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ANALYSIS OF THE EFFECT OF MATHEMATICAL MODELS OF CHEMICAL TRANSFORMATIONS ON THE IGNITION OF METHANE-OXYGEN MIXTURES

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This paper analyses the influence of mathematical models of chemical transformation on the ignition of methane-oxygen mixtures. The results of the analysis prove that, despite the widespread use of methane combustion processes for practical purposes and a fairly large number of publications, the development of kinetic schemes for methane combustion is still relevant. Using the example of solving the problem of determining the induction period of ignition of a methane-oxygen mixture in an adiabatic reactor, various kinetic schemes for methane ignition were tested in the work: two one-stage, one three-stage schemes and a scheme consisting of 156 reactions. The most accurate description of the experimental data on the delay times of an adiabatic explosion can be obtained only by using a more complex kinetics of methane oxidation, and the simplified kinetic mechanisms considered give overestimated temperatures of the mixture consisting of methane oxidation products.

Keywords: mathematical modeling; combustion and explosion; induction period.

Introduction

Mathematical modeling of flows of multicomponent and multiphase continuous media is widely used in various branches of science and technology and, sometimes, is the only reliable way to analyze the occurrence of emergency situations in the case of fast processes. The development of high-performance computing technology allows us to build increasingly complex mathematical models to describe fast processes in multiphase medium. In addition, the results of experimental studies of processes associated with methane combustion on a reduced scale (laboratory studies) cannot be fully used to describe full-scale processes, and conducting full-scale experiments can be difficult due to the high fire and explosion hazard of materials. To study such processes, it is necessary to use mathematical modeling methods.

A mathematical model of a multicomponent mixture, taking into account chemical transformations [1,3] in the approximation of a continuous medium, is a system of equations based on the laws of conservation of mass, momentum and phase energy, and can be solved numerically only by using an approach that allows reasonable application of splitting by physical processes. Physical splitting consists in dividing the calculation of the parameters of chemical transformations and hydrodynamic processes into two separate stages. In this case, the influence of chemical transformations on hydrodynamic processes

is taken into account in the form of source terms in the equations for the conservation of the energy of the mixture and the mass fractions of the components. The chemical transformations themselves can be described by using a system of chemical kinetics equations.

Despite the fact that methane oxidation (combustion) reactions are very widely used for practical purposes, and there quite a large number of publications, the development of kinetic schemes for methane combustion is still relevant at the present time. Therefore, this study analyzes the influence of mathematical models of chemical transformations on the dynamics of energy release during combustion of methane-oxygen mixtures in order to identify an effective kinetic mechanism for methane combustion, consisting of a minimal set of chemical reactions and allowing one to solve a wide range of practical problems.

1. Mathematical Model of Chemical Transformations in Adiabatic Reactor

One of the simplest and most effective ways to study the effect of mathematical models of chemical transformation on the combustion of methane-oxygen mixtures is to determine the adiabatic explosion delay (induction period).

Consider an *adiabatic reactor* i.e. a reactor in which there is no heat or mass exchange with the environment, so that all the heat obtained in the course of exothermic oxidation reactions is used to heat up the system. In such a system, under any initial conditions, the heat released during the reactions leads to a progressive heating of the mixture, ending in a thermal explosion. The time interval from the beginning of the process to the moment of a sharp increase in temperature is called the adiabatic induction period (*combustion delay*) t_{ad}. The duration of the induction period depends both on the initial conditions and on the thermophysical properties of the mixture and the parameters of the chemical reaction (rate constant, activation energy, thermal effect). During the process, the chemical composition of the reacting mixture and its temperature change. At the initial time $t = 0$, the following parameters are specified: the initial temperature T_0, the pressure P_0; the composition of the mixture is determined by the set of initial mole fractions of the components.

Since the system is ideally isolated, the gradients of concentration, temperature and pressure at the reactor walls are zero. The consequence of this is the absence of gradients throughout the entire process, i.e. concentrations, temperature and pressure change synchronously at all points of the reacting mixture.

