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To cite this article: A.V. Trotsyuk and P.A. Fomin 2019 *J. Phys.: Conf. Ser.* **1261** 012037

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# Reduced model of chemical kinetic and two-dimensional structure of detonation wave in rich mixtures of methane with oxidizer

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**Abstract.** Two-step reduced model of chemical kinetics of detonation combustion of methane mixtures is presented. The possibility of condensed carbon (soot) microparticles formation in reaction products is taken into account for the first time. The model is simple (only one ordinary differential equation in a main heat release zone) and physically grounded. It is in consistent with the second law of thermodynamics and Le Chatelier's principle. The model verification has been performed via numerical calculations of parameters and two-dimensional structure of detonation wave in the fuel-rich methane-oxidizer mixture. The irregular cellular structure of the wave with all its main features, observed in the experiments, was reproduced in the calculations. The dominant size of the detonation cell is in good agreement with experimental data and corresponding estimations in the frames of generally accepted Vasil'ev-Nikolaev model of detonation cell.

## 1. Introduction

Numerical modeling of parameters and multifront cellular structure of detonation wave in methane-oxidizer mixtures is the necessary step in solution of explosion safety problem in mining industry and design of engines, based on detonation combustion. It is problematic to use a detail system of chemical kinetic in such calculations owing to its cumbersome. Therefore, approximate kinetic models are frequently used for numerical calculations of multifront detonation waves in methane-oxidizer mixtures (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. Moreover, such models are not correspond to Le Chatelier's principle and the second law of thermodynamics. Therefore there is still an urgent need to develop simple but highly accurate approximate kinetic models for detonation combustion of methane.

In our articles [2-4] 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 [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 [2-4]. Unfortunately, this model cannot be used for the fuel-rich mixtures, in which  $a_1 \leq 0.5$ . In the present work a new modification of this model will be presented. It will be valid for all relations between fuel and oxidizer, including the mixtures with  $a_1 \leq 0.5$ . The model will be used in numerical



calculations of parameters and two-dimensional structure of detonation wave in the fuel-rich methane-oxidizer mixture.

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

The following mixture will be considered:  $\text{CH}_4 + a_1\text{O}_2 + a_2\text{N}_2$ .

The first step of the model is induction period and the second one corresponds to main heat release zone.

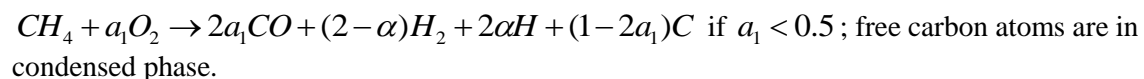
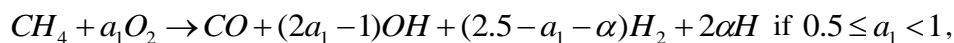
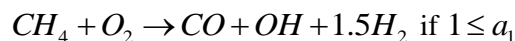
As is commonly done, we calculate the value of the induction parameter  $Y$  during the induction period of the chemical reaction in the gas mixture with variable pressures and temperatures by the formula [6]:

$$Y = \int_0^{t_i} \frac{dt}{\tau_i}$$

where  $\tau$  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  $t = t_i$ ),  $Y = 1$ . Arrhenius formula for calculation induction period  $\tau$  under constant temperature and pressure assumed to be known [7].

We also take into account that the induction period involves chemical reactions leading to decomposition of methane molecules, formation and increase in the number of reaction careers and (if concentration of methane in the mixture is high enough) condensed carbon (soot) microparticles formation. We replace the real multistep process occurring during the induction period with some brutto (overall) reaction. It is taken into account that by the end of the induction period, the temperature increase (and 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. The thermal effect of the overall reaction will also be much smaller than the thermal effect at the Chapman–Jouguet point of detonation wave. It is assumed additionally that all free atoms of carbon instantaneously transform into the condensed phase.

