Multi-front detonation structure in two-fuel mixtures—numerical modelling

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Abstract. A numerical simulation of a two-dimensional (2D) structure of the detonation wave (DW) in a two-fuel gaseous mixtures with air mixture at normal initial condition has been conducted. This study is based on a two-stage generalised model of detonation kinetics for a mixtures of two fuels first proposed by us. The computations have been performed in a wide range of channel height. The changes in the 2D front structure of the self-sustaining DW on variations of the height of the channel have been studied. From the analysis of the flow structure and the number of primary transverse waves in channel, the dominant sizes of the detonation cell for studied mixture have been determine. Numerical data on the detonation cell sizes have been carefully analyzed and compared with available experimental data.

1. Introduction
One of the most important problems in the theory of dynamic systems is the formation and destruction of ordered gasdynamic structures in a reactive medium. An example of such a self-organizing system is a multifront (cellular) DW steadily propagating in a reacting gas mixture. The complex three-dimensional and time-dependent structure of the front of these waves propagating in constant cross-section channels shows some order, whose geometrical parameter is the transverse size of the elementary cell of the DW ≈ a₀. Based on this value, it is possible to determine such parameters of detonation as critical conditions of detonation combustion, the critical energy of initiation detonation propagation limits, etc., i.e. to estimate the detonation hazard of gaseous mixture.

Depending on the chemical composition of the gas, DW in some mixtures have very regular cellular structure, whereas in other mixtures DW shows very irregular chaotic cell structure.

Extensive experience in 2D numerical simulation of the DW multifront cellular structure shows that the cell size in a flat model two-dimensional channel correlates well with the experimentally obtained cell size in a real three-dimensional DW. To date, numerical studies of the DW structure have been limited to gas mixtures of one fuel with oxygen, sometimes with inert diluents (nitrogen for modeling air mixtures, argon). Apparently, this can be explained by the lack of appropriate models of chemical kinetics that do not require expensive computations. However, multifuel gas mixtures are widely used in the chemical industry and in the power industry (for example, syngas, a binary mixture of hydrogen H₂ and carbon monoxide CO). Mixtures of heavy hydrocarbons with CO are widespread in nature, for example, as an accompanying gas in oil production. To solve the problems of explosion safety of such binary gas systems, it is necessary to have the ability to numerically model the parameters and the two-dimensional cellular structure of detonation in these mixtures.
For this purpose, we have developed generalized two-stage models of detonation kinetics for the two-fuel mixtures of syngas and hexane C₆H₁₄–CO with air. This made it possible in this work to perform 2D numerical modeling of the multi-front structure of the DW in two-fuel mixtures and to determine the detonation cells sizes.

2. Governing equations and model of chemical kinetics

The dynamics of the compressible chemically reactive medium is described by the two-dimensional Euler equations.

The chemical reaction in the DW is described by the two-stage model of the detonation kinetics (stage of induction period and main heat release stage).

The proposed model for syngas is an extension of the previously developed model of chemical kinetics of detonation combustion of hydrogen–oxygen mixtures \([1,2]\). It is assumed that there are no chemical transformations during the induction period; correspondingly, the molar weight of the gas remains unchanged, and the thermal effect of the chemical reaction is equal to zero. The main heat release takes place after the induction period. The value of heat release and all thermodynamic parameters of the reacting gas are described by one differential equation of the generalized kinetic model and by a set of algebraic equations, see all details in \([1,2]\).

The two-stage detonation kinetics for a C₆H₁₄–CO mixture is based on the generalized model of the detonation kinetics of methane-based gas mixtures proposed by us in \([3–5]\). Thermal decomposition of hydrocarbon molecules and their chemical transformation are assumed during the induction period. This process is described by one \textit{brutto}–reaction. As a result of the above-mentioned chemical processes, the average molar mass of the mixture changes insignificantly, there is an insignificant heat release. CO molecules are assumed to be chemically inert. After the induction period has expired, the stage of the main heat release begins. The description of this stage is carried out in the same way as for a mixture of synthesis gas, with a corresponding change in the constants included in the equations of the heat release kinetics.

