

Kinetics Based Adjustment of the Two-stage Combustion Model for Hydrogen

Ivan A. Zaev¹, Igor A. Kirillov²

¹Moscow Institute of Physics and Technology (State University),
Dolgoprudny, Moscow Region, 141700, Russia

²RRC Kurchatov Institute,
1, Kurchatov Sq., Moscow, 123182, Russia

1 Introduction

During the past decade the worldwide attention in the combustion community was paid to development of pulsed detonation devices (PDDs) as a prospective propulsion system and to hydrogen global energy as an alternative to traditional energetic and fuels (petroleum, natural gas, etc.).

Research and development in these areas are impossible without numerical experiment, especially CFD, which helps to understand deeper the physics and simplifies development of the products.

In the PDD development and in hydrogen safety most of the problems are related with confined reactive systems with complex multidimensional geometry. Hence, development of the robust and accurate models for chemistry is necessary (practical multidimensional CFD simulations using detailed kinetic schemas are extremely time-consuming and can be made only for decisive runs). In the present work the modification of the existed IPM model for hydrogen combustion is proposed.

One of the candidates on the role of chemistry model is the Induction Parameter Model (IPM), which is used in CFD simulations [1]. Detailed description of the model can be found in [1]. The advantage of the IPM model is the accurate reproduction of the ignition delay times, the trial to describe reaction as a one-variable process and its simplicity for implementation in CFD codes. But it was not given advices for the choice of the parameters of the heat release stage in a regular manner (e.g. see [1], where different sets are discussed). The different values of the parameters could give different heat release profiles after induction, that is very crucial for results obtained, because of the fact that time scale of the heat release is of the order (or larger) of the induction time scale and an accuracy in its simulation is obligatory as well.

In the present work the modification of the IPM model is proposed, which allows to model heat release more accurately (accounting for all the factors, which can alter it) and the procedure of the determination of the parameters of the model from-the-first-principles is developed.

2 Time scales of the heat release process in hydrogen combustion

Combustion of the hydrogen is a chain-branching process, which is characterised by two successive stages. During the first, induction, stage the active intermediate species are accumulated. Usually this stage is thermo neutral or slightly endothermic. When the amount of active intermediate species become large, they begin to recombine releasing the heat and the second, heat release stage begins. The duration of these stages is characterized by a time scales referred to as induction time t_i and heat release time t_{hr} .

In the present work kinetics of the hydrogen combustion is investigated using Constant Volume Adiabatic Calorimetric Bomb Reactor model, available in Chemical Workbench software suite. Description of the model can be found in the user guide of the program [2]. Induction and heat release times are defined as follows. Tangent line to the inflection point of the $T(t)$ dependence, obtained from calculations, is drawn. Its intersection with initial temperature level T_0 defines induction time t_i . Time scale between intersection points of the tangent line with initial temperature level T_0 and adiabatic temperature level T_{ad} is the heat release time t_{hr} .

The mixture, considered as example is H_2 -air with composition $H_2 : O_2 : N_2 = 2ER : 1 : 3.76$, where ER is equivalence ratio of the mixture. The range of initial temperatures and pressures is 1100 – 2100 K and 1 – 50 atm respectively, representing wide range of conditions, relevant for most conditions behind lead shock front of the detonation wave. Kinetic mechanism used in calculations is Marinov et al. mechanism [3].

On the Fig. 1 dependence of the heat release time on initial temperature is plotted for two specific cases. For the first one, the stoichiometric H_2 -air mixture is considered and initial pressure is set to 1 atm, 5 atm and 15 atm, see Fig. 1a. While temperature changes from 1100 K to 2100 K, heat release time increases from 0.01 millisecond to ~ 0.015 millisecond ($P_0 = 1$ atm) or decreases from 0.2 microseconds to 0.15 microseconds ($P_0 = 15$ atm). It means, that the dependence $t_{hr}(T_0)$ is power or Arrhenius law with extremely low for combustion processes activation energy.

The second case considers the dependence of the heat release time on initial temperature for varying mixture composition (primarily lean or stoichiometric conditions) at fixed initial pressure $P_0 = 1$ atm. In this case, $t_{hr}(T_0)$ remains to be power law. Specific plots are presented on the Fig. 1b. From the power law of the $t_{hr}(T_0)$ dependence the conclusion is drawn that the heat release rate is limited by the rate of the reactions with zero activation energy and large enthalpy, such as

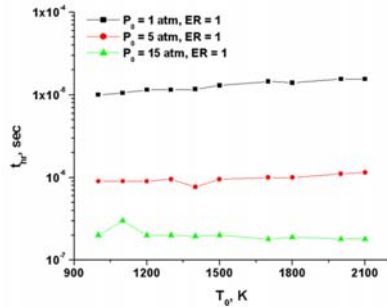
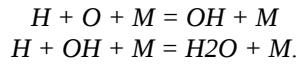