Consider a closed adiabatic reactor of constant volume containing a mixture of gases of variable composition from N_C components participating in N_R elementary chemical reactions. We write the j-th reaction as a generalized stoichiometric equation:

$$\nu_{1,j}A_1 + \nu_{2,j}A_2 + \ldots + \nu_{N_C,j}A_{N_C} \to \nu'_{1,j}A_1 + \nu'_{2,j}A_2 + \ldots + \nu'_{N_C,j}A_{N_C}.$$

Here A_k is the chemical symbol of the k-th substance (e.g., CH_4, CO_2, O_2, H, O, etc.), $\nu_{k,j}$ is the stoichiometric coefficient of the k-th substance in the j-th reaction, which indicates the number of moles (or molecules) of a given reagent entering the reaction as the initial substance, and $\nu'_{k,j}$ is the number of moles resulting from the reaction. The stoichiometric coefficients of substances that do not participate in the j-th reaction are equal to 0.

The rate of the j-th reaction in the gas phase is determined by the law of mass action (dependence on concentrations) and the Arrhenius law (dependence on temperature) and

can be expressed as follows:

$$W_j = k_{0_j} T^{b_j} \exp\left(-\frac{E_j}{RT}\right) \prod_{k=1}^{N_C} C_k^{\nu_{k,j}},$$

where k_{0_j}, T^{b_j}, E_j are the kinetic constants for calculating the rate of the j-th reaction, R is the universal gas constant. The quantities k_{0_j} of bimolecular and trimolecular reactions have the dimensions $m^3 \cdot mol^{-1} \cdot s^{-1}$ and $m^6 \cdot mol^{-2} \cdot s^{-1}$, respectively, and the activation energy E_j is $J \cdot mol^{-1}$.

The mathematical model of an adiabatic reactor is described by the energy balance equation for determining the temperature T of the reacting mixture and N_C equations for the molar concentrations C_k of each of the reagents [4,5]:

$$\frac{dT}{dt} = \frac{-\sum_{k=1}^{N_C} h_k \frac{dC_k}{dt}}{\sum_{k=1}^{N_C} c_{P_k} C_k},$$

$$\frac{dC_k}{dt} = \sum_{j=1}^{N_R} W_j(\nu'_{k,j} - \nu_{k,j}), k = 1, 2, \ldots, N_C,$$

where t is the time, h_k is the total specific molar enthalpy (J/mol), c_{P_k} is the isobaric molar heat capacity $(J/(K \cdot mol))$. The current mixture pressure can be calculated using the formula:

$$p = RT \sum_{I=1}^{N_C} C_i.$$

The heat capacity at constant pressure c_P and the total enthalpy h of each substance are calculated using approximate temperature dependences [6,7]:

$$h(T) = \Delta h^0(0) + [h^0(T) - h^0(0)],$$

$$[h^0(T) - h^0(0)] = T(a_1 - 2a_2 X^{-2} - a_3 X^{-1} + a_4 X + 2a_5 X^2 + 3a_6 X^3), (J/mol),$$

$$c_P(T) = a_1 + 2a_2 X^{-2} + 2a_4 X + 6a_5 X^2 + 12a_6 X^3, (J/(K \cdot mol)), X = \frac{T}{10000},$$

where a_i are the coefficients of the polynomial for each substance, $\Delta h^0(0)$ is the standard enthalpy of formation of the substance at $T = 0$. In this mathematical model, the thermal effect is taken into account according to Hess' law, which makes the model more correct.

To solve the problem of determining the induction period, this system must be supplemented with initial conditions for the concentrations and temperature of the gas mixture: $t = 0$, $T = T_0$, $C_k = C_{0k}$.