The main problem for creating a two-stage kinetics of multi-fuel mixtures is to determine the duration of the induction period \(\tau_{\text{ind}}\) in this type of mixtures. It is assumed that the induction time in an individual fuel-oxidizer mixture \(\tau_{\text{indF}}\) is known from experiment or from detailed kinetic calculations. Traditionally, the dependence of the induction time on temperature and the initial concentration of the mixture components is represented as an Arrhenius-type dependence:

\[
\tau_{\text{indF}} = A_F \exp\left(\frac{E_F}{RT}\right)[O_2]^{-1}
\] (1)

In present calculations, we used the following constants for individual mixtures: for hydrogen \(A_H = 5.38 \times 10^{14}\) mole s/cm³, \(E_H/R = 8631\) K \([6]\); for carbon monoxide \(A_{CO} = 1.38 \times 10^{14}\) mole s/cm³, \(E_{CO}/R = 15098\) K; for hexane \(A_{C_6H_{14}} = 1.86 \times 10^{17}\) mole s/cm³, \(E_{C_6H_{14}}/R = 1065\) K.

Several approaches are known to describe the induction period in a mixture of several fuels. In this paper, we will follow the semi-empirical algorithm proposed in \([7]\). There are also in \([7]\) several variants of algebraic formulas for determining the constants in an equation of type (1) for a binary fuel mixture. Following \([7]\), we assume that the induction period in a two-fuel mixture diluted by CO is described by an equation of the same form as for a mono-fuel mixture (1):

\[
\tau_{\text{indE}} = A_E \exp\left(\frac{E_E}{RT}\right)[O_2]^{-1}, \quad \text{where} \quad A_E = f_1(A_F, A_{CO}), \quad E_E = f_2(E_F, E_{CO}).
\] (2)

To calculate the constants \(A_E\) and \(E_E\), we proposed the following formulas \([8,9]\):

\[
A_E = A_{CO}(1 - \alpha) \exp(-k\alpha) + A_F(1 - (1 - \alpha) \exp(-k\alpha)),
\] (3)

\[
E_E = E_{CO}(1 - \alpha) \exp(-k\alpha) + E_F(1 - (1 - \alpha) \exp(-k\alpha)).
\] (4)

Here \(\alpha\) is the fraction of the main fuel \(F\) in the composition of the binary fuel with carbon monoxide. To select the functional form of the formulas (3) and (4) for \(A_E, E_E\) and determine the constants of these formulas, we used the experimental dependences of the detonation cell size on the concentration of the main fuel in the binary mixture \([10]\) and the Vasil’ev–Nikolaev analytical model of the detonation cell \([11]\). The equations of this model explicitly include the duration of the induction period \(\tau_{\text{indE}}\).
We found that formulas (2)–(4) at $k=13$ describe well the experimental curves [10] for a stoichiometric mixture of syngas with air (1- $\cdot$ ) O$+\cdot$ H$+\cdot$0.5Air. For a stoichiometric mixture with air (1- ) 2 O$+(\cdot$9.5$)C_6H_{14}+\cdot$Air of the hexane–CO binary fuel, the best agreement with experimental data is obtained at $k=23$.

This completes the construction of a generalized model of detonation kinetics for two-fuel mixtures. In further two-dimensional numerical simulations of the DW front structure, we checked the validity of this semi-empirical approach for determining the induction period in the above two-fuel mixtures.

3. Numerical method

The resultant system of equations is solved numerically, using the code based on the Godoyev-type finite-volume scheme with the fourth-order MUSCL-TVD reconstruction and the advanced HLLC algorithm for an approximate solution of the Riemann problem. In implementation of HLLC algorithm for the case of a chemically reacting mixture, the “energy relaxation method” is used. This method eliminates the problem of numerical solution of the Riemann problem for a medium with a complicated nonlinear equation of state (including that with a variable ratio of specific heats). Integration in time is performed with second-order accuracy by using additive semi-implicit Runge-Kutta methods. All details about these numerical algorithms can be found in [2–4,8,9].

