An Approach to Construction of Universal Global Kinetic Mechanisms of Hydrocarbons Combustion

Ivan A. Zaev[1], Igor V. Prokopovich[2]

[1]Kintech Lab, Ltd. and [2]Moscow Institute of Physics and Technology

Moscow, Russia

1   Introduction

Even with the significant increase of the computational power of modern high-performance computers last decade, their current capabilities for multi-dimensional modeling of combustion are limited to LES simulations of basic burner configurations or RANS simulations of real burners. Even in these simulations the primary choice of engineer for modeling the chemistry of combustion are the simplest mechanisms, consisting of several species and reactions (usually not larger than 10 species and 10 reactions), called global mechanisms of combustion. Only these simplest mechanisms allow to carry out a design parametric studies in reasonable time with available computer resources.

During a long history of the combustion research it was proposed several global kinetic mechanisms, capable to describe the combustion of a selected hydrocarbon fuel. Among these mechanisms it is necessary to mention the papers of Lindstedt and Jones [1], Westbrook and Dryer [2], Duterque [3], Frolov and Basevich [4], Varatharayan et al [5], Anderson et al [6], who developed a general recommendations for preparation of kinetic mechanisms, capable of describing the laminar flames [1 - 3, 6] and self-ignition [4, 5] of desired hydrocarbon in air.

In spite of the extensive usage of the developed global mechanisms in simulations of industrial burners[6, 7], these mechanisms posess several disadvantages: possibility to simulate only the limited number of combustion phenomena (e.g. either laminar combustion [1 - 3] or ignition [4, 5]), for which the global mechanism was developed; limited range of pressure, temperature and mixture compositions, where predictions of the mechanisms are accurate enough; extensive fitting of the reaction rates, when changing the process conditions; no explicit recommendations for adaptation of the existing mechanism for description of the new class of combustion phenomena.

The goal of the present paper is to propose the approach for construction of universal global kinetic mechanisms of hydrocarbons combustion, capable to describe several combustion phenomena simultaneously, without extensive fitting of the reactions rates.

2   Description of the Approach

The underlying disadvantage of the global mechanisms in describing the whole set of the combustion phenomena for a wide range of initial conditions is related with description of changes in mixture composition observed in experiments or simulations with detailed kinetic mechanisms, while neglecting the chemical nature of reactions. For example, the global mechanism of methane combustion in laminar flames includes a simple reaction of fuel burn out to CO and H_2O, while in

reality this process is complex: it is due to chain-branched reactions of fuel and radicals, producing new intermediate radicals.

In the approach to construction of the global mechanisms for hydrocabon combustion, proposed in the present paper, it is assumed that the global mechanisms, which model all the kinetic stages of combustion of the selected fuel in desired range of conditions, will be universal in terms of the both combustion phenomena (ignition and flames) and wide range of initial conditions.

Among the combustion phenomena to be modeled, the auto-ignition is the simplest one, where the combustion stages follows one by one. In other phenomena (laminar flames and turbulent combustion) these stages are mixed with parallel reactions of fuel and radicals. Thus, the development of the universal global mechanism should start from development of the global mechanism for auto-ignition and successive extension of this mechanism by global reactions, encountered in flames.

To obtain the global kinetic mechanism for auto-ignition, it is necessary to perform the sequence of steps, described below.

1. Identify the minimum set of species, required to describe the equilibrium composition of combustion products with prescribed accuracy in the desired range of initial conditions and mixture compositions. Based on this set of species identify the the independent set of the reactions between them, based on detailed kinetic mechanism. These species and reactions will form the initial part of the universal global mechanism.

