Reduced detonation kinetics and detonation structure in one- and multi-fuel gaseous mixtures

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Abstract. Two-step approximate models of chemical kinetics of detonation combustion of (i) one-fuel (CH₄/air) and (ii) multi-fuel gaseous mixtures (CH₄/H₂/air and CH₄/CO/air) are developed for the first time. The models for multi-fuel mixtures are proposed for the first time. Owing to the simplicity and high accuracy, the models can be used in multi-dimensional numerical calculations of detonation waves in corresponding gaseous mixtures. The models are consistent with the second law of thermodynamics and Le Chatelier’s principle. Constants of the models have a clear physical meaning. Advantages of the kinetic model for detonation combustion of methane has been demonstrated via numerical calculations of a two-dimensional structure of the detonation wave in a stoichiometric and fuel-rich methane-air mixtures and stoichiometric methane-oxygen mixture. The dominant size of the detonation cell, determines in calculations, is in good agreement with all known experimental data.

1. Introduction

Methane-air mixture is typical example of one-fuel gaseous mixture. The interest in modeling of detonation processes in gaseous mixtures containing methane has recently increased (explosion safety problems in mining industry). Numerical calculation of such processes needs the adequate models of chemical kinetics.

Typically the detailed systems of equations of chemical kinetics in hydrocarbons (including methane)-air mixtures are cumbersome. Therefore, approximate (reduced) kinetic models are frequently used for numerical calculations of multifront detonation waves (see, for example, calculation of detonation wave structure in methane-air mixture [1]). In contrast with the reality, in the frames of such models the heat release of chemical reaction does not depend on pressure and temperature and molar mass and adiabatic index of gaseous mixture assume to be constant. Therefore there is still an urgent need to develop simple but highly accurate approximate kinetic models for detonation combustion of methane, hydrogen peroxide and ozone.

One of the most suitable approximate models of chemical kinetics in one-fuel mixtures of hydrogen with oxygen, water vapor, and inert diluents is the model, presented in [2-5]. This model allows one to calculate molar mass evolution with the help of one differential equation, energy release and changes in thermodynamic parameters of the gas after the induction period with the help of several explicit algebraic formulas. The calculation of the induction period of chemical reaction is not included in the framework of this model. The model is also applicable for calculating thermodynamic parameters of the gas in the chemical equilibrium state. Explicit algebraic formulas are obtained for such calculations. The model is widely used to solve a wide range of research and application problems (for
example, modeling of cellular structure of detonation waves [6], gas-droplet detonation [7], detonation application of coatings [8], pulse detonation engine [9], and explosion processes in bubble systems [10]).

In our articles [11-13] we have presented the reduced model of chemical kinetics in methane-air mixtures: \( \text{CH}_4 + a_1 \text{O}_2 + a_2 \text{N}_2 \). This model is the further modification of the model [2-5] for detonation combustion of hydrogen-air mixtures and has similar advantages: clear physical meaning of constants, simplicity, high accuracy, consistency with the second law of thermodynamics and Le Chatelier’s principle. The model was successfully used for 2-D numerical calculations of detonation wave structure [12, 13]. Unfortunately, this model is valid only for \( a_i \geq 0.8 \). In the present work a new modification of this model will be presented. This model will be valid for \( a_i \geq 0.5 \).

There are not simple and physically grounded reduced models of chemical kinetics of detonation combustion of multi-fuel gaseous mixtures up to now. In the present work such models for \( \text{CH}_4/\text{H}_2/\text{air} \) and \( \text{CH}_4/\text{CO}/\text{air} \) will be presented for the first time.

2. Reduced model of chemical kinetics of detonation combustion of methane

We will consider the following mixture: \( \text{CH}_4 + a_1 \text{O}_2 + a_2 \text{N}_2, a_i \geq 0.5 \). We will not consider the mixture with \( a_i > 0.5 \), because fuel concentration for such mixture is well below the Lower Flammable Limit and out of detonation limit as well.