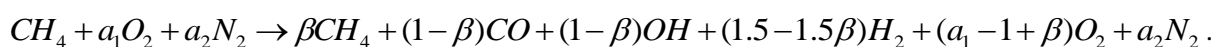
Thus, we assume that during the induction period, each methane molecule of the mixture is involved in the chemical brutto-reactions:



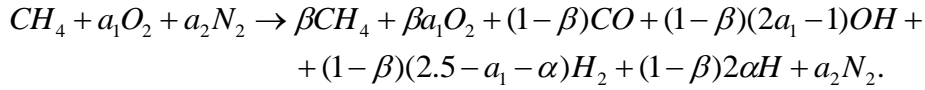
The value  $\alpha$  should be calculated from the condition: the thermal effect of the reaction at the end of the induction period  $Q_\tau$  is significantly smaller than the maximum possible heat effect of the chemical reaction  $Q_{\max}$  per one mole of  $\text{CH}_4$ . For example,  $Q_\tau / Q_{\max} \ll 1$  for  $1 \leq a_1$ . If  $0.8 \leq a_1 \leq 1$  then  $Q_\tau / Q_{\max} \leq 0.1$  at  $\alpha = 0$ . If  $a_1$  equals to 0.5, 0.6 and 0.7, then  $Q_\tau / Q_{\max} \leq 0.1$  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.

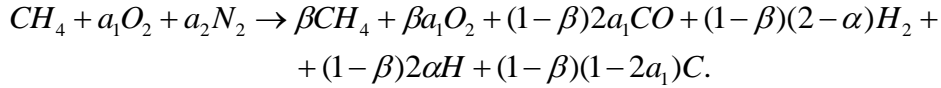
For  $1 \leq a_1$ ,



For  $0.5 \leq a_1 < 1$ ,



For  $a_1 < 0.5$  (soot formation),



According to [2, 3] it is possible to assume that

$$\beta = 1 - Y.$$

This formula takes into account that the value of  $\beta$  affects only the wave parameter profiles in the induction zone. Moreover, 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.

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

After induction period (during the second step of the reaction) the model includes a kinetic equation for the molar mass of the gas [5]

$$\frac{d\mu}{dt} = 4K_+ \frac{\rho^2}{\mu} \left(1 - \frac{\mu}{\mu_{\max}}\right)^2 - AT^{3/4}(1-\exp(-\Theta/T))^{3/2} \rho \left(\frac{\mu}{\mu_{\min}} - 1\right) \exp(-E/\Re T),$$

and formulas for the specific internal energy of the gaseous phase [5]:

$$U(T, \mu) = U_{\text{therm}}(T, \mu) + U_{\text{chem}}(\mu), \\ U_{\text{therm}}(T, \mu) = \left[ \frac{3}{4} \left( \frac{\mu}{\mu_a} + 1 \right) + \frac{3}{2} \left( \frac{\mu}{\mu_a} - 1 \right) \frac{\Theta/T}{\exp(\Theta/T) - 1} \right] \frac{\Re T}{\mu}, \\ U_{\text{chem}}(\mu) = E \left( \frac{1}{\mu} - \frac{1}{\mu_{\min}} \right), \\ U_{\text{chem}}(\mu) = E \left( \frac{1}{\mu} - \frac{1}{\mu_{\min}} \right),$$

where  $\rho$ ,  $T$  and  $\mu$  are the density, temperature, and the mean molar mass of the gaseous mixture;  $\Re$  is the universal gas constant;  $\mu_a$ ,  $\mu_{\min}$ ,  $\mu_{\max}$  are the molar masses of gas in the atomic, completely dissociated and completely recombined states;  $A$  and  $K_+$  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,  $U_{\text{therm}}$  and  $U_{\text{chem}}$  are thermodynamic and chemical parts of  $U$ .

It is assumed that particles of condensed carbon are in mechanical and heat equilibrium with the gas (i.e., the velocity and temperature of gas and soot particles are equal). The total volume of condensed particles is negligibly small. Condensed phase is incompressible. The characteristic sizes of soot particles is in tens of nanometers [8]; thus, these suppositions correspond to the reality. The partial pressure and total volume of particles and the pressure of saturated vapors of condensed phase are negligibly small.

