

# Numerical Simulation of Deflagration Initiation in Flows of Hydrogen-Air Mixes

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## 1 Introduction

Many authors produce investigations (physical and numerical) of flows with deflagration and detonation of air-hydrogen gas mixes. This is due to the problem of constructing of detonation engines with hydrogen as the fuel. Perspective results in this field where ideas of impulse detonation engines ([1-3] for example) and spin detonation engines [4]. Nevertheless it should be noted that this problem is far from real technical decision. One of the way of progress in decision of this problem is development of mathematical models and numerical methods for numerical simulation of initiation of deflagration of gas mix and transition of deflagration to stable detonation. Initially many authors used simplified model of chemical reaction of Levin at all. [1], on the basis of which essential results where provided, Fujiwara [4] for example. Nowadays, for the aim of detail investigation, in particular for preserving accurate energy balance full system of chemical reactions are using, which consist of 9, 16, 32 or more reactions. From the kinetic point process of transition to detonation can be treated as transition from slowly deflagration to branching chain reaction in hydrogen-air mix. This reactions where developed by N.N.Semenov [5]. In real physical experiments this deflagration initiation in flows appears via sudden hot spot appearance or near an obstacle on boarding surface. In this paper numerically investigated flows of reactive gas mixes in channels with obstacles with purpose to define regims of deflagration initiation.

## 2 Mathematical Model and Results of Calculation

System of equations for chemical reactions can be presented as follows:

$$\sum_{i=1}^n \alpha_{ij} A_i = \sum_{i=1}^n \beta_{ij} B_i, j = 1, \dots, M \quad (1)$$

where  $M, N$  – number of reactions and components of the mix,  $\alpha_{ij}, \beta_{ij}$  - coefficients of direct and inverse reactions. Arrhenius law is predicted for calculating speeds of changing molar concentration  $C_i$  of mix components:

$$\frac{dc_i}{dt} = \sum_{j=1}^M (\beta_{ij} - \alpha_{ij}) w_j(c, T), \quad (2)$$

$$w_j(c, T) = k_f(T) \prod_{i=1}^n c_i^{\alpha_{ij}} - k_b(T) \prod_{i=1}^n c_i^{\beta_{ij}}, \quad (3)$$

$$k_{f,b} = A_{f,b} T^{l_{f,b}} \exp(-E_{f,b} / RT) \quad (4)$$

For preserving of non decreasing of entropy condition coefficients of inverse reaction where calculated from equilibrium constants:

$$k_b / k_f = K = \exp\left[ \sum_{i=1}^n (\beta_{ij} - \alpha_{ij}) \left( \frac{G_i^0(T)}{RT} + \ln \frac{RT}{P_0} \right) \right], \quad (5)$$

where  $G_i^0(T)$  -Gibbs potential for mix component.

During numerical investigations systems (2)-(4) for hydrogen-air mix with different numbers of reactions and mix components where used. In the papers of different authors ([6-8] for example) meanings of coefficients  $k_{f,b}$  diverse essentially. Results of numerical simulation of flows with deflagration and detonation naturally essentially depends of what system of reactions and meanings of coefficients  $k_{f,b}$  are used. One of the aims of present work is testing of usage different systems of reactions and meanings of coefficients in model (2)-(4).

The next problem was solved numerically: in small closed volume, initially filled by hydrogen-air mix with atmospheric meanings of gas dynamics parameters at moment  $t=0$  temperature rising till meaning, at which reaction of deflagration should begin (approximately  $3 T_{amm}$ ). Numerical experiment consist of calculation of thermodynamics parameters and gas mix components concentration per time in small isolated volume. Meanings of molar concentration of components of gas mix where calculated by numerical decision of system (2)-(4) by implicit numerical method of Gear. Calculation where provided till concentration of hydrogen became equal to zero or till deflagration is not appearing at all. Thermodynamic parameters where found from meanings of Gibbs potential:

$$G(\rho, T, c_i) = \sum_{i=1}^N c_i [RT \ln(Pc_i / P_0) + G_i^0(T)] \quad H_i^0(T) = G_i^0(T) - T \frac{dG_i^0(T)}{dT},$$