Therefore, the problem of determining the induction period and analyzing the influence of mathematical models of chemical transformations on the dynamics of energy release during the combustion of methane-oxygen mixtures is reduced to the solution of a system of ordinary differential equations. This system of ordinary differential equations is very complicated even for numerical integration, since during the process described by these equations, the rates of concentration and temperature growth change very strongly, which makes the system unsolvable by simple explicit methods (the stiffness coefficient reaches

10^{12}). The problem of solution instability can be avoided by using the so-called implicit solution methods. Another way to avoid this problem is to eliminate fast stages by splitting the time scales. A detailed analysis of the methods for solving systems of stiff differential equations is given in [8].

In this study, to solve a system of stiff differential equations of chemical kinetics, we use the built-in MatLab ode15s method, which implements the implicit Gear method of a variable order of accuracy. The accuracy of the calculations directly depends on the parameters of the built-in solver, so the correct selection of the adaptive step, as well as setting the calculation error, plays an important role [9].

In order to determine the possibility of using a simplified kinetic model of methane-air mixture combustion in a combustion chamber, a detailed kinetic mechanism of methane combustion was considered, which was obtained on the basis of a modification of the widely known and repeatedly tested kinetic scheme of light hydrocarbon oxidation proposed in [10]. This kinetic scheme was modified by excluding methanol oxidation reactions. The resulting kinetic mechanism contains 156 reactions, 23 active reagents: H_2, O_2, H_2O, H, O, OH, HO_2, H_2O_2, CO, CO_2, CH_4, C_2H_6, CH, CH_2, CH_3, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, CHO, CH_2O, CH_3O and one inert component N_2. Therefore, a system of 25 differential equations (24 concentrations + temperature) is solved. Adiabatic induction periods are calculated for given compositions of methane-oxygen and methane-air mixtures at a given initial pressure. The criterion for determining the induction period t_{ad} is the attainment of the maximum rate of heat release.

The analyzed simplified mathematical models of chemical transformations were chosen to be models based on three chemical reactions, the rate constants of which are given in Table 1, as well as two one-step mechanisms of methane oxidation [11]:

$$CH_4 + 1.5O_2 \to CO + 2H_2O,$$

the rate constants of chemical transformations are presented as:

$$k_1 = 1.35 \cdot 10^{20} \exp\left(-\frac{30000}{RT}\right), \tag{1}$$

$$k_2 = 3.00 \cdot 10^{22} \exp\left(-\frac{45000}{RT}\right). \tag{2}$$

Table 1

Kinetics of methane oxidation from 3 reactions

No.	Reaction scheme	Direct reaction		
		A	n	$E_a, kkal/mol$
1	$CH_4 + 1.5O_2 \to CO + 2H_2O$	2.0e15	0	35.0
2	$CO + 1.5O_2 \to CO_2$	2.0e9	0	12.0
3	$CO_2 \to CO + 1.5O_2$	8.11e9	0	77.2

Figure 1 shows the dependence of the combustion period on the initial temperature and a comparison of one-stage mechanisms (1) and (2) with the mechanism of 156 reactions.

Figure 2 shows time dependencies of temperature for one-stage kinetic mechanisms when an adiabatic reactor reaches the stationary state in a comparison with the mechanism of 156 reactions.

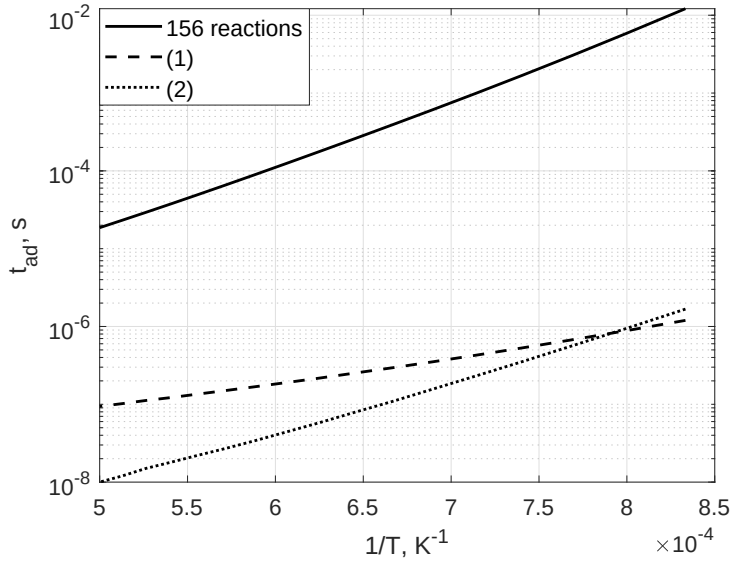

Fig. 1. Dependence of the combustion period on initial temperature for one-stage mechanisms.

