Numerical simulation of deflagration in hydrogen-air gas mixes

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Abstract. Verification of validity of different manifolds of chemical reactions and coefficients in Arrhenius formulae was made for numerical simulation of deflagration appearing in hydrogen-air gas mixes. Kinetic model of branching chain reaction was tested for initial stage of detonation of this kind of mixes. One dimensional numerical simulations of deflagration initiation where provided for small closed heat isolated region. 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. Numerical experiment consist of calculation of thermodynamics parameters of gas mix in small isolated volume. Meanings of molar concentration of components of gas mix where calculated by implicit numerical method of Gir for numerical decision. Calculation where provided till zero concentration of hydrogen or not appearing of deflagration at all. Characteristic feature of hydrogen-air gas mix deflagration is appearance of sudden explosion after long period of induction. In this induction period grows of radicals $H$, $O$ and $OH$ appears. Mass of radicals, nevertheless stay small, and one radical component transverse to the others. This explosion mechanism is branching chain reaction introduced by N.N.Semenov. In agreement with branching chain reaction theory during process of branching chain reaction radicals $H$, $O$, $OH$ many times initiates reaction 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 $O$, $OH$ (velocity of changing of this components concentration is equal to zero). For concentration of component $H$ one simplified differential equation is treated. 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. Algorithm was developed for numerical simulation of hydrogen-air mixes on the basis of theory branching chain reactions. Calculations provided demonstrate applicability of developed algorithm for numerical simulations of initial stage of deflagration of hydrogen-air mixes.

1. Introduction

Many authors produce investigations (physical and numerical) of flows with deflagration and detonation of air-hydrogen gas mixes. Employment of hydrogen as motor fuel instead of decreasing amounts of oil and gas is treated by many authors as main way of future energetic (so called hydrogen energetic). Main preference of hydrogen as a fuel is detonation fuel cycle which is more...
energetic preferable in comparing with ordinary fuel cycle. In connection with this preference (beyond the problems of producing, collecting and transporting hydrogen) problem of constructing hydrogen detonation engine is extreme actual. Perspective results are projects of pulsing detonation engine [1] and spin detonation engine [2,3]. Nowadays investigations in this field are provided mainly by mathematical modelling methods. Essential part of investigations is developing and improving of mathematical methods for numerical simulation of deflagration initiation and transition from deflagration to stable detonation in hydrogen-air gas mixes flows. From the kinetic point of view process of transition to detonation can be treated as transition from slowly deflagration to branching chain reaction in hydrogen-air mix. 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 of view 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].

2. Materials and methods

Equations of chemical reactions can be presented as follows:

$$\sum_{i=1}^{n} \alpha_{ij} A_i = \sum_{j=1}^{n} \beta_{ij} B_j, j = 1,..., M$$

(1)

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

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

(2)

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

(3)

$$k_{f,b} = A_{f,b} T^{\frac{m}{n}} \exp\left(-\frac{E_{f,b}}{RT}\right))$$

(4)

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

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

(5)

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

For numerical solving of system (2)-(5) for hydrogen-air mix different numbers of reactions and mix components are 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 essentially depends of what system of reactions and meanings of coefficients $k_{f,b}$ where used. One of the aims of present work is testing of 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 \( 3T_{atm} \)). Numerical experiment consist of calculation of thermodynamics parameters of gas mix in small isolated volume. Meanings of molar concentration of components of gas mix where calculated by implicit numerical method of Gir for system (2)-(4) numerical decision. Calculation where provided till zero concentration of hydrogen or not appearing of deflagration at all. Thermodynamic parameters where found from meanings of Gibbs potential:

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

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

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, \( NO_2 \) were neglected. During the initial period of process, period of induction, concentration of radicals \( H, O, OH \) (and \( NO, NO_2 \)) consequently grows and diminishing from \( H, O \) to \( HO_2 \) and \( H_2O_2 \) (look to Fig.2, A). Essential decreasing of concentration \( H_2, O_2 \) take place on the second stage of process. Time interval for both stage of process essentially diminishing with grows of initial temperature rising. 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 slowly character, which could be connected with slow deflagration of hydrogen (Fig.1A). Numerical decision of system (2)-(4) with 9, 16 and 26 reactions and coefficients, taken from [6], shows that grows of number of reaction don’t change essentially graphics of changing components concentrations from time. So, for investigations the next 9 most widespread reaction where choose:

**Table 1. Chemical reactions.**

| Reaction | Description | Notes |
|----------|-------------|-------|
| \( H_2 + O_2 = 2OH \) | \( H_2 + OH = H + H_2O \) | \( 2HO_2 = H_2O_2 + O_2 \) |
| \( H + O_2 = O + OH \) | \( H_2 + O = H + OH \) | \( HO_2 + M = H + O + O_2 + M \) |
| \( H_2 + M = 2H + M \) | \( H_2O_2 + M = 2OH + M \) | \( OH + H_2O = H + H_2O_2 \) |

**3. Results and discussions**

Two sets of coefficients meanings where used for system of equations (2)-(4), for reactions from Table 1: the first from [6] (for slow deflagration simulation), the second from [7] (for calculation on the basis of branching chain reaction theory). Graphics of mass concentration of mix components from time (coefficients from [6]) are drown on figure 1, A for for initial temperature rising \( 2.4T_{atm} \) and on figure 1, B for for initial temperature rising \( 2.6T_{atm} \). Small grows of temperature gradient change essentially speed of reaction.