$$h = \sum_{i=1}^N c_i H_i^0(T), \quad V = (RT \sum_{i=1}^N c_i) / P \quad (6)$$

Gas mix of 9 component :  $H_2, O_2, H, O, H_2O, OH, HO_2, H_2O_2, N_2$  was treated. Components as  $Ar, O_3, NO, NO_2$  where neglected. During the initial period of process, period of induction, concentration of radicals  $H, O, OH$ , (and  $HO_2, H_2O_2$ ) consequently grows and diminishing from  $H, O$  to  $HO_2$ , and  $H_2O_2$ , (look to. Fig.2, A). Essential decreasing of concentrations  $H_2$ , and  $O_2$  take place on the second stage of process. Time interval for both stage of process essentially diminishing with rising of initial temperature. In case of small initially temperature rising reaction is not appears at all or grows of  $H_2O$  and decreasing of  $H_2, O_2$  have very slowly character, which could be connected with slow deflagration of hydrogen (Figure 1a). Numerical decision of system (2)-(4) with 9, 16 and 26 reactions with coefficients, taken from [6], shows that grows of number of reaction don't change essentially graphics of changing components concentrations from time. So, for numerical

investigations the next 11 most widespread reactions where choose (Table 1,  $k_i$  denote speed of reactions).

**Table 1** Chemical reactions (component M in reactions means some collision partner of reaction)

$H_2 + O_2 - k_0 \rightarrow 2OH$	$H_2 + OH - k_{11} \rightarrow H + H_2O$	$H + O_2 - k_2 \rightarrow O + OH$
$H_2 + O - k_3 \rightarrow H + OH$	$HO_2 + M - k_5 \rightarrow H + O_2 + M$	$H + H_2O - k_6 \rightarrow H_2 + OH$
$2H + M - k_7 \rightarrow H_2 + M$	$2HO_2 - k_8 \rightarrow H_2O_2 + O_2$	$H_2O_2 + M - k_9 \rightarrow 2OH + M$
$2OH + M - k_{10} \rightarrow H_2O_2 + M$	$H + H_2O_2 - k_{11} \rightarrow OH + H_2O$	

During the calculations, in initial period of process, period of induction, concentration of radicals  $H$ ,  $O$ ,  $OH$ , (and  $HO_2$ , and  $H_2O_2$ ) consequently grows and diminishing from  $H$ ,  $O$  to  $HO_2$ , and  $OH$ . Essential decreasing of concentrations  $H_2$ , and  $O_2$  take place on the second stage of process. Time interval for both stage of process essentially diminishing with rising of initial temperature. In case of small initially temperature rising reaction is not appears at all or grows of  $H_2O$  and decreasing of  $H_2$ ,  $O_2$  have very slowly character, which could be connected with slow deflagration of hydrogen. Results of calculations are shown on Figure 1 (A,B).

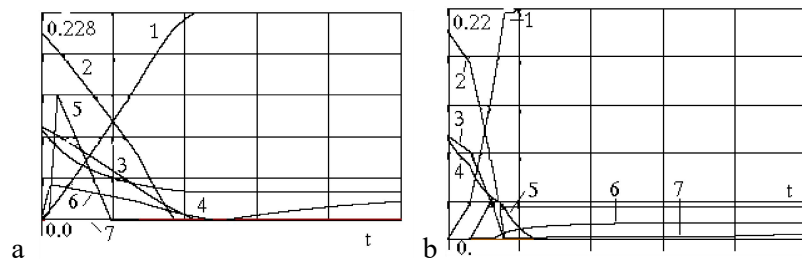


Figure 1: Graphics of molar concentration of mix components from time (constants from [6] where used for slow deflagration simulation). On Figure 1 a,b (initiation of deflagration as result of temperature increasing to 2.4 and 2.7 times consequently) line 1 –  $H_2O$  molar concentration, line 2 –  $H_2$  molar concentration, line 3 –  $O_2$ , line 4 –  $1/T$  – inverse to temperature, line 5 –  $H_2O_2$ , line 6 –  $H$ , line 7 –  $HO_2$  (graphics 5-7 multiplied by  $10^2$ ), on figure 1 B line 6-  $HO_2$ , line 7-  $OH$  (graphics 5-7 multiplied by  $10^2$ ).