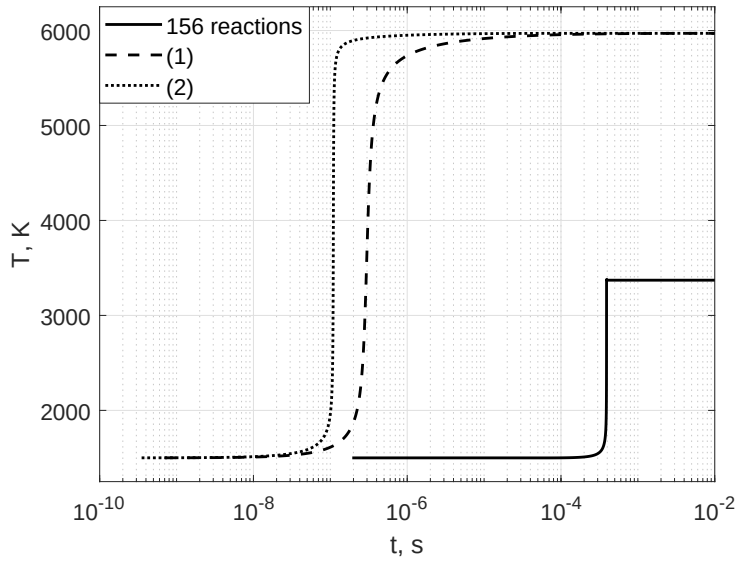

Fig. 2. Time dependence of temperature period on the initial temperature for one-stage mechanisms and reaching the stationary state at $p_0 = 1\ atm$, $T_0 = 1500\ K$.

As shown in the Figure 2, the temperature of combustion products obtained by one-stage mechanisms gives an overestimated value of the temperature, because in this case dissociation processes leading to endothermic reactions of decomposition of large molecules arising during the combustion process into smaller ones and a decrease in temperature are not taken into account.

Therefore, this approach and one-stage kinetic mechanisms of methane ignition and combustion can be applied only for a qualitative analysis in multiparameter studies of the process in the combustion chamber.

Figures 3 and 4 show calculations of the dependence of the combustion period on the initial temperature and the time dependencies of the temperature for the two-stage mechanism when an adiabatic reactor reaches the stationary state ($p_0 = 1\ atm$, $T_0 = 1500\ K$) in a comparison with the mechanism of 156 reactions.

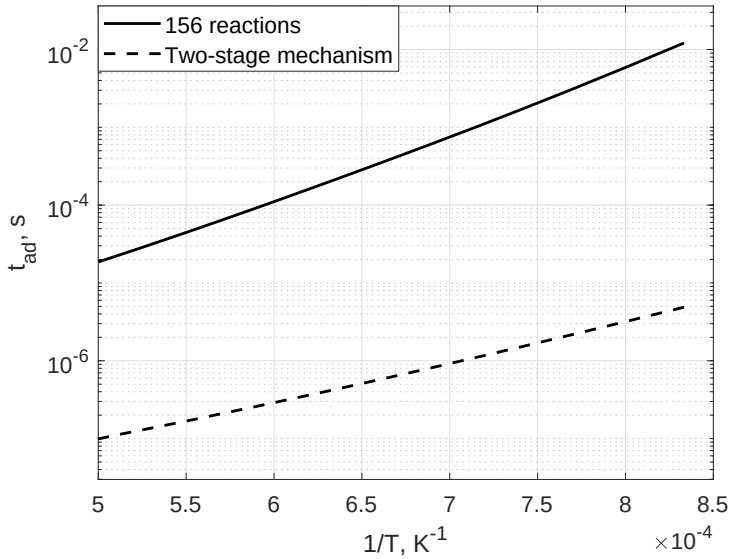

Fig. 3. The comparison of dependence of the combustion period on initial temperature of the two-stage mechanism with the mechanism of 156 reactions.