The model has two steps. The first step is induction period and the second one corresponds to main heat release. Note, that two-step model of chemical kinetic (including the induction step and the step of main heat release) for description of detonation processes in gaseous mixtures was used for the first time in [14].

As is commonly done, we calculate the value of the induction parameter \( Y \) during the induction period of the chemical reaction in the gas mixture with variable pressures and temperatures by the formula [15]:

\[
Y = \int_{t_0}^{t_i} \frac{dt}{\tau_i}
\]

where \( \tau_i \) is the induction period at constant parameters. At the beginning of the induction period, \( Y = 0 \), and at the end of it (the moment in time \( t = t_i \)), \( Y = 1 \). Semi-empirical relations have to be used to calculate \( \tau_i \). The value of \( \tau_i \) for the methane–air mixture will be calculated, for example, by the formula, recommended in [16] as the best for calculations of the cell size of the detonation wave.

We replace the real multistep process occurring during the induction period with some overall reaction chosen from the following general considerations. We take into account that by the end of the induction period, the temperature increase (and, hence, the total heat release due to chemical reactions) is low. Therefore, the overall reaction is chosen so that its thermal effect is much smaller than the maximum possible thermal effect of the complete recombination of the reaction products to form \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) molecules. Note that under this condition, the thermal effect of the overall reaction will also be much smaller than the thermal effect at the Chapman–Jouguet point.

We also take into account that the induction period involves chemical reactions leading to the formation and increase in the number of active centers and decomposition of heavy molecules. In our case, the heavy molecules are methane molecules. It is therefore assumed that during the induction period, all methane molecules decompose to form \( \text{CO} \) molecules. Single C atoms in the products of the overall reaction are neglected since the mixture contains a more than sufficient amount of oxidizer.

Thus, we assume that during the induction period, each methane molecule of the mixture is involved in the chemical reactions:

\[
\text{CH}_4 + a_1 \text{O}_2 \rightarrow \text{CO} + (2a_1 - 1)\text{OH} + (2.5 - a_1 - \alpha)\text{H}_2 + 2\alpha\text{H} \quad \text{if } 0.5 \leq a_i < 1,
\]

\[
\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + \text{OH} + 1.5\text{H}_2 \quad \text{if } 1 \leq a_i.
\]
The value \( \alpha \) should be calculated from the condition: the thermal effect of the reaction at the end of the induction period \( Q_i \) is significantly smaller than the maximum possible heat effect of the chemical reaction \( Q_{\text{max}} \) per one mole of \( \text{CH}_4 \). It is easy to show that \( Q_i/Q_{\text{max}} \ll 1 \) for \( 1 \leq a_1 \). If \( 0.8 \leq a_1 \leq 1 \) then \( Q_i/Q_{\text{max}} \leq 0.1 \) at \( \alpha = 0 \). If \( a_1 \) equals to 0.5, 0.6 and 0.7, then \( Q_i/Q_{\text{max}} \leq 0.1 \) at \( \alpha = 0.097, 0.067 \) and 0.036 respectively.

Let \( \beta \) be the fraction of un-decomposed methane. In the initial state, \( \beta = 1 \); during the induction period, \( \beta \) decreases monotonically; and at the end of the induction period, \( \beta = 0 \). According to the above, the chemical composition of the gas undergoes the following change during induction period.

For \( 1 \leq a_1 \),

\[
\text{CH}_4 + a_1\text{O}_2 + a_2\text{N}_2 \rightarrow \beta\text{CH}_4 + (1-\beta)\text{CO} + (1-\beta)\text{OH} + (1.5-1.5\beta)\text{H}_2 + \text{(a}_1\text{-1+}\beta)\text{O}_2 + a_2\text{N}_2.
\]