Graphics of molar concentration of mix components from time (coefficients for (2)-(4) where taken from [6]) are drawn on Figure 1, a for for initial temperature rising  $2.4 T_{atm}$  and on Figure 1, b for initial temperature rising  $2.7 T_{atm}$ . For the sake of evidence meanings of concentration of radicals  $O$ ,  $H$ ,  $OH$ ,  $HO_2$ ,  $H_2O_2$  are multiplied by  $10^2$ . Small grows of initial temperature leads to essentially changing of reaction velocity. It appears, that transition to the second stage of process (fast reaction) connected not only with grows of  $H$ , but mainly with grows of  $H_2O_2$  concentration.

Characteristic feature of hydrogen-air gas mix deflagration is appearance of sudden explosion after period of induction (Figure 1,a,b). In this induction period concentrations of radicals  $H$ ,  $O$  and  $OH$  slowly grows. Mass of radicals, nevertheless stay small, and one radical component transverse to the others. This explosion mechanism is branching chain reaction introduced by Semenov [5]. For construction model of branching chain reaction in [7] the set of reaction (with consequent coefficients of reactions  $k_0 - k_{11}$ ) from Table 1 where used. In agreement with branching chain reaction theory during process of branching chain reaction radicals  $H$ ,  $O$ ,  $OH$ ,  $HO_2$ ,  $H_2O_2$  many times initiate

reactions with other components of the mix. Nevertheless mass of radical components preserve small during the reaction, them almost fully disappeared in every time of the process. That's why method of "quasi - stationary concentration" is treated to components  $O$ ,  $OH$ ,  $HO_2$  (velocity of changing of this components concentration is equal to zero). For concentration of component  $H$  in [5] one simplified differential equation is treated with using speeds of reaction  $W_0 - W_5$ . Speed of changing  $H$  essentially grater then speed of changing "slow" components  $H_2$ ,  $O_2$ ,  $H_2O$ , that's why equation for  $H$  should be solved separately with the other time scale. In addition to the theory of Semenov [5] in this paper changing of  $H_2O_2$  also calculated as decision of differential equation, because of changing of this very component determines full process (see Figure 1, a,b). In agreement with [5,9] speeds of changing molar concentrations of  $H$ ,  $O$ ,  $OH$  can be written in such a way:

$$d[H]/dt = W_1 - W_2 + W_3 - W_6 - W_5 - 2W_7 - W_{11}; \quad (7)$$

$$0 = d[O]/dt = W_2 - W_3;$$

$$0 = d[OH]/dt = 2V_0 + 2W_2 - W_1 + W_6 + 2W_9 - 2W_{10} + W_{11}$$

$$0 = d[HO_2]/dt = W_5 - 2W_8,$$

from what  $W_2 = W_3$ . For  $[H]$  we get:

$$d[H]/dt = 2V_0 + 2W_2 - W_6 - W_5 - 2W_7 - W_{11},$$

from what

$$d[H]/dt = 2V_0 + 2k_2[H][O_2] - k_5[H][O_2][M]$$

$$- k_6[H][H_2O] - k_{11}[H][H_2O_2] - k_7[H]^2. \quad (8)$$

It can be written in the form with first and second order of  $[H]$ :

$$d[H]/dt = 2k_0[H_2][O_2] + \Phi[H] - k_7[H]^2, \quad (9)$$

where  $\Phi = 2k_2[O_2] - k_5[O_2] - k_6[H_2O] - k_{11}[H_2O_2]$ . For  $\Phi > 0$   $[H]$  – decision of (9) grows very fast, what is in agreement with branching chain reaction theory. For  $[H_2O_2]$  we get the next differential equation:

$$d[H_2O_2]/dt = k_8[HO_2]^2 - k_9[H_2O_2][M] + k_{10}[OH]^2[M] - k_9[H_2O_2][H] \quad (10)$$

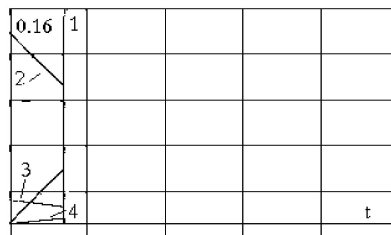


Figure 2. Graphics of mass concentration (initiation of detonation on the basis of simulation of branching chain reaction as result of temperature increasing to 2.5 times), line 1 –  $H_2O$  mass concentration, line 2 –  $H_2$  mass concentration, line 3 –  $O_2$ , line 4 –  $H_2O_2$  multiplied by  $10^2$ .