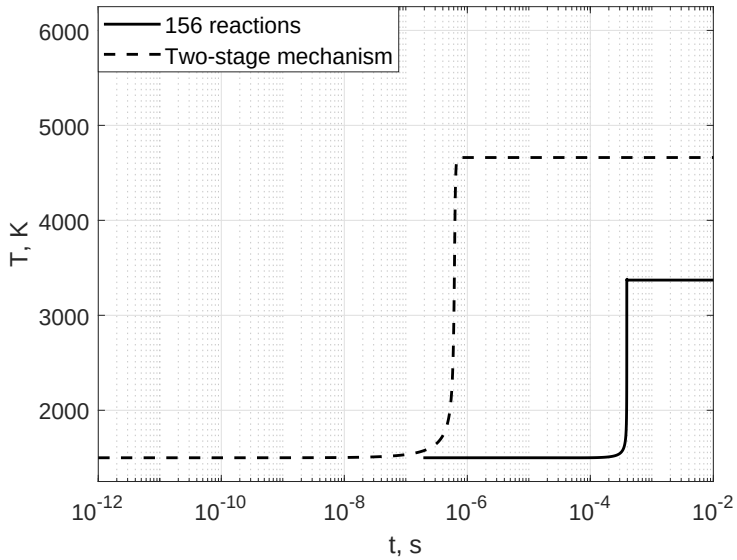

Fig. 4. Time dependencies of temperature period on the initial temperature for the two-stage mechanism and the mechanism of 156 reactions when an adiabatic reactor reaches the stationary state.

Despite the fact that the two-stage mechanisms of methane oxidation takes into account the dissociation of a carbon dioxide molecule, this is not enough to significantly

reduce the temperature of the methane combustion product mixture. This is indicated by the shorter combustion period and higher temperatures of combustion products (by 1500 K) compared to the detailed kinetic mechanism of 156 reactions.

2. Conclusion

As a result of the study, numerical solutions were obtained for various kinetic mechanisms to solve the problem of determining the combustion period of ignition of the methane-oxygen mixture in an adiabatic reactor: for two one-stage mechanisms, for one two-stage mechanism and for the mechanism of 156 reactions.

The analysis of the influence of those mathematical models of chemical transformation on the ignition of methane-oxygen mixtures makes it possible to conclude that only the mathematical model built on 156 reactions gives the result which is consistent with the experiment.

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АНАЛИЗ ВЛИЯНИЯ МАТЕМАТИЧЕСКИХ МОДЕЛЕЙ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ НА ВОСПЛАМЕНЕНИЕ МЕТАН-КИСЛОРОДНЫХ СМЕСЕЙ

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В данной работе представлен анализ влияния математических моделей химического превращения на воспламенение метан - кислородных смесей. Результаты проведенного анализа показывают, что, несмотря на широкое применение процессов горения метана в практических целях и достаточно большое количество публикаций, разработка кинетических схем горения метана является актуальной и в настоящее время. На примере решения задачи об определении периода индукции воспламенения метан - кислородной смеси в адиабатическом реакторе в работе были апробированы различные кинетические схемы воспламенения метана: две одностадийные, одна двух стадийная схема и схема, состоящую из 156–ти реакций. Было показано, что наиболее точное описание экспериментальных данных по временам задержки адиабатического взрыва удается получить, только используя более сложную кинетику окисления метана, а рассмотренные упрощенные кинетические механизмы дают завышенные температуры смеси, состоящей из продуктов окисления метана.

Ключевые слова: математическое моделирование; горение и взрыв; период индукции.

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