The total internal energy  $U^*$  and the density of gas-particles mixture  $\rho_*$  and the volume density of condensed phase are:

$$U^* = (1 - \bar{\alpha})U + \bar{\alpha}U^C, \quad \rho_* = \rho + \rho_C, \quad \rho = (1 - \bar{\alpha})\rho_*, \quad \rho_C = \bar{\alpha}\rho_*,$$

where  $\bar{\alpha}$  is the mass fraction of condensed phase in gas-particles mixture and  $U^C$  is the internal energy of condensed carbon.

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

$$\mu(\rho, T) = \frac{B\mu_{\min} - 2\mu_{\max} + \sqrt{D}}{2(A^* - 1)},$$

$$B = \frac{AT^{3/4}}{4K_+} (1 - e^{-\Theta/T})^{3/2} e^{-E/\Re T} \frac{\mu_{\max}^2}{\mu_{\min} \rho}, \quad D = (B\mu_{\min} - 2\mu_{\max})^2 + 4(B - 1)\mu_{\max}^2.$$

The heat capacity at constant volume and pressure are [9]:

$$C_V^* = (1 - \bar{\alpha})(U_T + U_\mu \mu_T) + \bar{\alpha}U_T^C, \quad C_P^* = C_V^* + (1 - \bar{\alpha}) \frac{\rho}{T} \frac{T/\mu \cdot \mu_T - 1}{1 - \rho/\mu \cdot \mu_\rho} (U_\mu \mu_\rho - \frac{P}{\rho^2}),$$

where

$$\mu_\rho = \frac{\mu}{\rho} \Lambda, \quad \mu_T = -\frac{3}{4} \cdot \frac{1}{T} \mu \Lambda + \frac{3}{2} \cdot \frac{e^{-\Theta/T}}{1 - e^{-\Theta/T}} \cdot \frac{\Theta}{T^2} \mu \Lambda - \frac{E}{\Re T^2} \mu \Lambda,$$

$$U_T = G + \frac{3}{2} \left( \frac{\mu}{\mu_a} - 1 \right) \frac{\Re T}{\mu} \cdot \frac{\Theta}{T^2} \cdot \frac{1}{e^{\Theta/T} - 1} \left\{ -1 + \frac{\Theta}{T} \cdot \frac{e^{\Theta/T}}{e^{\Theta/T} - 1} \right\},$$

$$U_\mu = \left\{ \frac{3}{4} \cdot \frac{1}{\mu_a} + \frac{3}{2} \cdot \frac{1}{\mu_a} \cdot \frac{\Theta}{T} \cdot \frac{1}{e^{\Theta/T} - 1} \right\} \frac{\Re T}{\mu} - G \frac{T}{\mu} - \frac{E}{\mu^2},$$

$$\Lambda = \frac{(\mu_{\max} - \mu)(\mu - \mu_{\min})}{2\mu_{\max} \mu - \mu_{\min}(\mu + \mu_{\max})}, \quad G = \left\{ \frac{3}{4} \left( \frac{\mu}{\mu_a} + 1 \right) + \frac{3}{2} \left( \frac{\mu}{\mu_a} - 1 \right) \cdot \frac{\Theta}{T} \cdot \frac{1}{e^{\Theta/T} - 1} \right\} \cdot \frac{\Re}{\mu}.$$

Velocity of sound  $c_*$  and adiabatic index  $\gamma_*$  in gas-microparticles mixture under consideration is:

$$c_*^2 = \frac{dP}{d\rho_*} = \gamma_* \frac{P}{\rho_*}, \quad \gamma_* = \frac{d \ln P}{d \ln \rho_*} = \frac{d \ln P}{d \ln \rho} = 1 - \frac{\rho}{\mu} \mu_\rho + \frac{\rho}{T} \left( 1 - \frac{T}{\mu} \mu_T \right) \frac{dT}{d\rho},$$