**Figure. 1** Graphics of mass concentration of mix components from time (constants from [6] where used for slow deflagration simulation), line 1 – \( 1/T \) – inverse to temperature, line 2 - \( H_2 \), line 3 – \( H_2O \),
evertheless mass component concentration is equal to zero). For concentration of 

d\[H]/dt = 2 V 

From what 
0 = d\[OH]/dt = W 

W 

d\[H]/dt = W 

changing molar concentrations of 

|

\[O\] 

\[H\] + wall = 0.5H + O 

H +O = H+OH branching of the chain, \( W_2 = k_3 [H] [O] \)

4) H + wall = 0.5H \_2 destruction of the chain on the wall, \( W_4 = k_{4} [H] \)

5) \( O\) +H+M= HO_2+M destruction of the chain inside the volume, \( W_5 = k_{5} [H] [O_2] \), 

where \( k_i \) calculated by (4). Coefficients of inverse reactions where calculated by (5).

In agreement with branching chain reaction theory during process of branching chain reaction radicals \( H, O, OH \) may not initiate reaction 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 \( O, OH \) (velocity of changing of this components concentration is equal to zero). For concentration of component \( H \) 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 in other time scale.In agreement with [5,7] speeds of changing molar concentrations of \( H, O, OH \) can be written in such a way:

\[
\begin{align*}
\frac{d[H]}{dt} &= W_1 - W_2 + W_3 - W_4 - W_5; \\
\frac{d[O]}{dt} &= W_2 - W_3; \\
\frac{d[OH]}{dt} &= 2V_0 + 2W_2 - W_1.
\end{align*}
\]

From what \( W_2 = W_1 \) and \( W_3 = 2V_0 + 2W_2 \) 

For \( [H] \) we will get:

\[
\frac{d[H]}{dt} = 2V_0 + 2W_2 - W_3, \quad \text{from what } \frac{d[H]}{dt} = 2V_0 + 2k_2 [H] [O_2] - k_4 [H] - k_5 [H] [O_2].
\]
With addition terms of second order of \([H]\):

\[
\frac{d[H]}{dt} = 2k_2[H_2][O_2] + \Phi[H] \cdot K[H]^2
\] (7)

where \(\Phi = 2k_2[O_2] - k_4 \cdot k_3[O_2]\), \(K = (k_2^2k_2/k_3k_4)[[O_2]/[H_2]]^2\). For \(\Phi \gg 0\) \([H]\) – decision of (5) grows very fast, what is in agreement with branching chain reaction theory. Molar concentration of “quasi-stationary” components \([O]\) and \([OH]\) can be found from algebraic equations:

\[
\begin{align*}
[O] &= [H] (k_2[O_2]/[H_2]);
[OH] &= 2[O_2] (k_0 + k_2[H]/[H_2]) / K1.
\end{align*}
\] (8)

The others components of the mix are found from consequent equations of system (2)-(4) with constants of reaction from [7]. Transition to algorithm of branching chain reaction should be used if condition \(\Phi \gg 0\) is true. Criteria of finishing using this algorithm is not explicit. In present work calculations with using branching chain reaction algorithm where finished when concentration of oxygen became sufficient small. In present work also assumption was made that \(W_e = 0\). This assumption means in other words that influence of walls is treated neglecting small for atmospheric pressure (near high border of “semi-island of deflagration”).

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 \(T_{\text{init}}\) which where calculated with using algorithm of branching chain reaction are drown on Figure 2, B. Calculation where provided till zero concentration of hydrogen or not appearing of deflagration at all. Characteristic feature of hydrogen-air gas mix deflagration is appearance of sudden explosion after long period of induction. In this induction period grows of radicals \(H, O\) and \(OH\) appears. Mass of radicals, nevertheless stay small, and one radical component transverse to the others. This explosion mechanism is branching chain reaction introduced by N.N.Semenov. In agreement with branching chain reaction theory during process of branching chain reaction radicals \(H, O, OH\) many times initiates reaction 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 \(O, OH\) (velocity of changing of this components concentration is equal to zero). For concentration of component \(H\) one simplified differential equation is treated. 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. Algorithm was developed for numerical simulation of hydrogen-air mixes on the basis of theory branching chain reactions. Calculations provided demonstrate applicability of developed algorithm for numerical simulations of initial stage of deflagration of hydrogen-air mixes.

5. References
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