In numerical simulations of propagating 2D detonation wave in straight channel we use an adaptive moving grids technique in the $x$ direction with local refinement in the vicinity of a leading shock front, propagating along $x$-axis. In the $y$ direction a uniform numerical grid has been used.

The code is parallelized with MPI library using the domain decomposition technique. The total number of numerical cells in the $x$ and $y$ directions were $N_x=2000$, $N_y=2000$ respectively. Numbers of CPU cores along $x$ and $y$ axes are $N_{prx}=16$ and $N_{pry}=16$.

4. Results and discussion

Numerical simulation has been performed for stoichiometric two-fuel mixtures of syngas and $C_6H_{14}$–CO with air at normal initial conditions $p_0=1$ atm and $T_0=298.15$ K.

The detonation cell size for the two-fuel mixtures has been determined in a procedure similar to that used in the numerical study of hydrogen mixtures [2]. The initial height of the channel $H$ has been chosen rather arbitrarily; usually, it was assumed to be slightly higher than the presumed transverse size of the cell $a_0$. Further variation of $H$ in the calculations affected the number of primary (main) transverse waves (TWs) remaining at the DW front after its initiation and the establishment of a self-sustained Chapman–Jouguet detonation regime. The value of $H$ has been found at which only two equal and antisymmetrically moving TWs remained on the front of the DW [2], thus, the cell size was determined as $a_0=H$.

Our experience in two-dimensional modeling of the structure of the DW front shows that for mixtures with an irregular cellular structure recorded in the experiment, in the numerical simulation of the DW, changes in the value of $H$ in a small range do not affect the structure of the DW with two main SW waves. And only a significant change in $H$ leads to the emergence of a new TW or the disappearance of the existing TW [3–5].

Therefore, for mixtures with an irregularly cellular structure, one can speak only of a certain range of characteristic values of the detonation cell size.

4.1. Multi-front structure of DW in syngas mixture

A two-dimensional multifront (cellular) DW structure has been numerically investigated in a stoichiometric mixture of syngas with air (1- $\cdot$ ) O$+\cdot$ H$+\cdot$0.5·Air for $=0.3$ (8.875% $H_2$ in mixture) and $=0.1$ (2.96% $H_2$ in mixture ). Analysis of 2D flow fields for $=0.3$ shows that at the front of the DW in this mixture at $H=a_0$ there are several secondary TWs and a significant numbers of tertiary and even smaller TWs. At some time moments, unburned gas packets are observed behind the DW front.
Figure 1. Detonation wave structure, numerical Schlieren flow field: (a) stoichiometric hydrogen–oxygen mixture; (b) stoichiometric hydrogen–air mixture.

So, the DW multifront structure is rather irregular, and the dominant size of the detonation cell is defined as \( a_0=0.35 \) cm.

Further, a series of calculations with the variation of \( H \) has been carried out for \( =0.1 \). It has been found that with a decrease of the hydrogen concentration in the mixture, the degree of irregularity of the multi-front structure of the DW front increases, the number of secondary TWs on the wave front increases, and the formation of unburned gas packets behind the wave front begins to occur more frequently. Such an increase in the irregularity of the DW structure corresponds to the experimental observations in [10]. For \( =0.1 \) detonation cell size is \( a_0=1.2 \) cm.

Comparison with experimental data [10] has shown that the relative increase in the cell size is in good agreement with the experimental data. Here \( a_{0(0)} \) is the transverse size of the detonation cell in a pure stoichiometric hydrogen–air mixture. So for \( =0.3 \) we have \( a_0/a_{0(0)}=1.17 \), while the experimental value \( a_0/a_{0(0)}=1.24\pm0.1 \). For \( =0.1 \) there are \( a_0/a_{0(0)}=4.0 \) and experimental value \( a_0/a_{0(0)}=3.1\pm1.1 \).

However, the calculated absolute values of the cell sizes in the syngas–air mixture and the experimental data (for \( =0.3 \) \( a_0=1.1\pm2.0 \) cm and for \( =0.1 \) \( a_0=2.0\pm4.2 \) cm) [10] are very different.