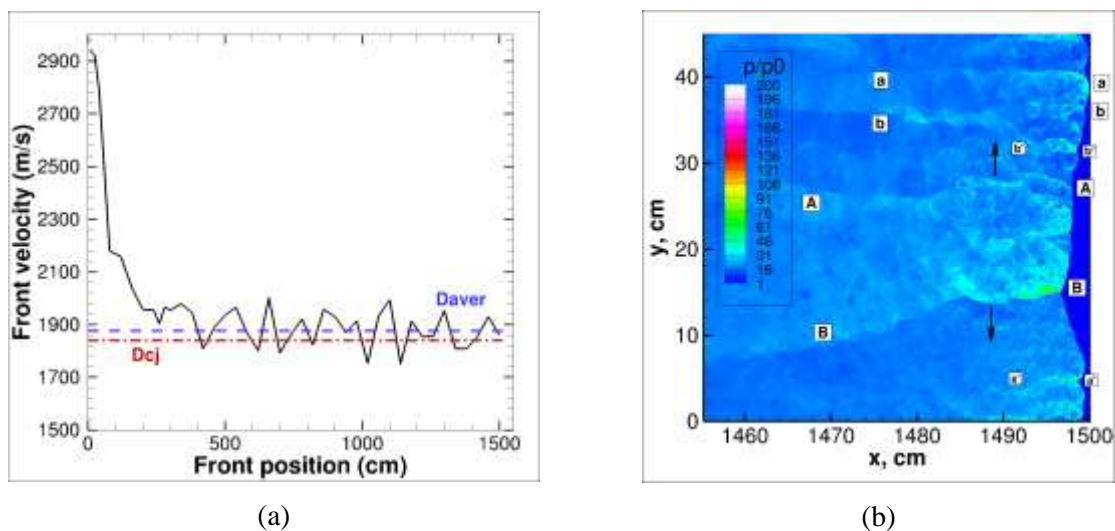
$$\frac{dT}{d\rho} = \frac{1}{1 - \alpha} \cdot \frac{dT}{d\rho_*} = - \frac{(1 - \alpha)(U_\mu \mu_\rho - RT/\rho\mu)}{(1 - \alpha)(U_T + U_\mu \mu_T) + \alpha U_T^C}.$$

### 3. Results of calculations of detonation wave parameters and structure in rich CH<sub>4</sub>/Air/O<sub>2</sub> mixtures

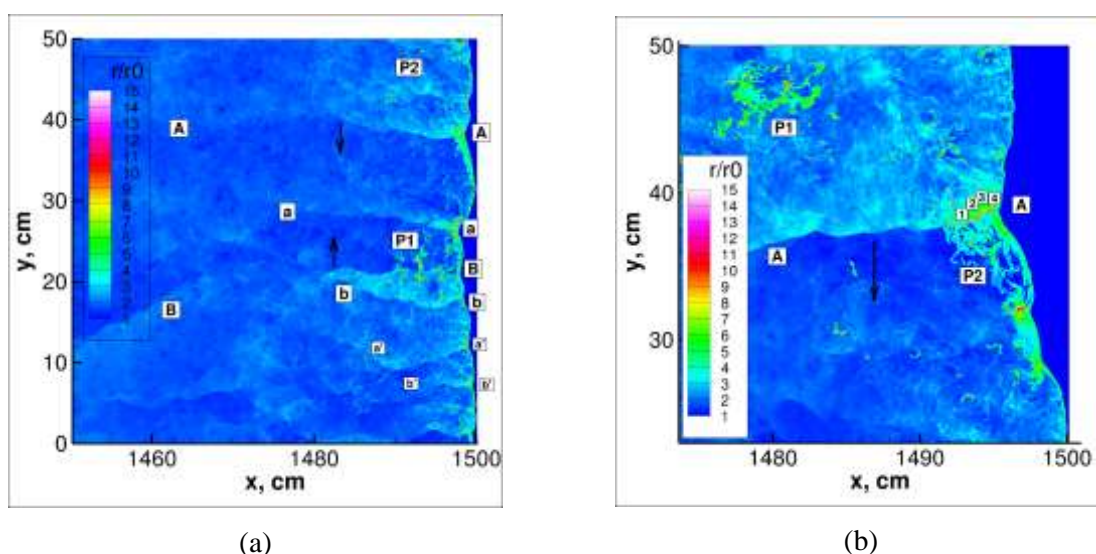
The kinetic model for detonation combustion of methane has been verified via numerical calculations of a two-dimensional structure of the detonation wave (DW) in a stoichiometric and fuel-rich (1.5CH<sub>4</sub>+2Air) methane-air mixtures and stoichiometric methane-oxygen mixture. The numerical algorithm and numerical grids, described in [2,3] are used. According to calculations, qualitative structures of detonation waves in all these mixtures are identical. Typical results of calculations are presented in Figures 1–2.  $H$  is the thickness of a channel,  $a_0$  is the detonation cell size,  $D_{aver}$  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 1a shows a front-propagation velocity (solid line) as a function of DW front position after the initiation in a channel  $H=45$  cm. Denotation has reached aquasi-steady propagation regime at the last 9÷10 meters. The multifront DW structures are investigated for steady propagating detonations.

