$[RH]/(k$_0$[O$_2$]$_o$)+k$_6$□M□/k$_0$ + cL, □ = 2f$_o$□□□ and then integrate (9) by changing variables T(x)= ln(t(x))RT$_o^2$/E with allowance for t(0) = 1:

$$t(x) = -\frac{1}{4\square\square\square}(-H-2\square\square\square+(2\square\square-H)\tanh\left[-\frac{x\square E(-2\square\square+H)}{2T_o^2R^2}+\frac{1}{2}\ln\left(\frac{2\square(1-\square)}{H-2\square}\right)\right]$$

And then

$$e^{\frac{ET(x)}{RT_o^2}} = \frac{1+\square\square\left[1/(1-\square)-2f_o\square\square\square/H(1-\square)\right]e^{\square}}{2f_o\square\square/H-\left[2f_o\square\square\square\square(1\square\square\square\square\square\square\square\square\square\square\square\square\right]e^{\square\square}} \quad (10)$$

where □□□□□□□H -2f$_o$□□□□)x/(cR^{2}T$_o^2$k) (11)

The system (1) can easy be transformed to the following relation [12]:

$$h(v_1,D) = \square\left(1-\square_{\square\square}\square\square\square\square\int_0^{x_1} H(x)dx\right) \quad (12)$$

where h(v$_1$,D) = D^2/2(k^2 - 1) is a function that describes detonation without losses, H(x) is the sum of "chemical" and heat losses, where, at the point x1 $v(x) = v1$ (the heat release is equal to the heat removal). □$_{\square\square}$□is the fraction of unreacted O$_2$ at the point of tangency of the Hugoniot's adiabatic curve and the Michelson's straight line. At this point, the fact that the numerator and denominator of the fraction on the right-hand side of Eq.(2) are simultaneously equal to zero, makes a detonation mode possible [12]. Thus, at the temperature T$_{oo}$, corresponding to the tangent point:

□□□□□□L/□□или □□□□□□□□□e$^{-E/RToo}$–□$^{2/3}$k$_1$[RH]/(k$_0$[O$_2$]$_o$(1-□))–k$_6$M/k$_0$)=Lc/□ (13)

Suppose that, at this point, the inhibitor has already been consumed; then

Lc/(2f$_o$□) = □$_{\square\square}$□□□□□□□$_{\square\square}$□□□□□□ (14)

From (10), it follows that ½ $L/(\square f_o) < 1$. It means [12] that in (14) □$_{\square\square}$□can be ignored.

Let us estimate □□H(x)dx. From (10) it is evident that:

2f$_o$□□□/H(1-□) - (2f$_o$□□□/H(1-□) -1)e$^{\square}$ < 1 then □ < - ln(1/(1-□) - H/(2f$_o$□□□(1-□)))

If the value of H/(2Q□□f$_o$) is not too close to 1, one can use the first term of the expansion into a series:

$$\square\square < H/(2\square\square\square f_o) + \ln(1-\square) \quad (15)$$

The second term in the right-hand side without violation of inequality could be omitted.

Then, using the expression for □ from Eq. (11), expressing x from it, replacing □ by its estimated upper limit from Eq. (15) and substituting f$_o$ = e$^{(-E/RTo)}$, one can obtain:

$$x = cR^2T_o^2k/\left[2(H-2\square e^{(-E/RTo)}\square\square)E(k-1)(3-k)\right]$$

Let □□H(x)dx ≈ H x. This estimation of H(x)dx we put in (12) and take into account that □$_{\square\square}$□□□□□□ 3 - k ~ 2, k/(k+1) = C$_p$/R, □□□□□$_{max}$ ~ □$^{2/3}$ ~ ¼. Then we obtain the equation (4).

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