2. Based on the analysis of the kinetic curves of the process identify the different stages of the combustion process and their type of the kinetics in desired range of initial conditions. The following variants are posible: simple or chain reaction with small heat release; the same type with notable heat release leading to thermal runaway; chain-branched reaction with small heat release; chain-branched reaction with notable heat release, leading to runaway. The type of the reaction can be identified, if the kinetic curve of the process is replotted in the coordinates, where these curves will take the form of straight lines. These are: $(\ln n(t), \ln w(t))$ and $(t, \ln n(t))$ for simple or chain reaction, $(1/T(t), \ln w(t))$ and $(t, n(t))$ - for simple or chain reactions with thermal runaway; $(t, \ln n(t))$ or $(t, \varphi(t))$ for chain-branched reaction; $(1/T(t), \ln \varphi(t))$ for chain-branched reaction with thermal runaway. In these expressions t is time, n is concentration of stable species, w is rate of formation/consumption of stable species, T is temperature and φ is branching factor of the reaction, defined as $d(\ln n(t))/dt$.

3. Identify the product of every stage, which is assumed to be a reagent for next stage. The sensitivity analysis is used for this purpose, where the sensitivity is evaluated as $S_{ij} = d(\ln \Delta t_i)/d(\ln c_j)$, Δt_i is duration of stage i, c_j is concentration of j-th species at start of i-th stage. The species, which produces the maximum sensitivity for i-th stage, will be the reagent for this stage and product for the previous one. The identified species and initial set of species, required to describe the chemical equilibrium, will form the full set of species of global mechanism.

4. Extend the initial set of the reactions by a sequence of stages, identified at two previous steps. If the stage is simple or chain reaction, than it can be modeled with equation $F \rightarrow R^*$, and if the stage is chain-branched reaction, it can be modeled with sequence of two reactions $F \rightarrow R^*$ (chain-initiation), $R^* + F \rightarrow R^* + R^*$ (chain-branching). For chain initiation reactions their rates are equal to corresponding chain initiation reactions in detailed mechanism; for simple, chain-propagation or chain-branched reactions the effective activation energy is estimated based on the slope on the curve $(\ln \Delta t_i, 1/T_0)$, where Δt_i is duration of the i-th stage, T_0 is initial temperature. Usually two or three kinetic stages of ignition are observed, thus only two or three remaining parameters are unknown - the pre-exponential factor for reactions rates of every stage. Fitting of these parameters requires just a few simulations, thus significantly reducing the computational work, in comparison with fitting the whole global mechanism.

5. Additional universal simplification can be made for combustion of hydrocarbons. The final stage of combustion is burn-out of CO to CO_2. Its global mechanism can be developed once and will be used for all other fuels.

6. Test of the accuracy of the developed mechanism and identification of its range of applicability in terms of initial conditions.

Extension of the auto-ignition mechanism to other combustion phenomena can be achieved by adding the global reaction, representing the flame reactions (usually one or two additional reactions). The obtained mechanism is applicable to both the auto-ignition and flame problems.

3   Case-Study: High-temperature auto-ignition and Plasma-Assisted Ignition of Methane

The goal of the present section is to demonstrate the steps of global mechanism development for methane auto-ignition and plasma-assisted ignition in the following range of conditions: initial temperature 1100 - 2000K, pressure 1 - 30 atm and mixture equivalence ration 0.5 - 2.0, which are of practical importance for methane explosions, detonation and combustion in industry and propulsion. The detailed mechanism of methane combustion [8] is used in kinetic simulations of auto-ignition and as reference for rates of elementary and global reactions.

In the selected range of conditions the equilibrium temperature of combustion products can be simulated with accuracy 100K if species H, O, OH, H_2O, CO, CO_2 are used. Due to conservation of 3 elements H, O, C only three reactions are required. These are reactions 6, 8, 9 in Table. Their rate constants are given from mechanism [8]

The analysis of the kinetic curves of methane auto-ignition shows, that the whole process proceeds in three stages. These stages are illustrated on Fig. 1. Left plot clearly shows, that the first stage is chain-branched reaction with small heat release as the chain-branching factor φ is nearly constant. Right plot shows that the second stage is chain-branched reaction with significant heat release, while the first stage (with small heat release) on the same plot is represented as single black point. The last stage is slow burn-out of CO and transition to equilibrium, universal for all hydrocarbons.