The calculations reproduce an irregular cell structure with all of its main features: random inconsistent movement of the main (primary) transverse waves (TWs), AA and BB on Figure 1b and Figure 2a; numerous secondary TWs, denoted by aa, bb, etc, and third order smaller TWs a'a', b'b', etc, that forming the hierarchy of perturbations of decreasing size at the leading shock front of detonation wave (see Figures 1–2); pockets of unburned mixture P1, P2 at a considerable distance behind detonation front (see Figure 2); fine (cellular) structure of the main TW AA, Figure 2b. Here 1, 2, 3, 4 are the fine TWs on the front of primary TW AA. This fine structure is manifested in experiments in the typical shape of transverse-wave trajectories recorded on soot imprints.



**Figure 1.** A rich methane-air ( $1.5\text{CH}_4 + 2\text{Air}$ ) mixture,  $T_0 = 298$  K,  $p_0 = 1$  atm in channel  $H=45$  cm: (a) front-propagation velocity (solid line) as a function of front position.  $D_{\text{aver}} = 1876$  m/s,  $D_{\text{CJ}} = 1840$  m/s.; (b) DW structure, normalized pressure  $p/p_0$  flowfield.



**Figure 2.** A rich methane-air mixture in channel  $H=50$  cm, normalized density  $\rho/\rho_0$  flowfield: (a) DW structure, double grid resolution simulation; (b) fine structure of the primary transverse wave AA, magnified fragment of the flowfield.

#### 4. Conclusions

Two-step reduced model of chemical kinetics of detonation combustion of methane mixtures is presented. The possibility of condensed carbon (soot) microparticles formation in reaction products is taken into account for the first time. The model is in consistent with Le Chatelier's principle and the second law of thermodynamics. It is simple and therefore can be used in numerical calculations of parameters and cellular structure of corresponding detonation waves.

The presented model has been verified in numerical 2-D calculations of detonation wave parameters and structure in stoichiometric CH<sub>4</sub>/Air and CH<sub>4</sub>/O<sub>2</sub> mixtures and fuel-rich CH<sub>4</sub>/Air mixture (1.5 CH<sub>4</sub> + 2 O<sub>2</sub> + 7.52 N<sub>2</sub>). The developed two-stage kinetic model and 2D numerical code give excellent results in the modelling of irregular cellular structures and detonation cell size in methane-based mixtures for classical DW in a straight 2D channel.

#### Acknowledgments

The authors gratefully acknowledge the financial support from Russian Foundation for Basic Research (Grant № 17-03-01351). The computations were carried out on MVS-10Q at Joint Supercomputer Center of the Russian Academy of Sciences (JSCC RAS).

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