Our 2D studies have shown that the reason for this is that for a pure hydrogen stoichiometric mixture, the calculated cell values are much less than the experimental values: for \( H_2+0.5 \cdot \text{Air} \), \( a_0=0.3 \) cm and experimental value \( a_0=1.0\pm1.5 \) cm; for \( H_2+0.5\cdot\text{O}_2 \), \( a_0=0.08 \) cm and experimental value \( a_0=0.14\pm0.16 \) cm.

A thorough study of this problem was carried out and numerous two-dimensional computational experiments were carried out, including those with an increased spatial resolution up to \( N_x=4000, N_y=4000 \). It was found that the dependence of the duration of the induction period \( \tau_{\text{indep}} \) for hydrogen mixtures (F=H\(_2\)) on the initial pressure (the initial concentration of the reacting components of the mixture) has a more complex character than that described by global kinetic models of the form (1) with constants from [6]. Based on the general theoretical concepts of the mechanism of chemical reactions in the gas phase, it is proposed to carry out this correction of the global kinetics (1) on the initial pressure of the reacting mixture \( p_0 \) as follows, namely, introducing a correction factor for the value of \( A_{12} \) (1). That is, replace the parameter \( A_{12} \) with \( f(p_0)A_{12} \). Here \( f(p_0) \) is a piecewise linear function. Based on our numerous numerical experiments, \( f(p_0)=1 \) at \( p_0\leq0.4 \) atm, at \( p_0=1.0 \) atm \( f(p_0)=2 \). At \( 0.4 \) atm\( <p_0<1 \) atm, the function \( f(p_0) \) can be represented by a linearly increasing dependence, but a more accurate determination of its functional form requires additional computational experiments.

Figure 1a shows the structure of a detonation wave in a channel with a height of \( H=a_0=0.16 \) cm; the calculation was carried out using the kinetics (1) corrected by the above method for \( H_2+0.5\cdot\text{O}_2 \) mixture. The field of numerical Schlieren visualization is shown. The figure 1a shows two almost
Figure 2. Detonation wave structure in a stoichiometric syngas-air mixture (\(\phi=0.3\)) in the channel with \(H=1.5\) cm, flow fields of: (a) numerical Schlieren-visualization; (b) normalized density.

Figure 3. Detonation wave structure in a stoichiometric syngas-air mixture (\(\phi=0.1\)) in the channel with \(H=2.5\) cm, flow fields of: (a) numerical Schlieren-visualization; (b) normalized density.

perfectly symmetric TW, designated as AA and BB, which form the detonation cell. This value of \(a_0\) fully corresponds to the above experimental data \(a_0=0.14\div0.16\) cm for \(p_0=1.0\) atm.

Determination of the cell size for a hydrogen-air \(H_2+0.5\cdot Air\) mixture showed that an additional correction of the \(A_{H2}\) value for the nitrogen content \(N_2\) in the mixture is required. This was done according to [12], instead of \(A_{H2}\) in formula (1) we use the expression \([2H_2+O_2+zN_2]/[2H_2+O_2]f(p_0)A_{H2}\). Here \([\]\) is the sum of moles of the mixture components.

Figure 1b shows the multi-front structure of the DW for a stoichiometric hydrogen-air mixture at \(p_0=1.0\) atm in the 2D channel, the height of which \(H\) was chosen so that after the DW reaches a steady-state propagation regime, two symmetric main transverse waves AA and BB remain at the DW front. That is, the height of the channel is in this case the transverse size of the detonation cell, \(H=a_0=1.4\) cm. This result \(a_0=1.4\) cm is in excellent agreement with the above experimental data.