Sensitivity analysis shows, that the CH_2O is the product of the first stage and reagent for the second stage, CO is the product of the second stage and reagent for the third stage. Reactions, reproducing the kinetics of these stages are shown in Table. Preliminary estimation of the pre-exponential factors and activation energies based on rate constants of elementary reactions and several kinetic simulations allows to reduce the unknow parameters of the mechanism to two: pre-exponential factor of reaction 2 and 3 in Table. The final version of the mechanism for methane auto-ignition is shown in Table and contains 10 species and 9 reactions. The results of mechanism validation are presented on Fig. 2 for a range of initial conditions and mixture compositions.

To illustrate the way for extension of the obtained global mechanism to other combustion phenomena, we will consider the important problem of plasma-assisted ignition of methane, which is supposed to be related with reactions of oxygen atom with fuel to initiate the chain-branched reactions [9].

According to general approach, described in previous section, the basis for the universal mechanism, which allows to describe both auto-ignition and plasma-assisted ignition of methane at high temperatures (>1100K), is the mechanism, given in Table. It should be extended by a single reaction, which describes the reaction of fuel with O atoms. As it is initiation reaction, its rate is equal to rate of elementary reaction $CH_4 + O = CH_3 + OH$, given in mechanism [8]. The equation of global reaction, for description of plasma-assisted ignition is $CH_4+O+1/2O_2 = CH_2O+H_2O$ (CH_2O is main chain carreir for the first stage in global mechanism). Results of mechanism validation are presented on Fig. 3 for a range of initial conditions, including the variable initial concentration of oxygen atom, reflecting the different plasma conditions.

4   Conclusions

In the present paper the approach to derivation of the universal global mechanisms of hydrocarbons combustion is proposed, which is based on the requirement to reproduce all stages of hydrocarbon self-ignition supplemented by additional reactions of fuel and radicals, relevant for other types of the combustion (plasma-assisted ignition, flames).

Based on the proposed approach the global mechanisms of methane self-ignition, consisting of 10 species and 9 reaction and allowing to simulate the ignition delay time with accuracy of 50% for temperature from 1100 to 2000 K and pressure from 1 to 30 atm in lean ($\varphi = 0.5$), stoichiometric ($\varphi = 1$) and rich ($\varphi = 2$) mixtures, is derived. Its extension to plasma-assisted ignition is also developed without any additional adjustment of the reaction rates and keeps the same accuracy as the base global mechanism.

The developed mechanisms can be applied to practical simulation of detonation and explosions in methane-oxygen-air mixtures for safety and propulsion applications, as well as in preliminary theoretical studies of plasma-assisted methane combustion to estimate the potential of new combustion technologies, using non-equilibrium plasma.

Acknowledgements

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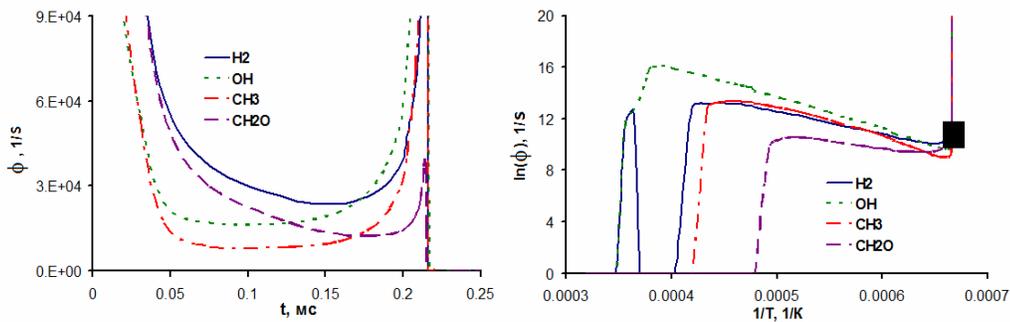
Figure 1. Dependence of branching factor ц on time t (left plot) and on current temperature T(t) (right plot) during methane self-ignition for species H_2, OH, CH_3, CH_2O. Initial conditions: stoichiometric CH_4-air mixture, 1500K, 10 atm
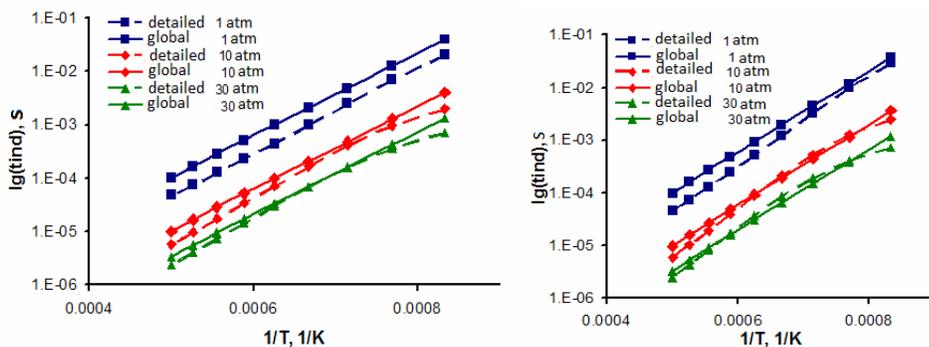