For \( 0.5 \leq a_1 < 1 \),

\[
\text{CH}_4 + a_1\text{O}_2 + a_2\text{N}_2 \rightarrow \beta\text{CH}_4 + (1-\beta)\text{CO} + (1-\beta)2\text{a}_1\text{-1}\text{O}_2 + [(1-\beta)(2.5-a_1-\alpha)]\text{H}_2 + + (1-\beta)2\text{a}_1\text{H} + \text{a}_1\beta\text{O}_2 + a_2\text{N}_2.
\]

We note that the value of \( \beta \) affects only the wave parameter profiles in the induction zone. The wave velocity, flow parameters at the Chapman-Jouguet point, and zone of main heat release do not depend on \( \beta \). Therefore, if the above conditions are satisfied, the particular form of the formula for calculating \( \beta \) affects the wave parameter profiles in the induction zone only quantitatively. As a rule, the chemical reaction rate increases at the end of the induction period. It is therefore reasonable to choose a formula for calculating \( \beta \) that it meets the above conditions, and the rate of decrease as the movement grew mixture in the induction zone. For example, the quantity \( \beta \) can be defined as

\[
\beta = 1 - Y.
\]

Within this kinetic model, the chemical composition of the gas during the induction period is calculated by explicit algebraic formulas. Therefore, the molar mass and the internal energy of the gas can be easily calculated by the well-known standard algorithms using the thermodynamic parameters of individual species.

After induction period (the second step of reaction) the model includes a kinetic equation for the molar mass of the gas [4]

\[
\frac{d\mu}{dt} = 4K_\mu \rho^2 \left(1 - \frac{\mu}{\mu_{\text{max}}}\right)^2 - AT^{3/4}(1-\exp(-\theta/T))^{3/2} \rho \left(\frac{\mu}{\mu_{\text{min}}} - 1\right)\exp(-E/RT)
\]

and formulas for the specific internal energy of the mixture [2-5]:

\[
U(T,\mu) = U_{\text{therm}}(T,\mu) + U_{\text{chem}}(\mu)
\]

\[
U_{\text{therm}}(T,\mu) = \left[\frac{3}{4} \left(\frac{\mu}{\mu_a} + 1\right) + \frac{3}{2} \left(\frac{\mu}{\mu_a} - 1\right) \frac{\Theta/T}{\exp(\Theta/T) - 1}\right] \frac{\Theta/T}{\mu},
\]

\[
U_{\text{chem}}(\mu) = E \left(\frac{1}{\mu} - \frac{1}{\mu_{\text{min}}}\right),
\]

where \( \rho, T \) and \( \mu \) are the density, temperature, and the mean molar mass of the gaseous mixture; \( \Theta \) is the universal gas constant; \( \mu_a, \mu_{\text{min}}, \mu_{\text{max}} \) are the molar masses of gas in the atomic, completely dissociated and completely recombined states; \( A \) and \( K_\mu \) are the rate constants of dissociation and recombination of the generalized reaction products; \( \theta \) is the effective excitation temperature of the vibrational degrees of freedom of the molecules; \( E \) is the mean dissociation energy of the reaction.
products; $U$ is the total specific internal energy of the gas, $U_{therm}$ and $U_{chem}$ are thermodynamic and chemical parts of $U$; $t$ is the time. The algorithm for calculation the model constants are presented in [12, 13].

The first and second terms in the kinetic equation correspond to recombination and dissociation reactions.

The model takes into account that the energies of dissociation of diatomic molecules (H$_2$, O$_2$, OH) into atoms are approximately equal to the energy of dissociation of H$_2$O molecule into OH and H and CO$_2$ molecule into CO and O. Thus, the recombination reaction heats are assumed to be identical and noted as $E$. It is taken into account that under detonation temperatures molecules CO and N$_2$ practically do not dissociate into atoms.

It is known that recombination reactions occur almost without the activation energy. Therefore, the activation energy of recombination reactions in the model is assumed to be zero. As a result, the first term in the kinetic equation has no exponent. The activation energy in the second term equals to $E$. The reason is that the difference between the activation energy of the dissociation reaction and that of the reverse recombination reaction equals the chemical reaction heat.