Molar concentration of "quasi - stationary" components  $[O]$ ,  $[HO_2]$  and  $[OH]$  can be found from algebraic equations:

$$\begin{aligned} [O] &= [H](k_2[O_2])/(k_3[H_2]); \\ [OH] &= (2[O_2][H_2]k_0 + k_6[H_2O][H] + 2k_9[H_2O_2][M] + k_{11}[H_2O_2][H]) / (k_1[H_2] + 2k_{10}[M]); \\ [HO_2]^2 &= k_5[H][O_2][M] / (2k_8). \end{aligned} \quad (11)$$

The others components of the mix are found from consequent equations of system (2)-(4) with constants of reaction from [6] (that is not unique possible constant values, for example other one can be found in [7]). Transition to algorithm of branching chain reaction should be used if condition  $\Phi > 0$  is true. Criteria of finishing using this algorithm is not explicit. In present work calculations with using branching chain reaction algorithm were finished when concentration of oxygen became sufficient small. All formula valid with assumption that influence of walls is treated neglecting small for atmospheric pressure (near high border of "semi-island of deflagration" [5]). Results of calculation on the basis of formula (9)-(11) are shown on the Figure 2 where are drawn graphics of mass concentration of mix components from time (coefficients where taken from [6]) for initial temperature rising  $2.5 T_{atm}$  which were calculated with using algorithm of branching chain reaction

### 3 Numerical simulation of reactive gas mixes flows in channels with obstacles

The system of the equations of ideal gas and the kinetic equations in the integral form for two dimensional flows with source term which are velocities of changing gas mix components can be presented as follows:

$$\frac{d}{dt} \int_V \vec{Q} dV + \oint_S \vec{n} F dS + \Phi = 0 \quad (12)$$

$\vec{Q} = (\rho, \vec{m}, \rho e, \rho c_i), i = 1, \dots, n$  - vector of conservative unknowns,  $c_i = \rho_i / \rho$  mass concentration of mix component,  $\Phi = (0, 0, 0, 0, 0, \rho f_i)$  - source term,

$$F = (\vec{m}, \vec{m} \vec{m} / \rho + P I, \vec{m}(e+p) / \rho, \vec{c}_i \vec{m}) \text{ vector of flows, } P = \rho R_b T \sum_i \frac{c_i}{\mu_i},$$

$$e = R_b T \sum_i \frac{c_i}{\mu_i} (\gamma - 1) + V^2 / 2 + \sum_i c_i h_i$$

- pressure and full energy of volume unit  $i$   $c_i h_i$  - internal energy of chemical reactions.

Common feature of non-linear TVD and ENO difference methods is calculation of flows on the border of finite volume on the basis of approximate-state Riemann solvers. In this paper those approximate-state Riemann solvers were defined (initially find in [8]) for arbitrary number of gas mix components on the basis of Roe-Pike method. TVD difference scheme of Chacrarvarthy - Osher [9] of third order of accuracy was used. Modification of numerical method [8] consist of using pure upwind variant of this scheme. This variant of scheme made it possible to avoid oscillations of values of radicals concentration during time period of deflagration appearance. The aim of calculation was simulation of deflagration initiation in flows of reacting gas mixes on the basis of two kinetic models. Numerical simulation of two dimensional flows of hydrogen-air mixes with deflagration were provided for some configurations of axisymmetrical channels with obstacles. For numerical simulation of flows in axi-symmetrical channels, especially channels with obstacles, construction of calculation curvilinear grids sometimes is not a simple problem. Difficulties in this case appears, when using of calculation grid, constructed absolutely write theoretically, produce oscillations and wrong results in gas dynamics calculation. This situation demands using compromise and iterations between constructing of grid and numerical simulation of physical process. In this paper curvilinear structured grids where constructed by algorithm of author [10] developed on the basis of decision of system of PDE equation of parabolic type

### 3.1 Flow in non-reflecting nozzle.

Axisymmetrical channel with non-reflecting nozzle initially filled with hydrogen-air mix with little amount of water (it involved as collision partner in reaction 5 and 7 of Table 1) with atmosphere meanings of gas dynamics values. At the initial moment shock wave of intensity  $M_{sh.w.}=1.9$  began to move from the left side of the region. During the spreading of shock wave on the top bound of the region (conical surface) deflagration of gas mix appears. On Figure 3 a-c level lines of temperature and meanings of water concentration (in write column) in consequent time moments are drawn. Change of this concentration inside the flow demonstrate deflagration appearance. On Figure 3 d,e graphics of temperature (d) and concentration of water (e) along top boundary of the channel in consequent time moments are drawn. On Figure 3 ,f calculation grid is situated.