Figure 2. Ignition delay time for lean (left plot, equivalence ratio 0.5) and stoichiometric (right plot) methane-air mixtures.
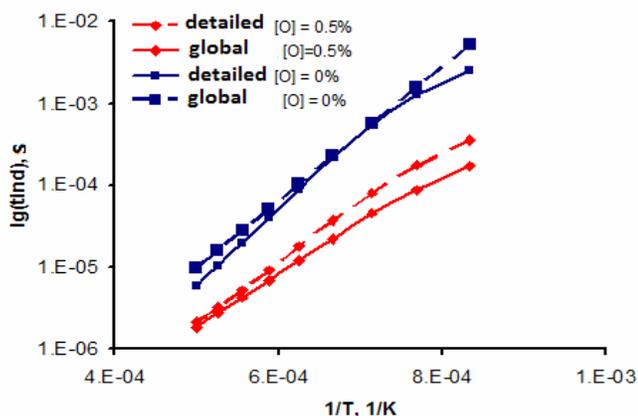

Figure 3. Ignition delay time for stoichiometric methane-air mixture at plasma-assisted ignition. T = 1200 - 2000K, P = 10 atm.

Table: Global mechanism of methane auto-ignition in air (units, cm3, s, kcal and K).

Reaction No. and equation	Reaction rate
1. $CH_4 + O_2 \rightarrow CH_2O + H_2O$	$10^{-10,181} e^{(-56,89/R\,T)} [CH_4][O_2]$
2. $CH_4 + CH_2O + O_2 \rightarrow 2CH_2O + H_2O$	$10^{-8,73} e^{(-40/R\,T)} [CH_2O][O_2]$
3. $CH_2O + O_2 \rightarrow CO + H_2O + O$	$10^{-12,7} e^{(-40/R\,T)} [CH_2O][O_2]$
4. $CH_2O + OH \rightarrow CO + H_2O + H$	$10^{-14,2444} T^{1,18} e^{(0,45/R\,T)} [CH_2O][OH]$
5. $CH_2O + H \rightarrow CO + H + H_2$	$10^{-13,41} T^{1,05} e^{(-3,28/R\,T)} [CH_2O][H]$
6. $H + O_2 \leftrightarrow O + OH$	$10^{-7,3565} T^{-0,6707} e^{(-17,04/R\,T)} [H][O_2]$
7. $OH + CO \leftrightarrow H + CO_2$	$10^{-16,1021} T^{1,228} e^{(-0,07/R\,T)} [OH][CO]$
8. $H + OH + M \leftrightarrow H_2O + M$	$10^{-25,2171} T^{-2} [H][OH][M]$
9. $O + H_2 \leftrightarrow H + OH$	$10^{-19,0808} T^{2,67} e^{(-6,29/R\,T)} [O][H_2]$