Figure 1a. Dependence of the heat release time on initial temperature for stoichiometric H_2 -air mixture at different initial pressures

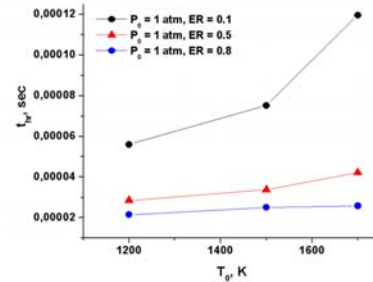


Figure 1b. Dependence of the heat release time on initial temperature for H_2 -air mixtures of different composition (ER) at 1 atm initially

Results of the calculations of the heat release time as function of initial pressure P_0 and initial mixture composition ER is presented in the Figs. 2a and 2b. Dependences $t_{hr}(P_0)$, calculated in the wide range of conditions (temperatures $T_0 = 1200$ K and $T_0 = 1500$ K, equivalence ratios $ER = 1$ and $ER = 2$) and plotted in double-logarithmic scale ($-\lg t_{hr}$, $\lg P_0$), are straight lines with the equal positive slopes, see Fig. 2a. It means that heat release time is a power function of the initial pressure.

For two sample initial temperatures $T_0 = 1200$ K and $T_0 = 1500$ K at pressure $P_0 = 1$ atm the plots $t_{hr}(ER)$ are plotted on the Fig. 2b (logarithmic scale for both axis). Increase of the ER from lean to stoichiometric conditions results in decrease of t_{hr} . At $ER = 2$ plot of $t_{hr}(ER)$ attains minimum and after that increases.

Summarizing the results of the calculations, presented above, the approximation formula for heat release time in H_2 -air mixtures is proposed

$$t_{hr}(T_0, P_0, ER) = 10^{-5} \cdot \left(\frac{T_0}{1100} \right)^{0.64 - 0.055 \cdot P_0} \cdot P_0^{-1.5} \cdot ER^{-0.6}, \quad (1)$$

where t_{hr} in seconds, T_0 in K, P_0 in atm.

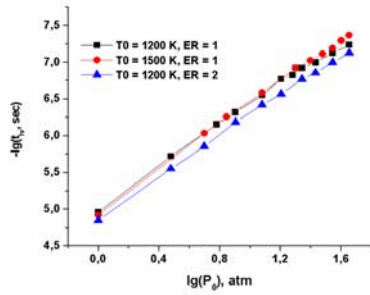


Figure 2a. Dependence of the heat release time on initial pressure for stoichiometric H₂-air mixture at different initial temperatures

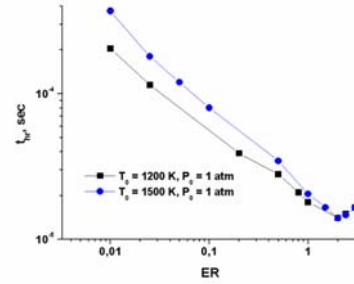


Figure 2b. Dependence of the heat release time on initial mixture composition of H₂-air mixtures at different temperatures and 1 atm initially

3 Kinetics based estimation of the two-stage model parameters

On the basis of the previous section, related to heat release time during hydrogen combustion in air, the following modification of the IPM model is proposed.

It was shown that heat release time is a power function of initial pressure and temperature for a specific mixture. To account for these results, the rate $\dot{\omega}_r$ in the equation for the second, heat release, stage [1] must be rewritten as

$$\dot{\omega}_r(T, P, ER) = \tilde{a} \cdot \left(\frac{P}{P_{ref}} \right)^{n_p} \cdot \left(\frac{T}{T_{ref}} \right)^{n_T} \cdot (1 - f_{hr})^{n_f} \cdot \exp\left(-\frac{\tilde{b}}{T}\right). \quad (2)$$

In this definition T_{ref} and P_{ref} are reference temperature and pressure, for which all the parameters are calculated according to relations

$$\tilde{a} = \frac{1}{t_{hr}(T_{ref}, P_{ref}, ER)}, \quad n_p = - \frac{d \ln[t_{hr}(T_{ref}, P_0, ER)]}{d \ln P_0} \Big|_{P_0=P_{ref}}, \quad n_T + \frac{\tilde{b}}{T_{ref}} = - \frac{d \ln[t_{hr}(T_0, P_{ref}, ER)]}{d \ln T_0} \Big|_{T_0=T_{ref}}. \quad (3)$$

The value of n_f remains undefined. In the next section it will be shown that for hydrogen mixtures $n_f = 1$.

4 Kinetics of the heat release in hydrogen combustion

In general, the hydrogen-oxygen or hydrogen-air combustion is characterized by 10 unknown variables: mole fractions of species H₂, O₂, H₂O, H, O, OH, HO₂, H₂O₂, temperature T and density. Existence of the three conservations laws (elements O and H and energy) allows to reduce the number of the variables to seven.