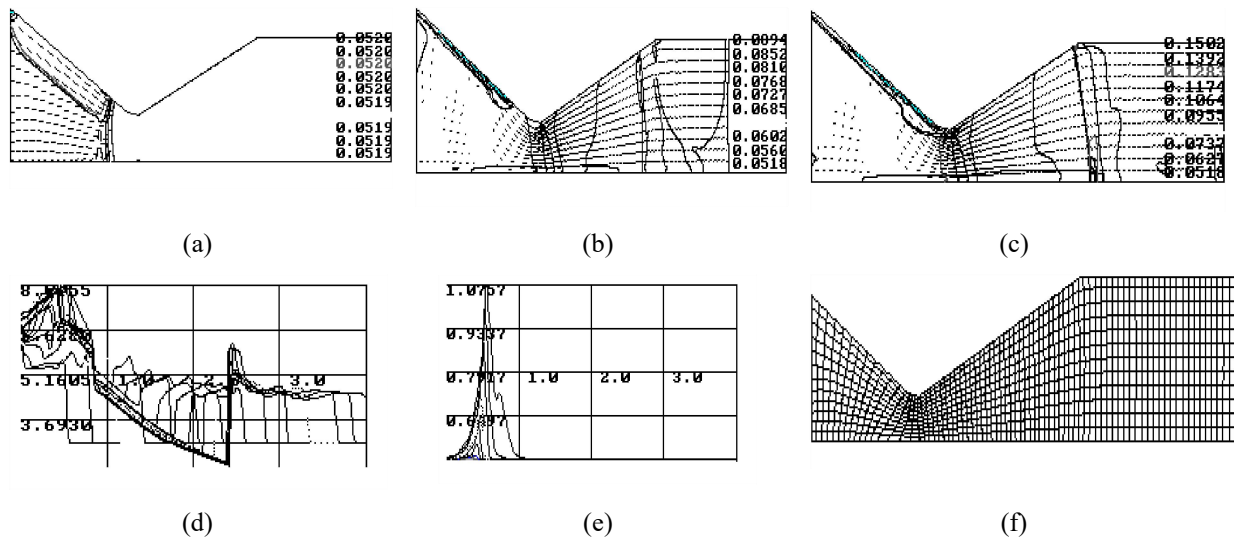


Figure 3. (a) - (c) – vectors of velocity , level lines of temperature and in write column corresponding to level lines meanings of molar concentration of  $H_2$  in consecutive time moments; (d), (e) – graphics of temperature (d) and concentration of water (e) along top boundary of the channel in consequent time moments, (f)-calculation grid.

### 3.2 Flow in cylinder with obstacles.

Calculation region consist of cylinder with three obstacles . Formulation of the problem is similar to the previous one. Shock wave of initial intensity  $M_{sh.w.}=2.2$  spreading from the left boundary of the region. Initiation of deflagration appears at the boundary of obstacles and, later near axe of symmetry. On Figure 4 a - e level lines of temperature and water concentration (at the same picture) in consequent time moments are drawn.On Figure 4 g,h graphics of temperature (h) and concentration of water (g) along axe of symmetry of the channel in consequent time moments are drawn. On Figure 4 ,f calculation grid is situated.

## 4 Summary

Algorithm of numerical simulation of transition from slow deflagration to detonation are developed on the basis of branching chain reaction theory. Graphics of mass concentration of mix components from time (coefficients from [7]) for initial temperature rising  $3.2 T_{atm}$  which where calculated with using algorithm of. branching chain reaction are drawn on Figure 2, B.