For a specified caloric equation of state, the rate constants of direct and reverse chemical reactions in the kinetic equation cannot be arbitrary but should be correlated with allowance for the second law of thermodynamics. Therefore, the form of the temperature-dependent pre-exponent of the dissociation rate constant was obtained from the condition that thermodynamic potentials of the gas have an extremum in chemical equilibrium ($d\mu/dt = 0$).

The recombination rate constants differ from each other insignificantly. In the kinetic model, therefore, they are assumed to be identical and equal to $K_r$. Formula for calculation $U_{therm}$ was derived by analyzing the mean number of degrees of freedom of molecules versus temperature. Formula for calculation $U_{chem}$ is based on the assumption that the dissociation energy of diatomic molecules and the energy of dissociation of H$_2$O molecule into OH and H and CO$_2$ into CO and O equal to $E$.

The presented model can also be used to calculate thermodynamic parameters of the gas in chemical equilibrium ($d\mu/dt = 0$ in).

3. Reduced models of chemical kinetics of detonation combustion of multi-fuel gaseous mixtures CH$_4$/H$_2$/air and CH$_4$/CO/air

In case of multi-fuel gaseous mixtures CH$_4$/H$_2$/air and CH$_4$/CO/air it is assumed that during induction period in detonation wave H$_2$ and CO are not involved in chemical transformation. Therefore, in these mixtures the same chemical process in the induction zone as in CH$_4$/Air mixture occurs.

To calculate induction period of multi-fuel gaseous mixtures under consideration, an algorithm, presented in [17], should be used. Constants of Arrhenius formulas for calculation induction period of chemical reaction in one-fuel mixtures of CH$_4$, H$_2$ or CO with O$_2$/Air assumed to be known.

After induction period the same formulas for calculation internal energy, molar mass and adiabatic index, as for CH$_4$/Air mixtures, should be used.

4. Results of calculations of detonation wave structure in CH$_4$/Air/O$_2$ mixtures

Advantages of the kinetic model for detonation combustion of methane has been demonstrated via numerical calculations of a two-dimensional structure of the detonation wave in a stoichiometric and fuel-rich (1.5CH$_4$+2Air) methane-air mixtures and stoichiometric methane-oxygen mixture. The numerical algorithm, presented in [4, 5] is used. According to calculations, qualitative structures of detonation waves in all these mixtures are identical. Typical results of calculations are presented in Figures 1 and 2; $H$ is the thickness of a channel, $a_0$ is the detonation cell size, $D_{ave}$ is the average velocity of detonation wave front; $D_{CJ}$ is Chapman-Jouguet detonation wave velocity (calculation, based on detailed equations of chemical equilibrium). Figure 1: $T_0 = 298$ K, $P_0 = 1$ atm, $H = a_0 = 45$ cm, $x_{front} = 1500$ cm, $D_{ave} = 1876$ m/s, $D_{CJ} = 1840$ m/s. Figure 2: $T_0 = 298$ K, $P_0 = 1$ atm, $H = a_0 = 50$ cm.
Figure 1. Detonation wave structure (normalized pressure $P/P_0$ field) in fuel-rich (1.5CH$_4$ + 2Air) mixture. AA and BB – primary transverse waves; aa and bb – secondary transverse waves; a’a’ and b’b’ – tertiary transverse waves.

Figure 2. “Thin” structure of transverse wave (normalized density $\rho/\rho_0$ field (enlarged) in fuel-rich (1.5CH$_4$ + 2Air) mixture. AA – primary transverse wave; a”a” and b”b” – secondary transverse waves on the primary transverse wave AA. P1, P2 and P3 – pockets of unburnt mixture.

The calculations reproduce an irregular cell structure with all of its main features; random inconsistent movement of the main transverse waves; numerous secondary transverse waves, forming the hierarchy of perturbations of decreasing size at the leading shock front of detonation wave; regions of unburned mixture at a considerable distance behind detonation front; fine (cellular) structure of the transverse wave. These secondary waves are responsible for the small-cell network inside the main cell in soot imprints in experiments. The fine structure is manifested in the typical shape of transverse-
wave trajectories recorded in soot imprints. Results of calculations of parameters and dominant cell size of detonation waves reveal good agreement with available experimental data.