For the system under consideration, a large set of kinetic simulations shows that in the range of conditions: $0.7 < ER < 3$, $1100 < T_0 < 1700$, $P_0 < 50$ atm the following observations for heat release stage are valid: 1) substances HO₂, H₂O₂, O, OH are in quasi steady state; 2) chain-branching reactions $H + O_2 = O + OH$ and $O + H_2 = H + OH$ are in quasi-equilibrium. So, additional six algebraic relations exist, reducing the number of independent variables to one.

In result, the system is described only by one parameter and this statement justifies the validity of the IPM model. It is worth noting that the same result was obtained in the work [4].

It was noted in the Section 3, that parameter n_f can not be determined from data about t_{hr} . This is due to the fact, that heat release time reflects the behavior of a maximum heat release rate, while equation (2) is intended to model time dependence of the heat release rate and related with the chemistry of this stage. The major part of the heat is released in the reaction $H + OH + M = H_2O + M$. Its rate is proportional to product $H \cdot OH \cdot M \approx C \cdot H$,

where C is approximately constant, because of the concentrations of the mixture $[M]$ and OH are constant during to heat release. It means, that the order of the reaction is unity, $n_f = 1$.

5 Examples and conclusions

All the results above were obtained for H_2 -air mixtures, but they are applicable to H_2 - O_2 and other mixtures as well.

Parameters of the rate of the heat release stage depend only on mixture composition (for suitably selected P_{ref} and T_{ref}). For stoichiometric H_2 - O_2 mixture they are $\tilde{a} = 1,7 \cdot 10^5 \text{ s}^{-1}$, $n_p = 1,5$, $n_T = 0$, $n_f = 1$, $\tilde{b} = 0 \text{ K}$; for stoichiometric H_2 -air mixture they are $\tilde{a} = 4,34 \cdot 10^4 \text{ c}^{-1}$, $n_p = 1,5$, $n_f = 1$, $\tilde{b} = 0 \text{ K}$.

On the Fig. 3a the ZND profile of the steady detonation wave is plotted on the basis of the detailed chemistry kinetic calculation and calculations with the proposed IPM model modification (2). Initial conditions are $P_0 = 1 \text{ atm}$, $T_0 = 300 \text{ K}$. On the same figure the ZND profile, calculated with the parameters of the IPM model from [1] is presented as well and overestimates the scale of the heat release zone.

On the Fig 3b the temperature trace in the adiabatic calorimetric bomb of the constant volume is plotted on the basis of the detailed chemistry kinetic calculation and calculations with the proposed IPM model modification (2). Initial conditions are $P_0 = 1 \text{ atm}$, $T_0 = 1300 \text{ K}$.

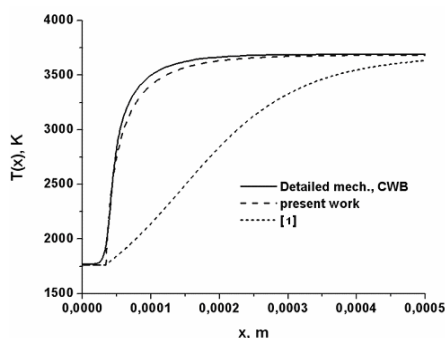


Figure 3a. ZND profile of the steady detonation wave in stoichiometric H_2 - O_2 mixture. Initial temperature 300K, initial pressure 1 atm

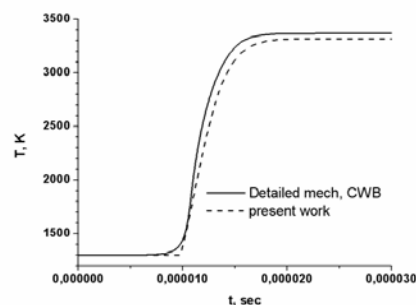


Figure 3b. Temperature change during combustion of the stoichiometric H_2 - O_2 mixture at adiabatic constant volume conditions. Initial temperature 1300K, initial pressure 1 atm

Results presented in this work show, that the modified model of the heat release in hydrogen combustion works good in wide range of conditions and for various mixtures. So, two main goals, to modify heat release model to account for influence of the local state parameters of the mixture on heat release and to propose regular, from-the-first-principles, method of recovery of the parameters of that model, are succeeded. In addition, the applicability of such a one-parameter model to simulation was proved in the series of kinetic calculations with detailed chemical mechanism.

References

- [1] Sichel M, Tonello NA, Oran ES, Jones DA (2002) A two-step kinetic model for numerical simulation of explosions and detonations in H_2 - O_2 mixtures. Proc. R. Soc. Lond. A, vol. 458, 49-82
- [2] <http://www.kintech.ru>
- [3] Li J, Zhao Zh, Kazakov A, Dryer FL (2004). An Updated Comprehensive Kinetic Model of Hydrogen Combustion. International Journal of Chemical Kinetics, Vol. 36, p. 566-575
- [4] Eckett CA (2001), Numerical and analytical studies of the dynamics of gaseous detonation. Ph.D. thesis, University of California, Pasadena