Modification of algorithm [6] of calculation of initiation of deflagration in flows of hydrogen-air mixes , consist of using pure upwind variant of Chakravarthy-Osher difference scheme was provided. This variant of scheme made it possible to avoid oscillations of values of radicals concentration

during time period of deflagration appearance. Calculations of some flows with initiation of deflagration in hydrogen-air mixes in channels with obstacles by this algorithm modification were provided. For decision of system of kinetic equation two algorithms were used: decision of fool system of kinetic equation for multistage hydrogen-air reaction, and algorithm based on Semenov's theory of branching chain reaction. For calculation performing structured curvilinear calculation grids where constructed by author's algorithm, based on decision of system of PDE equation of parabolic type.

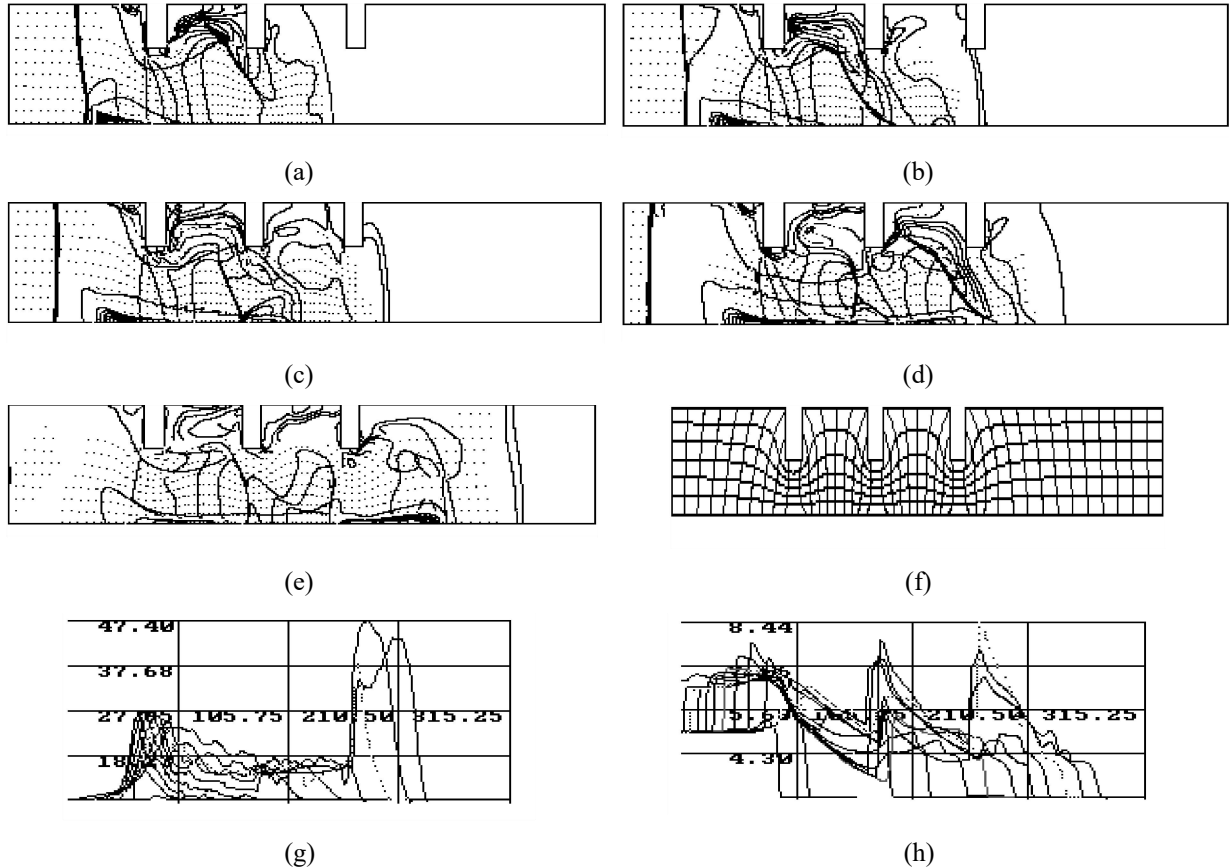


Figure 4. (a) - (e) – vectors of velocity , level lines of temperature and water concentration (on the same picture); (f) - calculation grid, (g), (h) – graphics of concentration of water (g) and temperature (h) along axe of symmetry of the channel in consequent time moments.

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