After the correction of the kinetics of the induction period of the form (1) for hydrogen mixtures, we carried out refining 2D studies of the multi-front structure of DW in a stoichiometric syngas–air mixture. Figure 2 shows the structure of the DW front at \(\phi=0.3\) (8.875% \(H_2\) in mixture) and figure 3 at \(\phi=0.1\) (2.96% \(H_2\) in mixture). The height of channel \(H\) is selected so that \(H=a_0\) in the figures we see
Figure 4. Detonation wave structure in a stoichiometric hexane-air mixture ($\phi = 1.0$) in the channel with $H = 3.4$ cm, flow fields of: (a) numerical Schlieren-visualization; (b) temperature, K.

Figure 5. Detonation wave structure in a stoichiometric C$_6$H$_{14}$–CO–Air mixture ($\phi = 0.082$) in the channel with $H = 9$ cm, flow fields of: (a) numerical Schlieren-visualization; (b) normalized density.

two equal in intensity and almost symmetric main transverse waves AA and BB. Hereinafter aa, bb, c … the secondary TWs are designated; P1, P2 indicate the pockets of unburned gas. The results of 2D modeling $a_0 = 1.5$ cm for $\phi = 0.3$ and $a_0 = 2.5$ cm for $\phi = 0.1$ are in excellent agreement with the experimental data (for $\phi = 0.3$ $a_0 = 1.1 \div 2.0$ cm and for $\phi = 0.1$ $a_0 = 2.0 \div 4.2$ cm [10]).

4.2. Multi-front structure of DW in binary C$_6$H$_{14}$–CO mixture

To test the applicability of the proposed two-stage model of detonation kinetics for hydrocarbon fuels for describing detonation processes, as the first stage, we calculated the DW multi-front structure in a stoichiometric hexane-air mixture ($\phi = 1.0$, 2.163% C$_6$H$_{14}$ in the mixture). Figure 4 shows the structure of the DW front in this mixture. Based on the analysis of two-dimensional calculations for different values of $H$, we determined the cell size in the range $a_0 = 3.3 \div 3.4$ cm. This is in good agreement with the experimental values $a_0 = 2.8 \div 3.8$ cm [10].

Numerical simulation of a stoichiometric two-fuel mixture C$_6$H$_{14}$–CO with air was carried out immediately with a significant dilution of the mixture with carbon monoxide to $\phi = 0.082$, that is, 0.131% C$_6$H$_{14}$ in the mixture. Figure 5 shows a typical DW multi-front structure in this mixture.
Based on calculations of 2D detonation in various channels, the size of the detonation cell was determined by us as $a_0 = 9 \pm 10$ cm. The structure of the front for this mixture is extremely irregular. Along with two main TWs, which are often not entirely symmetric and equal in intensity, there are several rather intense and extended secondary TWs at the front. A significant number of pockets of unburned mixture are observed behind the DW front. At a number of points in time, tertiary TWs are also observed, which are even smaller in size. The cell size obtained in the simulation is in good agreement with the experimental data [10] $a_0 = 8.2 \pm 9.5$ cm.

5. Concluding remarks
A two-stage model of the generalized chemical kinetics of detonation combustion of two-fuel mixtures with the addition of carbon monoxide CO as a second (additional) fuel has been proposed. The main (base) fuel can be either hydrogen or any gaseous hydrocarbon. Modeling has been carried out for heavy hydrocarbon hexane and hydrogen. Oxygen with any degree of dilution with nitrogen can be selected as an oxidizing agent. Simulation has been carried out with oxygen and air as oxidant.

A numerical study of the multi-front structure of the detonation wave front has revealed that as the degree of dilution by CO the two-fuel mixture increases, the size of the detonation cell increases and the degree of irregularity of the cellular structure of the wave increases. These conclusions are in good agreement with experimental observations for the investigated mixtures. The size of the detonation cell obtained in 2D simulation is in good quantitative agreement with experimental data in a wide range of the dilution ratio of the mixture with carbon monoxide – from a pure mono-fuel mixture of the main fuel to a two-fuel mixture with several percent of the main fuel.

It has been shown that it is necessary to correct the global kinetics of the induction period $\text{indH}_2$ for hydrogen mixtures according to the initial pressure of the fresh mixture (i.e., according to the initial concentration of the reacting components), as well as the content of nitrogen $\text{N}_2$ in the mixture.

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