5. Conclusions
Approximate models of chemical kinetics of detonation combustion of (i) one-fuel (CH$_4$/air) and (ii) multi-fuel (CH$_4$/H$_2$/air and CH$_4$/CO/air) gaseous mixtures are developed. Owing to the simplicity and high accuracy, the models can be used in multi-dimensional numerical calculations of detonation waves in corresponding gaseous mixtures.

The validity of the model for CH$_4$/Air/O$_2$ mixture are shown. For this purpose numerical calculations of detonation wave structure in stoichiometric CH$_4$/Air and CH$_4$/O$_2$ mixtures and fuel-rich CH$_4$/Air mixture are performed. Chemical reaction in these calculations is described by the presented model of chemical kinetics. The calculations reproduce an irregular cell structure with all of its main features; random inconsistent movement of the main transverse waves; numerous secondary transverse waves, forming the hierarchy of perturbations of decreasing size at the leading shock front of detonation wave; regions of unburned mixture at a considerable distance behind detonation front; fine (cellular) structure of the transverse wave. These secondary waves are responsible for the small-cell network inside the main cell in soot imprints in experiments. The fine structure is manifested in the typical shape of transverse-wave trajectories recorded in soot imprints. Results of calculations of parameters and dominant cell size of detonation waves reveal good agreement with available experimental data.

Further research is planned to apply the proposed model of the detonation kinetics for numerical 2-D calculations of detonation wave parameters and structure in multi-fuel mixtures CH$_4$/H$_2$/Air and CH$_4$/CO/ Air.

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References
[1] Oran E S, Weber J W, Stefanii E I, Lefebvre M H and Anderson J D 1998 Combust. Flame 113 147-163
[2] Nikolaev Yu A 1978 Combust. Explos. Shock Waves 3 468–471
[3] Nikolaev Yu A and Fomin P A 1982 Combust. Explos. Shock Waves 1 53–58
[4] Nikolaev Yu A and Zak D V 1988 Combust. Explos. Shock Waves 4 461–464
[5] Fomin P A and Trotsyuk A V 1995 Combust. Explos. Shock Waves 4, 455–457.
[6] Trotsyuk A V 1999 Combust. Explos. Shock Waves 5 549–558
[7] Nikolaev Yu A and Fomin P A 1984 Combust. Explos. Shock Waves 4 447–455
[8] Gavril'enko T P, Grigoriev V V, Zhdan S A, Nikolaev Yu A., Boiko V M and Papyrin A N 1986 Combust. Flame 66 121–128
[9] Zhdan S A, Mitrofanov V V and Sychev A I 1994 Combust. Explos. Shock Waves 5 657–663
[10] Fomin P A and Vasil'ev A A. 2001 J. Loss. Prev. Proc. Ind. 6 521–526
[11] Fomin P A, Fedorov A V. and Tropin D A. 2014 Combust. Explos. Shock Waves 1 87–96
[12] Fomin P A, Trotsyuk A V and Vasil'ev A A 2014 Combust. Sci. Technol. 10–11 1716–1735
[13] Trotsyuk A V, Fomin P A and Vasil'ev A A 2015 J. Loss. Prev. Proc. Ind. 36 394–403
[14] Korobeinikov V P, Levin V A, Markov V V and Chernyi G G 1972 Acta Astronaut. 17 529–537
[15] Strickland-Constable R F 1949 Proc. Third Symp. on Combustion and Flame, and Explosion Phenomena, 33(1) 229
[16] Soloukhin R I 1970 Proc. 7th Int. Shock Tubes Symposium (University of Toronto Press. Toronto and Buffalo) 662–706
[17] Vasil'ev A A 2007 Combust. Explos. Shock Waves 3 282–285